Synthesis and Novel Applications of Cerium Dioxide

Rafaela Cristina de Carvalho [Thesis]
Technological University Dublin

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Synthesis and Novel Applications of Cerium Dioxide

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A thesis presented to
Technological University Dublin for the award of
Doctor of Philosophy
August 2019

Prepared under the supervision of Professor J.F. Cassidy and Dr A.J.Betts

School of Chemical and Pharmaceutical Sciences and Applied Electrochemistry Group
August 2019
Abstract

Cerium dioxide nanoparticles (NPs) were synthesised using a novel precipitation procedure and their function explored in a range of applications. The impact of different factors on CeO$_2$ NPs synthesis including temperature and reactant concentration were evaluated experimentally and optimised. The resulting nanoparticles (with an average size of 35 nm) was then characterised by a range of physical and spectroscopic techniques including dynamic light scattering, scanning electron microscopy in conjunction with energy dispersive spectrometry, X-ray diffractometry, Brunauer–Emmett–Teller isotherm measurement, Raman spectroscopy, UV-visible spectroscopy and X-ray photoelectron spectroscopy. A new nanoparticle synthetic route, the “frozen NH$_4$(OH) cubes method”, was developed, resulting in a higher yield of NPs and shows much promise.

CeO$_2$ NPs in both colloidal and powder forms was utilised as a catalyst under the irradiance of a sun simulator to degrade Methyl Orange dye (MO) and the important pharmaceutical compound Diclofenac (DCF). The degradation efficiency of MO and DCF was found to be 100% in 85 min and 56% in 3h respectively with the CeO$_2$ NPs. The products of photodegradation of DCF were identified through combined liquid chromatography/mass spectrometry and a degradation pathway was proposed involving a ring cyclisation process.

CeO$_2$ NP and commercial TiO$_2$ NP were utilised in thin layers (~40nm) to fabricate model resistive switching (memristor-like) devices. A new mechanism was proposed for their operation. This involves the formation of p-n junctions resulting from reactions involving the
semiconductor layer’s inherent point defects. These occur in the presence of large electric field gradients such as those occurring in thin layer solid-state electrolytic cells.

By utilising the photocatalytic properties of CeO$_2$ NPs in a photoanode incorporated into a novel Photoelectrochemical Fuel Cell (PEFC), low levels of organic pollutants (formic acid and DCF) in a model wastewater were degraded, along with the production of electrical current. Comparison was made with PEFCs using the standard TiO$_2$ photocatalyst which indicated that the CeO$_2$ NPs were inferior (i.e less photoactive) and were not re-usable.

Finally, the CeO$_2$ NPs were also utilised as catalysts in electrochemical sensors incorporated in disposable screen-printed carbon electrodes (SPCE). It was found that a vacuum heat treatment was essential in order to confer the necessary catalytic action on the CeO$_2$ NPs. Investigations were conducted using cyclic voltammetry and square wave voltammetry (SWV) for the enhanced detection of commonly used pharmaceutical products including Acetaminophen, Aspirin and Caffeine. A Limit of Detection (LOD) of 0.4 µmol L$^{-1}$ and Limit of Quantification (LOQ) of 0.12 µmol L$^{-1}$ was obtained which is comparable with other involving more difficult fabrication methods. Furthermore, DCF and its degradation products were also detected using this new SWV-SPCE-CeO$_2$ system.

Finally, future approaches involving the use of CeO$_2$ NPs in a range of photocatalytic, electronic and electroanalytical (sensor) fields were discussed and recommendations are given.
DECLARATION

I certify that this thesis which I now submit for examination for the award of Doctor of Philosophy is entirely my own work and has not been taken from the work of others, save and to the extent that such work has been cited and acknowledged within the text of my work.

This thesis was prepared according to the regulations for postgraduate study by research of the Technological University Dublin and has not been submitted in whole or in part for another award in any university.

The work reported on in this thesis conforms to the principles and requirements of the University's guidelines for ethics in research.

The University has permission to keep, lend or copy this thesis in whole or in part, on condition that any such use of the material of the thesis is duly acknowledged.

Signature _______________________________ Date ________________

ID No.: _________________
Acknowledgements

I would like to express my sincere gratitude to all those who have supported me in any way during the last four years and in particular at the final stages of completing this work.

Firstly, I wish to place on records my heartfelt and sincere thanks to my supervisors Prof. J.F. Cassidy and Dr A.J. Betts for providing me with an opportunity to complete my PhD thesis. I greatly appreciate their contributions of time and ideas to make my work productive and stimulating. I’m very grateful for their help and guidance, for answering my 1000’s of questions and for their enthusiasm and encouragement for every time I wanted to give up on research. John many thanks for always showing me the positive side of everything – not only in research but also in life. Tony many thanks for always reminding me to smile, your energy has always made my day better. Both of you are very generous and I’m very lucky to have had you as my supervisors.

To Prof. H. Byrne who has always been an inspiration and made Focas a great place to work, and still does everything for postgraduate students to have an easier life, none of this would be possible.

I would like to thank the TUD for affording me the use of their equipment and facilities. The laboratory technicians in, Focas, Kevin Street and Grangegorman – Luke, Brian, Denise, Ola, Brian, Grant and Martin were always there to provide any chemicals that I may not have had or helping with the instrumentation.

Most of all I would like to thank my Brazilian and Irish families. A special thank you for my boyfriend Eoghan Kirwan for listening to me talking about PhD problems for uncountable hours and supporting me for all these years. Many thanks to my friend Dr Gerard Bree for reading my thesis and offering many suggestions along the way. Thanks to all AEG and lab friends for sharing the good and bad days of Science.
Abbreviations

ACN - Acetonitrile
ACOP – Acetaminophen
AFM - Atomic force microscopy
ASA - Aspirin
BET - Brunauer-Emmett-Teller
BDDE - Boron doped carbon diamond
BRB - Britton-Robinson Buffer
CB – Covalent band
CAT – Catechol
CE – Counter electrode
C.C – Carbon cloth
CC - Chronocoulometry
CCD - Coupled with a charging device
CAF - Caffeine
CV – Cyclic voltammetry
DLS – Dynamic Light Scattering
DCF – Diclofenac
DCU - Dublin City University
DP - Degradation products
DFT - Density Functional Theory
DWD - Drinking Water Directive
EC – European Commission
E_F - Fermi level
EPA – Environmental Protection Agency
EP - Electrochemical pre-treatment
$E_p$ - Peak potentials
Eq. - Equation
EU – European Union
EDS – Energy dispersive X-ray
EFTEM - Energy-filtering transmission electron microscopy
$E_g$ – Energy gap
EIS - Electrochemical impedance spectroscopy
eV – Electron volt
Et al – Et alia
Fig. – Figure
FWHM – Full width half maximum
FCC – Face-centered cubic
FA – Formic Acid
HPLC – High-performance liquid chromatography
HQ – Hydroquinone
HRS – High Resistance state
HER - Hydrogen evolution reaction
HRTEM - High-resolution transmission electron microscopy
$h\nu$ - Photon energy
IEP - Isoelectric point
ITO – Indium Tin Oxide
LC-MS – Liquid chromatography-Mass spectroscopy
LMCTC - Ligand-to-metal charge transfer complex
LRS – Low resistance state
LOD - Limit of detection
MPL – Microporous layer
MO – Methyl orange
NSAID – Non-Steroidal Anti-Inflammatory Drug
NHE – Normal hydrogen electrode
nm – Nanometer
NP – Nanoparticle
NRs – Nanorods
NRF - Nano Research Facility
ORR – Oxygen reaction reduction
PCPs - Pentachlorophenol
PBS – Phosphate buffer solution
PEFC – Photoelectrochemical fuel cell
P-F - Poole-Frenkel
PP - Propylene
PVC – Polyvinyl chloride
PZC – Potential of zero charge
RT – Retention Time
ReRAM – Resistive Random-Access Memory
RE – Reference electrode
R.S.D - Relative standard deviation
RS – Resistive switching
ROS - Reactive oxygen species
SE - Schottky emission
SEM – Scanning Electron Microscope
SDGs - Sustainable Development Goals
SOFCs - Solid-oxide fuel cells
SPCE - Screen-printed electrode
SCLC - Space-charge-limited conduction
SWV - Square wave voltammetry
TCO – Transparent conductive oxides
THF – Tetrahydrofuran
UV – Ultraviolet
VB – Valence Band
VCMs – Valence change memory devices
VHT - Vacuum heat treatment
WWTPs – Wastewater Treatment Plants
XRD – X-ray diffraction
XPS – X-ray photoelectron spectroscopy
WE – Working electrode
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CHAPTER 1

GENERAL INTRODUCTION
1.1-Water in the environment.

The goal of producing clean and sustainable energy has become a major concern (worldwide) in the last few decades, due to issues of air pollution from the use of fossil fuels and greenhouse gas emissions. Such problems have led to drastic changes in the climate. Studies show that worldwide, July 2019 was characterised by unusually warmer temperatures across the world's land and ocean surface, with an average of increase +0.04°C [1].

The use of energy from renewable sources requires the development of new efficient energy conversion techniques and storage capacities. The leaders of 170 countries have created a plan called the Sustainable Development Goals (SDGs) which aims to change this reality by the year 2030. Two of the seventeen goals are to ensure availability and sustainable management of water and sanitation for all and to ensure access to affordable, reliable, sustainable and energy for all [2].

There are many sources of organic waste in the world, most of which are generated as a result of agricultural, industrial and domestic activities. Others sources arise from natural phenomena, such as the decay of organic material. Water is the main source of sustenance and survival of every living species. It is of most importance in regions where water can be scarce due to climate change and the occurrence of natural disasters. Water scarcity is currently one of the most serious problems in the world because of the enhanced need for water by a fast-growing population, in combination with the exhaustive reduction of water resources, and lack of a proper distribution framework for water management [3]. Either management of water from a fresh source should be optimised or wastewater treatment techniques need to be further developed by industries to provide adequate quality and supply of water. Much research is
being carried out on various wastewater treatment techniques which can then be used for such purposes as farming, bathing or even reusing it in a recycling process [3,4].

1.2 - Wastewater treatment.

In many developed countries, wastewater treatment and prevention of industrial pollution is of crucial importance, as population and industrial density increase every year. Conventional water-treatment technologies often cannot completely decompose organic contaminants in aqueous media, due to the higher stability and lower reactivity of some organic contaminants (insoluble nature of many) [5]. Organic pollutants in drinking water pose a harmful threat to both humans and aquatic organisms.

The most common treatments for water with organic pollutants are adsorption with activated carbon, air stripping, and chemical water treatments (e.g chlorination, ozonation). Although these are generally inexpensive, they are not often effective in stopping living contaminants reproduction (e.g organisms such as virus, bacteria) and they cannot efficiently remove heavy inorganics metals or organic contaminants [4]. Non-chemical treatments (e.g UV, plasma) are usually effective in preventing the reproduction of viruses and bacteria, but are not effective at removing chemicals. The main disadvantage is that they are often expensive techniques and require a higher level of energy consumption (thus are not a “green” technology) [5]. However, as non-destructive technologies, they transfer contaminants from water to adsorbents or to the air and as a result, they often require further treatment. Moreover, some organic compounds are not removed by these commonly used treatments because of their low adsorbabilities or low reactivities [5, 6]. The principles of green chemistry suggest that it is important to utilise processes that reduce energy consumption and minimise the use and
generation of harmful substances [7]. Catalytic technologies provide an opportunity to improve and optimise the environmental sustainability of treating wastewater containing low concentrations of organic pollutants. Adsorbing toxic contaminants on a catalyst surface and then transforming them in situ to non-toxic or substantially less toxic compounds is the basis of catalytic water remediation techniques [6].

Residual pharmaceutical products are often found in effluent wastewaters due to the difficulty of their removal by conventional remedial wastewater treatments. These organic pollutants reach the environment through the direct disposal of pharmaceutical compounds which have not been metabolised from human waste or have simply been disposed of inappropriately. (There is considerable interest in the use of metal-oxide nanoparticles as photo-catalysts in order to degrade these pharmaceuticals [8, 9]). Pharmaceutical compounds (endocrine disruptive) such as Diclofenac (DCF) may have a long-term adverse effect on organisms [10]. DCF is often not completely removed from wastewater due to its inherent stability (poor degradation), and high worldwide consumption rates (e.g. estimated at 179.8 tons per year in Europe, where the highest use is in Germany, 86 tons and in the UK 26.13 tons per year) [11]. It is considered an important issue due to the frequent measurement of the occurrence of the presence of DCF in many drinking water sources. The main factor for this impact is that DCF is naturally degraded in sunlight and its photo-transformation products could be more toxic leading to the formation of other potential pollutants (e.g. metal complexes) possessing antibacterial and cell destruction capacities [12].

Waste Water Treatment Plant (WWTP) effluent discharges account for a significant amount of pharmaceuticals released into the environment [13]. The main impact of these
compounds on the environment are however largely unknown. Although concentrations of the pharmaceuticals detected have been reported to be too low to have any detrimental effects on human health, there is still the question whether these pharmaceuticals will have an adverse effect, and, if they do, what kind of effect they have on other organisms [10]. In a recent study, trace amounts of illicit drugs, including cocaine (100%) were found in freshwater shrimp, as well as lidocaine (95%), alprazolam (88%), ketamine (76%) and the banned pesticide (which is not approved for use used in EU) fenuron (86%) in biota samples in rivers across the rural area of UK [14]. In the 21st century, one of the most important challenges is still to supply potable water worldwide. Although in Ireland, the water supply is of relatively good quality, in 2009 the Environmental Protection Agency (EPA) listed heavy metal pollutants, among others such as nitrates and pentachlorophenol (PCPs), as a major threat to our drinking water supply [15].

Since the 1980s, the EU has applied guidelines that aim to improve water quality controls. In February 2018, the European Commission (EC) adopted its recast proposal for a Directive of the European Parliament and of the Council on the quality of water planned for human consumption, the so-called Drinking Water Directive (DWD)[16]. This proposal aims to update water quality standards, to introduce other ways to carry out the monitoring of water, to improve the information on water quality and to devise standards for materials in contact with drinking water [16]. The EC has created a watch list of 10 substances for which data and information need to be gathered since they pose a potential risk to the aquatic environment. These include Diclofenac (DCF), 17-beta-estradiol, and 17-alpha-ethinylestradiol [17]. Ireland is an important pharmaceutical industrial centre, with nine out of the ten of the largest
pharmaceutical companies located in the country. This potentially places the country’s aquatic environment at risk and forces the water industries to search for new technologies to remove contaminants such as DCF from wastewater [17].

1.3 – The use of solar light

Solar technologies could potentially offer a solution towards a sustainable future for mankind, as it's expected that the energy supply from fossil fuels may be compromised in the near future. The use of renewable energy sources, of which solar is considered as the most important is likely to grow. Photochemical processes could be considered as a short term goal. Solar photocatalytic processes have made considerable progress in recent years due to their economic, technological and environmental attractiveness [18]. However, new engineering tactics (chemical, physical and biological) are still necessary to make solar photochemistry a major part of producing electricity. The goal of waste minimisation and the desire to use “green” technology will offer further provide opportunities for solar chemical processes [19].

In areas where sunlight is abundant, when direct solar radiation is not blocked by clouds, the visible light irradiance can reach up to 1000 W m\(^{-2}\) [20]. Therefore the use of this radiation for photocatalysis should be explored. Additionally, the solar process can be used on-site and therefore avoids risks associated with transporting and handling of hazardous wastes (e.g spent carbon and volatile organic compounds). The solar spectrum consists up into around 52 to 55% infrared (above 700 nm), 42 to 43% visible (400 to 700 nm), and only 3 to 5% ultraviolet (below 400 nm). Solar photons from the visible and near-UV spectrum are considered energetic enough to be used in photochemical processes. Infrared photons are normally of insufficient energy in photochemistry, due to the high wavelength range [21].
1.3.1 – Photocatalysis

As mentioned previously, solar photocatalytic processes have made considerable progress. Photocatalysis consists of the combination of conduction band electrons (e\textsuperscript{−}) and valence band holes (h\textsuperscript{+}) generated once the nanoparticulate of a metal oxide (e.g TiO\textsubscript{2}, CeO\textsubscript{2}, ZnO) is irradiated with light energy. The photogenerated electrons could reduce the organic molecule (e.g dyes, pharmaceuticals drugs, pesticides) or react with electron acceptors such as O\textsubscript{2} adsorbed on the metal-oxide surface or dissolved in water, reducing it to superoxide radical anion O\textsubscript{2}•\textsuperscript{−}. The photogenerated holes can oxidize the organic molecule to form R\textsuperscript{+} or react with OH\textsuperscript{−} or H\textsubscript{2}O oxidizing them into OH• radicals [6].

The photocatalysis can also occur without the need of catalytic and is known as photolysis. Such process involves the electronically excited state of an organic molecule which is either simply unstable and/or quenched by ambient O\textsubscript{2} to produce singlet oxygen – which then oxidises the molecule. This mechanism is well known to occur when the organic molecule is a dye and it is named as dye (photo)sensitisation, this usually involves the initial electronic excitation of the dye, D, to D*, by light of sufficient energy, so that D* is able to then inject an electron into the conduction band of the metal-oxide, which in turn then reacts with ambient O\textsubscript{2} present in the system [7]. This dye is unstable and able to react further to produce colourless degradation products which means that dye absorbs onto the metal oxide surface however its loss of colour is not necessarily an indication of the destruction of the organic molecules but only the bleaching of the dye [8].
1.4 – Nanotechnology

Nanotechnology may play a key role in the development of water treatment technologies [22]. This technology can be considered as the study, manipulation or building of devices, materials, and objects that are at the nanoscale, typically < 100 nm [22]. At this scale, many properties of materials depend strongly on their size. Nanomaterial synthesis can be categorised according to whether their assembly follows the top-down approach (size reduction from bulk materials) or bottom-up method (material synthesis from atomic level). The latter approach is the route more often utilised in research for preparing nano-scale materials, with the advantage of producing uniform nanoparticles of shape and distribution size [18]. Nanotechnology also provides the ability to manipulate atoms and molecules in an almost unlimited number of new compounds (e.g through doping) [23].

Many current studies utilise nanoparticle (NP) semiconductor photocatalysts which have enhanced properties when compared to their bulk form [24]. As an example, with adsorption where surface sites of the adsorbent (catalyst) are utilised, bulk materials may lack adequate surface area. This characteristic is because the surface-to-volume ratio increases immensely with the decrease in the size of the semiconductor catalysts from bulk to nano dimensions, thus improving their reactivity [8, 25].

Also when a material is reduced to the nanoscale, it often presents new physical and chemical properties, including optical, electrical and magnetic properties [8]. The surface energy per nanoparticle increases notably with decreasing size, as the reactivity also increases due to the increase of atoms on the crystal surface [8]. Often, this increase in surface energy immediately results in an increase in organic contaminant removal even at small concentrations
of the contaminant. The management and use of nanocatalysts may also lead to a reduction of waste generation, principally in post-treatment, since a smaller amount of nanomaterial will be used compared to its bulk form [25, 26]. Until now, nanoparticles of many elements, especially the metal oxides have been investigated and exploration of new nanostructures is in progress [8, 9].

1.5 – Cerium Dioxide (CeO₂) and Its Applications

Cerium (Ce) is the twenty-sixth most abundant of all elements, being half as abundant as Cl and 5 times as abundant as Pb [27]. It is non-toxic and relatively inexpensive [28]. Ceric (IV) salts are orange-red or yellowish in colour, while cerous (III) salts are usually white. Cerium, the second element in the lanthanide series, exists in two common oxidation states, Ce³⁺ (e.g in Ce₂O₃, cerium trioxide) and Ce⁴⁺ (e.g as CeO₂, cerium dioxide more commonly known as ceria or cerium (IV) oxide), with the electronic structure [Xe] 4f⁰, over the state [Xe]4f⁴ for Ce³⁺ [29]. In this thesis, two nomenclatures will be used; CeO₂ NP or nanoceria. In practice CeO₂ exists as a substoichiometric oxide, CeO₂₋ₓ [30]. CeO₂ is the most common polymorph of cerium oxide, it will be the focus of the rest of this thesis.

Nanoceria has attracted substantial attention due to its relatively high abundance and its characteristic of showing a large increase in the surface-to-volume ratio with respect to the bulk form. This makes CeO₂ NP more reactive than bulk CeO₂ [9]. Ceria is also a semiconductor and the crystal structure of CeO₂ NP has a high-level of oxygen deficiency. This deficiency increases with the decrease in the size of the nanoparticle and yields a high oxygen-ionic conductivity at high temperatures which makes it useful in the widely known high-temperature solid oxide fuel cell (SOFC) applications as a solid electrolyte [31, 32].
However, in terms of catalytic activity, CeO$_2$ NP is the main oxide utilised for catalytic reactions, with Ce$_2$O$_3$ being used as an intermediate oxide for example in high-temperature catalytic converters (where harmful emissions from fuel-burning are converted to harmless gases) as in the conversion of CO to CO$_2$ [11]. Heterogeneous catalysis by CeO$_2$ NP was investigated through the photodegradation of methylene blue dye by Pouretedal et al. [33]. They reported that the dye degraded only at a slow rate under UV irradiation in the absence of CeO$_2$ NP. Once the CeO$_2$ NP were added, it led to an increase in the degradation efficiency of the dye with an optimum degradation efficiency of 90% within 125 min [33]. Other applications of ceria include use as gas sensors [34] and UV absorbents [35] due to their particular properties based on the redox behaviour between Ce$^{4+}$ and Ce$^{3+}$ and the formation of oxygen vacancies [36]. CeO$_2$ has been used in chemical mechanical polishing since 1960, due to its ability to catalyse the hydration of silicon dioxide surfaces [32]. In the medical field, many studies have suggested the ability of nanoceria to scavenge reactive oxygen species (ROS) at the cellular level, since ROS are often instrumental in many diseases [37].

1.6 – Non-stoichiometric Cerium Dioxide

The non-stoichiometric form of CeO$_2$ exhibits a broad range of stoichiometries, CeO$_{2-x}$, where $x \leq 0.28$ [38]. It exhibits both ionic and electronic conduction with ionic being prevalent at temperatures above 500ºC [38].

Cerium trioxide has a hexagonal lattice while Cerium dioxide crystallises in the space group (Fm$\bar{3}$m), fluorite structure, in which Ce$^{4+}$ cation is surrounded by eight equivalent O$^{2-}$ ions [39]. In CeO$_2$, the Ce$^{4+}$ cation is located at each edge of a cube with each O$^{2-}$ coordinated to four Ce$^{4+}$, as shown in Fig. 1.1 (a) [39]. The unit cell of ceria is a face-centred cubic (FCC)
structure composed of Ce$^{4+}$ ions, the Ce$^{4+}$ ions forming a cubic array and all the tetrahedral sites around the Ce$^{4+}$ ions are occupied by the oxygen ions, whereas the octahedral holes remain vacant (Frenkel or Schottky defects). Since there are four cerium ions and eight oxygen ions inside the cell, the 1:2 stoichiometry is maintained, and the lattice constant of the cubic unit cell is 0.541 nm [40].

Figure 1.1 The FCC crystal structure of CeO$_2$. (a) without defects, (b) with intrinsic defects, including the reduction of Ce$^{4+}$ to Ce$^{3+}$. Adapted from Ref. [41].

As is indicated in Fig 1.1, Ce$^{3+}$ ions have a higher ionic radius (1.034 Å) as compared to the Ce$^{4+}$ ions (0.92 Å). The introduction of the oxygen vacancies and the accompanying Ce$^{3+}$ ions lead to a distortion of the local symmetry [41]. Defects in ceria can be either intrinsic or extrinsic. Intrinsic defects are formed due to thermal disorder in the crystal, which can be produced by the reaction between the solid and surrounding atmosphere, whereas the extrinsic
defects are due to either an impurity or arise from the introduction of a foreign dopant [42, 43].

Point defects consist of vacant lattice sites, atoms in non-regular lattice positions (interstitials), and the introduction of an impurity atom instead of a vacant hole. Several properties (e.g. conductivity, luminescence and diffusion) can be enhanced or reduced by the existence of these defects [44]. Furthermore, it is not possible to produce a single crystal completely free of defects and as temperature increases, defects become even more significant [31].

In the case of intrinsic defects, the coordination number of Ce⁴⁺ to O²⁻ may reduce from eight to seven at elevated temperatures (>500°C). This in turn reduces the Ce⁴⁺ to the Ce³⁺ ions as two electrons from an oxygen atom are transferred to two Ce ions surrounding the oxygen ion which leaves the unit cell and a vacancy site is formed, as shown Fig. 1.1 (b) [45]. Oxygen vacancies are formed together with O₂ gas and 2Ce⁴⁺ are reduced to 2Ce³⁺ (equation 1.1). The formation of these oxygen vacancies can be described by Kröger-Vink defect notation, which is described further in Appendix I [46].

\[
2\text{Ce}^{4+}_\text{ce} + \text{O}^{2-}_\text{o} \rightleftharpoons \frac{1}{2} \text{O}_2 \text{(gas)} + \text{V}_\text{o}^{**} + 2\text{Ce}^{3+}_\text{ce}
\]  

(1.1)

The formation and loss of vacancies and the inclusion of commonly used trivalent dopants, such as Gadolinium and Niobium, is described below using the Kröger-Vink notation (equations 1.2 and 1.3 respectively), where CeCe is a Ce⁴⁺ ion, Ce'ce is the Ce³⁺ ion, Oo refers to lattice oxygen, Gd is the tri-valent element dopant atom, Gd'ce means electron-acceptor trivalent ion formed in ceria, Nbce refers to a metal cation in the vicinity of a cerium atom, and V_o^{**} refers to oxygen vacancies [30];

\[
\text{Gd}_2\text{O}_3 \rightleftharpoons 2\text{Gd'}_\text{ce} + \text{V}_\text{o}^{**} + 3\text{O}_\text{o}
\]  

(1.2)

\[
\text{Nb}_2\text{O}_5 \rightleftharpoons 2\text{Nb}_\text{ce} + 2e^- + 5\text{O}_\text{o}
\]  

(1.3)
Extrinsic defects in nanoceria are created for example when a tri-valent dopant is substituted for a Ce$^{4+}$ ion and the tri-valent oxide is instantaneously converted into the tri-valent ion and O-vacancy in the material with the oxygen atoms released from the crystal matrix (equation 1.2). Electrons may also be generated from doping with a pentavalent dopant (equation 1.3).

This process leads to an increase in the concentration of O-vacancies itself and the conversion rate from Ce$^{4+}$ to Ce$^{3+}$ which can be predicted solely from Equation (1.2) and has been widely reported in the literature [47, 48].

1.7 - Stability of Cerium dioxide

An important characteristic of CeO$_2$ is its behaviour in aqueous media. Pourbaix diagrams (potential-pH) are commonly utilised to describe the stability of metal oxides, such as CeO$_2$ in an aqueous environment. These diagrams present information regarding the pH-dependent stability and reactivity of various species along with associated redox species.
Figure 1.2 E-pH diagram of Ce–H₂O–H₂O₂ system. The maximum concentration of Ce³⁺ and soluble Ce⁴⁺ species is assumed to be 1 M. Adapted from Ref [49].

Fig. 1.2 shows a simplified Pourbaix diagram (potential-pH diagram) for cerium using the concentration of soluble Ce species at 1 M. The diagram was proposed by Yu et al. and shows the regions of stability for solid phases like CeO₂ or hydroxide forms like Ce(OH)₃, and the areas with a majority of soluble cerium species (Ce(IV): [Ce(OH)]³⁺, [Ce(OH)₂]²⁺ and Ce(III): Ce³⁺).

The use of the Pourbaix diagram is a simple way to illustrate the formation of species such as Ce(OH)₃, which according to this only occurs at high pH and the observation of Ce⁴⁺ precipitates such as CeO₂, which requires oxidation. It can be observed in Fig 1.2, that Ce³⁺
may be oxidised by dissolved O$_2$ or by application of a potential to form Ce$^{4+}$ species such as Ce(OH)$_4$ or CeO$_2$·2H$_2$O after an increase of pH to 5.6, (the redox potential of O$_2$/H$_2$O couple is higher than Ce(OH)$_4$/Ce$^{3+}$ when the pH is greater than 5.6), justifying the weak stability of Ce$^{3+}$ ion precursor solutions in this pH range [50]. However, one notable feature is that when the pH is between 3 and 7, all the Ce$^{3+}$/Ce$^{4+}$ phase transition lines are in the region contained within the two H$_2$O$_2$ lines, one being oxidation and the other being reduction. This suggests that H$_2$O$_2$ could have dual functions, being either an oxidising or a reducing agent for the Ce$^{3+}$/Ce$^{4+}$ transition. Yu et al. confirmed experimentally that peroxide tends to be a reducing agent for Ce$^{4+}$ at lower pH values and an oxidising agent for Ce$^{3+}$ at higher pH values [49]. Such findings indicate that kinetic factors contribute to the formation of intermediate species and makes the stability of CeO$_2$/Ce$_2$O$_3$ a challenge.

1.8 – Titanium dioxide (TiO$_2$) applications and history

Numerous studies of titanium dioxide have been carried out since Fujishima and Honda reported in the early ’70s its ability to split water into H$_2$ and O$_2$ using TiO$_2$ immobilised on an anode [51]. Since then, the use of TiO$_2$ nanoparticles (TiO$_2$ NP) as a photocatalyst in the remediation of harmful organic molecules in wastewater [52,53,63,64] became very well known and understood. It has opened the way for its use in the destruction of many organic compounds through the mineralisation process, where CO$_2$ and water are formed.

There are numerous examples of TiO$_2$ NP use as photocatalysts. For example, Yizhong et al. and others showed that the degradation of many commercial dyes was possible using the photocatalysis of aqueous suspensions of TiO$_2$ NP [53,54,55]. TiO$_2$ NP is very important in a
wide range of commercial applications, such as paints and toothpaste and serves as a UV absorbent for sun cream among other uses [56].

Titanium dioxide occurs widely in nature, usually in minerals and is normally found in three different crystalline forms: brookite (orthorhombic), anatase and rutile (both tetragonal), each with different properties. Rutile is the most abundant and thermodynamically stable [57]. Anatase is the best crystal form for photochemical experiments, as reported by Linsbigler et al. [54] and Tanaka et al. [55], because of its enhanced charge-carrier movement and the greater number of surface hydroxyl groups. The best-known photocatalyst (Degussa P25-Evonik) is a mixture of anatase (70–80%) and rutile (20–30%), which favours reduced recombination effects [58-60] and also improved electron-hole separation [61]. TiO₂ NP exhibits remarkably high chemical stability in aqueous conditions (as can be seen in Fig 1.3) over a prolonged period of time as its reactivity and photoactivity with water [62].
Figure 1.3 E-pH diagram of Ti–H₂O system. Calculated for [Ti⁴⁺] = 10⁻³ mol L⁻¹ at 25°C (Dashed lines: O₂/H₂O and H₂O/H₂ redox couples. Adapted from Ref [63].

In this work, a widely used commercial photocatalyst TiO₂ NP Degussa P-25 is utilised with the purpose of comparing its functionality to CeO₂ NPs. Degussa P-25 is a highly stable material and has an average particle size smaller than 30 nm having a surface area of 50 m²g⁻¹ [58].

1.9 – Aims and Objectives of thesis work

As previously described, it is important to utilise processes that are sustainable, with the aim to reduce energy and to minimise the use and generation of harmful materials. The use of nanotechnology also plays an important rule in this project as nanosize improves the reactivity
of the reactions at play. This work targets different applications of CeO$_2$ to achieve some of the principles of green chemistry [2]. The aim of this study is to investigate the use of CeO$_2$ semiconducting nanoparticles as mediators on electrode surfaces and to improve electroanalysis of pollutants and consequently contribute to energy saving and environmental remediation. And thus compare the results obtained with the widely used commercial photocatalyst TiO$_2$ NP Degussa P-25. With the aim of improving the earth sustainability, devising a method for water remediation, developing a model for a low energy data storage device and investigating simple sensors rather than complex instrumental methods, the following are the 5 objectives of the work:

- To initially synthesise nanosized cerium dioxide using a novel method and to characterise this material.
- To investigate the use of nanoceria in the photodegradation of diclofenac and to carry out the analysis of its degradation products.
- To use semiconducting nanoparticles as substrates for memristors for potential use as energy-saving devices for data storage.
- To design a photoelectrochemical cell (PEFC) using a flexible and inexpensive electrode incorporating CeO$_2$ NP.
- To use CeO$_2$ NP as the catalyst for the detection of diclofenac and other organic compounds using a disposable electrode.

Cerium oxide is a semiconductor capable of transitioning between oxidation states leading to high mobility of oxygen species. However, there are many aspects of its functionalities that need to be explored, which makes it ideal for further study.
1.10 – Novelty of this work

Currently, many groups are pursuing research into different applications of CeO₂ NP. This work initially explores the use of a novel synthesis of CeO₂ NP which is simple, cost-effective, and eco-friendly compared to most of the methods reported in the literature. These typically use expensive and toxic chemicals for doping (e.g. Pd, Cd) and often need thermal treatment such as autoclave and microwave-assisted synthesis. The CeO₂ NP produced by this novel synthesis will be utilised as a catalyst without any doping to photodegrade DCF under solar irradiation (other research groups have used doping agents in other semiconductors (e.g. TiO₂, ZnO, Fe₂O₃) to enhance its reactivity and degrade organic pollutants in WWTP.

These nanoparticles will also be used in resistive random access memory studies, in which a new model for the mechanism of a low energy device is proposed. Such a mechanism is distinct from those is reported in the literature and suggests a new approach using electrochemical and point defect chemistry concepts. Another novel aspect of the work carried out is the design of a new photoelectrochemical cell (PEFC), prepared using a flexible and inexpensive electrode, with the aim of investigating its use for an optimised PEFC. Finally, the use of nanoceria in an electrochemical sensor is explored. Ultimately this could be used in a portable analytical device for the determination of DCF and other compounds. CeO₂ NP can thus be used to photodegrade DCF by solar simulation and also employed in the electroanalysis for DCF detection and thus contributing to the improvement of water quality. Thus this project aims to contribute to new insights in several investigations of CeO₂ applications, with the intention of providing new options for sustainable chemistry and thus ultimately leading to a better understanding of CeO₂ functionalities in a range of applications.
1.12 - References

[1] https://climate.nasa.gov/effects/ accessed on 08/05/19


CHAPTER 2

CERIUM DIOXIDE NANOPARTICLES SYNTHESIS AND CHARACTERISATION
Chapter 2 - Cerium Dioxide Nanoparticles Synthesis and Characterisation.

2.1 – Introduction

Cerium dioxide is a useful material whose properties can depend on the crystal structure, which typically has a high oxygen deficiency and a redox behaviour between Ce$^{4+}$ and Ce$^{3+}$.

2.1.1 – Synthesis Methods

The synthesis of CeO$_2$ NPs with known composition, uniform morphology, and controlled size is of considerable interest in materials science. Until recently, most ceria-based materials were produced at high temperatures (>300°C), over long periods (24h), due to the need to obtain reproducibility and nanoparticles with the required physical and chemical properties. More recently, alternative strategies have been developed, offering the advantages of the use of lower temperatures and thus less energy, utilising simple equipment, easier control of conditions and flexible post-treatments [1-5].

CeO$_2$ NPs have been synthesised by a variety of techniques such as precipitation, sonochemical methods, crystallisation, microemulsion, mechano-chemical, thermal decomposition, sol-gel, thermal hydrolysis amongst others and are widely reported [1-6]. Hydrosolvothermal methods and precipitation in high-boiling point solvents are most commonly applied in the synthesis of high-quality CeO$_2$ NPs. Experimental parameters, such as temperature, acidity, surfactant use, concentration, and reaction time, offer flexibility and can be varied to tune NP formation [7].
Recently, efforts have been made to develop environmentally friendly and economically efficient pathways for the fabrication of CeO$_2$ NPs via an aqueous-phase synthesis method [3-5]. Not only can the physical properties of nanoscale ceria be exploited, but also the chemical properties can be investigated and utilised in applications such as catalysis, photocatalysis, chemical mechanical polishing and in electrochemical devices [8]. One of the most important applications of these NPs is the photocatalytic performance of CeO$_2$ NPs, which is strongly dependent on the particle size, due to the higher content of oxygen vacancies and thus an increase in the photocatalytic activity [9].

2.2 - Experimental

The aim of this work is to prepare CeO$_2$ NPs by precipitation in the absence of a capping agent by a novel and relatively simple method optimised and improved from that reported by Yan Wei et al. [10]. The prepared nanoparticles were characterised and their photocatalytic activity was studied for the photodegradation of several organic pollutants. Ceria was chosen because it has interesting physicochemical properties that are less well understood in comparison to other metal oxides, as previously discussed in sections 1.5 and 1.6 of chapter 1.

2.2.1 - Materials

All chemicals were purchased from Sigma, Fisher Scientific or from Acros Organics and they were used as received without further purification. The CeO$_2$ NPs were synthesised by a precipitation method. Ultrapure water (18.2 MΩ·cm) was used to prepare the solutions and for washing the final precipitate. The raw materials used for the synthesis of these nanoparticles were as follows:

- Cerium (III) Nitrate hexahydrate 99.5% (Ce(NO$_3$)$_3$.6H$_2$O) (Sigma)
- Ammonium Hydroxide 56.6\% (NH\(_4\)OH) 14.8 M (Acros)
- Nitric Acid 70\% (HNO\(_3\)) 15.4 M (Fisher)

2.2.2 – Equipment

The synthesised nanoparticles were characterised in terms of their structural, optical and photocatalytic properties. Dynamic Light Scattering (DLS), which can provide information regarding size distribution, polydispersity of particles and zeta potential (which determines the stability of a colloid), was performed by using a Malvern Nano series Zetasizer. The general morphologies were examined by using a Hitachi SU 6600 FESEM scanning electron microscope (SEM) operating at 10.0 kV. The Energy Dispersive X-Ray (EDX) spectrum (Oxford Instruments X-Max Silicon, Drift Detector for Energy Dispersive X-Ray) of CeO\(_2\) NPs was analysed to evaluate its elemental composition. A diffractometer (Siemens D-500) with an anode of Cu and a wavelength of 0.15406 nm (Cu K\(_\alpha\)) was used to obtain X-ray diffraction (XRD) patterns. The diffractograms were recorded over a 2\(\theta\) of 20º-80º and the diffractometer operated at 40 kV and 30 mA. Scherrer’s equation (equation 2.1 later) was employed to determine the primary particle size of a given crystal phase based on the most intense diffraction peak. A Carbolite 201 furnace was utilised to anneal the samples.

The composition of the synthesised crystalline CeO\(_2\) NPs was analysed by using Raman Spectroscopy (Horiba Jobin Yvon, LabRAM HR 800). The optical properties were studied by UV-visible spectroscopy using a Perkin Elmer, Lambda 900 spectrometer. Diffuse reflectance spectra were collected using a 60 mm Spectralon coated integrating sphere with a range from 200 to 2500 nm, for the measurement of samples of high optical density. The X-ray photoelectron spectroscopy (XPS) system at DCU utilised was a VG Microtech electron
spectrometer at a base pressure of $1 \times 10^{-9}$ mbar. The photoelectrons were excited with a conventional Mg K$_\alpha$ (hv = 1253.6 eV) X-ray source and an electron energy analyser operating at a 20 eV pass energy, yielding an overall resolution of 1.2 eV. The specific surface area of the CeO$_2$ nanopowders was carried out by low-temperature nitrogen adsorption measurements with a Micromeritics Gemini VII BET surface area analyser. Samples were degassed under nitrogen flow at 30 °C for 10 mins, 60 °C for 10 mins and then 230 °C for 3 hrs. The sample surface area was analysed by a multipoint Brunauer-Emmett-Teller (BET) method.

2.2.3 -Methodology

2.2.3.1 - Preparation of CeO$_2$ nanoparticles.

The synthesis of CeO$_2$ NPs was performed using two methods, namely a Standard method (A) and another termed the “Frozen NH$_4$(OH) cubes method (B)”. For method A, a solution of 0.1 mol/L Ce(NO$_3$)$_3$.6H$_2$O was prepared, after which it was added dropwise at a rate of 4 mL/min into a 2 mol/L ammonium hydroxide solution. For method B, a solution of 0.1 mol/L Ce(NO$_3$)$_3$.6H$_2$O was added dropwise at a rate of 4 mL/min into a viscous solution of 2 mol/L ammonium hydroxide, made using ice cubes from a silicone tray. It should be pointed out that method A and B are chemically the same, the only difference between them is that for method B, the 2 mol/L of ammonium hydroxide is frozen (which makes the solution more viscous) and for method A the solution is at room temperature. For both methods, the mixture was stirred vigorously for 40 min at room temperature.
Figure 2.1 Photographs showing a comparison between solutions obtained after adding 0.1 mol/L Ce(NO₃)₃.6H₂O into solution from (a) Standard method on the left-hand side, and from the much darker (b) Frozen NH₄(OH) cubes method on the right-hand side.

Finally, purple Ce(OH)₄ particles were produced and the excess ammonia was removed by washing and centrifuging several times at a rotation rate of 1000 rpm for 5 min at 25°C. Figure 2.1 shows the difference in appearance between method A and B, in which it's very clear that the Frozen NH₄(OH) cubes method (B) produces a darker colour, indicating thus that this solution is more concentrated. A purple coloured precipitate, that has a texture of a paste, was obtained which was collected by discarding the supernatant (liquid). The purple colour is indicative of Ce³⁺ oxidising to Ce⁴⁺. The precipitate obtained from method B was twice the quantity than that precipitate from method A. The precipitate was then washed with water to ensure that the hydroxide was removed and the mixture was then sonicated for 5 min at 25°C. After that, 100 mL of ultrapure water was added and 1 mol/L of HNO₃ was added drop-wise to
the suspension until it became transparent, and a pH value of 1.4 was achieved. The colloid was then heated for 30 min at 60°C and a yellow hydrosol containing CeO₂ NPs was obtained. This hydrosol was further characterised using DLS and UV-Vis (see Fig 2.2) and utilised in Chapter 3 to photodegrade Methyl Orange. The prepared hydrosol was then dried in an oven at 200°C for 2 h and the powder sample produced was annealed in the furnace at a selected temperature of 300°, 600°, and 900°C for 2 h and then stored for further use. It was then utilised in chapter 3, 4, 5, 6 and 7 as the semiconducting nanopowder.

The precursor used for precipitation was a nitrate (Ce(NO₃)₃. The precipitating agent was NH₄(OH), added drop-wise to form a homogeneous distribution, and providing enough reactant for hydroxide precipitation. Finally, a thermal treatment was performed to allow the growth of CeO₂ NPs.

Vigorous stirring breaks down large particles which can be formed in the initial reaction into smaller nanostructures. In addition, sonication can also help to break up the large agglomerations that may form during centrifugation. Drops of nitric acid were used to adjust the pH and to act as a steric stabiliser of the nanoparticles in order to obtain a stable hydrosol dispersion. A flowchart of the nanoceria synthesis is shown in Fig 2.2:
2.3– Results and Discussion

2.3.1-Experimental Design.

CeO$_2$ NPs were prepared by a novel precipitation method. Using an experimental design approach. The size of nanoparticles is directly affected by changes in the precursor salt concentration and the temperature of the reaction [10]. Therefore, the effective parameters were determined for CeO$_2$ NP synthesis. It should be noted that only the results for the standard method (A) are shown for the experimental design, due to its similarity to results obtained using the other method (B). The impact of different factors like temperature and reactant concentration were evaluated from the initial experiments and it was determined that the
dominant factors were the cerium nitrate initial concentration and the temperature of the reaction, these conditions were tested in duplicate samples. Dynamic Light Scattering (DLS) was used to determine the stability and size distribution of CeO$_2$ NPs. Fig 2.3 displays a particle size distribution graph of three measurements of the nanoceria hydrosol dispersion utilising a cerium nitrate initial concentration of 0.007 M. The graphs for 0.1, 0.05, and 0.07 M are not shown due to the similarity of the results. However, a table with a comparison of the results obtained is displayed in Table 2.1.

**Figure 2.3** Particle size distribution graph of three measurements of the nanoceria hydrosol dispersion utilising cerium nitrate initial concentration of 0.007 M. This graph was taken from the CeO$_2$ NPs synthesised using the standard method (A).
Table 2.1 Size distribution and mean size of nanoceria dispersion at different cerium nitrate initial concentrations.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Size range (nm)</th>
<th>Mean size (nm)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.007</td>
<td>2.3 – 8.7</td>
<td>6.1</td>
<td>3.0</td>
</tr>
<tr>
<td>0.05</td>
<td>6.5 – 10.1</td>
<td>8.2</td>
<td>1.3</td>
</tr>
<tr>
<td>0.07</td>
<td>3.1 – 13.5</td>
<td>7.6</td>
<td>4.0</td>
</tr>
<tr>
<td>0.1</td>
<td>1.6 – 8.7</td>
<td>5.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

It was found that the initial concentration of cerium salt had a significant effect on the final distribution of particle size, ranging from 8.2 nm (0.05 M) to 5.5 (0.1 M). It should be noted that such an effect has not been previously reported. The concentration of 0.1 M was selected due to the smallest mean size of 5.5 nm. The influence of temperature during the final heating step on particle size was also evaluated. Three aliquots separate were separated and heated for 30 min each at 25 ºC, 60 ºC, and 100 ºC. The results of size distribution are shown in the table below.

Table 2.2 Size distribution of CeO₂ hydrosol dispersion treated at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mean size (nm)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25ºC</td>
<td>152.1</td>
<td>53.2</td>
</tr>
<tr>
<td>60ºC</td>
<td>5.5</td>
<td>2.4</td>
</tr>
<tr>
<td>100ºC</td>
<td>4565</td>
<td>1268</td>
</tr>
</tbody>
</table>
From these results, it can be concluded that the variation of temperature following CeO$_2$ synthesis has a significant effect on its particle size, and this optimization has not been previously reported in the literature. The temperature of 60 °C was selected due to the mean size of 5.5 nm being the smallest particle size obtained.

The zeta potential (ζ) is a measure of the electrostatic charge repulsion/attraction between particles and is known to affect the stability of any particle in suspension. In order for a suspension to be stable, the zeta potential value should be above +30 mV for acidic media or −30 mV for alkaline [11]. Fig 2.4 displays a bimodal zeta potential distribution of three measurements of the stock solution (hydrosol) at pH=1.4.

**Figure 2.4** The average zeta potential of three measurements of a stock suspension of CeO$_2$ hydrosol dispersion after 30 days of storage. Average ζ-potential of +34.1 mV and sd=8.2 mV. The measurement was performed on a sample of CeO$_2$ NPs obtained using the standard method (A).
Fig 2.4 shows that the stock suspension has an average zeta potential above +30 mV. The broadening of the zeta potential distribution could be due to the ionic strength of the CeO$_2$ hydrosol dispersion at such low pH. Barany et al. reported that the isoelectric point (IEP) of CeO$_2$ NPs corresponds to pH 6.8 and, at lower pH values, an increase of positive $\zeta$-potential values is observed. This agrees with the results found in this work; such results can be explained by the enhanced adsorption of H$^+$ ions on the surface and an increase of the positive charge density of the nanoparticles [12].

To sum up, the experimental design was investigated to optimise CeO$_2$ synthesis. The optimum concentration and temperature were found to be 0.1 M and 60°C respectively and the CeO$_2$ hydrosol (final product of CeO$_2$ NPs synthesis) was found to be stable for over 30 days, according to the result shown in Fig. 2.4.

2.4-Characterisation of CeO$_2$ nanoparticles

2.4.1 – Size and morphology - Scanning electron microscopy (SEM).

The SEM image of the nanopowder sample annealed at 300 °C shown in Fig 2.5 shows the size and morphology of the CeO$_2$ NPs (nanopowder after annealing at 300°C). Spherical shapes were observed ranging between 27-52 nm (with a mean size of approx. 35 nm). Fig 2.6 shows an image of the hydrosol dispersion (the final product of CeO$_2$ NPs synthesis), which was composed of homogeneous nanoceria. An agglomeration can be observed, with a mean nanoparticle size of approximately 35 nm, which was consistent with the result found from the powder sample, displayed in Fig 2.5. The particle size, as determined by SEM imaging, contrasts with that measured by DLS (table 2.1 and 2.2), a phenomenon, which has also been reported by other groups [9,10,13]. A possible reason for this difference in size is that the
particle size may vary with pH as a result of a change in zeta potential since Fig 2.5 and 2.6 were taken in the dry state and the DLS was from an acidic suspension of CeO$_2$ NPs. Only SEM images from the standard method (A) are shown. Similar images were also obtained by the other Frozen NH$_4$(OH) cubes method (B).

**Figure 2.5** SEM image of the CeO$_2$ powder nanoparticles. Synthesised with the optimum concentration (0.1 M) of the precursor salt, heated at 60°C and further annealed at a temperature of 300°C. This image was taken from the resultant nanoceria produced by the standard method (A) and the nanopowder was reconstituted into a suspension in water and subsequently cast on a carbon tab and dried. Mean size is 35 nm.
Figure 2.6 SEM images of CeO₂ hydrosol dispersion (final product of ceria synthesis). Synthesised with the optimum concentration (0.1 M) of the precursor salt, and then heated at 60°C. This image was taken from the resultant CeO₂ NPs from the standard method (A). Mean NP size is 35 nm.

2.4.2 – Elemental analysis (EDS).

The EDS spectrum of the CeO₂ NPs was collected and the data depicted in Fig 2.7 shows the main peaks related to Cerium and Oxygen (atomic percentage of 68.16% for O and 31.84% for Ce). There are two peaks relating to Silicon and Carbon, the C peak is most likely from the Carbon tabs utilized in this analysis, and the tiny trace of Si is possibly due to sample preparation (glassware). It should be noted that only the EDS spectrum from the standard
method (A) is shown. Identical data were produced from the Frozen NH₄(OH) cubes method (B).

Figure 2.7 EDS spectrum of the synthesised CeO₂ powder nanoparticles. Synthesised with the optimum concentration (0.1 M) of the precursor salt, heated at 60°C and further annealed at a temperature of 300°C. This spectrum was taken from the resultant nanoceria from the standard method (A).

2.4.3 –X-ray diffraction (XRD).

Crystal phases and crystallinity of the synthesised nanoparticles were confirmed by XRD, with spectra shown in Fig 2.8. The XRD diffraction patterns of CeO₂ powder samples
annealed at a temperature of 300°C, 600°C, and 900°C respectively are plotted. Eight peaks with 20 values of 28.6°, 33.2°, 47.5°, 56.4°, 59.2°, 69.9°, 77.1°, and 79.8° correspond to the (111), (200), (220), (311), (222), (400), (311) and (420) planes that can be indexed as face-centred cubic phase of CeO₂, as reported in previous studies [2]. These results were confirmed by comparison with the joint committee on powder diffraction standards (JCPDF cards nº75-8371)[2].

Figure 2.8 XRD patterns of CeO₂ nanoparticles obtained after annealing at 300° C (1), 600°C (2) and 900°C (3), respectively. Synthesised with the optimum concentration (0.1 M) of the precursor salt, heated at 60°C and further annealed at different annealing temperatures. The spectra were taken from the resultant CeO₂ NPs produced by the standard method (A).
XRD peaks became sharper with increasing annealing temperature and their Full-width half maximum (FWHM) decreased, indicating that the crystallinity of nanoceria powder is improved by the annealing process at higher temperature. However, as the crystallite size gets smaller, the peaks broaden, and conversely the more narrow the peak, the larger is the crystal [2]. Mullins et al. reported that each shape of CeO$_2$ (111) exposes defects at edges and corners as well as an undetermined number of vacancies on their faces. This indicates that the O-vacancy formation energy will vary from face to face. Consequently, oxidation and reduction reactions are expected to occur at different rates on the different faces [16].

From Scherrer’s formula (Eq.2.1) the average crystallite size $L$ was calculated, $L$ is given by:

$$L = \frac{K \lambda}{\beta \cos \theta}$$

where $\lambda$ is the X-ray wavelength in nanometer (nm), $K$ is a constant related to crystallite shape, normally assumed to be 0.9, although it can be 0.89 or 0.9 for Full-Width Half Maximum (FWHM) of spherical crystals with cubic unit cells [17]. $\beta$ is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians. The values of $\beta$ in the 2$\theta$ axis of diffraction profile must be in radians. Using this expression, the crystallite sizes of CeO$_2$ NPs annealed at temperatures of 300ºC, 600ºC and 900ºC were calculated to be 2.4 nm, 8.8 nm and 26.6 nm respectively. As expected, increased annealing temperature results in larger crystal domains, which agrees with the data found in the literature [2]. Only the XRD spectrum samples obtained from the standard method (A) is shown, due to the similarity with the data produced from the Frozen NH$_4$(OH) cubes method (B).
2.4.4 – Raman Spectroscopy.

The interatomic bonding characteristics of the CeO$_2$ nanoparticles were also confirmed by using Raman spectroscopy, shown in Fig 2.9. The Raman spectra were recorded using the 532 nm excitation wavelength (solid-state diode laser (50 mW) narrow bandwidth version with double edge filter upgrade (cut off to 50 cm$^{-1}$)) and x50 objective with a diffraction grating of 600 grooves/mm coupled with a charging device detector (CCD). Manual calibration of the grating was carried out using the 520.7 cm$^{-1}$ Raman line of crystalline silicon. Raman spectra were acquired in the 200 to 1000 cm$^{-1}$ region with an acquisition time of 15 s per spectrum and averaged over 5 accumulations. It should be pointed out that Raman scattering is highly sensitive to laser instabilities, and a sample can be subject to saturation/degradation at the higher laser power density levels [18].
Figure 2.9 Typical Raman spectrum of the synthesised CeO$_2$ NPs annealed at (a) 900°C (b) 600°C and (c) 300°C. The Raman spectra were recorded using the 532 nm excitation wavelength with an x50 objective and a diffraction grating of 600 grooves/mm, with an acquisition time of 15 s per spectrum was used and averaged over 5 accumulations. In the range 200 to 1000 cm$^{-1}$. This spectrum was taken from the resultant CeO$_2$ NPs produced using the standard method (A).
The Raman spectra obtained for samples annealed at 300°C, 600°C and 900°C shows peaks at 464 cm$^{-1}$, 466 cm$^{-1}$ and 467 cm$^{-1}$ respectively, which typically correspond to the F$_{2g}$ Raman active mode of a fluorite type cubic structure. This can be assigned to the symmetric mode of oxygen atoms around each Ce$^{4+}$ since it is the only allowed Raman mode in these metal oxides [13].

This Raman active mode is attributed to the asymmetrical stretching mode of the Ce-O8 vibrational unit and is very sensitive to any disorder in the oxygen sub-lattice resulting from thermal doping or grain size induced non-stoichiometry [18,20]. The Raman active modes were shifted from 464 cm$^{-1}$ to 467 cm$^{-1}$ as annealing temperature increased from 300°C to 900°C, due to particle size variation, which is in agreement with results found by Babitha et al. and also supports the XRD results [18]. The FWHM was found to be 10.8 cm$^{-1}$, 19.2 cm$^{-1}$ and 31.5 cm$^{-1}$ for 300°C, 600°C and 900°C respectively. Figure 2.8 shows that the intensity of Raman peaks is shifted upwards with an increase in annealing temperature. This intensity difference might be due to the increase in vibrational amplitudes of the nearest neighbour bonds due to the increase in particle size and has also been reported by other research groups [15,21].

2.4.5 – UV-Vis Spectrophotometry.

The optical properties of synthesised nanoceria were examined by UV-visible spectrophotometry and results are presented in Fig 2.10 UV-Vis spectra of the nanoceria hydrosol dispersion exhibited a well-defined absorption peak located at 298 nm which confirms that CeO$_2$ NPs are optically active. The absorption band between 275 nm and 300 nm is attributed to charge transfer from O$^{2-}$ $\rightarrow$ Ce$^{4+}$, while the shoulder between 320-350 nm is attributed to inter-band transitions of CeO$_2$ [22].
As can be seen in Fig 2.10 the absorbance of samples produced by method B is higher than method A. A possible reason for such a difference in concentration could be that when frozen NH₄OH cubes reacted with the added droplets of Ce(NO₃)₃, they did so in a more controlled manner and at constant rate, where the Ce³⁺ cations were isolated later to be oxidised to Ce(OH)₄ and eventually to CeO₂. On the other hand, the standard method may have produced a higher initial local concentration of NH₄OH even when reacted drop by drop with Ce(NO₃)₃.
This may have resulted in less controlled nucleation of particles of Ce(OH)$_4$ leading to a lower concentration of CeO$_2$ NPs ultimately being formed.

Another possible explanation for this difference of concentration of CeO$_2$ NPs could be that with the rapid supersaturation of NH$_4$OH in water, the first nucleus to form allows the nucleation to happen thus forming crystalline Ce(OH)$_4$ nuclei structures. In the case of the Frozen NH$_4$OH cubes method initially, the crystals of NH$_4$OH could also act as the second nucleation site producing sites and a larger number of nuclei for initiation of Ce(OH)$_4$ formation. For example, with the crystals in a solution, the system is subject to shearing forces from the crystals, and the crystal nuclei structures could be sheared off a growing crystal, thus increasing the number of nuclei available in the system [23].

The bandgap energy was estimated on the basis of the maximum absorption band of CeO$_2$ nanoparticles and it was found to be 4.1 eV according to Eq. (2.2). Similar bandgap values of CeO$_2$ synthesised through precipitation have been found by Khan et al. and by other groups [24,10]

\[
E_g = \frac{1240}{\lambda_{\text{max}}} \text{ (eV)}
\]  

(2.2)

where $E_g$ is the bandgap energy in eV and $\lambda$ is the wavelength (nm) of the synthesized nanoparticle and 1240 is the value of Planck’s constant (h= 4.14x10$^{-15}$ eVs) multiplied by the speed of light (c=2.99 x 10$^8$ ms$^{-1}$). This equation is a facile way of expressing the relationship between bandgap wavelength and energy. It has been noted that most of the bandgap values of CeO$_2$ reported in the literature are usually calculated by using the lambda maximum or $\lambda_{\text{max}}$ [2, 10,24]. However, the bandgap value should be estimated from the absorption coefficient ($\alpha$)
for a given photon energy \( (h\nu) \), where the difference in energy between the initial and final state is equal to the photon energy plus or minus the energy of any other particle (e.g., a phonon) that participates in the transition, and is also dependent upon the density of available final states [25].

The resulting absorbance \( (\alpha) \), which is the logarithmic ratio between the light intensities in the absence and the presence of the material along the light path, with the allowed direct bandgap semiconductor can be presented as the following equation [26]:

\[
\alpha (h\nu) = A * (h\nu - E_g)^{1/2}
\]  

(2.3)

For the bandgap calculation, \((ah\nu)^2 \text{ (eV/cm)}^2\) is plotted against the incident photon energy \( h\nu \), which is known as the Tauc plot. The x-axis intercept of a line drawn on the linear part of the curve gives the value of the direct \( E_g \) of CeO\(_2\), as can be seen below.
Figure 2.11  Plot of $(\alpha h v)^2$ vs. the incident photon energy for the estimation of direct optical band gap energies (a) from the nanoceria hydrosol (final product of ceria synthesis). The data was the same used in Fig. 2.10. (b) from the CeO₂ nanopowder annealed at 300ºC, 600º and 900ºC using diffuse reflectance. The inner graph shows the raw data for the Tauc plot.

Figure 2.11 (a) shows the Tauc plot where the actual band gap value of the synthesised CeO₂ was found to be 3.7 eV for the nanoceria hydrosol and Fig 2.11 (b) the $E_g$ of CeO₂ nanopowder annealed at 300ºC, 600º and 900ºC which was found to be 3.30 eV, 3.27 eV and
3.23 eV respectively. It should be noted that the films prepared from a dispersion of the nanopowders in water drop cast onto a quartz slide and the films resulting were not uniform; hence the noise observed in the insert plot for the raw data of Fig 2.11 (b). The possible reason for the difference in the bandgap of nanoceria hydrosol and the CeO$_2$ nanopowder could be that the HNO$_3$ present in the hydrosol formulation could be shifting the wavelength to higher energy. As could be seen in Fig 2.11 (b) there was a bathochromic shift (redshift) as annealing temperature increased. However, there is another important factor that affects the energy of the bandgap, which is the number of O-vacancies and/or the conversion from Ce$^{4+}$ to Ce$^{3+}$ ions. It has been reported by Patsalas et al. that the bandgap of CeO$_2$, where cerium exists in the Ce$^{4+}$ ionization state and when there are no oxygen vacancies present, is roughly 4 eV, but with Ce$^{3+}$ ions in the crystal lattice, which could be considered a part of a Ce$_2$O$_3$ species, this ionisation creates a trap state above the CeO$_2$ valence band which corresponds to the Ce$^{5d}$ - Ce$^{4f}$ transition. Furthermore, in their work it was found that the red shift in the bandgap is due to the presence of Ce$^{3+}$ at grain boundaries and the gap decreases with the increase in Ce$^{3+}$ concentration which forms localised gap states in the bandgap [27]. In addition to this, another paper by Yin et al. describes the experimentally observed Ce$_2$O$_3$ bandgap typically ranging between 3.03 eV to 3.7 eV. However, $E_g$ depends on the synthesis procedure, growth and post-growth process temperatures, and the size of the nanoparticles [28]. Such findings suggest that the synthesised undoped nanoceria in this work contains a mixture of cerium atoms in the Ce$^{4+}$ and Ce$^{3+}$ states along with the accompanying oxygen vacancies.

Some groups have tried to quantify Ce$^{3+}$/Ce$^{4+}$ concentration using UV-vis spectrophotometry and consequently, have measured the change in bandgap values. The
change in $E_g$ can usually be performed by doping CeO$_2$ with transition-metal ions such as Fe, Mn, Ti, and Co. This results in the formation of localised energy states that are closer to the conduction band and thus decreasing the bandgap [29]. However, the change in $E_g$ has been measured using diffuse reflection techniques, which can be inaccurate due to the existence of the specular reflectance [30]. Also, the 1.0 nm fixed bandwidth instruments can affect the peak resolution and bring about a decrease in the signal-to-noise ratio [30].

2.4.6 - X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out in Dublin City University (DCU) in the Nano Research Facility (NRF) with the help of the senior technician responsible for the equipment. This analysis was carried out in order to qualify and quantify the surface chemical structures and the ionisation states of the synthesised CeO$_2$ NPs. In an attempt to analyse the oxidation state of cerium ions, cerium 3d spectra were measured, in which the shifts in binding energies were calibrated using the C 1s peak as a reference at a binding energy of 284.8 eV. The XPS spectra of the Ce 3d level can be deconvoluted and separated into Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ peaks. The peaks in the range 875-895 eV were assigned to the Ce 3d$_{5/2}$ while peaks between 985-910 eV correspond to Ce 3d$_{3/2}$ levels as can be seen in Fig. 2.12 [31].
The software CasaXPS ® was used to carry out the calculations of integrated areas of the peaks. Peaks were fitted with a Gaussian line shape over a Tougaard background [31]. The assignment of Ce$^{4+}$ 3d component (3d$_{5/2}$: 888.3 eV; 3d$_{3/2}$: 906.5 eV) and Ce$^{3+}$ 3d component (3d$_{5/2}$: 879.2 eV, 891.1 eV; 3d$_{3/2}$: 903.7 eV) from XPS spectra agrees with results found in the literature [31]. The estimation of Ce$^{3+}$/Ce$^{4+}$ ratio was found to be 59.44% for Ce$^{3+}$ and 40.87% for Ce$^{4+}$, which agrees with the result found for diffuse reflectance where $E_g$ of 3.23 eV indicates a higher concentration of Ce$^{3+}$. It should be noted that the XPS spectrum suffers from a huge background interference with varying FWHM and it can lead to significant over or
underestimation of $\text{Ce}^{3+}$ content. Paparazzo et al. reported that several cases of peak fitting of Ce3d spectra which are affected by inaccuracies and inconsistencies [37]. In addition to the underestimation of $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio, it should be pointed out that the XPS technique is performed under high vacuum conditions (mbar). Thus the interpretation of this data can be ambiguous, leading to the inaccuracy of the calculated ionisation states of cerium due to the increase in the O-vacancy concentration observed under such vacuum conditions. This issue has been reported by Qiu et al. [32]. However, it seems that in the literature this factor has not been taken into consideration. There is seldom mention of this interference and the limitation of this technique [33,34,36]

2.4.7 - Brunauer–Emmett–Teller (BET) analysis

BET measurements were carried out in DCU in the NRF with the help of the senior technician responsible. The BET theory is commonly used in systems of multilayer adsorption in order to quantify specific surface areas. This is the measure of how much-exposed surface area a structure has. Table 2.3 shows the specific surface area of the optimum synthesised CeO2 NPs formed under different annealing temperatures (Appendix I shows the raw data).

**Table 2.3** The specific surface area of CeO2 nanopowders annealed at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing temperature (ºC)</th>
<th>Specific surface area (m²/g)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂-1</td>
<td>300</td>
<td>95.42 ± 0.02</td>
<td>2.41 ± 0.08</td>
</tr>
<tr>
<td>CeO₂-2</td>
<td>600</td>
<td>68.24 ± 0.05</td>
<td>8.81 ± 0.12</td>
</tr>
<tr>
<td>CeO₂-3</td>
<td>900</td>
<td>34.21 ± 0.01</td>
<td>26.63 ± 0.15</td>
</tr>
</tbody>
</table>
The results obtained indicate that the crystallite size found by XRD analysis, increases as the annealing temperature increases, and the surface area decreases as the annealing temperature increases. This finding is in agreement with the data reported by Zhlobak et al. where the CeO$_2$ presented a decrease in the surface area with an increase in annealing temperature. However, the values are slightly different in their work like the sample annealed at 600°C showed a surface area of 45 m$^2$/g [36]. The possible reason for this difference could be due to the synthetic method; in their work CeO$_2$ NPs were stabilised with sodium citrate.

2.5 – Conclusions

This chapter describes the synthesis and characterisation of CeO$_2$ NPs. CeO$_2$ NPs morphology and surface chemistry can vary widely depending on the synthesis method used. A new method was developed for the fabrication of CeO$_2$ NPs by using frozen NH$_4$(OH) cubes as a precipitating agent to precipitate Ce(OH)$_4$ from cerium nitrate, resulting in a greater yield of nanoparticles, along with an experimental design strategy to evaluate the best parameters and conditions for the methodology was also employed.

CeO$_2$ NPs were produced with a mean size of 35 nm for the hydrosol (final product of ceria synthesis) measured by SEM. The distribution size measured by DLS differs from SEM, where DLS presents a smaller nanoparticles distribution. However, the CeO$_2$ used for DLS measurement was in acidic suspension. The CeO$_2$ NPs were monodisperse, uniformly distributed nanoparticles for the powder form (dried hydrosol), then annealed at 300ºC, 600ºC and 900ºC resulting in CeO$_2$ NPs with FCC structure. The nanoceria particles showed a strong UV-vis absorption below 300 nm. The direct band gap was found to be 3.7 eV using the Tauc plot principle. The EDS and Raman results analysis confirmed the CeO$_2$ composition and
structure respectively. The BET specific surface area agreed with increased crystallite size as the annealing temperature increased. XPS measurement estimated the concentration of cerium states in the synthesised sample, where Ce$^{3+}$/Ce$^{4+}$ ratio was found to be 59.44% for Ce$^{3+}$ and 40.87% for Ce$^{4+}$.

Compared to other methods, chemical precipitation, which was selected for this work, is more attractive due to the use of inexpensive salt precursors, simple operation, and ease of potential mass production. Future studies should focus on a better understanding of how this synthetic technique affects the properties of nanoceria, in particular the concentration of oxygen vacancies. For this doping studies are recommended. It is expected that CeO$_2$ NPs can find many different potential applications. Two will be further explored in this work, namely catalyst sensors and in low energy electronic materials devices.
2.6 - References


CHAPTER 3

PHOTOCATALYSIS OF ORGANIC POLLUTANTS
Chapter 3 – Photocatalysis of organic pollutants.

3.1 – Introduction

In this chapter, the use of CeO₂ NPs was explored for the photodegradation of organic compounds and the identification of degradation products was carried out. Firstly, a quick discussion is given on semiconductor photochemistry.

3.1.1 Semiconductor Photochemistry

In a semiconductor, the molecular orbitals interact to form broad energy bands. The electronic structure of semiconductors (e.g. CeO₂, TiO₂, ZnO, CdS, ZnS) is characterised by an occupied valence band (VB) filled with electrons and conduction band (CB) [1]. Electronic conduction is generated by the movement of holes in the valence band and also by the movement of electrons in the conduction band for an undoped semiconductor. The energy difference between the lowest energy level of the CB and the highest energy of VB is known as the bandgap (\(E_g\)), the electron volt (eV) and the Fermi level can be considered to be a hypothetical energy level of an electron (\(E_F\)) which is mid-way between the VB and CB [2].

Irradiation of a semiconductor with photons of energy equal to or exceeding the \(E_g\) results in promotion of an electron from the VB to the CB, leaving a hole (h⁺) behind in the VB. Conduction is achieved by movement of the h⁺ in VB and also by the movement of this new e⁻ in the CB [2-3]. Figure 3.1 shows a schematic energy level diagram of these activities. The Fermi level lies halfway between VB and CB for an undoped and intrinsic semiconductor (in which the number of charge carriers is determined by the properties of the material itself and not due to the number of impurities present) [3].
Figure 3.1 Valence band model for an undoped, intrinsic semiconductor. The valence band is filled with electrons and holes. Adapted from Ref. [1].

The typical energy bandgap for many semiconductors (Table 3.1) falls in the region of 1-3 eV approximately and is in the visible light region of the electromagnetic spectrum, as previously discussed in chapter 2. Semiconductors absorb light below a threshold wavelength \( \lambda_g \), the fundamental absorption edge, which is related to the bandgap energy. Table 3.1 lists the \( E_g \) for many semiconductors reported in the literature. One such compound which is often utilised for photocatalysis is TiO\(_2\) NPs. Its \( E_g \) is listed in this table as 3.2 eV (anatase) and 3.0 eV (rutile) [2].
Table 3.1 Bandgap energy, $E_g$, and corresponding wavelength $\lambda_{bg}$ for a selected few undoped semiconductors that are in widespread use [1].

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>$\lambda_{bg}$ / nm</th>
<th>$E_g$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>350</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>390</td>
<td>3.2</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>390</td>
<td>3.2</td>
</tr>
<tr>
<td>CeO (This work (nanopowder))</td>
<td>335</td>
<td>3.2</td>
</tr>
<tr>
<td>TiO$_2$ (anatase crystal form)</td>
<td>390</td>
<td>3.2</td>
</tr>
<tr>
<td>TiO$_2$ (rutile crystal form)</td>
<td>410</td>
<td>3.0</td>
</tr>
<tr>
<td>CdS</td>
<td>520</td>
<td>2.4</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>590</td>
<td>2.1</td>
</tr>
<tr>
<td>CdS</td>
<td>730</td>
<td>1.7</td>
</tr>
<tr>
<td>CdTe</td>
<td>890</td>
<td>1.4</td>
</tr>
<tr>
<td>InP</td>
<td>950</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Solar irradiation generally starts at about 300 nm, but only around 5% of the solar spectrum (in the UV region) can activate TiO$_2$ NPs. As TiO$_2$ absorbs only light of $\leq$410 nm, it does not use sunlight very effectively. This is due to the fact that 95% of the total energy of the solar spectrum lies at wavelengths above this value [1]. Aside from TiO$_2$ NPs another oxide, CeO$_2$ NPs is a potential choice as a photocatalyst, as it is abundant, inexpensive and can be prepared in a facile way, as discussed previously in chapter 2. In contrast, the synthesis of the commonly used TiO$_2$ photocatalyst usually requires high energy (temperatures typically above 1000°C) and carefully controlled conditions, as previously discussed in chapter 1. However, TiO$_2$ has a much smaller bandgap compared to cerium dioxide, as will be discussed further in the sub-chapters. Table 3.2 shows a list of some of the values of $E_g$ for CeO$_2$ NPs found in the literature, its respective preparation method and the photocatalytic degradation efficiency for
different organic pollutants. As can be seen in Table 3.2 there appears to be a wide variation in the reported $E_g$ values, probably due to the various production methods utilised.

<table>
<thead>
<tr>
<th>$E_g$ (eV)</th>
<th>Synthetic method</th>
<th>Photocatalytic degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>Hydrothermal</td>
<td>0.03 mM Amido black, achieving 45.6% degradation efficiency in 170 min with 1 g/L catalyst, using a 250 W high-pressure mercury lamp [4].</td>
</tr>
<tr>
<td>3.6</td>
<td>Self-propagating solution combustion method</td>
<td>40 ppm DR-23 dye, achieving 80% degradation efficiency in 90 min with 0.5 g/L catalyst, using a 125 W low-pressure mercury lamp [5].</td>
</tr>
<tr>
<td>3.5</td>
<td>Microemulsion</td>
<td>50 ppm RO 16 dye, achieving a full degradation in 2h with 0.03 g/L catalyst, using a 400 W high-pressure mercury lamp [6].</td>
</tr>
<tr>
<td>3.2</td>
<td>Co-precipitation</td>
<td>10 ppm Diclofenac, achieving 56% degradation efficiency in 3h with 1 g/L catalyst, using a solar simulator.</td>
</tr>
</tbody>
</table>

### 3.1.2 Mechanism of Heterogeneous Photocatalysis.

In the last 40 years, the field of heterogeneous photocatalysis has undergone a large number of developments due to its use in the energy and environmental fields [4-7].

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Heterogeneous photocatalysis is defined as the acceleration of a photoreaction in the presence of a catalyst [3]. The main applications of photocatalysis are in the use of semiconductor materials for solar water splitting into H₂ and O₂ and in the purification of water-containing low concentrations of organic pollutants [8]. This is due to the ability of the semiconductors (Table 3.1) to oxidise organic and inorganic compounds in air and water through redox processes, initiated by the generation of electron and hole pairs. The photocatalyst harnesses UV radiation from sunlight or artificial light and uses the energy to break down molecules; such as organic materials, organic acids, estrogens, pesticides, dyes among other compounds [9].

A key concept of photocatalysis by semiconductor is that the flow of electrons and holes must be equal in order to maintain charge balance. If they are not, then either the surface becomes electrostatically charged and the process stops, or another electrode must be present to complete the electrical circuit. These species (e⁻ and h⁺), produced by the absorption of light, can then either recombine or they may migrate to the surface of the CeO₂ particle, where they can then react with other species at the photocatalyst-solution-interface [3,10].

Furthermore, photo-generated electrons in CB (solid/liquid) may reduce dissolved oxygen to water, producing reactive oxygen species (ROS) including superoxides O₂⁻, HO₂⁺, H₂O₂ and hydroxyl radicals OH•. These by-products are very strong oxidants capable of oxidising organic contaminants that may be present in water [1-3]. Consequently, a large number of these oxygenated species are typically formed on the surface of a CeO₂ photocatalyst under UV exposure, thus facilitating the rapid photodegradation of large organic compounds into smaller molecules, as shown in figure 3.2. In other words, the UV light can excite the
electrons from the VB to the interband Ce 4f levels or from the Ce 4f levels to the conduction band, CB leading to the formation of e⁻ and h⁺ [10].

The e⁻/h⁺ pair recombination can happen in a very short time (nanoseconds). As a result, the electrons return to the ground state of the semiconductor, and thus the photocatalysis can be stopped. Alternatively, competition between radical and e⁻/h⁺ pair reactions can take place on the surface of CeO₂. Some species are capable of seizing the photogenerated electron (e.g. Ag⁺, Pd⁺), thus preventing recombination. This can allow the holes to do their job more effectively [11]. Absorption of light energy by CeO₂ to form e⁻/h⁺ pairs and subsequent combination with anions to form radicals are presented in Equations 3.1 and 3.2 respectively.

In Eq.3.2 the holes oxidise OH⁻ producing hydroxyl radicals.

\[ \text{CeO}_2 (h^+) + \text{OH}^- \rightarrow \text{OH}^- + \text{CeO}_2 \]  

\[ \text{CeO}_2 \xrightarrow{h^\nu} \text{CeO}_2 (h^+…e^-) \]  

**Figure 3.2** Pictorial representation of a photocatalytic degradation mechanism of an organic contaminant involving the reaction of CeO₂ NPs under UV-light irradiation. Adapted from Ref [5].
The reaction rate in a photocatalytic process is a function of light intensity: starting with a linear dependence at a low light intensity, having a transition at moderate light levels, and becoming light-intensity independent after the light exceeds intensity a certain value (saturation) [12]. This type of behaviour comes from a large number of reactions involved during the photocatalytic process, such as the generation and annihilation of oxidation sites, and the evolution of OH• radicals [9]. The e− and h+ recombination process can take place both on the surface of the particle and in its interior, with the latter situation being one of the problems of heterogeneous photocatalysis. Ultimately the photocatalytic reaction finally resulting in the formation of carbon dioxide and water, if the reaction goes to completion, which is known as mineralisation [8].

In this work, the energy source to provide UV radiation was a xenon short-arc lamp which produces a bright white light that closely mimics natural sunlight, and generates significant ultraviolet radiation. Fig 3.3 displays the xenon lamp spectra which has strong spectral lines in the UV region. An air mass 1.5G filter was used to modify the spectral output of the arc lamp to match the specific solar conditions.
3.1.3. Photodegradation of dyes and diclofenac.

There is considerable interest in the use of metal-oxide nanoparticles as photo-catalysts in order to degrade organic contaminants, especially in wastewaters. TiO$_2$ NPs is conventionally used in such studies [11,14]. This chapter investigates the use of CeO$_2$ NPs as a possible alternative to TiO$_2$ NPs as a metal-oxide photo-catalyst for the photodegradation of organic compounds.
Many dyes are stable, and highly coloured organic compounds. However, they may present a risk for the environment when they enter aquatic systems. Due to the increase in industrial processes in the textile and clothing manufacturing industries, these effluent streams must be treated [15]. Methyl Orange (MO) is a dye widely utilized for different industrial and academic purposes (biological experiments), or as an acid-base indicator in analytical chemistry. Fig 3.4 shows the chemical structure of MO. It comprises an azo group (N=N) which bridges two aromatic rings, with a sulfonate group (H-S(=O)₂-OH) on one aromatic ring.

![Chemical Structure of Methyl Orange](image)

**Figure 3.4** Chemical Structure of Methyl Orange (IUPAC name Sodium 4-\{(4-(dimethylamino)phenyl)diazenyl\}benzene-1-sulfonate).

The photocatalytic ability of CeO₂ was demonstrated through the photodegradation of MO dye as an organic compound model pollutant. It was reported that the ceria photocatalytic activity is also determined by nanoceria particle size. According to Zholobak et al., 1–2 nm nanoceria did not show any photocatalytic activity for MO photodegradation. Once the particle size was increased to 16 nm, however, CeO₂ NPs exhibited a degradation amount efficiency of 43% of MO under UV irradiation [15].
Another water contaminant of environmental concern is diclofenac (DCF). It is a non-steroidal anti-inflammatory drug (NSAID) which is commonly used to reduce pain and inflammation. It is the active ingredient used in Voltarol® that is commonly used for migraines, and for physical injuries like sprains and strains [16] and is commonly detected in water sewage effluents, as previously discussed in chapter 1. The structure of DCF is presented in Figure 3.5.

Figure 3.5 Chemical Structure of Diclofenac sodium salt (IUPAC name sodium (2-[2-(2,6-dichloroManynilino)phenyl]acetate).

Diclofenac is difficult to remove using conventional wastewater treatment plant (WWTP) with a removal efficiency typically being around 30-70% [16]. A recent study conducted by the Environmental Protection Agency (EPA) Ireland quantified five pharmaceutical residues including Diclofenac, Mefenamic acid, Trimethoprim, Carbamazepine and Gemfibrozil, measured in effluent and seawater for 3 and 12-month intervals in Dublin Bay and Galway Bay, as most WWTPs are located in the country’s coastal
areas. They confirmed that the DCF residues of interest was present in low concentrations, with DCF having a concentration of 2.8 µg/L and 1.1 µg/L in effluent water and seawater respectively in Galway Bay, and concentrations of 2.3 µg/L and 0.6 µg/L for effluent water and seawater respectively in Dublin Bay over a 12 month period [17].

The harmful effects of DCF on different organisms in aquatic environments have been demonstrated recently [18,19]. Diclofenac can influence the biochemical functions of fish such as trout, zebra fish and mussels leading to tissue damage [18]. Chronic toxicity experiments were carried out on rainbow trout. After 28 days of exposure to about 1 µg/L of diclofenac cytological changes were observed in the trouts kidneys, gills, and liver. At a concentration of 5 µg/L, drug bioaccumulation occurred in liver, kidney, gills, and muscles was observed [19].

The main natural process of degradation DCF is photo-transformation by sunlight, which can cause an adverse impact on the environment. This is due to DCF reactivity where it can interact/combine/aggregate with other pollutants of the same or different class of chemical compound [20].

Up to now, no reports have been found in the literature on the use of nanoceria to carry out the photodegradation of diclofenac, although the use of TiO2 NPs for the same purpose has been investigated by Espino-Estévez et al [11]. In their research, Pd and Ag were deposited on the surface of TiO2 nanoparticles and the photodegradation rates were enhanced by a factor of 1.93 times, under UV irradiation. The highest rate of degradation was obtained when TiO2 doped with Pd was used, compared to bare TiO2. The type of metal utilised had an effect on the mechanism of the reaction, and different photoactivity for the decomposition of several organic compounds was observed. However, the addition of this precious metal, would make
this catalyst more expensive and hence would not be a practical option for use in a WWTP [11].

3.2 – Experimental

3.2.1 – Materials

Ultrapure water (18.2 MΩ·cm) was used for the freshly prepared solutions. All chemicals were obtained from Sigma, Fluka and Fisher Scientific and were used as purchased without further purification, as listed below:

- Acetonitrile (ACN) LC-MS grade (Fisher)
- Commercial Cerium (IV) oxide NPs in 10 wt% water suspension (<25nm) (Sigma)
- Formic Acid (FA) LC-MS grade (Fisher)
- Methyl Orange (MO) analytical grade (Fluka)
- Sodium Diclofenac analytical grade (DFC) (Sigma)
- Synthesized Cerium dioxide nanoparticles (<35 nm) (Described in chapter 2)
- Titanium dioxide (TiO₂) analytical grade (Degussa – P25) (Fisher)
- Water LC-MS grade (Fisher)

3.2.2 – Equipment

Photocatalytic experiments were performed in a water bath system in an attempt to maintain the reaction at a constant temperature near room temperature. A solar simulator, as can be seen in Fig 3.6 (ABET SUN 2000), based on a Xenon Mercury arc lamp 1 kW was used as the light source, emitting radiation between 280 to 420 nm.
Figure 3.6 Photograph of the solar simulator (ABET SUN 2000) used in this work. The arrows show the direction of the emitted light.

All reactants in the photoreactor (not inside photoreactor but in a beaker placed beneath the light source) were stirred using a magnetic stirrer and a Thermo Scientific megafuge 16R centrifuge was utilised to separate the nanoparticles. To monitor the reaction progress, the decrease of absorbance at 276 nm (wavelength of DCF) was measured using a UV-Vis spectrophotometer (Lambda 900) and a pair of 1.0 cm matched quartz cells.

In order to identify the products of photodegradation of DCF an Agilent 6500 Series TOF Q-TOF LC/MS coupled with a UV detector was utilised. The method was obtained from Kovacic et al. and it was optimized and adapted for these conditions [21]. For separation, the
column used was a Zorbax Eclipse plus C18 (2.1 x 50 mm with 1.8 \( \mu \text{m} \) particle size). The flow rate of mobile phase was 0.3 mL/min, and the injection volume was 5 \( \mu \text{L} \). The mobile phase was isocratic (45% of A and 55% of B) with a composition of solvent A (H\(_2\)O + 0.1% Formic acid (FA)) and solvent B (ACN + 0.1% FA). The separation was performed at a temperature of 40ºC. Mass spectroscopy was carried out in both negative and positive electrospray ionization (ESI – (+)) modes, with a capillary voltage of 3500 V, and a nebuliser pressure of 40 psi. The drying gas flow was set to 9 L/min, with a sheath gas (N) of 400ºC, the skimmer of 35 V, a fragment voltage of 100 V and collision energy of 20 V. The mass range was set from \( m/z \) 50 to \( m/z \) 500 with a spectra acquisition rate of 1 Hz. The software “Mass Hunter workflow” was used to identify the degradation products. The spectra of the reused CeO\(_2\) NPs was analysed by using Raman Spectroscopy (Horiba Jobin Yvon, LabRAM HR 800).

3.2.3 - Methodology

The photodegradation of MO and DCF was studied in the presence of CeO\(_2\) hydrosol (final product of CeO\(_2\) synthesis) for MO and with CeO\(_2\) nanopowder for DCF. It should be noted that as previously discussed in chapter 2, method B (frozen NH\(_4\)(OH) cubes) showed a higher concentration of NPs. However, it did not affect the results of photocatalysis, which employed both types of NPs obtained from the two methods A and B. An initial MO concentration of 2 mg/L was prepared. The DCF concentration was varied from 10 mg/L to 30 mg/L (in accordance with typical reported environmental concentration levels and levels with proven toxic effects) [17]. The solutions of MO and DCF were kept at room temperature while being irradiated.
The distance between the solutions and the light source was approximately 10 cm, and it was illuminated from the top (light source) to the bottom (sample), as can be seen in Fig 3.7. All reactants in the beaker were stirred with a magnetic stirrer to ensure that the catalyst was uniformly distributed during the course of the reaction. With respect to the adsorption onto the CeO$_2$ particles, the beaker was kept in the dark for 20 min initially to attain adsorption/desorption equilibrium between the organic pollutants (MO, DCF) and the CeO$_2$ NPs surfaces.

**Figure 3.7** Diagram illustrating the arrangement of Photodegradation apparatus.

Figure 3.7 shows a representation of the photodegradation apparatus. In order to determine the percentage of dye and DCF degradation, the samples were collected at regular intervals of 20 min. For the DCF photodegradation reaction, centrifugation was performed at 5000 rpm for
5 min at 10°C in order to remove the nanoparticles, this process was very important to make sure that there were no residual NPs were present which could be detrimental for the subsequent LC/MS analysis. All experiments were performed at pH 7.

To carry out the absorption measurements, the sample absorbances of MO and DCF were measured at $\lambda_{\text{max}}$ of 465 nm and 276 nm respectively. The absorbance of both solutions at an initial ($A_o$) and after a specific time ($A_t$) was used in conjunction with Beer’s Law (Eq.3.3) to calculate the degradation efficiency [13].

$$A = \epsilon \cdot b \cdot c$$  \hspace{1cm} (3.3)

where $A$ is the absorbance (optical density), which has no units, $\epsilon$ is the molar absorptivity/extinction coefficient of the organic pollutant, Lmol$^{-1}$ cm$^{-1}$, $b$ is the length of the light path, in cm and $c$ is the concentration of the organic pollutant in solution in mol/L.

UV-Vis spectroscopy was used to calculate the MO/DCF degradation efficiency using equation 3.4:

$$\text{degradation (\%)} = \frac{C_o - C_f}{C_o} \times 100$$  \hspace{1cm} (3.4)

where $C_o$ and $C_f$ are the initial and final concentration of MO/DCF solutions.

3.3 – Results and Discussion

3.3.1 - Photodegradation of Methyl Orange in acid media

As a model organic pollutant, methyl orange was selected because it is stable in acid media. The same experiment was initially carried out with Methylene blue (MB), but it did not
show stability in the nanoceria hydrosol conditions at pH 1. The decrease in the absorbance value at 480 nm corresponding to the peak for the absorption spectra of MO Fig 3.8 (a), which is typical of a substituted azobenzene, was utilised to determine the extent of degradation of MO [7]. Figure 3.8 shows the photodegradation over time of Methyl Orange at 2 mg/L carried out under simulated solar light irradiation. It is clear that MO degrades in the absence of photocatalyst but only at a very slow rate. As the nitric acid present in the formulation of CeO₂ NPs hydrosol can also decompose dye, the efficiency of nanoceria hydrosol was compared to that of HNO₃ at the same % v/v used for CeO₂ hydrosol production and MO without any catalyst. The pH of the solution was determined to be 3.0.
The complete decolourisation of MO was observed after only 20 min of illumination. The half-life $t_{1/2}$ of the decaying concentration of MO under HNO$_3$+UV was 71 min and for CeO$_2$ + UV was only 10 min. This rapid decrease in absorbance could be explained by the electrostatic interaction between the CeO$_2$ NPs (adsorbent) and MO (adsorbate). The $\zeta$-potential measurement carried out in chapter 2 of +32.3 mV confirms that CeO$_2$ has a positively charged surface strongly favouring the adsorption of the negatively charged MO dye molecules.
[22]. However, the observed photobleaching may have been due to dye photosensitisation, mechanism as discussed previously in Chapter 1 (section 1.3.1) rather than photocatalysis of MO. Where an oxidised radical of the MO that is unstable was able to react further to produce colourless degradation products [34].

The presence of CeO$_2$ NPs leads to an increase in degradation efficiency compared to HNO$_3$ alone, which reaches up to 90% degradation in 45 min with 1.5% v/v of nanoceria, as can be seen in Fig. 3.9. Above 2% v/v, it was no longer possible to carry out the absorption measurements, possibly due to the saturation of active catalyst surface sites, making it clear that MO is not stable under solar simulation and in acid media. The possible reason for the instability could be the MO pK$_a$ of 3.4, as at low pH. This is attributed to protonation at the azo group to form the azonium ion. The dimethylamino group has a lower affinity for protons and the production of the ammonium ion results in a weaker absorption as reported by Oakes et al. and di-protonation becomes important at still lower pH [23]. It was reported by Zholobak et al. that colloid solutions of CeO$_2$ NPs stabilised by sodium citrate did not exhibit good photocatalytic activity for MO photodegradation under UV irradiation. They reported a degradation efficiency of 43% in 2h, compared to TiO$_2$ and ZnO that fully degraded MO over the same time period [15].
Figure 3.9 Graph showing the photodegradation efficiency of MO at 2 mg/L versus time under different concentrations of CeO₂ hydrosol (final product of CeO₂ synthesis).

Positive holes are considered the main species responsible for oxidation at low pH, while hydroxyl radicals are considered as the predominant species involved in oxidation at neutral or high pH levels [24]. The protonation of the dye, as a result of variation of pH, can change its adsorption characteristics and thus alter the redox activity of the catalyst. For this reason, the degradation rate constant for the decomposition of MO was not calculated, due to the possible existence of a dual degradation mechanism arising from the reactivity of both CeO₂ and HNO₃. Oakes et al. for example, reported that the degradation of MO in acid media followed a second-
order rate constant [23]. However, in this work the CeO$_2$ hydrosol demonstrated an excellent degradation of MO achieving 100% decomposition in only 85 min.

3.3.2 – Photodegradation of Diclofenac sodium salt.

As previously discussed in chapter 2, CeO$_2$ was subjected to a thermal treatment; it was annealed at a set temperature of 300°C, 600°C or 900°C. The annealing temperature has a significant effect on the catalyst activity, as it can affect the physical properties of the material, such as porosity, surface area, and crystal size. It has been reported by Zhou et al. that CeO$_2$ nanostructures have highly actively exposed crystal planes such as \{110\} as can be seen in Fig 2.8 (section 2.4.3) in Chapter 2. These it can significantly increase its catalytic activity due to the higher reactivity of this plan [25].

A calibration plot for DCF was obtained. Concentrations ranging from 10 to 100 mg/L (in the range of EPA quantification as previously discussed [17]) were prepared and DCF concentration was then measured by measuring the absorbance at $\lambda_{\text{max}}$ of 276 nm. A calibration plot of absorbance versus concentration yielded a straight line going through the origin in accordance with Beer’s law with a slope equal to 0.0364 dm$^3$mg$^{-1}$ and a correlation coefficient value of 0.9950, which is shown in Figure 3.10.
Figure 3.10 Calibration plot for sodium diclofenac ($\lambda_{\text{max}}$ 276 nm). Absorbance vs the concentrations of 0-10 mg/L at pH 7. Duplicate measurements were carried out.

3.3.2.1 – Investigation of degradation efficiency under various conditions.

Control experiments were recorded in order to ensure that degradation took place only solely due to the presence of the CeO$_2$ NPs. Comparisons of DCF degradation was carried out in the presence and absence of nanoceria. A separate test was undertaken for the assessment of the efficiency of removal of CeO$_2$ NPs, since CeO$_2$ can absorb at around 276 nm. In order to determine if the mechanism of this photocatalysis is oxygen dependent, deoxygenation of the
system was also carried out using oxygen-free nitrogen gas in order to remove the solution’s dissolved oxygen.

Figure 3.11 Plot showing the variation in degradation efficiency over time of DCF (10 mg/L) under various conditions; in the presence and absence of nanoceria (1 g/L), the efficiency of removal of CeO₂ nanopowders, nanoceria in the absence of radiation (solar light) and the deoxygenated system at pH 7.

It can be seen in Figure 3.11 that some degradation of 10 mg/L DCF occurred under solar light (photolysis) without nanoceria being present, but the degradation efficiency is enhanced
in the presence of CeO₂ nanoparticles (photocatalysis). For the oxygen-free system, no degradation took place under the same conditions, thus demonstrating that the reaction is oxygen-dependent. No change in absorbance of the irradiated sample with nanoceria was observed, which indicates that the centrifugation at 5000 rpm for 5 min at 10°C was sufficient to remove the CeO₂ NPs from the sample solution and therefore would not cause any interference in the absorbance of diclofenac. When the reaction was performed in the dark, a slight decrease in DCF concentration occurred, possibly some due to surface adsorption, which reached equilibrium after about 20 min. The reason for this adsorption could possibly be that DCF is negatively charged due to the presence of the carboxyl group (C(=O)OH). On the other hand, CeO₂ (like many other metal oxides) becomes charged by the adsorption of hydrogen ions (H⁺) at low pH or hydroxide ions (OH⁻) at high pH, while remaining essentially uncharged at pH 7 [26]. Furthermore, the isoelectric point (IEP) which is the pH where CeO₂ carries no net electrical charge can vary from 5 to 8 [22].

The plot of % degradation versus irradiation time presented in Fig 3.11 indicates that, over the 120 min irradiation time, diclofenac was degraded by 56% in the presence of CeO₂ NP, while in the absence of CeO₂ NPs it was only degraded by 35%. Therefore, the degradation of DCF was enhanced 1.6 times more than it was in the absence of CeO₂ NPs.

As mentioned before (section 3.1.2), the photocatalytic activity depends on the ability of the catalyst to separate the electron hole-pair. The rate of separation and recombination are key factors for good photocatalysis. The h⁺ can oxidize the ions OH⁻ to produce radicals OH• in the VB. Meanwhile, the e⁻ in the CB can reduce oxygen to form the superoxide radical anion O₂•⁻. The apparent incomplete degradation of DCF determined by UV measurements may be
due to the formation of products which also absorb at 276 nm, possibly leading to a saturation of available surface sites. Such behaviour has also been reported by Rizzo et al. for a TiO$_2$ catalyst [27].

3.3.2.2 – Optimisation of the photodegradation reaction.

An optimum amount of CeO$_2$ should be utilised to avoid unnecessary excess catalyst and to ensure the sufficient absorption of light photons for efficient photodegradation. The degradation efficiency of DCF (10 mg/L) was analysed at different photocatalyst dosages ranging from 0.5 to 1.5 g/L (as reported by other authors [11, 24]). Figure 3.12 indicates that the photodegradation efficiency of DCF increased with an increase in the amount of photocatalyst from 0.5 to 1 g/L and then decreased with a photocatalyst loading of more than 1g/L. One possible explanation for this observation could be due to the agglomeration of a large number of CeO$_2$ NPs above 1g/L which could cause interference due to light scattering.
Although it can be observed in figure 3.12 that the % degradation increased over time, it is not always linear for some catalyst concentrations. This could be due to the limited mass transport of reactants during the stirring regime; even though the solution was continuously stirred with a magnetic stirrer throughout the degradation experiment, it was difficult to reproduce the same level of stirring for all the samples. Furthermore, is not possible to ensure that the same amount of nanoparticles (consistency) are removed at each time interval. If a new stirring system was introduced such as a flow rate apparatus, in which the flow of liquid can be accurately controlled using a pump or another system. In which a well-defined mass transport regime was applied, perhaps a more linear increase of degradation efficiency could
be obtained. However, from the results presented the optimum concentration for CeO₂ NPs was 1 g/L. This agrees with the data reported by Pouretedal et al., whereby the same concentration of CeO₂ was utilised for the most efficient photocatalysis of MB [24].

Figure 3.13 displays the degradation efficiency of DCF catalysed by nanoceria annealed at 300°C, 600°C and 900°C. The nanosized CeO₂ annealed at 900°C showed the highest photoactivity among the prepared nanoparticles. This could be explained by the fact that, since the annealing temperature is very high it could have increased the concentration of point defects such as oxygen vacancies (Ce³⁺) as previously discussed in chapter 2, where the bandgap was found to be 3.23 eV. Reed et al. reported that the increase of oxygen vacancies is not only confined to high vacuum or high-temperature conditions, it’s also related to the particle size. CeO₂ can be thought of as an “oxygen buffer” that provides or removes oxygen to/from the surrounding environment by responding to a lack or excess of oxygen in that environment [43]. This makes CeO₂ NPs unique and is currently a matter of debate since its lattice can also expand as the particle size decreases, leading to a decrease in oxygen release and reabsorption [43].

Pouretedal et al. reported that CeO₂ nanopowder produced at 600°C showed the best performance in the photodegradation of 20 mg/L of Methylene Blue using UV and a degradation efficiency of 90% was achieved in 125 min [24]. The possible reason for the difference in the behaviour of the annealed nanoceria to our work (900°C) could be that in their case a different synthetic method (hydrothermal synthesis) was employed. In contrast, for this work, the use of higher temperature (900°C) to remove any impurities such as NH₄⁺, NO₃⁻ on the surface of the nanoparticles was essential in order to improve the nanoceria catalytic performance.
As can be observed in Fig 3.13, the commercial Sigma CeO$_2$ NPs annealed at 900°C showed similar degradation efficiency to the 900°C synthetic sample. This indicated that the synthesis of the in house CeO$_2$ annealed at 900°C is both cost-effective and a novel procedure which showed slightly enhanced catalytic performance when compared to the commercial nanoceria supplied from Sigma Aldrich (with an average particle size of 25 nm).
3.3.2.3 – *Comparison of diclofenac degradation catalyzed by CeO$_2$ and TiO$_2$.*

TiO$_2$ P25 is well known for its high stability and is the photocatalyst standard material widely used for a variety of organic and inorganic species. It has an average particle size of 25 nm and a surface area of 50 m$^2$/g. Its performance has been well documented in the literature [28, 29]. A comparison between the photocatalysis of DCF (10 mg/L) with the catalyst, CeO$_2$ synthesised in this work and the commercial TiO$_2$ (P25) was carried out. Figures 3.14 and 3.15 show the UV-Vis spectra obtained for DCF being degraded using CeO$_2$ NPs and P25 respectively. The same concentration of each catalyst was utilised (1 g/L). In these spectra, it can be seen that the absorption intensity of diclofenac gradually decreased with increasing irradiation exposure time.
Figure 3.14 Absorption spectra of DCF (10 mg/L) during photodegradation with CeO$_2$ NPs (1 g/L) annealed at 900ºC. (1) 0 min; (2) 20 min; (3) 40 min; (4) 60 min; (5) 80 min; (6) 100 min; (7) 120 min; (8) 140 min; (9) 160 min; (10) 180 min; (10) 200 min. Carried out under solar simulator, at pH 7.

A rapid decrease seems to occur after an equilibration time between the CeO$_2$ NPs/DCF. This is due to the initial occurrence of surface adsorption of DCF on CeO$_2$ NPs under dark conditions. After the first 20 min of the solar irradiation, the absorbance declined rapidly, then more gradually before finally levelling off at longer times. It should be noted that the photodegradation was carried out for 240 min. However, no decrease of absorbance was
observed after 200 min. This was most pronounced at 276 nm and it could possibly be attributed to the formation of aromatic compounds which can be detected at the same wavelength as DCF, or possibly even due to some residual diclofenac molecules being still left in solution. It was suggested by Calza et al. that DCF/TiO₂ photodegradation intermediates are formed by attack of hydroxyl radicals on the side chain favouring the inclusion of OH groups on the aromatic ring, which would produce aryl-hydroxy diclofenac intermediates. Those could be transformed into quinine, amine and chlorophenol derivatives. Eventually, cleavage of the C-N bond leads to the formation of 4-chlorocatechol and 2,6 dichlorophenol [14].

There appeared to be a slight shift in λ_{max} at 335 nm, 285 nm, 235 nm over time. An isosbestic point can be seen at 250 nm with a shoulder peak growing on both sides at 248 nm and 255 nm. It could indicate that only two species that vary in concentration contribute to the absorption around the isosbestic point [12]. Such increases in the absorption intensities could characterize the formation of intermediate oxidation compounds possessing double bonds [11]. For example, Cavalheiro et al. reported the formation of an absorption band at 250 nm associated with the by-product 8-chlorocarbazole-1-acetic-acid [30].

It was proposed by Espino-Estevez et al. that the two main intermediates that are generated in the highest quantities in DCF photo elimination performed by TiO₂ doped with Ag and Pd are hydroquinone and catechol. Lower concentrations of carboxylic acids were also produced; such as formic>oxalic>malonic>maleic acids and also some chloride, ammonium and nitrate ions [11].

In contrast, figure 3.15, P25 TiO₂ NPs shows complete degradation of DCF after 2 h (120 min) of irradiation with 10 mg/L as the initial DCF concentration using 1 g/L TiO₂ (P25). In
comparison for CeO$_2$ NPs under the same conditions degraded DCF by 56%. Furthermore, there are no distinct peaks formed at 250 nm as shown in figure 3.15. However, in 3.14 there is a small peak at 245 nm; which indicates that nanoceria might be transforming other diclofenac by-products and thus increasing these intermediates' concentration during the exposure to solar simulation.

**Figure 3.15** Absorption spectra of DCF (10 mg/L) during photodegradation with TiO$_2$ (1 g/L). (1) 0 min; (2) 20 min; (3) 40 min; (4) 60 min; (5) 80 min; (6) 100 min; (6) 120 min; (7) 140 min. Carried out under solar simulator, at pH 7.
It is important to mention that there is a slight difference between the band gaps of TiO\textsubscript{2} (anatase/rutile) and CeO\textsubscript{2} which are 3.0 and 3.2 eV respectively (Table 3.2). This may influence this difference in photodegradation efficiency possibly due to the rapid recombination of electrons and holes that might occur for CeO\textsubscript{2} with a higher E\textsubscript{g}. There are other factors too that could be influencing the mechanism of DCF degradation by CeO\textsubscript{2}; such as the fact that cerium dioxide is highly non-stoichiometric in nature (e.g. it has more inherent defects than TiO\textsubscript{2}) and therefore contains large numbers of various point defects (oxygen vacancies, cations interstitials etc)[31,32]. As previously discussed in chapter 1 in section 1.7 where the Pourbaix diagram suggests that at pH 7 and potential of 0 V (conditions of this experiment) CeO\textsubscript{2} is not thermodynamically stable and its subjected to reaction with peroxides, which may influence its photoactivity. However, for TiO\textsubscript{2} under the same conditions, there is no interference from peroxide species and it is stable (section 1.8).

There are many claims regarding the improvement of visible-light-absorbing semiconductor photocatalysts reported in the literature, for example, using dopants [4,6,7,11]. However, in some cases, as for example the photobleaching of a dye, the mechanism could have been due to dye photosensitisation, or photolysis, rather than photocatalysis [33]. Another possible explanation for the DCF photodegradation by CeO\textsubscript{2} NPs is that perhaps the diclofenac is forming a visible-light-absorbing ligand-to-metal charge transfer complex (e.g. LMCTC) with the nanoceria. This can be seen at the end of the reaction when the colour of the nanopowder changed from yellow to brown. Furthermore, the decrease in the concentration of DCF may involve the electronically excited state of the LMCTC, and the mechanism might not
be due to photocatalysis. Therefore, further studies exploring the use of action spectra and photonic efficiency should be carried out [33,34].

TiO₂ photocatalysts are better able to completely degrade DCF, while it appears that CeO₂ cannot fully degrade DCF. The main benefit of using ceria rather than the traditional TiO₂ is the simplicity and low cost of the novel preparation method outlined in this work (section 2.2.3).

3.3.2.4 – Effect of the initial concentration of DCF and kinetics.

Figure 3.16 shows the plots of absorbance versus time at $\lambda_{\text{max}}$ of 276 nm, for the concentrations of 10, 20 and 30 mg/L of DCF catalysed by 1 g/L of CeO₂ NPs under solar simulation.
Figure 3.16 (a) The plot of absorbance versus time for the photodegradation of diclofenac at concentrations of 10 mg/L, 20 mg/L and 30 mg/L of DCF catalyzed by 1 g/L of CeO$_2$ carried out under solar simulation for 3h, at pH 7. (b) Histogram summarizing the degradation efficiency at different concentrations of DCF after 3h irradiation (180 min).

The histogram in Fig 3.16 shows a small reduction in the degradation efficiency as the concentration of DCF increased. For all three DCF concentrations after 3 h of solar irradiation, the initial concentration halved. This was possibly due to the adsorption of more organic molecules onto the surface of the nanoparticles, thereby reducing the active sites available for further reaction. Furthermore, some of the photons also might have been absorbed by the organic molecule reducing the number of available sites rather than the photocatalyst itself.
which then reduced the rate of photo-activation of the nanoparticles at the higher concentrations.

As previously mentioned the degradation intermediates of DCF could also have contributed to the absorbance obtained during the spectroscopic analysis. Thus absorbance intensity values recorded that were assumed to be solely due to the DCF but could also have some additional contribution from other compounds as well. This could have caused interference with the results obtained for the change in absorption over time and subsequently affected the kinetic models of the photocatalytic degradation process. Due to the mutual effects of heterogeneous photocatalysis reactions and the possible influence of these many factors mentioned before, it was difficult to evaluate the rates of degradation of DCF catalysed by CeO₂ NPs. For this simple reason, kinetic plots were not used to characterise the mechanism.

However, in an attempt to gain insight into the kinetics of degradation of DCF, the data from Fig 3.15 was utilised using Beer’s Law as previously discussed. The degradation of 10 mg/L of DCF using TiO₂ as the catalyst was modelled using both pseudo-first order (Langmuir-Hinshelwood model) Eq.3.5 and zero-order kinetics, Eq.3.6 as follows.

\[
\ln \frac{C_0}{C_t} = k_{app}t
\]  

(3.5)

where \(C_0\) was the initial concentration of DCF (mg/L), \(C\) was the concentration at time \(t\) (min), and \(k_{app}\) was the apparent first-order rate constant (mol dm\(^{-3}\)min\(^{-1}\))

\[
C_t = -kt + C_0
\]  

(3.6)
where $C_0$ was the initial concentration (mg/L), $C$ was the concentration at time $t$ (min), and $k$ was the zero-order rate constant ($\text{mol dm}^{-3}\text{min}^{-1}$).

Figure 3.17 (a) displays the plots for the pseudo-first-order model for the degradation of 10 mg/L of DCF. According to Eq.3.5, the line of best fit should pass through the origin but the intercept obtained was slightly below this -0.1.

**Figure 3.17** (a) Plot of $\ln \left( \frac{C_0}{C_t} \right)$ versus time for the pseudo-first-order model. (b) Zero-order kinetic model for the degradation of DCF at 10 mg/L catalysed by TiO$_2$ nanoparticles (1 g/L) at pH 7 under the solar simulator.
According to Eq. 3.6 for the zero-order kinetic model the intercept should be the initial concentration \((C_0)\) of the sample, and the intercept obtained was 9.4 mg/L or \(2.95 \times 10^{-5}\) mol/L for the zero-order model as can be seen in figure 3.17 (b).

It has been reported by Espino-Estevez et al. that the photocatalytic degradation of DCF using a doped TiO\(_2\), followed a pseudo-first-order kinetic model (Langmuir – Hinshelwood) [11]. From the experimental results from this work, the data tended to suggest a pseudo-first-order kinetic model more closely compared to the zero-order model, the regression coefficient obtained being \((R^2=0.9875)\) and \((R^2=0.9833)\) respectively. This result suggests that the photodegradation of DCF photocatalysed by TiO\(_2\) fits more closely the pseudo-first-order kinetic model. Another study by Rizzo et al. indicates that, at low concentrations of diclofenac, (5–20 mg/L) the data suggested a pseudo-first-order reaction, but for higher concentrations (40 and 80 mg/L) and after an increase in TiO\(_2\) concentration, the data did not follow a pseudo-first-order model anymore. Instead a second-order kinetic model was a better fit for this reaction [27].

3.3.2.5 – Analysis of intermediates and degradation pathway of Diclofenac

It is evident that the degree of DCF degradation using CeO\(_2\) NPs did not attain 100%, as can be seen in Fig. 3.13. As discussed previously it was not possible to obtain complete degradation of DCF probably due to the presence of intermediates and/or products produced during the photodegradation reaction. There are a number of reports on the evaluation of degradation processes of DCF through mass spectroscopy under different conditions [30,35-38]. However, there are some difficulties to overcome such as the formation of a large number of unpredictable and unstable compounds that could complicate their identification; and the
absence in some cases of commercial standards that could be used to confirm their identity. In order to obtain information about the fragments’ ions, an LC-MS analysis was carried out and it revealed potential degradation products of DCF. Figure 3.18 represents the total ion chromatograms (TIC) in positive mode of 10 mg/L DCF standard (dashed line) and the degradation sample (solid line) after 3h of solar irradiation.

![Figure 3.18](image_url)

**Figure 3.18** Total ion chromatograms of 10 mg/L DCF standard (dashed line) and the degraded sample (solid line) after 3h of solar irradiation using 1 g/L of CeO$_2$ NPs. Analysis was carried out under ESI (+). Conditions are detailed in the experimental section 3.2.2.
As can be seen in Fig 3.18, the standard DCF (dashed line) has a retention time (RT) of 1.14 min and the irradiated DCF sample (solid line) shows a decrease in the concentration of DCF peak to half of its original value as discussed previously with the UV-Vis results. The irradiated sample also shows several new peaks at lower RTs than DCF and for further discussion, these will be referred to as degradation products DP1=0.32 min, DP2=0.61 min and DP3=0.88 min (as identified in Fig 3.18). Their shorter RT values suggest that the DPs are smaller molecules (fragments) than DCF.

![Figure 3.19](image-url)

**Figure 3.19** Total ion chromatograms of 10 mg/L DCF standard (dashed line) and the degraded sample (solid line) after 3h of solar irradiation using 1 g/L of CeO₂ NPs. The analysis was carried out under ESI (−). Conditions are detailed in the experimental section 3.2.2.
The DP1, DP 2, DP3 and DP4 appeared all at the same RT for both the positive and negative mode, as can be seen in Fig 3.18 and Fig 3.19. In order to characterise the chemical structures of DPs firstly, the fragmentation of DCF was studied. Fig. 3.20 shows the mass spectrum of DCF. Three molecular ion peaks (MH+, MH+2, and MH+4) at \( m/z \) 296/298/300 can be observed and its characteristic isotopic species \(^{35}\text{Cl} \) and \(^{37}\text{Cl} \). These three isotopic peaks have a relative intensity in ratio 9:6:1 and are characteristic of the presence of two chlorine atoms. The relative size of the peaks can be worked out from the 75% probability that each Cl atom will be \(^{35}\text{Cl} \) and the 25% probability it will be \(^{37}\text{Cl} \). It should be noted that this probability is coming from the relative abundances of all the different stable isotopes of Cl and it will add up to 100%. Furthermore, chlorine-35 is about 3 times more abundant than chlorine-37 [39].

The compound ion at \( m/z \) 278 from the protonated DCF is a most likely result of water loss (18u) corresponding to dehydration \([\text{M+H–H}_2\text{O}]^+ \). The cation at \( m/z \) 250 is due to a loss of CO (28u) \([\text{M+H–H}_2\text{O–CO}]^+ \). The species with \( m/z \) of 215 is most probably formed via the further loss of a chlorine atom \([\text{M+H–H}_2\text{O–CO–Cl}]^+ \).
Figure 3.20 Mass spectrum plot of the protonated 10 mg/L DCF standard, showing [M+H]$^+$ at $m/z$ 300, 298, 296, 278, 250 and 215. Under ESI (+). For RT=1.14 min.

The mass spectrum displayed in Fig 3.21 for the negative mode shows a deprotonated molecular ion of DCF. Three molecular ion peaks (MH$^-$, MH$^-2$, and MH$^-4$) at $m/z$ 294/296/298 as seen for positive mode and its characteristic isotopic species ($^{35}$Cl and $^{37}$Cl). The relative intensity is the same as for ESI (+) with a ratio of 9:6:1. While the main fragment ion occurs at $m/z$ 250 ($-44$), which represents the loss of CO$_2$ in the ionisation source [M–H–CO$_2$]$^-$ with a ratio of 3:2.
Figure 3.21 Mass spectrum plot of 10 mg/L DCF standard, showing [M−H]− at \( m/z \) 294, 296, 298, 250 and 252. Under ESI (−). For RT=1.14 min.

In the case of the DPs, the molecular ions [M+H]+ and [M−H]− were investigated and identified, as DCF. Subsequently, the structures of the DPs were determined based on the fragmentation pathway observed in the ESI-MS spectra. Figure 3.22 shows the DPs identified in the positive mode.
Figure 3.22 Mass spectrum plot of the irradiated sample from 10 mg/L DCF standard, after 3h of simulated solar irradiation using 1 g/L of CeO$_2$. Showing [M+H]$^+$ at (a) $m/z$ 296, (b) 202, (c) 230 and (d) 387. Under ESI (+). For RT= (a) 1.14, (b) 0.32, (c) 0.61 and (d) 0.88 min.
Figure 3.23 Mass spectrum plot of the irradiated sample resulting from 10 mg/L DCF standard, after 3h of simulated solar irradiation using 1 g/L of CeO₂. Showing $[\text{M−H}]^-$ (a) at $m/z$ 294 and (b) 258. Under ESI (−). For RT=1.14 and 0.88 min respectively.

Figure 3.22 and 3.23 display the mass spectra for positive and negative modes respectively. It can be seen that the first DP1 appeared at 0.3 min and corresponding to $m/z$ of 202, DP2 =0.6 min corresponding to $m/z$ 230 and DP4=0.8 min corresponding to $m/z$ 387 for $[\text{M+H}]^+$ and DP3=0.8 min corresponds to $m/z$ 258 for $[\text{M−H}]^-$. The degradation products are stable since they were reproducibly detected when the sample was retested after several weeks. DP1, DP2, DP3 and DP4 were identified by the METLIN library Database [40] with a 98.2%, 86.6% and 94% score, respectively. These results are listed in Table 3.3. The DP1 (3-Chloro-9H-Carbazole), DP2 (8-Chloro-9H-Carbazole-1-Carbaldehyde) and DP3 (2(8-Chloro-9H-Carbazol-1-yl) acetic acid) have been also found by Aguera et al [35]. DP4 has not been
assigned. However, considering the high molecular mass obtained, it can be hypothesised that it’s a dimer and is formed from high mass DCF photoproducts coexisting in the reaction mixture possibly arising from a free radical reaction. Such compounds have also been reported by other groups [36,37].

Table 3.3 Summary of degradation products formed during the photodegradation of 10 mg/L of DCF under solar simulator after 3h, using 1 g/L of CeO$_2$.

<table>
<thead>
<tr>
<th>Compound (ionization mode)</th>
<th>RT (min)</th>
<th>Formula</th>
<th>Name</th>
<th>Experimental mass (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP1 (ESI+)</td>
<td>0.32</td>
<td>C$_{12}$H$_8$NCl</td>
<td>3-Chloro-9H-Carbazole</td>
<td>202.1804</td>
</tr>
<tr>
<td>DP2 (ESI+)</td>
<td>0.61</td>
<td>C$_{13}$H$_9$NOCl</td>
<td>8-Chloro-9H-Carbazole-1-Carbaldehyde</td>
<td>230.2482</td>
</tr>
<tr>
<td>DP3 (ESI−)</td>
<td>0.88</td>
<td>C$_{14}$H$_9$NO$_2$Cl</td>
<td>2(8-Chloro-9H-Carbazol-1-yl) acetic acid</td>
<td>258.0328</td>
</tr>
<tr>
<td>DP4 (ESI+)</td>
<td>0.88</td>
<td>unassigned</td>
<td>unassigned</td>
<td>387.1836</td>
</tr>
</tbody>
</table>

Once the possible intermediates were identified, an attempt to describe a photodegradation pathway was made as shown in Scheme 3.1. Only qualitative information is presented as a kinetic and quantitative study was not possible due to the lack of suitable standards enabling quantitative identification of intermediates for the compounds identified. It is possible that the
The presence or absence of some photoproducts is correlated to the rate of the reactions, as discussed previously where the degradation efficiency of DCF was found to be 56% after 3h. The fact that DCF could also adsorb onto the surface of nanoceria, may also influence the yield of the degradation products, as reported by Martinez et al., using the catalyst TiO$_2$ [37]. Therefore, structures that are shown in Scheme 3.1 should only be considered as proposals, which require further confirmation.

The chemical structure of the molecule DCF is a hybrid between a fenamic and an acetic acid class derivative. A key functional group is the secondary amino group (N-H), bridging two aromatic rings and representing the source of a series of potential intramolecular H-bonds towards a chlorine atom of one of the compounds aromatic ring. The carboxyl group of the other aromatic ring in DCF is also significant. Other H-bonds are likely formed between the carboxyl groups of two different molecules of DCF, which face together in a dimer: the dimer form represents a structural unit of the solid-state of DCF, like those most found in carboxylic acids [38].

The most important photocatalytic reaction pathway observed is the photocyclisation (ring closure) to the corresponding monohalogenated carbazole. This occurs via a loss of chlorine and hydrogen atoms (dehydrochlorination), followed by structural reorganization forming a new ring, 2-(8 chloro-9H-carbazol-1yl)acetic acid (DP3). This product could be the precursor of dimer formation, as also reported by Martinez et al. [37]. This reaction is then followed by a possible loss of CO and dehydrogenation reactions. Then it is followed by another loss of CO. The formation of carbazoles is important since it is related to the phototoxicity caused by DCF. Further studies should be carried out to determine the toxicity
of the intermediates formed from the degradation of DCF [37,41]. As mentioned previously in order to confirm the exact mechanism of DCF photodegradation, further fragmentation of the precursor ions (m/z 202, 230 and 258) should be performed. It should be noted that there are more than 30 potential intermediates reported in the literature, and degradation products are formed through several different processes; such as photolysis, photocatalysis and atmospheric plasma among others [21,30,35-38].

**Scheme 3.1** Proposed reaction mechanism for the photodegradation of diclofenac under solar simulator exposure, using CeO$_2$ NPs.
Aguera et al. proposed a phototransformation pathway for DCF under sunlight exposure and the $m/z$ at 202, 230 and 258 were also identified. In their work, it was described as a loss of CO, HCl and also CO$_2$ molecules. They suggested that the presence of the carboxyl group in the structure of the DPs through the loss of CO$_2$ is the key to understanding the fragmentation pathway. However, it's necessary to carry out MS$^2$ and possibly MS$^3$ fragmentation (LC-MS/MS) where further decarboxylation would also take place [35].

3.3.2.6 – Catalyst reuse

A literature survey indicated a lack of studies regarding the reuse of CeO$_2$ NPs in catalysis studies, which has often been used for the degradation of different compounds outlined earlier in Table 3.1. However, there was a need to prove that this catalyst can be reused as reported for TiO$_2$ [11]. For this reason, an investigation of the reuse of both in-house and Sigma Aldrich ceria nanopowders was carried out. The nanoparticles were removed from the sample after 3h of the first photocatalysis cycle and then washed with water and ethanol, followed by drying in the oven for 2h at 200ºC. The same procedure was repeated using 10 mg/L of DCF for the homemade and Sigma Aldrich CeO$_2$ NP. However, no photocatalytic activity was detected within 3h of monitoring. It should be noted that the nanoparticles recovered from the first cycle of reaction were brown coloured compared to the initial colour of the fresh CeO$_2$ which was yellow.

Based on the catalytic behaviour and physical appearance of the reused nanoceria supplied from both the in house and Sigma, it can be suggested that the nanoparticles were subjected to absorption of the organic molecules onto their surface. This could have inhibited and caused
the poisoning of the oxygen species, consequently preventing the further catalytic activity of CeO$_2$.

**Figure 3.24** Raman spectrum of the reused CeO$_2$ NPs annealed at 900ºC after 3h of irradiation under the solar simulator. The Raman spectra were recorded using the 532 nm excitation wavelength with an x50 objective and a diffraction grating of 600 grooves/mm, with an acquisition time of 15 s per spectrum was used and averaged over 5 accumulations. Data was collected in the range 200 to 1000 cm$^{-1}$.
In an attempt to understand why CeO$_2$ NPs are not photoactive after reuse it under the same photocatalytic conditions, a Raman spectrum was carried out and is presented in Fig 3.24. As can be seen, the peak that corresponds to the F$_{2g}$ Raman active mode of fluorite type cubic structure, shifted by 16 cm$^{-1}$. As shown previously in chapter 2 in section 2.4.4 there are no other peaks in the Raman spectrum. In contrast in Fig 3.24 low intense peaks can be seen at 273 cm$^{-1}$, 335 cm$^{-1}$, 708 cm$^{-1}$, 816 cm$^{-1}$ and 919 cm$^{-1}$. Thus, peaks appear on high and low energy sides of F$_{2g}$ and it suggests that it could be associated with intrinsic oxygen defects present in the nanoceria lattice. Schilling et al. reported that charged O$_2$ species can be adsorbed at the surface vacancy sites. Bands in the 480-600 cm$^{-1}$ region are generally associated with the presence of oxygen vacancies that are accompanied by the formation of reduced Ce$^{3+}$ sites [42]. Therefore, the change in wavelength of the cubic coordination around Cerium ions in the Raman spectrum corresponds to a convolution of vibrations. Perhaps such a change in the nanoceria structure could be the reason for the loss of the photocatalytic activity of CeO$_2$ NPs, possible due to the irreversibility of Ce$^{3+}$ to Ce$^{4+}$ formation. However, further studies should be carried out, such as Transmission electron microscopy (TEM) in order to understand the actual changes in the inner structure of CeO$_2$ NPs. It should be noted that above 1000 cm$^{-1}$ no peaks were observed.

3.4 - Conclusions

The goal of this chapter was to evaluate CeO$_2$ NPs degradation of the dye MO and sodium diclofenac a well-known pharmaceutical/organic pollutant. It was found that CeO$_2$ hydrosol was an excellent photocatalyst and fully degraded MO. The maximum degradation efficiency of DFC was 56% over a period of 3h. It is well known that the photocatalytic
efficiency is affected by the reaction environment, such as the concentration of the organic and catalyst, irradiation time, pH of the solution, and the energy of the photons incident generated by the UV light source. It is worth mentioning that there is a limitation with using undoped CeO$_2$ NPs as a photocatalyst as it possesses a wider bandgap (3.2 eV) energy compared to TiO$_2$ (e.g. 3.0 eV of rutile).

In this study, the photodegradation of DCF utilising CeO$_2$ and TiO$_2$ NPs was compared. It is clear that TiO$_2$ is more efficient and fully degraded DCF. It was shown that the titania showed superior photostability and possessed a narrower bandgap compared to nanoceria. In order to improve nanoceria photocatalytic activity, doping studies should be carried out. The benefits of using ceria rather than the traditional TiO$_2$ is the simplicity and low cost of the preparation method as described previously. In order to better understand the catalytic properties of CeO$_2$, analytical techniques that focus on surface reduction (e.g XPS), could provide additional information into the defect chemistry of nanocrystalline materials. Furthermore, it is essential to establish the identity of the light-absorbing species (e.g. semiconductor, LMTC) and studies of the action spectrum and photonic efficiency should be carried out.

An important feature neglected in past research is the identity of the intermediates formed during the photocatalytic reaction. However, even with 56% of DCF degradation achieved, it was possible to identify several degradation products of this reaction. In this study, three major molecules were identified (3-Chloro-9H-Carbazole, 8-Chloro-9H-Carbazole-1-Carbaldehyde and 2(8-Chloro-9H-Carbazol-1-yl) acetic acid). It is important to study this transformation pathway in some depth, for the simple reason that the intermediates might be more toxic to the
environment in comparison to the parent compound (DCF). Therefore, it is important to study the environmental fate of pharmaceuticals overall in such photolytic wastewater treatments.

3.5 - References


CHAPTER 4

A Novel Mechanism for a facile memristor-type device based on CeO$_2$ and TiO$_2$.

Chapter 4 – A Novel Mechanism for a facile memristor-type device based on 
CeO$_2$ and TiO$_2$ nanoparticles.

4.1 – Introduction

This chapter describes the fabrication and investigation of a simple memristor-like device using 
CeO$_2$ and TiO$_2$ nanoparticles.

4.1.1 – Memristor

A memristor or Resistive Random-Access Memory (RRAM also known as ReRAM) is 
a resistive switching memory. It has been proposed as one of the next generations of non-
volatile memory technologies and it is normally constructed with a metal/semiconductor/metal 
configuration (a sandwich of a semiconductor between two outer conducting electrodes. The 
metal oxide is in the middle layer (with thickness in the nm range), which is responsible for the 
resistive switching (RS) [1, 2].

The typical behaviour of bipolar resistance switching includes a “figure of eight” current-
potential profile, along with a transition from a high resistance state (HRS) to a low resistance 
state (LRS) or vice versa [3]. This characteristic has the potential for use as a low energy 
memory storage device in computing or other applications such as neuromorphic devices [1].

A number of different configurations have been reported in the last decade for the 
production of metal oxide memristive devices. These include NiO [4], ZnO [5], and TiO$_2$ which 
is the material with the largest number of publications reported in many memristors [6-9]. CeO$_2$ 
is an alternative semiconductor that can either be electrochemically deposited [10] or sputtered
It should be noted that there are only limited reports on the fabrication of cerium dioxide nanostructures for resistive switching devices [12].

As described earlier in chapter 1 (section 1.5) cerium, is the twenty-sixth most abundant element and exists in two oxidation states, Ce$^{3+}$ (e.g. Ce$_2$O$_3$) and Ce$^{4+}$ (e.g. CeO$_2$). The latter is more commonly used due to its polymorphy [13]. CeO$_2$ is a semiconductor and plays a role in many different applications due to its desirable properties, often resulting from a large oxygen deficiency content in its crystal structure (which typically increases with the decrease in the size of the CeO$_2$ NPs). CeO$_2$ is highly non-stoichiometric and point defects are formed (as temperature increases) from Ce$^{4+}$ to Ce$^{3+}$ in reduced ceria (CeO$_{2-x}$) by the formation of oxygen vacancies [10]. The fluorite cubic crystal structure (FCC) of CeO$_2$ allows it to accommodate high levels of point defects disorder and properties such as ionic conduction and mixed ionic-electronic conductivity can be altered by controlling the concentration of these defects [14].

4.1.2 – Mixed conductor mechanisms.

Many suggested mechanisms have been put forward to explain resistive switching and also memristance, and TiO$_2$-based devices are the most commonly found in the literature [6-9]. The high resistance material is generally believed to be stoichiometric TiO$_2$. Models for the operation of a memristor are often based on the formation of a high resistance (or semiconducting) TiO$_2$ layer contiguous with a conducting (low resistance) region. This was originally proposed by Strukov [15]; subsequent modifications have appeared through the years [16, 17].
As described by Gao et al., a number of different processes have been proposed for the operation of memristors [18], depending upon the materials used. Examples include Mott (insulator-metal) transitions, Schottky barrier (semiconductor-metal) behaviour at electrode interfaces, charge trapping or de-trapping, polaron melting and ordering (in polymeric memristors), electric field-induced generation of crystalline defects and the creation or destruction of conducting filaments through the thin film between both outer electrodes [18].

However, for Valence Change Memory Devices (VCMs) [21], the oxygen vacancies formed at the anode which are thought to migrate to the other electrode are thought to be responsible for the transition from a high resistance state (HRS) to a low resistance state (LRS) [19, 22]. This mechanism seems to have gained considerable attention and is proposed in many reviews of memristor operation [20, 23]. Various electrochemical models have also been proposed, based on the Nernst Planck equation to calculate the diffusion and migration currents [24, 25].

In the VCM mechanism, electrons trapped in oxygen vacancies are able to form a conductive strand or filament [21]. This filament consisted of oxygen vacancies, is formed under an applied current which leads to motion of oxygen ions along the driving force applied. This is believed to facilitate charge transport. Another mechanism proposed relies on the electrochemical dissolution and deposition of an active electrode metal such as Ag\(^{+}\) or Cu\(^{2+}\) [21]. It involves the growth of a conducting metallic filament growth and refers to oxygen ion current and proposes a very high local temperature rise for filaments; formation up to 1000ºC [21]. One problem, however, with this filament model is the presence of an insulating layer
adjacent to one electrode making charge transport across the solid-state electrolyte very unlikely.

Furthermore, the reaction takes place at room temperature, where electrical conductivity ($\sigma$) in transition metal oxides such as TiO$_2$ is the product of both electron ($n$) and hole concentrations ($p$) and mobility terms ($\mu_n$ and $\mu_p$ respectively) and is given by $e(n\mu_n + p\mu_p)$ where $e$ is the elementary charge ($1.6\times10^{-19}$C) [22]. Therefore, under ambient conditions, the ionic conductivity element, $\sigma_i$ which normally contributes, is insignificant becoming significant (only at high temperatures > several hundred °C). Beyond that, if the mechanism of RS involved movement of ionic species, the resultant current produced should decay over a time period of a few seconds. Instead, it has been demonstrated that a constant current occurs in which a p-n junction plays a crucial role in the charge transport [30, 31].

Thus although several models have been suggested to explain the resistive switching behaviour of metal oxides. There is still much debate regarding the exact nature of the charge carriers of these devices. Ismail et al. reported, in their review of conduction mechanisms of resistive switching, devices, describing a wide range of different mechanisms, sometimes for the same device [26].

4.1.3 – Models.

Generally, ReRAM modelling has concentrated on models based on the materials science and chemistry of the devices, whereas the memristor, predicted from electronic engineering theory, tends to include more physics and mathematics-based approaches [15].
In 1971, Chua et al. noted that there are six different mathematical relations connecting pairs of the four fundamental circuit variables: charge, \( q \), magnetic flux, \( \phi \), current, \( I \) and voltage, \( V \). The ‘missing’ element, the memristor with memristance \( M \) provides a functional relationship between charge and flux [27]. Figure 4.1 shows the current-voltage characteristics for the four fundamental circuits, with the characteristic pinched hysteresis loop of the memristor in the bottom right (figure of eight).

**Figure 4.1** Diagram showing a typical current-voltage characteristic for the resistor, capacitor, inductor and memristor. Adapted from Ref [47].
When Strukov et al. announced their discovery of a memristor they included a simple model based on treating the memristor as two space-conserving variable resistors in which they considered the velocity of the boundary, \( w \) between TiO\(_2\) and TiO\(_{2(2-x)}\) phases within the inner layer. The results provide a simplified explanation for reports of current-voltage anomalies, including switching and hysteretic conductance, multiple conductance states and apparent negative differential resistance, especially in thin-film, two-terminal nanoscale devices, that have been appearing in the literature for nearly 50 years [28]. This model has been both highly criticised and widely used, both as is and with other extensions.

The trend in building memristor device models is currently towards the more general (in that they can model more devices and types of devices), experimentally-informed (in that the model can be understood in terms of the physical processes happening in the device), easy-to-simulate models. Nonetheless, none of the changes in the definition of the memristor put forward by Chua et al. have changed the basic concept, that of a non-linear resistor which relates the time integral of the current to the time integral of the voltage and produces pinched (although now not necessarily self-crossing) \( V-I \) curves which generally shrink with increasing frequency [27].

In order to provide new insights into the fundamental principles of resistive switching behaviour, a different mechanism is proposed in this thesis. This relies upon concepts derived from point defect models arising in solids in combination with the operation of an electrolytic cell utilising electron/electron-hole carriers and the existence of a p-n junction and a space charge layer. The intention of this work is to present a simple method for the fabrication and
study of such devices and to suggest a possible new mechanistic approach to our understanding of resistive switching [29-31].

4.2 – Experimental

All chemicals were purchased from Sigma and Fisher Scientific and were used without further purification:

4.2.1 – Materials

- Al and Cu panels (Supplied by Henkel Ireland Ltd) (dimensions of 10 cm × 2.5cm × 2 mm)
- Cerium dioxide synthesised (described in Chapter 2)
- Clamp
- Degussa P25 analytical grade (TiO$_2$) (Sigma)
- Ethanol Absolute analytical grade (Fisher)
- Felt insulator

4.2.2 – Equipment

A potentiostat (CHI 600A) was used to control the potential by where the reference and auxiliary connections were linked to one aluminium panel, while the working electrode connection was linked to the other. Another potentiostat (SOLARTRON - SI1287 in conjunction with 1255B) was used to monitor electrochemical impedance spectroscopy (EIS) experiments. A dummy cell was utilised for calibration of the instrument (See appendix III). The general morphologies were examined by using a Hitachi SU 6600 FESEM operating at
10.0 kV. The EDX spectrum (Oxford Instruments X-Max silicon) was used to evaluate the elemental composition. To carry out the measurement of the inner layers film thickness an Asylum MFP-3D-BIO AFM was utilised.

4.2.3 – Methodology

It should be mentioned that the experiments were performed to explore the use of CeO$_2$ and compared to TiO$_2$ NPs which is well established for memristors. Suspensions of either CeO$_2$ or TiO$_2$ (Degussa P25), 0.076 g was prepared in 2-propanol (10 cm$^3$) and sonicated for 5 min. 10 μL of this suspension were then placed on an aluminium or copper panel to form a circle of about 1 cm in diameter. This was allowed to dry in a fume hood and another panel (Cu or Al) was clamped on top of the first, ensuring that both were insulated (using felt insulator) from the clamp. However, with the CHI 600A potentiostat, the current was saturated at 100 mA, above approximately 0.6 V, and so potentials lower than 0.6 V were typically applied. The clear advantage of this device is its ease of construction which is readily apparent in Fig 4.2.
**Figure 4.2.** Expanded view of Al-CeO$_2$ or TiO$_2$-Al device. A thin film of CeO$_2$ or TiO$_2$ NP was placed between aluminium and copper alloy plates which were carefully separated but electrically connected through the CeO$_2$/TiO$_2$ thin film interlayer. A sandwich-like assembly was formed.

### 4.2.4 - Characterisation of Memristor device.

Results for CeO$_2$ memristor characterization in a similar fashion are shown in comparison to well-known TiO$_2$ since it’s the focus of this thesis. The SEM images provided insight into the structure and morphology of the CeO$_2$ nanoparticles on Al plate. As shown in figure 4.3 (b) compared to 4.3 (a) the CeO$_2$ nanoparticles are aggregated. Moreover, a dense population with small nanoparticles with a mean size of 35 nm (Fig 2.4, chapter 2) on the surface of the substrate can be seen.
Figure 4.3 (a) SEM images of Aluminium panel before adding nanoceria; the (b) image of Al panel after drop-casting CeO$_2$ NP. (c) EDS, Elemental analysis of Al panel with drop cast CeO$_2$ NP on the surface.

The EDS analysis can be seen in figure 4.3 (c), the image shows the composition expected for an Al panel coated with CeO$_2$. All elements including cerium, oxygen and aluminium were detected. Also, some traces of carbon possibly emanating from the instruments chamber’s contamination as a result of the use of conductive carbon connections. Figure 4.4 displays the atomic force microscopy (AFM) measurement. Due to the roughness of the Al panel, this value
should be considered as an estimation of the thickness of CeO₂ NPs on the Al, which was found to be 40 nm ± 0.85 nm.

Figure 4.4 AFM measurement of CeO₂ cast on an Al lap shear.

4.3 - Results and Discussion

It is important to highlight that, in the literature, a control or reference device in which two metals have been directly electrically linked is seldom if ever shown. Figure 4.5 is a cyclic voltammogram (plot of current as a result of an application of a linear potential ramp) of such
a control assembly. It consists of an aluminium panel clamped directly on top of an aluminium lap panel which was obtained at room temperature. Here the current measured as a result of a linear potential ramp from 0 V to 0.6 V and back to −0.6 V and then returning to 0 V is presented. As expected, the result is essentially a plot of Ohm’s law, by which the resistance is calculated to be 5Ω. This corresponds to a limiting low resistance and serves to act as a control assembly device. Similar ohmic behaviour was observed when an aluminium panel was clamped directly on top of Cu with an area of 0.5 cm² in an identical system.

![Plot showing typical ohmic behaviour of a blank (control) device comprising two plates Al/Al panels clamped together. Scan rate = 10 mVs⁻¹.](image)

**Figure 4.5** Plot showing the typical ohmic behaviour of a blank (control) device comprising two plates Al/Al panels clamped together. Scan rate = 10 mVs⁻¹.

4.3.1 – TiO₂ Memristor.

TiO₂ was taken as a model system in the first instance as much of the literature on memristor focuses on TiO₂ [6-9]. Figure 4.6 shows a typical current-voltage (I-V) data of an
assembly Al/TiO₂/Al assembly in a 30 cycle voltammogram respectively. This data was obtained from the imposition of a potential scan rate of 10 mV/s over an applied potential range of −0.6 to +0.6 V. As demonstrated by Strukov et al., even at such low applied voltages, nanoscale devices can be subjected to a large electric field that can promote the movement of charged species. In the current case, the electric field was found to be 3x10⁷ Vm⁻¹ [28]. The initial starting potential was 0 V. This demonstrates a classic memristor behaviour, with a transition from a high resistance state (low current) to a low resistance (high current) state. The potential was applied to the Aluminium electrode with respect to the aluminium electrode for figure 4.6 (a). The current in this figure appears to be much larger than those most often reported in the literature, since most assemblies in the literature are prepared using microfabrication facilities, yielding significantly smaller surface areas [11, 32]. However, for this simple device the contact area is much greater; of the order of 0.5 cm².
Figure 4.6 A plot of current against the potential displaying typical behaviour of a bipolar resistive random access memory (or memristor) of a structure of Al/TiO$_2$/Al assembly. Where CE/RE was Al (top electrode) and WE (bottom electrode). Scan rate: 10 mVs$^{-1}$

Figure 4.6 shows a triangular (non-ohmic) switching behaviour, such hysteresis observed at large negative voltages could be due to a discontinuity in the current-time profile. For the sake of clarity, only 6 cycles are shown; the first three initial scans are overlaid together with the 28th, 29th and the 30th consecutive scans. Similar behaviour was demonstrated by Gale et al. for an Al/sol-gel TiO$_2$/Al and also by other authors [33, 34]. The clear advantage of this simple device is its ease of construction.

It should be noted that Al/TiO$_2$/Al is more correctly represented as Al/Al$_2$O$_3$ (OH)/TiO$_2$/Al$_2$O$_3$ (OH)/Al. However, conventional representation is Al/TiO$_2$/Al [36]. It is proposed that in the Al/TiO$_2$/Al device, there is a possible effect of the Al$_2$O$_3$ layer (passive film), or even a more complex mixed-phase (hydrated aluminium oxide outer layer) which may
also well act as a source of holes (h*). The chemical reaction between an Al₂O₃/bottom electrode and TiO₂ has been confirmed experimentally by Jeong et al. using high-resolution transmission electron microscopy (HRTEM), an analytical TEM technique using energy-filtering transmission electron microscopy (EFTEM), and an in situ x-ray photoelectron spectroscopy (XPS). XPS results suggest that the Al is readily oxidised by extracting oxygen ions from the TiO₂ surface and thus causing its reduction [34].

Such findings have been proposed and supported by Yang et al. and Jeon et al., which suggests that there is an overall oxygen deficiency present in the middle region of the TiO₂ interlayer [34, 35]. However, this contradicts the belief that only oxygen vacancies at the metal-oxide interface play a critical role in the reversible switching between a high resistance state and a low resistance state. Figure 4.7 shows a Bode plot recorded with a DC potential of 0.4 V and an AC amplitude of 10 mV. A step-change in resistance for Al/Al and Al/TiO₂/Al was observed, where the transition occurs from 200.4 Hz to 1.22 Hz (HRS to LRS) with impedance changes between 0.5 Ω to 1.43 x 10⁶ Ω thus indicating possibly changes in the effect of the Schottky barrier of TiO₂ within the Al₂O₃ layer.
Figure 4.7 A plot of frequency against the impedance (Bode plot) displaying typical behaviour of a bipolar resistive random-access memory (or memristor) of a structure of Al/TiO$_2$/Al assembly. Where $\Delta E = 10$ mV and DC = 0.4 V. Frequency scan commenced at $10^3$ Hz and finished at 0.5 Hz.

In pure TiO$_2$ samples (such as Degussa P25) formed at high temperatures (typically above 1273 K), the following equilibria describing defect chemistry reactions can happen [37]. This can result in either the creation of n-type TiO$_2$ (equations (4.1)-(4.3)) or p-type TiO$_2$ (equation (4.4), represented by Kröger–Vink notation), where $(\bullet\bullet)$ represent a double positive charge and $(e')$ signifies a negatively charged electrons. (See Appendix II).

$$O^\circ_2 \Leftrightarrow V_o^{**} + 2e' + \frac{1}{2} O_2$$  \hspace{1cm} (4.1)
2O\textsuperscript{\textcircled{o}} + Ti\textsuperscript{\textcircled{T}} \rightleftharpoons Ti\textsuperscript{\textbullet\bullet\bullet} + 3e' + O_2 \quad \quad \quad (4.2)

2O\textsuperscript{\textcircled{o}} + Ti\textsuperscript{\textcircled{T}} \rightleftharpoons Ti\textsuperscript{\textbullet\bullet\bullet\bullet} + 4e' + O_2 \quad \quad \quad (4.3)

O_2 \rightleftharpoons 2O\textsuperscript{\textcircled{o}} + V_{Ti}'''' + 4h^* \quad \quad \quad (4.4)

where V_{o}'''''' corresponds to an oxygen vacancy with a double positive charge. Equation (4.1) explains why the presence of oxygen vacancies has been attributed to an n-type TiO_2 semiconductor. In this notation, Ti\textsuperscript{\textbullet\bullet\bullet} denotes cationic Ti\textsuperscript{3+} in an interstitial site and Ti\textsuperscript{\textbullet\bullet\bullet\bullet} represents Ti\textsuperscript{4+} in an interstitial site. In these, reactions e' is a Ti\textsuperscript{3+} atom in a titanium lattice site (quasi-free electron) and h^* is an O\textsuperscript{−} anion in an O\textsuperscript{2−} lattice site (a quasi-free hole)[38].

The notation of the lattice components according to the Kröger-Vink [37] and the traditional notation are shown in Table 5.1 below and it can be described for both CeO_2 and TiO_2.
Table 4.1 Notations of the CeO$_2$ Lattice Species along with the Kröger -Vink notation and net charge [37].

<table>
<thead>
<tr>
<th>Traditional notation</th>
<th>Meaning</th>
<th>Kröger-Vink Notation</th>
<th>Net Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_{Ce}^{4+}$</td>
<td>Ce$^{4+}$ ion in the cerium lattice site</td>
<td>Ce$^{4+}_{Ce}$</td>
<td>Neutral charge</td>
</tr>
<tr>
<td>Ce$_{Ce}^{3+}$</td>
<td>Ce$^{3+}$ ion in the Cerium lattice site (quasi-free electron)</td>
<td>Ce$_{Ce}^{3+}$</td>
<td>-1</td>
</tr>
<tr>
<td>V$_{Ce}$</td>
<td>Cerium vacancy</td>
<td>V$_{Ce}^{4-}$</td>
<td>-4</td>
</tr>
<tr>
<td>Ce$^i$</td>
<td>Ce$^{i+}$ ion in the interstitial site</td>
<td>Ce$^{i+}$</td>
<td>+3</td>
</tr>
<tr>
<td>Ce$^{ii}$</td>
<td>Ce$^{ii+}$ ion in the interstitial site</td>
<td>Ce$^{ii+}$</td>
<td>+4</td>
</tr>
<tr>
<td>O$_{O}^{2-}$</td>
<td>O$^{2-}$ ion in an oxygen lattice site</td>
<td>O$_{O}^{2-}$</td>
<td>Neutral charge</td>
</tr>
<tr>
<td>V$_{O}$</td>
<td>Oxygen vacancy</td>
<td>V$_{O}^{2+}$</td>
<td>+2</td>
</tr>
<tr>
<td>O$_{O}^{-}$</td>
<td>O$^{-}$ ion in the oxygen lattice site (quasi-free hole)</td>
<td>h$^{+}$</td>
<td>+1</td>
</tr>
</tbody>
</table>

Degussa P25 (TiO$_2$) comprises a mixture of anatase and rutile nanoparticles (in the ratio 80:20) with an average size of 21 nm. SEM images of this material indicate that it forms nodules with a porosity level of about 30-40% [39,40]. Such TiO$_2$ material is hydrophilic in nature as it generally contains a high number of surface hydroxyl groups with a high specific surface area of 50 $m^2/g$ [40]. As a consequence of being formed at such high temperatures, the P25 TiO$_2$ is most probably highly non-stoichiometric in nature and therefore contains various
point defects including quasi-free electrons and quasi-free electron holes, oxygen vacancies, titanium vacancies and titanium interstitials, as reported in Nowotny et al. [22]. In practice, such defects arise from the processing conditions (such as production temperature) and the presence of either reducing (hydrogen-rich) or oxidising (oxygen-rich) environments. Such defects may react according to the equilibria described by equations 4.1-4.4. However, these equilibria only apply at high temperatures.

When TiO₂ NPs are connected between two metal electrodes in a memristor configuration such as the assemblies at room temperatures described previously and a positive potential is applied (region 1 in Figure 4.6 then oxidation occurs at the anode (equation (4.5)) to form a p-type TiO₂ as follows, since the V_o** remains, while the electrons pass into the electrode and oxygen is evolved. This electrochemical evolution of oxygen has been observed experimentally in TiO₂ based memristor assemblies [18, 33, 42].

\[
O^\cdot_o \rightarrow V_o^{**} + 2e' + \frac{1}{2} O_2
\]  

(4.5)

Alternatively the anode material may also be oxidised [33, 42].

\[
2Al + \frac{3}{2}O_2 \rightarrow 3V_o^{**} + Al_2O_3 + 6e'
\]  

(4.6)

Meanwhile, at the cathode n-type TiO₂ is formed through the reaction [42]:

\[
2Ti^{x}_{Ti} + 2e' \rightarrow 2Ti_{Ti}'
\]  

(4.7)
Here, Ti$_{Ti}$' corresponds to a Ti$^{3+}$ species in a Ti$^{4+}$ vacancy, leading to an overall single negative charge. Such a reduction has previously been reported by Ella Gale et al. and is widely reported in the literature [33,42,43]. There is a difference in the nature of the Ti$^{3+}$ depending on its position. If it is situated in a titanium lattice site (Ti$^{4+}$), it is seen as a quasi-electron. If it is situated in an interstitial site, i.e.: a (Frenkel-like defect) it is Ti$_{i}$[37].

Therefore, at the negative electrode (cathode), n-type TiO$_2$ forms and at the anode p-type TiO$_2$ is created at the same time. The operation of p-type TiO$_2$ at room temperature has been reported by Nowotny et al. [44]. In the low resistance state, a forward-biased p-n type junction appears when the p-type and n-type regions extend from the metal electrode surfaces and meet in the middle (forming a space charged layer) with enhanced current carrying capability. The space regions close to the p–n interface lose most of their mobile charge carriers, forming the space charge layer in the middle. The electric field formed by the space charge layer opposes the diffusion process for both electrons and holes. This accounts for the resulting increase in current at 0.5 V in Figure 4.6. During the initial electrochemical reaction (4.5) and (4.7), O$^{2-}$ anions migrate to the anode and this has been observed experimentally [18]. Thus, at the cathode, the formation of Ti$_{i}$O$_{2n-1}$ (e.g. Ti$_2$O$_3$ or possibly even a Magnéli phase) occurs [1]. Once the n and p region are formed, the charge is subsequently passed by electron and hole movement as shown in the schematic presented in figure 4.8 (a) and (b).
In region 2 in Fig 4.6 (from 0.5 V to 0.0 V), there is a decrease in the applied potential and a corresponding decrease in the driving force of the current, although the two reactions (4.5) and (4.7) still happen in the same direction, but to a lesser extent. It should be stressed, in this proposed model it is the movement of holes and electrons that are responsible for the current rather than the movement of ionic species.

In contrast, in region 3 in Fig 4.6 (from 0.0 V to −0.5 V), there is a reversal of the two reactions mentioned above. While regions 1 and 2 operate to increase the population of the electrons and holes at the cathode and anode respectively, in region 3 these populations decrease. However, there is a residual build-up of O₂ (effectively h*) and Ti (III) species (e') which still allows for a reasonable current through the reversal of the original reactions (4.6, 4.7) and (4.8). By the time we get to region 4 (from −0.5 V to 0.0 V) the movement of electrons...
and holes have decreased substantially and the device returns rapidly to its original high resistance (ohmic) state. Fig 4.8 shows a schematic representation of the process above.

While memristive behaviour is seen for the initial scans in Fig.4.6, it is not shown after the consecutive cycles and response changes to that of a pure resistor, indicating a change in the first mechanism. This is also reported elsewhere [3, 28]. In 2011, Chua et al. published a paper in which they suggest that any 2-terminal electronic device can switch between two resistances upon the application of an adequate voltage, and as a result, present pinched hysteresis loops thus acting as memristors [27].

Figure 4.9 displays the currents obtained from the application of selected constant potentials (in 0.1 V increments). The current time behaviour at each fixed potential was recorded for a period of 10s. Figure 4.9 shows the current evolution for an Al/TiO₂/Al device, where the resulting constant current indicates a non-diffusional behaviour. This confirms that the current is produced by the rapid movement of electrons or holes rather than from ionic species. It is clear that the current is steady and stable, apart from most the negative potentials, with a certain noise at the start of −0.5 V. It should be noted that generally chronoamperometric studies are not used in this field.
Figure 4.9 Current resulting from the application of fixed potentials for 0.5s and 10s in 0.1 V steps ranging from 0.1 V to 0.5 V on the top side (a) and (b) respectively. And −0.1 V to −0.5 V on the bottom side (c) and (d) for Al/TiO$_2$/Al. This data comes from the same device as that measured in Fig. 4.6.

In the case of the high negative potentials (−0.4 V and −0.5 V), an initial current decay is evident before a steady-state current was attained. This initial decay is possibly influenced by the dual-layer Al$_2$O$_3$/(OH) passive film created and the chemical change of the titanium oxide
thin layer sandwiched between two aluminium electrodes [45,46]. In the Al/TiO$_2$/Al device, the space charge layer is forward biased, which leads to the generation of a low resistance state and ultimately a constant current at both positive and negative fixed potentials. Such constant currents are not observed for the mass transport of ionic species, only at p-n junctions, where the movements of electrons and holes suggest a non-diffusional behaviour.

As can be observed in Figure 4.9, the current is also constant for the few first milliseconds, indicating a linear current–time dependence which suggests a non-diffusion controlled process occurring at the Al electrode.

4.3.2 – CeO$_2$ Memristor

As mentioned in the previous subchapter (section 4.1.1), CeO$_2$ is an alternative semiconductor to TiO$_2$ and there are only a few limited reports on the fabrication of cerium dioxide nanostructures for resistive switching devices [11, 47]. Cerium oxide prepared by precipitation from aqueous salt solutions followed by annealing at elevated temperatures is highly non-stoichiometric in nature and therefore contains various point defects [48].

Figure 4.10 (a) and (b) shows the typical current-voltage (I-V) data obtained from an assembly Al/CeO$_2$/Cu over 4 cycles and an Al/CeO$_2$/Al assembly in a 15 cycle voltammogram, respectively. For the sake of clarity, only 6 cycles are shown in Fig 4.10 (b), where by the first three initial scans are overlaid, together with the 13$^{th}$, 14$^{th}$ and the 15$^{th}$ consecutive scans, indicating that the Al/CeO$_2$/Al is more stable than Al/CeO$_2$/Cu. This data was obtained from the imposition of a potential scan rate of 10 mVs$^{-1}$ over an applied potential range of −0.6 to +0.6 V. The initial potential was 0 V. This demonstrates a classic memristor behaviour, with a
transition from a high resistance state (low current) to a low resistance (high current) state. The potential was applied to the copper electrode with respect to the aluminium electrode for Figure 4.10 (a).

**Figure 4.10** A plot of current against potential displaying typical behaviour of a bipolar resistive random access memory (or memristor) of an Al/CeO$_2$/Cu assembly. (a) where Cu panel is WE and Al is combined CE/RE. (b) The $I$-$V$ curve of a structure of Al/CeO$_2$/Al assembly. Scan rate: 10 mV/s.

It can be observed in Figure 4.10 that two different bipolar curves with different levels of hysteresis are evident. Figure 4.10 (a) shows a highly hysteretic curved switching behaviour, whereas 4.10 (b) shows a triangular switching behaviour in the forward scan. The same memristive behaviour was apparent for the TiO$_2$ memristor, and the same type of mechanism based on p-n junction and electrolytic cell is proposed for CeO$_2$ devices (equation 4.5 and 4.8). It should be stressed, that in this new model, it is the movement of holes and electrons that are
responsible for the current, rather than the movement of ionic species, where at the anode
equation 4.5 (p-type CeO$_2$) previously shown and at the cathode the n-type CeO$_2$ is formed
through the reaction:

$$2\text{Ce}^{x+} + 2e' \rightarrow 2\text{Ce}e'$$

(4.8)

It is proposed that the potential energy barrier for electrons produced at a
metal/semiconductor interface or junction, which is effectively a Schottky barrier, could lead
the difference between the devices. For an Al/CeO$_2$/Cu assembly, the formation of the CuO
layer can occur at the interface of the Cu electrode/CeO$_2$ electrolyte, and the Schottky barrier
produced a p-type CuO and concomitantly an n-type CeO$_2$. The mixed-phase of the aluminium
oxide layer, acting as a source of holes ($h^*$) [26, 36]. Once again the Al/CeO$_2$/Al device is more
reproducible on repeated runs and displays superior stability in comparison to the Al/CeO$_2$/Cu
assembly.

Figure 4.11 (a) and (b) shows a Bode plot recorded with a DC potential of 0.3 V and 0.5
V respectively and an AC amplitude of 10 mV. A change in resistance for Al/Al and
Al/CeO$_2$/Al was observed, whereby a transition occurs from 109 Hz to 0.79 Hz and an
impedance of step transition 0.3 Ω to 2.22 x 10$^6$ Ω, indicating a change in the effect of the
Schottky barrier of CeO$_2$ NPs within the aluminium oxide layer, while for Al/CeO$_2$/Cu device
a transition takes place from 850 Hz to 3.9 Hz (HRS to LRS) with an impedance of 915 Ω to
2.67 x 10$^7$ Ω. Such results are in agreement with the transition observed in Figure 4.10 (a) and
(b) from the high resistance state to the lower resistance state.
Figure 4.11 A plot of frequency against the impedance displaying typical behaviour of a bipolar resistive random-access memory (or memristor) of a structure of Al/CeO$_2$/Al assembly. Where $\Delta E=10$ mV and $DC= 0.3$ V (a). And for Al/CeO$_2$/Cu assembly, $\Delta E=10$ mV and $DC= 0.5$ V. Frequency scan commenced at $10^3$ Hz and finished at 0.5 Hz.
Figures 4.12 and 4.13 show the currents obtained from the application of selected constant potentials (in 0.1 V increments) to the copper electrode with respect to the aluminium electrode, for Al/CeO$_2$/Cu assembly and Al/CeO$_2$/Al respectively. The current evolution at each fixed potential was recorded for a period of 10s and is largely steady, time-independent. This suggests that the current is produced by the rapid movement of electrons or holes and not ionic species. It has been proposed by Kilner et al. that the transition from n-type to p-type conduction occurs at low temperatures (<100°C), and the ionic conduction only becomes significant above 500°C which further supports the concept that the charge is carried by electrons and holes, rather than by ions [49].
Figure 4.12 Current-time (chronoamperometric) plots at fixed potentials for 0.5 s and 10 s in 0.1 V steps ranging from 0.1 V to 0.5 V on the top side (a) and (b) respectively and −0.1 V to −0.5 V on the bottom side for Al/CeO$_2$/Cu (c) and (d). This data comes from the same device as that measured in Fig 4.1 (a).

It is apparent in Fig 4.12 (c) that the current behaviour is different when a high negative potential is applied (−0.4 V and −0.5 V). An initial current decay is observed before a steady current was attained for −0.4 V, while for −0.5 V the current decreases for −0.2 V increments. This could be explained by the fact that two different electrodes were used in this assembly.
(copper and aluminium), possibly resulting in a dual passive film and reproducing changes to the current profiles.

Figure 4.13 Current transients at fixed potentials for 0.5 s and 10s in 0.1 V steps ranging from 0.1 V to 0.5 V on top side (a) and (b) respectively and −0.1 V to −0.5 V on bottom side for Al/CeO$_2$/Al (c) and (d). This data comes from the same device as that measured in Fig 4.9 (b).

Figure 4.13 (a) shows the existence of a constant current indicative of a non-diffusional behaviour, apart from the most positive potential, with a certain amount of noise at 0.3 V. As can be observed in Figure 4.12, 4.13 (b) and (d) the current is constant for the first few
milliseconds, indicating a linear current–time dependence which represents a non-diffusion controlled process occurring at the Al and Cu electrode. The space layer or p-n junction is forward biased, which results in the generation of a low resistance state and ultimately a constant current at both positive and negative fixed potentials.

4.4 – Conduction mechanism model of ReRAM.

The conduction mechanism of resistive switching memory can vary according to the material used in the middle interlayer and the type of bottom and top electrodes utilised. The barrier height between the electrode and the oxide interface has a major influence in its conductance, in which the oxide trap plays a key role [50]. Conduction mechanisms in ReRAM, are divided into two groups (A) the electrode-limited paths, including Schottky emission (SE) and (B) the bulk-limited paths, like hopping, space-charge-limited conduction (SCLC), ohmic conduction, and Poole-Frenkel (P-F) emission. It is important to identify the exact physical transport mechanism and its relationship with resistive switching phenomena [26, 51].

In this work SE, P-F Emission models and SCLC were explored in an attempt to explain the conductive mechanism of Al/CeO₂/Cu and Al/CeO₂/Al assemblies. As previously discussed and reported by different groups [26,44,50], the conduction mechanisms cannot be described by a single model due to the complexity of ReRAM. A brief description of each model will be provided: (1) the Schottky emission happens when thermally-activated electrons injected over the energy barrier into the conduction band of the oxide [26]. It can be determined by fitting to ln(I) vs. E^{1/2}. (2) The P-F emission occurs when trapped electrons get excited into the conduction band of the oxide. It should exhibit linear fitting when the I-V characteristic is plotted on ln(I/E) vs. (E^{1/2}) graph. (3). In the SCLC regime, the current is dominated by charge
carriers injected from the contacts and the current-voltage characteristics become quadratic ($I \sim V^2$). The current is then only dependent on the mobility and no more on the charge carrier density. The typical SCLC is observed by two regions when the $I-V$ is plotted on a double-logarithmic scale. The $I-V$ relation follows ohmic law ($I \text{ vs. } V$) in low field regime, and Child’s Law ($I \text{ vs. } V^2$) in high field regime, Fig 4.14 which is the region known as trap-unfilled of SCLC [26].

In order to demonstrate how a single device can fit different models as observed for Al/CeO$_2$/Al, or just not fit any model, as for Al/CeO$_2$/Cu, the HRS and LRS for negative and positive potential were plotted for both devices. The graphs for Al/CeO$_2$/Cu are not shown due to the poor fit of these simple conduction models. The data utilised to fit the models were extracted from Fig 4.10 (b).
Figure 4.14 Plot showing the best fit for the space-charge-limited conduction model for the Al/CeO$_2$/Al assembly (HRS region).

As can be seen in Fig 4.14, the SCLC showed a good fit for the region 1 of Al/CeO$_2$/Al. Figure 4.14 shows the SE fit for LRS (region 2). As observed for this assembly, the best fit occurs for SCLC. Taroni et al. reported that motion of charge carriers inside the space charge region of an inversely biased p-n junction is numerically solved, taking into account the influence of the density of electron-hole pairs on the electric field. However, there are significant variations in the theoretically predicted current signals and it could only be predicted at low fields [53].
The possible explanation for this behaviour is the high field characteristic of such a device. It should be pointed out that systematic discussion about the fundamental nature of these RS devices (memristors) is almost absent within the memristor community. Abraham et al. demonstrated that the ideal memristor is a non-physical active device and any physically realizable memristor is a nonlinear composition of resistors with active hysteresis. Therefore, in their view, a memristor should not be considered the fourth circuit element [52].

**Figure 4.15** Plot showing the best fit for the Schottky emission model for the Al/CeO$_2$/Al assembly (LRS region).
As previously discussed the conduction mechanisms cannot be described by a single model due to the inherent complexity of ReRAM, as it may involve the operation of many different models [26]. The physical understanding of the resistive switching mechanisms remains a challenge due to the lack of direct characterisation technologies [52]. An attempt has been made to explain the conduction mechanism with Schottky, PF emission, and SCLC. However, they still do not explain the real mechanism of these devices.

4.5 – Conclusions

A simple metal-semiconductor-metal device comprising TiO₂ or CeO₂ NPs cast from a suspension of Degussa P25 or cerium dioxide nanoparticles synthesised as described in chapter 2 was prepared and placed between two metal plates (Cu/Al and Al/Al panels). This device demonstrated memristive behaviour. These assemblies displayed potential-current plots that were distinctly non-ohmic in nature generally with enhanced currents in their initial scans. A mechanism is proposed which relies upon the formation of p and n-type regions within the semiconductor material ultimately leading to the formation of a space charge layer resulting in a significant level of current (in the milliamps range) being obtained during testing. The devices also exhibited steady constant currents upon the imposition of potential steps, most notably at higher potential magnitudes (both anodic and cathodic) indicating non-ionic movement.

In this study, a device of very simple construction is demonstrated along with a mechanism, which is different from the widely published mechanism, consisting of movement of oxygen vacancies. The field of memristors is rapidly growing; a recent reference lists a table of commercial devices along with their characteristics [17]. The first commercial suggestion
for memristor use for purposes was memory because the memristor’s small feature size could offer an increase in memory density, and would not require much power (reduced energy) and could be used for multi-state memory. There are few attempts described in the literature to improve the memristive behaviour and thus complement the information regarding its mechanism and model, which depends on the material’s device and the active layer. However, the conduction mechanisms cannot be described by a single model due to the complexity of ReRAM [26]. The physical understanding of the resistive switching mechanisms remains a challenge due to the lack of direct characterization technologies. In this chapter, a new semiconductor model was proposed of operation arising from point defect chemistry concepts. This is expected to provide new insights into the fundamental principle of resistive switching behaviour, thus suggesting a new mechanistic approach that has to be confirmed by understanding how defects in solids interact with external electric fields and the use of mathematical models such as Density Functional Theory (DFT) could be recommended for future work.

4.6 – Reference


[47] https://www.theregister.co.uk/Print/2011/12/27/memristors_and_mouttet/ accessed 07/08/19


CHAPTER 5

PHOTOANODE DEVELOPMENT FOR USE IN A PHOTOELECTROCHEMICAL FUEL CELL
Chapter 5 - Photoanode Development for the photoelectrochemical fuel cell.

5.1 - Introduction

This chapter presents results obtained from the development of a novel photoanode based on carbon cloths coated with CeO2 and TiO2 NPs and a new design of a photoelectrochemical fuel cell.

5.1.1 – Photoelectrochemical fuel cell

Fuel cells are electrochemical devices that can convert chemical energy into electrical power [1]. The main advantages of such a device is the quiet operation, high thermodynamic efficiency and zero pollutant emissions [2]. Photoelectrochemical fuel cells (PEFCs or PECs) are used in organic waste degradation [1, 2], solar energy conversion [3, 4], removal of aqueous pollutants [5, 6] and photocatalytic sterilisation [7, 8]. A PEFC consumes fuels and at the same time utilises solar energy or another source of irradiation to generate electrical power when a photoanode is exposed to electromagnetic-radiation [9]. This device is an attractive subject nowadays, due to the growth in wastewater contamination caused by organic pollutants, as previously discussed in chapter 1 and 3 [5]. The double environmental benefits of a PEFC are that waste material can be consumed and solar radiation can be converted into a useful form of energy, namely as electricity.

Waste organic pollutants may actually be useful as a potential fuel for PEFCs. The reason for this is that organics yield many electrons on oxidation due to their high-energy density, much more per mole than hydrogen, which is the typical compound of choice for most commercial fuel cells. Fuel cells are normally categorised by the type of electrolyte utilised
and by the start time, that can vary from 1 s for proton exchange membrane fuel cells (PEM fuel cells, or PEMFC) to 10 min for solid oxide fuel cells (SOFC) [10]. Furthermore, organic compounds as a fuel can avoid issues associated with hydrogen use for fuel cells, which is difficult, expensive and dangerous to compress, store and transport [9].

5.1.2 - Mechanisms of Photoelectrochemical Fuel Cells

As shown in Fig 5.1, a PEFC consists of a photoanode that supports an immobilised semiconductor photocatalyst (in this case – CeO₂), a cathode that comprises another electrocatalyst such as an air-cathode (with Platinum) and a liquid phase serving as an electrolyte. In such a device, the anode and cathode are connected to an external load (resistor linked to a data logger). When the photocatalyst is an n-type semiconductor and the electrocatalyst is usually a noble metal (e.g. Pt), the photoanode acts as the negative electrode and the cathode as the positive electrode (e.g. electrons move from the anode to the cathode) through the electrical circuit connecting both [5]. The direction of the external current depends on the electric potential of each electrode. When the cathode is in contact with an aqueous electrolyte, its potential depends on the presence or absence of oxygen. In the presence of oxygen, the cathode behaves as an oxygen electrode and in this project, the PEFC should catalyse the oxygen reduction reaction (ORR) [9]. Oxygen reduction in aqueous solutions occurs mainly through two different pathways under acidic conditions: either a four-electron reduction pathway from O₂ to H₂O or a two-electron pathway from O₂ to H₂O₂ as shown in equation 5.1 and 5.2 [11].

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (5.1)
\]
In a PEFC, the recombination of photogenerated electron-hole pairs is significantly reduced via the external electric field, compared to a photocatalytic process. This causes the photogenerated holes to rapidly transfer to the surface of the electrode and consequently to oxidise the target pollutant (organic compound). This mechanism has been described in chapter 3 (section 3.1.2) in Fig 3.2.

5.1.3 – Semiconductor immobilised on a photoanode.

A photoanode is usually made of material onto which a nanocrystalline or thin semiconductor film is immobilised or deposited. In most cases, nanocrystalline TiO₂ is the
preferred semiconductor photocatalyst, due to its stability and high photoactivity, as previously mentioned in chapter 1 [12].

The immobilisation of a semiconductor onto a suitable solid support matrix (conductive support) eliminates the need for post-treatment removal of NPs, as occurs for photocatalysis. This is the major benefit of this technique, although, it may decrease the surface area available for the photoanode reaction [13].

There are a number of transparent conductive oxides (TCOs) utilised as photoanode materials, including indium-tin-oxide (ITO) and fluorine-doped tin oxide (FTO), commonly utilised in the traditional planar PEFC cells. However, the use of these glass substrates is not suitable for transportation due to their fragility, and high large-scale production cost [14]. Two of the goals of this study were to explore potential low-cost, highly stable, and flexible conductive substrate to develop a novel design of PEFC. Thus, the aim is to explore the use of CeO$_2$ NPs utilising different materials as conductive supports and to introduce the developed photoanode into a novel PEFC design.

There are relatively few reports on the use of semiconductors deposited on conductive textiles, such as carbon cloth or carbon paper. Most of the reports feature WO$_3$ or TiO$_2$ immobilised onto carbon cloths through hydrothermal synthesis [15-17]. In general, carbon cloths are flexible, conductive, and stable in most liquid electrolytes as well as being low cost materials. Furthermore, carbon cloth materials can offer high surface areas and exhibit excellent mechanical, electronic, and catalytic properties, which are the most desired characteristics expected for their use in PEFC devices [15].
Cyclic voltammetry (CV) is an electroanalytical technique often utilised for initial electrochemical studies of redox systems. It is generally used to study the electrochemical properties of an analyte either in solution or adsorbed onto an electrode surface and is very useful for obtaining kinetic and diffusion parameters [18]. The principle of CV involves the application of a triangular potential ramp and investigates the transport of electroactive species in solution carried out by diffusion. This along with the heterogeneous kinetics of the reaction determines the resultant current [18]. The current measured is directly proportional to the concentration of the analyte present in solution [18, 19].

When a potentiostat applies a positive bias to the working electrode (WE), it increases the oxidising power of the WE and so it increases the chances that electroactive species present in the solution will be oxidised. The opposite occurs by applying a negative potential, as this causes the reduction of an electroactive compound [18].

In cyclic voltammetry, the electrode potential ramps linearly versus time in cyclical phases. The rate of voltage change over time during each of these phases is known as the experiment's scan rate (Vs^{-1}). A standard CV experiment utilises a cell employing three electrodes: a reference electrode (RE), a working electrode (WE), and a counter electrode (CE). This arrangement is commonly referred to as a three-electrode electrochemical cell. The potential is applied between the working electrode and the reference electrode, while the current flows between the working electrode and the counter electrode. Additionally, an electrolyte is usually added to the sample solution to ensure sufficient solution conductivity [19].

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5.1.4.1 – Working electrodes (WE)

In this chapter, a three-electrode configuration is utilised. The potential applied to the WE determines the availability of the electrons at the WE. Its surface defines the interface where the redox reaction of interest takes place. Materials normally utilised for the fabrication of a WE usually include inert, conducting and catalytic materials, such as Pt, Au and glassy carbon (GC). Additionally, the WE should be durable and therefore resistant to chemical attack [18]. As it is the most important electrode to examine the reaction under study, the WE may require some pre-treatment to remove surface contaminants. The electrochemistry is affected greatly by its surface chemistry of carbon-oxygen functionalities and its cleanliness; e.g., absence of adsorbed impurities [20]. This can often be achieved by polishing with a micro-sized abrasive such as aluminium oxide ($\text{Al}_2\text{O}_3$) which exposes a fresh clean surface followed by rinsing in pure water and organic solvent. However, for this study, carbon cloth will be utilised. It only requires a simple pre-treatment (washing process) to reduce any adhered surface contaminant [20].

5.1.4.2 – Reference electrode (RE)

There are several REs commercially available, as shown in Table 5.1. A RE is used as a reference point against which the potential of other electrodes can be measured in an electrochemical cell [21]. It has a well defined and stable equilibrium potential. The most common REs can be related back to the hydrogen reaction that takes place on Pt at 1 atm, 25ºC. This is known as the normal hydrogen electrode (NHE) and it is set to 0 V. The potentials of other REs are then measured relative to this value. The RE used in this chapter is the mercury mercurous sulphate (Hg/Hg$_2$SO$_4$) system in aqueous saturated potassium sulphate (K$_2$SO$_4$). It
was chosen in order to eliminate chloride, which could interfere with the electrocatalytic experiments conducted in this work, as chloride can adsorb onto the electrode surface \[22\]. Table 5.1 shows how the potentials of different RE vary and illustrates how they are related to each other.

**Table 5.1.** Potential of reference electrodes in aqueous solution at 25°C \[23\].

<table>
<thead>
<tr>
<th>Reference Electrodes</th>
<th>E vs. NHE (V)</th>
<th>E vs. SCE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg/HgO, NaOH (0.1 M)</td>
<td>0.926</td>
<td>0.685</td>
</tr>
<tr>
<td>Hg/Hg(_2)SO(_4), H(_2)SO(_4)(0.5 M)</td>
<td>0.681</td>
<td>0.439</td>
</tr>
<tr>
<td>Hg/Hg(_2)SO(_4), K(_2)SO(_4) (sat’d)</td>
<td>0.642</td>
<td>0.401</td>
</tr>
<tr>
<td>Hg/Hg(_2)Cl(_2), KCl (0.1 M)</td>
<td>0.334</td>
<td>0.092</td>
</tr>
<tr>
<td>Hg/Hg(_2)Cl(_2), KCl (1 M)</td>
<td>0.280</td>
<td>0.039</td>
</tr>
<tr>
<td>Hg/Hg(_2)Cl(_2), KCl (sat’d) SCE</td>
<td>0.241</td>
<td>0</td>
</tr>
<tr>
<td>Ag/AgCl, KCl (sat’d)</td>
<td>0.197</td>
<td>0.044</td>
</tr>
<tr>
<td>NHE</td>
<td>0</td>
<td>−0.241</td>
</tr>
</tbody>
</table>

where E is the voltage relative to the normal hydrogen electrode (NHE) and mercurous chloride in aqueous saturated potassium chloride (also known as a saturated calomel electrode, (SCE)).

5.1.4.3 – *Auxiliary/Counter electrodes*

Counter or auxiliary electrodes (CE or AE) are usually made of Pt foil, glassy carbon or graphite. In this work, a graphite rod was employed as a CE. For electrochemical experiments, it is necessary that the surface area of the CE is much larger than that of the WE to guarantee
that the half-reaction occurring at the CE can happen fast enough in order to avoid a limitation of the reaction at the WE [21].

5.1.4.4 – Supporting electrolyte

In an attempt to reduce the migration of electroactive ions caused by the electric field, a high concentration of an inert supporting electrolyte is necessary. It is important to have the concentration of the supporting electrolyte at least 100 times more concentrated than the active species [1]. In this work, the concentration of supporting electrolyte was 0.1 M, while the concentration of electroactive species was much less (typically sub-millimolar levels).

5.1.4.5 – Electrode preparation

The method by which the electrode is prepared can have an influence on electrochemical surface reactions such as the electrocatalysis of the ORR [18]. The compound to be immobilised on the electrode can be attached to the electrode by different techniques such as vacuum deposition, layer by layer deposition [24], or adsorption [25]. This chapter describes the incorporation of CeO₂ NPs on to a polymer in combination with solvent evaporation. The main preparation method chosen was electrodeposition, which was adapted and optimised from Younis et al. [26]. It should be noted that until now, there were no reports found in the literature regarding the immobilisation of CeO₂ on to carbon cloths (C.C).

5.2 – Experimental

Unless specified otherwise, all chemicals were purchased from Sigma Aldrich, Acros Organics or from Fisher Chemical and were used as received without any further purification. All solutions were prepared using ultrapure water (18.2 MΩcm).
5.2.1 – Materials

- Acetone 99.9% (Acros)
- Cerium dioxide nanoparticles synthesized in Chapter 2.
- Cerium nitrate hexahydrate 99.5% (Ce(NO₃)₃ · 6 H₂O) (Sigma)
- Ethanol absolute analytical grade (Acros)
- Formic Acid 98% (FA) (Acros)
- Methylene Blue analytical grade (MB) (Fisher)
- Polyvinyl chloride analytical grade, high molecular weight (PVC) (Sigma)
- Potassium Chloride analytical grade (KCl) (Acros)
- Potassium Ferrocyanide (K₄Fe(CN)₆ · 3 H₂O) (Fisher)
- Potassium nitrate analytical grade (KNO₃) (Fisher)
- Sodium sulfate analytical grade (Na₂SO₄) (Across)
- Sodium diclofenac (DCF) (Sigma)
- Titanium (IV) isopropoxide 99.9% (TTIP) (Sigma)
- Tetrahydrofuran anhydrous 99.9% (THF) (Sigma)

5.2.2 – Equipment

All voltammetric measurements were performed on an Eco Chemie B.V, Electrochemical work station, model Autolab PGSTAT 12 (The Netherlands) using GPES software (version 4.9). Measurements were conducted using a three-electrode one compartment configuration in which the WE was a carbon cloth with a geometric area of 1 cm². The CE consisted of a
graphite rod and the RE was a Hg/Hg₂SO₄, K₂SO₄ (sat’d). Scanning microscopy (SEM) images were obtained using a Hitachi SU 6600 FESEM model. An acceleration voltage of 20 kV was employed. EDS (Oxford Instruments X-Max Silicon, drift detector for energy dispersive X-Ray) of the carbon cloths were used to confirm their elemental composition. A diffractometer (Siemens D-500) with an anode of Cu and a wavelength of 0.15406 nm (Cu Kα) was used to obtain X-ray diffraction (XRD) patterns. The diffractograms were recorded over a 2θ of 20°-80° and the diffractometer operated at 40 kV and 30 mA to characterise the carbon cloths. Diffuse reflectance spectra as described earlier were collected using a 60 mm Spectralon coated integrating sphere with a range from 200 to 2500 nm for the measurement of samples of high optical density with a Perkin Elmer Lamda 900 UV/VIS/NIR spectrometer. A Carbolite 201 controllers furnace was utilised to anneal the samples. The photoelectrocatalytic experiments were conducted by using a SUN 2000 Solar simulator with a Xe short arc lamp 1kW from ABET Technology. A data acquisition system (Pico Technology) with an ADC 20 analog to digital converter was employed to monitor the cell voltage/current.

5.2.2.2 – Other materials

- Copper wire
- Carbon Cloth with Micro-porous layer (MPL) 10 x 10 cm with 30% of PTFE treatment (Fuel Cell Store)
- Vulcan/Platinum carbon Cloth (Vulcan) - 0.2 mg/cm² Pt-C 20% - 5 x 5 cm with 30 wt% of PTEF treatment (Fuel Cell Store)
- Plain Carbon Cloth (C.C) -25 x 20 cm (Fuel Cell Store)
- Graphite rod counter electrode (GCE) (Alfa Aesar)

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• Petri dish (7 cm diameter) (Fisher)
• Mercury - Mercury (I) sulphate in saturated potassium sulphate reference electrode, potential at 298K = 0.64 V (NHE) \[11\] (Radiometer Analytical)
• Ultrasonic cleaner (Emmi – 20HC)
• Water Bath - (Heidolph).

5.2.3 – Methodology

5.2.3.1 – Anode Preparation

*Enright et al.* reported that the incorporation of TiO\(_2\) onto a conducting carbon ink with a polymer and then solvent evaporation leads to the production of a carbon ink anode (WE) using Cobalt (II) phthalocyanine (CoPc) \[1\]. This procedure was utilised as the first preparation method (S1). Three types of support substrate for carbon cloth (plain C.C, MPL, and Vulcan) were used and divided into pieces of 1 cm\(^2\) each. The carbon cloth was ultrasonically cleaned for 5 min in ethanol followed by washing in ultrapure water and drying with a stream of N\(_2\). A dispersion of nanoceria (0.25 g) synthesised in Chapter 2 was then dispersed in 6.25 mL of THF and 4.35 mg of PVC were then added. The latter acted as a support and stabilised the catalyst on the carbon fibres. The dispersion was stirred for 20 min and a portion of plain C.C, MPL or Vulcan was then dip-coated with the prepared CeO\(_2\) material placed for 30 min. This was left to dry overnight in the fumehood to allow solvent evaporation. The samples were then characterised by using a range of techniques.

The second preparation method (S2) was based on the work of *Younis et al.* in which ITO was utilised as a glass conductive support for the fabrication of memristors, and CeO\(_2\) was
electrodeposited on to the ITO surface [26]. The three samples of carbon cloth (plain C.C, MPL and Vulcan) with an area of 1 cm² and graphite rod were used as the working and counter electrodes respectively. Conductive silver epoxy and resin hardener from Radionics Ltd were used to prepare the copper wire connections to the carbon cloth. The two electrodes were separated by approximately 1 cm. The RE was a Hg/Hg₂SO₄, K₂SO₄ (sat’d). Electrodeposition of CeO₂ was carried out using an Autolab electrochemical workstation potentiostat and a standard three-electrode setup was utilised in an undivided cell. The substrate was first cleaned with ethanol followed by water, for 5 min each under ultrasonication in both cases. The substrate was carefully rinsed with ultrapure water and then electrodeposition (cathodic) was carried out in a solution of 0.01 M Ce(NO₃)₃ · 6H₂O at −1.4 V for 20 min, at 30ºC. The potential applied in the literature [26] was −1.05 V with an Ag/AgCl reference. Utilizing the values in Table 5.1, the potential was calculated to be −1.4 V for a Hg/Hg₂SO₄ reference. The samples were then removed from the electrodeposition bath and were left to dry in the fumehood overnight, followed by characterisation of their properties.

In order to compare the functionality of the novel PEFC configuration, the plain carbon cloth was coated with TiO₂ using the method reported by Zhai et al. via an in situ deposition and subsequent annealing procedure [16]. A cleaned plain C.C was soaked in a beaker with 10 mL of TTIP ethanol solution (V_{TTIP}/V_{ethanol} =1/10 ) respectively. This beaker was placed inside another beaker filled with water and it was covered and kept for 10 h. As the water evaporated over time, the TTIP could be hydrolysed in this moist environment. After the reaction, the plain C.C was dried in the ambient environment, and then it was annealed at 400ºC for 3h resulting in TiO₂ incorporation onto the C.C labelled (TiO₂-C.C).
5.2.3.2 – Carbon cloth electrode characterisation.

In order to better understand the behaviour of carbon cloth as an electrode, a 5 mM Potassium Ferrocyanide solution in 0.1 M KCl (supporting electrolyte) was prepared [16]. This system has electrochemical characteristics which are well-known, and its behaviour using a GC electrode (WE) was used to compare results obtained for C.C, MPL, and Vulcan. Prior to the analysis, the GC was cleaned/activated via polishing with water-alumina slurry on a cloth polishing pad (5 µm). The three substrates were then cleaned with ethanol in an ultrasonic bath for 5 min followed by washing with ultrapure water. This treatment exposes a fresh reactive surface. The same standard three-electrode setup in an undivided cell was utilised to characterise the electrochemical behaviour of the substrates each of geometric area of 1 cm². The cyclic voltammogram was performed applying potentials ranging between −0.7 V to +0.7 V vs Hg/Hg²SO₄ at a scan rate of 0.1 V/s.

5.2.3.3 – Formic acid (FA) voltammetry characterisation experiments.

Formic acid was used as a model pollutant for the investigation of the voltammetric response of FA in solution, as it is a by-product found in the mineralisation of many organic pollutants. In this work, 16 mM FA was prepared in 50 mL of 0.1 M KCl and cyclic voltammetry experiments were carried out. C.C, MPL, and Vulcan were used as the WE (1 cm²), graphite as CE and Hg/Hg²SO₄ as RE respectively, as described above. The light source was the solar simulator and the solution was irradiated for 10 min during the C.V, with an applied potential ranging between −1 to +1V vs Hg/Hg²SO₄ at a scan rate of 0.05 V/s. This experiment was recorded both under dark and light conditions to enable comparison of the effect of light on the generated current.
5.2.3.4 – Configuration of PEFC

As previously discussed, one of the goals of this work was to develop a new design for a PEFC. In order to improve the efficiency of this device, the distance between the anode and the cathode was minimised, and the two electrodes had similar areas. Most recent studies [1, 15,16,27], reported the electrode distance to be above 5 cm, and in an attempt to minimise the ionic resistance of the cell, this distance should be reduced [9]. The second parameter considered was the choice of the photoanode material. Here, the use of substrates such as plain C.C, MPL and Vulcan could be a great alternative as conductive support, due to their flexibility, high surface area and low cost.

Figure 5.2 shows the new proposed configuration of the PEFC, in which the cell is contained in a Petri dish. The maximum volume of the cell is 65 mL. The use of an air cathode (Vulcan carbon cloth) for this configuration could also contribute to the efficiency of this device, due to a high load of a suitable catalyst (Pt) to improve the kinetics of oxygen reduction [28]. It was also utilised/tested as a photoanode in order to explore the use of the same material as anode/cathode. The air cathode (diameter of 7 cm) is placed with the face of Pt/C in contact with the electrolyte+fuel. This side of the carbon cloth is waterproof (hydrophilic). The other side is exposed to the air to enable oxygen from the surrounding environment to react (hydrophobic). Thus, no additional aeration to this device is needed. The air cathode has also been used by many other groups, in PEFC applications [1, 27, 29]. It should be pointed out that for the configuration of this cell, the cathode should have a central hole with the same geometrical area as the anode, in order to allow the photoanode to be accessible by the light.
source, as can be seen in Fig 5.2. The photoanode consisted of a plain carbon cloth with a geometrical area of 19 cm$^2$ coated with either CeO$_2$ or TiO$_2$ NPs.

A copper wire connection was made individually for the photoanode and cathode, and the distance between them was 1 cm. A 1 kΩ resistor was connected between the anode and cathode and served as a load resistor through which current was measured. This connection was then linked to an ADC convertor (Picolog), to measure the cell voltage which was

Figure 5.2 Diagram illustrating set up of the novel PEFC design. Top view from above bottom-cross-section view.
measured for 500s (with the data logger positioned across the load resistance). The cell potential was converted to current using Ohm’s law. The light source was a solar simulator.

5.3 – Results and Discussion

5.3.1- CeO₂ Photoanode Characterisation

The electrochemical synthesis of CeO₂ NPs begins with oxygen being electrochemically reduced at the surface of the WE, resulting in an increase in the local pH value in the vicinity surface, while under neutral conditions the ORR occurs in equations (5.3) and hydrogen evolution reaction (HER) in equation (5.4). The resultant increase in the local pH leads to the precipitation of Ce(OH)₄ (equation (5.5)) at a suitable temperature (30°C) [26].

It should be noted that the mechanism proposed for the electrochemical synthesis of CeO₂ NPs was adapted from Younis et al. [26]. In their study, it was reported that the nitrate was reduced after applying a negative potential (equation 5.6). In this chapter, it is proposed that ORR occurs rather than nitrate reduction, as in practice the oxygen reaction should be favoured compared to the reduction of nitrate. At higher pH, O₂ tends to oxidise Ce(III) to Ce(IV) species like Ce(OH)₄, which means that in the presence of oxygen the solution may evolve towards an equilibrium in which both Ce³⁺ and Ce⁴⁺ species exist.
\[ \begin{align*}
\frac{1}{2} O_2 + 2e^- + H_2O & \rightarrow 2OH^- \quad \text{E}^{\circ} = -1.4 \text{ V vs. Hg/Hg}_2\text{SO}_4 \quad (5.3) \\
2H_2O + 2e^- & \rightarrow H_2 + 2OH^- \quad (5.4) \\
4Ce^{3+} + O_2 + 14 H_2O + 12OH^- & \rightarrow 4Ce(OH)_4 + 12 H_2O \quad (5.5) \\
Ce(OH)_4 & \rightarrow CeO_2 + 2H_2O \quad (5.6) \\
NO_3^- + H_2O + 2e^- & \rightarrow NO_2^- + 2OH^- \quad (5.7)
\end{align*} \]

To confirm the composition of the coating formed during the dip-coating (S1) and electrodeposition (S2), an elemental EDS analysis was carried out, on the three types of carbon cloths (MPL, C.C and Vulcan) samples which were then compared.
Figure 5.3 EDS and elemental mapping spectra. MPL, dip-coated with nanoceria suspension (S1) (a) EDS elemental analysis and (b) elemental mapping. MPL electrochemical deposition of CeO$_2$ NPs (S2) (c) EDS elemental analysis and (d) elemental mapping.
Figure 5.4 EDS and elemental mapping spectra. Plain C.C, dip-coated with nanoceria suspension (S1) (a) EDS elemental analysis and (b) elemental mapping. Plain C.C electrochemical deposition of CeO$_2$ NPs (S2) (c) EDS elemental analysis and (d) elemental mapping.
Figure 5.5 EDS and elemental mapping spectra. Vulcan, dip-coated with nanoceria suspension (S1) (a) EDS elemental analysis and (b) elemental mapping. Vulcan, electrochemical deposition of CeO$_2$ NPs (S2) (c) EDS elemental analysis and (d) elemental mapping.

The images presented in figures 5.3 (a) and (b) indicated that for MPL S2 there is a higher weight % of Cerium (37.38%) than for S1 (16.32%). Some other elements can also be seen in the EDS elemental analysis (K, Cl, F). Fluorine probably arises from the PTFE present in the carbon cloth. The source of potassium is unknown but it is possibly due to some
interference from EDS detector. Chlorine probably came from the reactants utilised for this method.

Figure 5.4 (a) and (b) displays EDS from the plain carbon cloth sample (C.C), which indicated the highest concentration of Ce and it was found to be S2 (22.48%) compared to S1 (10.65%).

Fig 5.5 (a) and (b) shows results obtained for the Vulcan sample S1 which presented the lowest loading of Ce (0.48%), while for S2 it was much higher (63.45%). For all samples, it could be seen that carbon was present as expected and from the elemental mapping, it is very clear that cerium was present throughout the carbon cloth area. The figures below show the SEM images of the control samples of plain C.C, MPL, Vulcan, and the respective samples dip-coated in nanoceria suspension (S1) and following electrodeposition of CeO₂ (S2).
Figure 5.6  (a) SEM image of bare plain C.C (b) dip-coated with nanoceria suspension (S1) (c) and electrochemical deposition of CeO$_2$ (S2).
Figure 5.7 (a) SEM image of bare MPL (b) dip-coated with nanoceria suspension (S1) (c) and electrochemical deposition of CeO$_2$ NP (S2).

It can be noted in Figure 5.7 and 5.8 that cracks are apparent which could be due to the electron beam from SEM or the vacuum conditions and perhaps due to the flexible layers. However, it can be seen that for Fig 5.7 (c) and 5.8 (c) that the entire area of the carbon surface is covered by the CeO$_2$ layer, compared to the Fig 5.7 (b) and 5.8 (b) where the NPs are spread out and sometimes unevenly agglomerated.
Figure 5.8 (a) SEM image of bare Vulcan (b) dip-coated with nanoceria suspension (S1) (c) and electrochemical synthesis of CeO$_2$ NP (S2).

It can be seen from figures 5.6 (c), 5.7 (c) and 5.8 (c) that the electrochemical synthesis of CeO$_2$ NP showed a better uniformity of CeO$_2$ NP deposition compared with that from the nanoceria suspension. In the latter case, it can be seen clearly that the NPs were aggregated along the surface area of the carbon fibres compared to the uniform development of a compact layer from the electrodeposition. Thus, the electrochemical synthesis of CeO$_2$ was adopted as
the main method of CeO$_2$ immobilisation on the photoanode. In order to identify the crystalline properties of CeO$_2$ electrodeposited on carbon cloth, XRD testing was conducted. Figure 5.9 shows the crystal structure of CeO$_2$ – C.C species, the peaks at 26º and 44º reveals the reflections of Carbon (002) and Carbon (100), respectively. The other crystal planes are assigned to the diffraction patterns of CeO$_2$, as previously discussed in chapter 2, in which the same patterns are observed in Fig 2.8 (chapter 2). However, the peaks in CeO$_2$ – C.C are less intense than the CeO$_2$ nanopowder, as the CeO$_2$ – C.C was not annealed.

![XRD spectrum patterns of CeO$_2$ – C.C electrodeposited in a plain carbon cloth substrate.](image)

**Figure 5.9** XRD spectrum patterns of CeO$_2$ – C.C electrodeposited in a plain carbon cloth substrate.
5.3.2– Electrochemical behaviour of Carbon cloths

In order to better understand the electrochemical behaviour of the three substrates, cyclic voltammetry was performed, using three different carbon cloths (plain C.C, MPL and Vulcan) as the WE. Results were then directly compared to those obtained with the well known G.C electrode, using $K_4Fe(CN)_6$ as a probe. Due to the novelty of immobilising $\text{CeO}_2$ into carbon cloths, it was necessary to gain insight into the behaviour of this photoanode.

![Cyclic voltammogram recorded in 5 mM potassium ferrocyanide in 0.1 M KCl at a bare G.C as WE with a geometric area of 0.07 cm$^2$ and a scan rate of 0.1 V/s.]

**Figure 5.10** Cyclic voltammogram recorded in 5 mM potassium ferrocyanide in 0.1 M KCl at a bare G.C as WE with a geometric area of 0.07 cm$^2$ and a scan rate of 0.1 V/s.
Figure 5.10 shows the C.V of the redox system Potassium-Ferri/Ferrocyanide using a G.C as the WE. A classic cyclic voltammetric curve was obtained, in which the current was measured as a function of applied potential. It has been established as a standard procedure for the characterisation of electrochemical processes, where by Fe$^{2+}$ oxidises on the way forward and Fe$^{3+}$ reduces on the way backwards. When analysing a voltammogram, it is important to consider whether the electron transfer rate is reversible or quasi/irreversible in nature.

In order to identify the type of voltammogram, such as that of the ferro/ferricyanide system, the peak-to-peak separation ($\Delta E_p = E_{pa} - E_{pc}$) should be measured. For a one-electron transfer at 25ºC, the $\Delta E_p$ should approach 57 mV in the fully reversible system for 1 electron. A value greater than 60 mV suggests that the electron transfer is quasi-reversible. Electrochemical reversibility requires that the electron transfer kinetics are fast relative to the predominant rates of mass transport [30]. Understanding the interfacial electron-transfer and heterogeneous electron-transfer reactions and consequently, the rate constant ($k^o$) is a fundamental physical and chemical factor [31]. The standard rate constant is simply a measure of the kinetic facility of a redox couple. A system with a large $k^o$(0.1 to 10 cm$^{-1}$) will achieve equilibrium faster than a system with a small $k^o$ [30]. The electrode reaction rate constants $k^o$ for G.C, C.C, MPL and Vulcan will be estimated from the $\Delta E_p$ in the voltammograms of Fig 5.10, 5.11, 5.12 and 5.13.
Figure 5.11  Cyclic voltammogram recorded in 5 mM potassium ferrocyanide in 0.1 M KCl at a bare C.C as WE with a geometric area of 1 cm² and a scan rate of 0.1 Vs⁻¹.

Similar curves to 5.10 are presented in Figures 5.11 and 5.12, except that a certain noise is observed, possibly due to the large currents involved and perhaps a limitation of the potentiostat. Compared to the GC electrode the area of the carbon cloth is 14 times bigger. These results indicate that the electrode presented similar behaviour towards the ferri/ferrocyane redox couple as the well-known G.C.
Figure 5.12 Typical Cyclic voltammogram recorded in 5 mM potassium ferrocyanide in 0.1 M KCl at a bare MPL as WE with a geometric area of 1 cm² and a scan rate of 0.1 Vs⁻¹.

The values of the surface rate of heterogeneous constant $k^0$ for the redox couples can be estimated using equation 5.9 [25]. The parameter $Ψ$ is expressed as [36]:

$$Ψ = \frac{k^0}{[π D_o v (F/RT)]^{1/2}} \quad (5.9)$$

where $D_o$ is the diffusion coefficient and $v$ is scan rate and $F$, $R$, $T$ have the normal meanings.
Using the cyclic voltammogram of 5 mM K₄[Fe(CN)₆] in 0.1 M KCl at the G.C electrode, with the scan rate of 0.1 \text{Vs}^{-1} as shown in Figure 5.10. The measured value of $\Delta E_p$ was 222 mV which corresponds to 0.10 of the dimensionless rate parameter $\Psi$ from Table 5.2. Then, the $k^o$ value at 278 K can be estimated to be $2.8 \times 10^{-3}$ \text{cm} \text{s}^{-1} using $D_0 = 6.3 \times 10^{-6}$ \text{cm}^2\text{s}^{-1} [32] and $v = 0.1 \text{Vs}^{-1}$ according to Eq 5.9.

**Table 5.2** Relationship between the standard rate constant and separation of anodic and cathodic peak potentials. Adapted from [31].

<table>
<thead>
<tr>
<th>$\Delta E_p$/mV</th>
<th>$\Psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>144</td>
<td>0.25</td>
</tr>
<tr>
<td>176</td>
<td>0.16</td>
</tr>
<tr>
<td>220</td>
<td>0.10</td>
</tr>
<tr>
<td>288</td>
<td>$5.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>382</td>
<td>$2.0 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

The values of standard rate constant $k^o$ for other redox couples are similarly estimated and are summarised in Table 5.3. These are estimated, not taking into account i$R$ drop in the system. However, their relative values indicate that MPL behaves better than plain C.C.

**Table 5.3** Electrode reaction parameters obtained from cyclic voltammetric measurements

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$\Delta E_p$/mV</th>
<th>$k^o$ \text{cm} \text{s}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>222</td>
<td>$2.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>C.C</td>
<td>340</td>
<td>$1.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>MPL</td>
<td>180</td>
<td>$3.4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Figures 5.10, 5.11 and 5.12 displays voltammograms that are electrochemically quasi-reversible systems, in which the potential difference between the cathodic and anodic peak potentials, $\Delta E_p$ is more than 57 mV. The results displayed in Table 5.3 for the rate constant indicates that the electrode MPL would achieve a faster electrochemical kinetics for the redox couple $[\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4-}$ compared to the well-known G.C.

Another important piece of information that can be taken from the voltammograms is the electro-active surface area of the electrodes. The electrochemical reaction of $\text{K}_4\text{Fe(CN)}_6$ which diffuses to the electrode surface is described according to the following equation for a quasi-reversible electron transfer process, Randles–Ševčík (RS) equation [31]:

$$I_p = 299000 \, n^{3/2} \, \alpha^{1/2} \, A \, D^{1/2} \, C \, v^{1/2}$$  

(5.10)

Where $I_p$ is peak current in amps, $n$ is the number of electrons transferred ($n = 1$ for $[\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4-}$), $\alpha$ is the transfer coefficient (usually assumed to be close to 0.5), electrochemically active surface area (cm$^2$), diffusion coefficient (cm$^2$s$^{-1}$), concentration of ferrocyanide (mol/cm$^3$) and scan rate (Vs$^{-1}$), respectively. The diffusion coefficient of potassium ferrocyanide is 6.3 x10$^{-6}$ cm$^2$s$^{-1}$ at 25º C [32].

The effective area of a C.C and MPL were estimated in order to compare the real electrochemical area for both electrodes. Table 5.4 indicates the real electrochemical surface area of C.C and MPL.
Table 5.4 Real electrochemical and geometrical surface area of the SPCE-CeO₂ and SPCE.

<table>
<thead>
<tr>
<th>Geometrical surface area WE (cm)²</th>
<th>A real (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.C</td>
<td>1</td>
</tr>
<tr>
<td>MPL</td>
<td>1</td>
</tr>
</tbody>
</table>

The results displayed indicate that the real electrochemical area of C.C is 6.7 times bigger than that of the MPL. Such a significant difference in the area of C.C is probably due to the carbon fibres increasing the exposed area (as can be seen in the SEM images). In contrast, the MPL has PTFE that could be insulating some of the areas of the carbon cloth.

However, in Fig 5.13 the voltammogram for the Vulcan electrode, a broad curve is reminiscent of a significant capacitive (non-Faradaic) contribution. This could be accounted for the interference caused by the presence of 20% Platinum on the Vulcan Carbon support catalyst. For the other materials, there is no catalyst coating. Furthermore, the chlorides (present in the electrolyte) could also affect the kinetics of the platinum oxide formation/reduction process, possibly due to its Cl adsorption at the platinum surface rather than hydroxyl radicals (or water). Where the adsorption of chlorides on the platinum surface could compete with OH⁻, this competitive specific adsorption could have retarded or restrained the kinetic conditions on the electrode surface [22]. Therefore, despite the presence of the Pt, this is not a good ferri/ferrocyanide redox couple behaviour, thus indicating poor electron transfer capability.
Figure 5.13  Cyclic voltammogram recorded in 5 mM potassium ferrocyanide in 0.1 M KCl at a bare Vulcan as WE, with a geometric area of 1 cm$^2$ and a scan rate of 0.1 Vs$^{-1}$.

5.3.3 – Voltammetric characterisation of formic acid.

In order to select the best photoanode for the PEFC application, FA was utilised as the model organic compound. The voltammogram obtained for formic acid at a CeO$_2$-coated- C.C, MPL and Vulcan electrode in dark, light and blank conditions are shown in figures 5.14, 5.15 and 5.16 respectively.
Figure 5.14 Cyclic voltammograms of CeO$_2$-C.C recorded in 16 mM FA in 0.1 M KCl in dark (solid line), with light from the under solar simulator (dashed line), and under blank conditions (dotted line), without CeO$_2$ on the photoanode. The WE was a CeO$_2$ – plain carbon cloth (area =1 cm$^2$) for dark and light conditions. The scan rate was 0.05 V s$^{-1}$.

As can be seen in figure 5.14, there is a clear difference between the three conditions employed. FA voltammetry in the dark and blank yields only a small current, indicating that there is only small oxidation of FA at the bare surface of the carbon cloth-based electrode in both light and dark conditions. This is in contrast to the much larger current generated with CeO$_2$ upon light exposure from the solar simulator for the coated layer. This large difference
in current magnitudes between dark and light reflects the rate at which photogenerated holes are absorbed by FA, thus confirming that enhanced FA oxidation occurs due to CeO₂ photocatalysis. This is possibly due to the FA being readily oxidised; such behaviour has also been observed by Enright et al. when the photoanode was a carbon ink coated with TiO₂ [1]. However, in his study, it was observed a steady current, rather than a peak current, suggesting the oxidation for the CeO₂–plain carbon cloth is kinetically faster than the carbon ink coated with TiO₂.

![Cyclic voltammograms recorded in 16 mM FA in 0.1 M KCl in dark (solid line), with light from the under solar simulator (dashed line), and under blank conditions (dotted line), without CeO₂ on the photoanode. The WE was a CeO₂–microporous carbon cloth (MPL) (area =1 cm²) for dark and light conditions. The scan rate was 0.05 Vs⁻¹.](image)

**Figure 5.15** Cyclic voltammograms recorded in 16 mM FA in 0.1 M KCl in dark (solid line), with light from the under solar simulator (dashed line), and under blank conditions (dotted line), without CeO₂ on the photoanode. The WE was a CeO₂–microporous carbon cloth (MPL) (area =1 cm²) for dark and light conditions. The scan rate was 0.05 Vs⁻¹.
The same behaviour was not observed, when the photoanode (WE) was MPL. However, the current produced by light and dark conditions is essentially the same, even slightly higher under dark conditions. This behaviour may be ascribed to the larger amount of cerium coated on the carbon cloth and also possibly could be due to its different morphology. Although MPL is a good quality electrode (see Table 5.3) perhaps the coating is reducing its quality. As it is a microporous layer, the film formed is more likely thicker than for the plain carbon cloth. Furthermore, the layer thickness is an important factor to take into consideration. For a photoelectrocatalysis, thicker layers can block active sites and prevent the formation of photogenerated holes [1].

The different CVs observed (lower photocurrent) for MPL and Vulcan shown in figures 5.15 and 5.16 respectively, compared to the plain carbon cloth (shown in figure 5.14), could also be due to the presence of 30 wt% of PTFE treatment on the carbon cloth (MPL). It is also possible that the hydrophobic surface of these electrodes may have led to the repulsion of the water on this material adversely affecting its behaviour (and the electron transfer capability).
Figure 5.16 Cyclic voltammograms recorded in 16 mM FA in 0.1 M KCl in dark (solid line), with light from the under solar simulator (dotted line), and under blank conditions (dashed line), without CeO$_2$ on the photoanode. The WE was a CeO$_2$ – Vulcan carbon cloth (area =1 cm$^2$) for dark and light conditions. The scan rate was 0.05 Vs$^{-1}$.

The voltammogram in Fig 5.16 shows a FA CV using the Vulcan electrode. It is clear that the voltammetry is different compared to that of C.C and MPL, as was also observed during the electrode calibration in potassium-ferri/ferrocyanide. There is no substantial difference between the three conditions investigated (light, dark, and blank). This behaviour may also be attributed to the layer thickness, and once more the 20% Pt present in this carbon cloth may be
adversely affecting its behaviour. That could also be favoured by the morphology of the deposited film especially due to the surface roughness surface of the prepared electrode. Perhaps chloride from the electrolyte may be adsorbed on the electrode surface inhibiting the adsorption of HCOOH. Such behaviour has also been found by Guillaume et al. [22]. The vulcan electrode did not show a good result for it to be used as a photoanode. However, it was used as the air cathode, due to the Pt catalyst layer for the promotion of the ORR. In summary, of the three types of carbon cloth for FA PEFC performance, the plain carbon cloth (C.C) showed the best results, considering the electrochemical response under light conditions differential. Therefore, the photoanode chosen for further experiments was the electrodeposited CeO₂ onto the plain carbon cloth (CeO₂-C.C).

In order to evaluate the effect of concentration of FA and the changes in current utilizing the novel photoanode (CeO₂-C.C) under the solar simulator, a photocurrent profile was carried out. Figure 5.17 shows the dependence of the level photocurrent as a function of FA concentration. It is apparent that the current increases as FA concentration rose as expected. The increased concentration of FA leads to the greater abstraction of photo-formed holes from the surface-bound of CeO₂ [1].
Figure 5.17  Linear sweep voltammogram (LSV) recorded for a CeO$_2$-C.C (area =1 cm$^2$). Sweep at 0.1 V s$^{-1}$ in 0.1 M KCl with incremental amounts of FA added with exposure to the solar simulator. Photocurrents increased with FA concentrations of 0, 16, 36, 66 and 86 mM.

The photocurrent increased with potential up to $-0.2$ V vs Hg/Hg$_2$SO$_4$, possibly because at such low potentials the photocatalytic process is governed by slow electron transport within the CeO$_2$ layer. Similar behaviour has also been observed by Plieth et al. using TiO$_2$ as a photocatalyst [33].
5.3.4 – The use of the novel CeO$_2$-C.C PFC configuration

The photocurrent of the PEFC device was measured in a one-compartment cell with a two-electrode configuration as shown previously in figure 5.2. In this instance, the CeO$_2$-C.C was employed as a photoanode (WE), and an air cathode (Vulcan) as the cathode. Various organic compounds were tested as potential fuel for this device using the configuration in Fig 5.2. All runs were repeated at least two times to check the reproducibility. As can be seen, in Fig 5.18 there is an increase in current over time independent of the system operating at light or dark condition. This could possibly be due to the fuel also being oxidised by the Pt/C from the air cathode.

![Graph showing photocurrent response](image)

**Figure 5.18** Photocurrent response of CeO$_2$-C.C to solar irradiation of 16 mM FA (a) in 0.1 KCl M solution. The voltage was collected for 500s with a Pico technology ADC-20 data logger across a 1 kΩ resistor. The light was switched on at 100s and switched off at 300s.
As can be seen, there is no significant transition between light and dark conditions. This confirms that there is no interior bias between the two electrodes in the as-prepared PEFC system. The possible explanations for this behaviour could be the thickness of the CeO$_2$ layer along the carbon fibres or possibly may be due to the instability of the layer.

Figure 5.19 shows an SEM image of the CeO$_2$ - C.C used after exposure to FA in an individual cell. As can be seen even at a short time exposure to a low concentration of acid, the uniform layer of CeO$_2$ (Fig 5.6 (c) from S2) was dislodge from the carbon fibres surface, indicating that the CeO$_2$ layer desorbed from the surfaces of the fibres. It should be mentioned that a neutral medium was also tested (e.g. 10 mg/L of methylene blue). However, the CeO$_2$ layer also sloughed off in this case.

![Figure 5.19: SEM image of CeO$_2$-C.C used in the PEFC system after exposure to FA in 0.1 M KCl](image)

**Figure 5.19** SEM image of CeO$_2$-C.C used in the PEFC system after exposure to FA in 0.1 M KCl.
In an attempt to identify the issues with the performance of CeO$_2$-C.C PEFC system, several key changes were made, including exploring the use of different electrolytes. For example, it could be possible that Cl$^-$ from the KCl electrolyte could be forming H$_3$O$^+$ or HCl on the photoanode surface and perhaps the reason for CeO$_2$ being spalled off from the carbon fibres (chemical dissolution from HCl). Therefore, HNO$_3$ and Na$_2$SO$_4$ were used instead as the electrolyte. However, there was no improvement in the PEFC results. An attempt was then made to explore different times of CeO$_2$ electrodeposition, to increase or reduce the layer thickness of the CeO$_2$ coating along the carbon fibres. The deposition time was varied from 20s to 20 min and subsequently tested in the PEFC system. The thickness varied from approximately 300 nm to 1.05 µm, as can be seen in figure 5.20 for the 20s and 30 min deposition time. However, no significant changes were observed in the PEFC efficiency.

**Figure 5.20** SEM images of CeO$_2$-C.C, under different electrodeposition time (a) 30 min (b) 20 s.
With a view to understanding if the issue with the PEFC system was solely due to the CeO\(_2\) coating, a comparison with TiO\(_2\) was carried out. This material is well known as an efficient photocatalyst and has been widely employed in such a capacity [34].

5.3.5 - TiO\(_2\) Photoanode Characterisation

As previously discussed, the synthesis of TiO\(_2\) was carried out using the method of Zhai et al., in which TTIP and ethanol were utilised [16]. In order to validate the experiment, a standard arrangement (Fig 5.2) was used with the standard photocatalyst. For this procedure, the hydrolysis yields a milky suspension of hydrated TiO\(_2\) on the carbon fibres before annealing at 400\(^\circ\)C. Figure 5.21 shows the elemental analysis of TiO\(_2\) - C.C. As expected titanium and carbon can be seen in the EDS spectrum.

![EDS spectrum of the synthesised TiO\(_2\) - C.C](image)

**Figure 5.21** EDS spectrum of the synthesised TiO\(_2\) - C.C via an in situ deposition and subsequently annealed at 400\(^\circ\) for 3h.
Figure 5.22 shows the SEM images of the TiO$_2$-C.C, and it can be seen that TiO$_2$ particles adhered along the carbon fibres, in the form of isolated islands. It is clear that the coating is not as uniform as the CeO$_2$ coating. The photoelectrocatalytic properties of TiO$_2$-C.C were then tested in the novel PEFC configuration.

![SEM image of synthesised TiO$_2$-C.C](image)

**Figure 5.22** SEM image of the synthesised TiO$_2$-C.C via an in situ deposition and subsequently annealed at 400º for 3h

For the bandgap determination, $(a\nu)^2$ (eV/cm$^2$) is plotted against the incident photon energy $\nu$. This is known as the Tauc plot, as previously discussed in chapter 2. The x-axis intercept of a line drawn on the linear part of the curve gives the value of the direct bandgap of TiO$_2$, as can be seen in Fig 5.23. The bandgap value determined for TiO$_2$-C.C was found to
be 3.02 eV, thus suggesting that there is a higher content of rutile than anatase, as shown in Table 3.1 in chapter 3. It should be noted that there is no result of band gap value for CeO$_2$-C.C possibly because the layer of CeO$_2$ along the carbon fibres was yellow, but with the black background of the carbon cloth it was not possible to obtain a reflectance or perhaps it was due to the lack of optical density for CeO$_2$-C.C

![Graph](image)

**Figure 5.23** Plot of $(\alpha h\nu)^2$ vs. the incident photon energy for the estimation of direct optical band gap energies from the TiO$_2$-C.C via an in situ deposition and subsequently annealed at 400º for 3h.
5.3.6 – The use of the novel TiO$_2$-C.C PEFC configuration

It should be pointed out that there are many recent reports on the use of TiO$_2$ immobilized in the anode, of a PEFC system [1, 9, 12]. In these studies, TiO$_2$ is usually synthesised in self-organised nanotubes via electrochemical anodization and subsequently doped with graphene oxide (GO) or cadmium selenide (CdSe), as reported by Kim et al. and by other authors [15,16, 27].

The purpose of using this simple TiO$_2$ synthesis into carbon cloth is just to confirm and investigate if the TiO$_2$-C.C can be used as an alternative to the CeO$_2$-C.C photoanode in the novel PEFC configuration (as shown in Fig 5.2). Figure 5.24 shows the photo-response behaviours of the TiO$_2$-C.C PEFC system, using two different organic compounds (FA and DCF) as fuels. The possible difference in the behaviour of TiO$_2$-C.C compared to CeO$_2$-C.C could be the higher stability of TiO$_2$ over CeO$_2$ under neutral pH, as can be seen in Pourbaix diagram shown in chapter 1 (section 1.7 and 1.8) [35].
Figure 5.24 Photocurrent response of TiO$_2$-C.C to solar irradiation of (a) 16 mM FA and (b) 500 mg/L DCF in 0.1 KCl solution. The voltage was collected for 500s with a Pico technology ADC-20 data logger across a 1 kΩ resistor. The light was switched on at 100s and switched off at 400s for FA, and switched on and off every 80s for DCF.

As can be seen, a responsive photocurrent is obtained when the illumination is turned on. An instantaneous current response was found both in the presence and absence of light.
Background dark currents indicate the existence of a dark reaction and is believed that it could be due to the consumption of the fuel (FA or DCF) at the anode in the dark due to polarity. Such behaviour has also been reported by Enright et al. [1]. The instant increase of voltage under the solar light irradiation confirms that an interior bias existed between the two electrodes and that the novel PFC configuration could work well under the light illumination conditions. Through the measurement of voltage across a fixed load resistance of 1kΩ, the current was calculated via Ohm’s law and the current density was obtained upon the exposure of the photoanode to the solar simulator. The resultant current density was found to be 4.7 and 0.5 \( \mu \text{A/cm}^2 \) for FA and DCF respectively. This value was calculated by using the difference of current obtained from the transition from dark to light (e.g. 60 \( \mu \text{A} \) and 6\( \mu \text{A} \) for FA and DCF respectively) divided by the real electrochemical area of C.C electrode (12.8 cm\(^2\)).

The performance of the TiO\(_2\)-C.C PEFC configuration is good considering that it involved a simple procedure for fabricating an undoped TiO\(_2\) photocatalyst. A recent study from Xie et al., using a complex heterostructured doped ZnFe\(_2\)O\(_4\)/TiO\(_2\)-NTs photoanode and an air cathode PEFC system [27], a Ti sheet was used as the conductive support/anode and a complex two-step procedure of synthesis. The current density obtained with several organic compounds as fuel (e.g. MB, tetracycline hydrochloride and oxytetracycline hydrochloride) ranged from 11.4 to 34.2 \( \mu \text{A/cm}^2 \), concentrations of 0.1 mM were used under solar radiation. The bandgap of the photoanode was only 2.07 eV due to doping [27].

It should be noted that the TiO\(_2\)-C.C could be reused up to 4 times with similar current density values obtained, confirming its stability. The novel configuration of this PEFC device showed good preliminary results. However, the evaporation of the electrolyte/fuel even when
the cell was kept in a water bath or when a UV source equipped with water jacked vessel was a problem. This issue can adversely affect the PEFC performance due to the reduction of the level of electrolyte/fuel leading to the loss of contact with the Pt/C of the air cathode as the liquid evaporates. Clearly, there are clear advantages of using such a simple method to fabricate this photoanode relative to other methods of catalyst preparation, where its much more complex and time-consuming [15,16, 27]. This system uses an undoped CeO$_2$ or TiO$_2$ on an inexpensive carbon cloth and operates at room temperature.

5.4 – Conclusions

Photoelectrochemical fuel cells have experienced rapid development in the past few years due to progress in nanomaterials. There is an evident benefit in using the synthesis of TiO$_2$ on carbon cloths and to synthesise CeO$_2$-C.C on the same material (plain carbon cloths). It is a relatively facile method for fabrication of anodes, compared with the more commonly used methods of catalyst deposition. It requires no thermal treatment and is low cost. This method utilised undoped CeO$_2$ NP deposited on an inexpensive carbon cloth, which has the advantages of being a flexible conductive substrate, inexpensive, and stable, and it has not been reported previously in the literature. Preliminary results, however, showed that CeO$_2$-C.C was not stable under the conditions of the PEFC, most likely due to poor adhesion of CeO$_2$ onto the C.C. However, good photocurrent responses for FA oxidation were obtained when a traditional three-electrode system was utilised. In order to show the functionality of the novel PEFC configuration, TiO$_2$-C.C was utilised and it showed promising results with maximum current density values of 4.7 $\mu$A/cm$^2$ and 0.5 $\mu$A/cm$^2$ for FA and DCF respectively. This, if compared favourably with recent studies, showed very promising results.
The goal of this project was to explore the application of CeO$_2$ in a PEFC system. It is worthwhile to explore not just carbon cloths but other conductive supports as well the synthesis of CeO$_2$ nanorods (NRs) since they can be more effective due to the existence of direct electrical pathways for photogenerated charges along the 1D nanostructure, as reported by other authors [15,16]. Perhaps they may well demonstrate good performance in the degradation of organic contaminants such as FA and DFC. The novel PEFC configuration should be improved in order to avoid the evaporation of the electrolyte/fuel operation. Perhaps the use of a quartz plate on the top of the cell could overcome this issue since it would enable light to traverse and prevents evaporation. The use of a flow-through cell could also be an alternative worth exploring. A heat sink placed in between the light source could also possibly be beneficial. In order to improve the resistance of the cell different ratios of anode/cathode could also contribute to cell performance. A larger cathode would enhance the oxygen reduction reaction and consequently increase the rate of resultant photoanode oxidation reaction, ultimately leading to improved pollutant degradation and higher PEFC power output. However, there are clear benefits of using such a simple method (combining carbon cloths and catalyst) to fabricate this photoanode, in comparison to other methods of catalyst production. This simple PEFC uses an undoped CeO$_2$ or TiO$_2$ on an inexpensive carbon cloth and operates at room temperature and shows promise once certain problems are resolved.
5.5 - References


CHAPTER 6

ELECTROANALYSIS OF PHARMACEUTICAL COMPOUNDS
Chapter 6 – Electroanalysis of pharmaceutical compounds

6.1- Introduction

In this chapter, the use of electrochemical techniques for the determination of pharmaceutical compounds will be explored. In the last decade, the use and investigation of electrochemical techniques in the analysis of pharmaceutical drugs and other compounds have shown promising results.

6.1.1 – Analytical Techniques

There are a wide range of analytical techniques available for quantification of pharmaceutical compounds, notably spectrophotometric techniques (UV-Visible), Fourier-transform infrared spectroscopy, Raman spectroscopy, fluorimetry spectroscopy, nuclear magnetic resonance, mass spectrometry. Chromatographic techniques (Thin Layer Chromatography, High-Performance Liquid Chromatography, Ultra High-Pressure Liquid Chromatography, Liquid Chromatography-Mass Spectrometry and Gas Chromatography among others) [1,2]. These analytical techniques can provide a high degree of specificity and selectivity necessary for the accuracy of an analytical method.

HPLC has historically been the most widely utilised technique for the detection of organic compounds. Typically, a UV detector is used, which is capable of monitoring a wide range of wavelengths. The choice of wavelength detection is critical to guaranteeing that all UV-absorbing components are detected [1]. However, there are disadvantages to this technique. HPLC can be costly due to the requirement for the use of expensive organic solvents for the mobile phases; the high price of columns, which if not well conserved, can adversely affect the
column long term reproducibility due to the nature of column packing. It can also be difficult to troubleshoot the problem (time-consuming) such as pressure variation, contamination in the detector components and it can be costly to develop new HPLC methods where the choice of pH and solvents can be critically important. Furthermore, HPLC and UV-Vis spectroscopy possess low sensitivity for certain compounds and some may not even be detected [2]. In addition, when performing simultaneous determinations of organic molecules, the peaks can overlap, leading to a misinterpretation of the estimation of the amounts present of each compound.

6.1.2 - Electrochemical methods

The use of electrochemical techniques in the analysis of pharmaceuticals drugs and other compounds has shown promising results, and the investigation of these methods has increased in recent years. This interest in electrochemical techniques can be credited partially to more sophisticated instrumentation (e.g potentiostats with higher sensitivity) and is also due to an interest in obtaining a better understanding of the techniques themselves. When compared with other analytical techniques, electrochemical methods provide simple, rapid, selective detection using relatively low-cost instrumentation. There is no need for the use of expensive solvents, gases and chromatographic columns with electroanalytical techniques [3-7].

The efficacy of the electrochemical methods is largely determined by the electronic conductivity of the working electrode surface. Therefore, in order to improve the electrochemical performance of this electrode, a typical strategy is to design composites combining electrocatalytically active materials with conductive additives to modify the working electrode surface. However, the main issue typically encountered during the
fabrication of a sensor device is the preparation of the working electrode, as it is the key component in the electroanalytical technique. There are numerous materials that have been developed to solve this issue, with carbon-based materials showing particular promise. These include glassy carbon electrodes [8], carbon paste electrodes [3], graphene electrodes [9], boron-doped carbon diamond electrode (BDDE) [6], modified glassy carbon electrodes and screen-printed carbon/graphite electrodes [10,11]. The use of catalysts materials to improve the stability and conductivity of the WE has become an area of interest for electroanalysis [8].

Additionally, over the last decade, many studies using electroanalytical methods for quantification of pharmaceuticals in aqueous media have been reported [3,12, 39-43]. For example, an amberlite XAD-2 and titanium dioxide nanoparticles modified glassy carbon paste was developed for the detection of imipramine, trimipramine and desipramine which are used to treat depression [5]. The electrochemical behaviour of these drugs was investigated using cyclic voltammetry (CV), chronocoulometry (CC) and electrochemical impedance spectroscopy (EIS) [5]. A research group from Brazil developed a working electrode using BDDE and square wave voltammetry (SWV) for the determination of cocaine and screening of the most common adulterants (benzocaine, caffeine, lidocaine, phenacetin, paracetamol, and procaine) in seized cocaine samples [6]. Khairy et al. developed a screen-printed electrode coated with CeO₂ NPs and it was utilised for the simultaneous detection of paracetamol, codeine and caffeine using DPV and enhance in the conductivity of the WE was observed [32].

A carbon nanotube paste electrode modified in situ with Triton X 100 was developed for the individual and simultaneous determination of acetaminophen (ACOP), aspirin (ASA) and caffeine (CAF). The electrochemical behaviour of these three molecules was analysed
employing CV, EIS, CC. After optimisation of analytical conditions employing this electrode at pH 7.0 in PBS (0.1 M), the limits of detection (LOD) of $2.58 \times 10^{-8}$ M, $8.47 \times 10^{-8}$ M and $8.83 \times 10^{-8}$ M for ACOP, ASA and CAF respectively were obtained [3].

6.1.3 – Screen-printed carbon paste electrodes

Relatively conductive carbon electrodes can be fabricated through the use of a screen-printing technique that offers the possibility of manufacturing large numbers of identical electrodes in a reproducible, low-cost, and disposable format. It also allows the integration of chemically functionalised materials to the electrode surface in a straightforward way. Screen-printing fabrication has two main advantages over other methods of electrode manufacture. Primarily, the electrode area, thickness, and structure can be simply and accurately controlled. Secondly, the incorporation of catalysts can be achieved simply by adding them to the screen-printing ink (paste) forming the working electrode. Conversely, a disadvantage of screen printing is that it is limited to flat surfaces [10].

Screen-printed electrodes (SPCE) are produced by spreading a thixotropic liquid across a mesh screen allowing control of the shape and size of the resultant electrode. The thixotropic ink normally consists of a variety of compounds such as graphite, carbon black, organic solvents and a polymeric binder [13]. The electrochemical performance of fabricated electrochemical sensing platforms depends on a number of diverse parameters such as the formulation of the working electrode (binder/solvent combinations) and it is not openly found in the literature. This is because of its commercial value [4]. Currently, SPCE find applications in diverse areas of electrochemistry; however, it has been used most often in the bioelectrochemical field for sensing applications [15,11]. Figure 6.1 (a) shows the screen-
printed electrode used in this study and Fig 6.1 (b) shows a cross-section image of an SPCE where the substrate is propylene (PP). A conducting silver layer is generally deposited underneath active layers of non-porous and porous carbon, in order to decrease the electrical resistance and consequently minimise the $iR$ drop during voltammetric analysis [10,16].

Figure 6.1 (a) Photograph of disposable SPCE (DRP 110) from Metrohm-DropSens. The working and counter electrodes are made of graphite and the reference electrode is made of silver paste. (b) A scanning electron microscope image of a cross-section of a screen-printed porous carbon electrode. Adapted from Ref. [16].

6.1.4 – Molecules for electroanalysis

A formulation of drugs containing acetaminophen (paracetamol: N-acetyl-p-aminophenol) abbreviated as ACOP, acetylsalicylic acid (ASA) and caffeine (CAF) (see structure in section 6.3.1.4) is used to relieve pain from common discomforts such as
headaches, muscle aches, menstrual cramps, colds and sinus infections. However, an increased dosage of this combination of drugs may induce nausea, diarrhoea, abdominal pain, seizures, and an irregular heartbeat, and in the worst-case scenario, it can cause hepatic toxicity and kidney damage. For this reason, the determination of these substances in trace quantities is important [3]. Electrochemical techniques using modified electrodes have been investigated for the estimation of levels of ACOP, ASA and CF when present individually as well as their simultaneous determination in certain pharmaceutical formulations [3, 17-19].

The purpose of this study is to compare the sensitivity and selectivity of the SPCE-CeO$_2$/SPCE-Bare with and without vacuum heat treatment.

6.2 – Experimental

6.2.1 – Materials

Unless specified otherwise, all chemicals were purchased from Sigma Aldrich, Acros Organics or from Fisher Chemical and were used as received without any further purification. All solutions were prepared using ultrapure water (18.2 MΩcm). The Britton-Robinson buffer solutions (BRB) (pH 2.0 – 12.0) were prepared with a mixture of 0.04 M of acetic, boric, and phosphoric acid solutions. The pH was adjusted using a 2 M NaOH or either a 0.2 M HCl solution.

- Acetaminophen 99% (ACOP) (Sigma)
- Acetic Acid 99.5 % (CH$_3$COOH) (Fisher)
- Boric Acid 99% (H$_3$BO$_3$) (Acros)
- Caffeine 99.8% (CAF) (Fisher)
- Excedrin ® - Bayer (purchased from a Dublin pharmacy) (each tablet contains 250 mg ACOP, 250 mg ASA and 65 mg CAF).

- Hydrochloric acid 37% (HCl) (Fisher)

- Phosphoric acid 98% (H₃PO₄) (Fisher)

- Acetylsalicylic acid 99% (ASA) (Sigma)

- Sodium hydroxide pellets (NaOH)(Acros)

- Synthesized Cerium dioxide NPs (Described in chapter 2)

6.2.2 – Equipment

As described earlier all voltammetric measurements were performed on an Eco Chemie B.V, Electrochemical Work Station, model Autolab PGSTAT 12 (The Netherlands) using GPES software (version 4.9). All measurements were conducted using a three-electrode one compartment configuration, in which the working electrode was graphite based with a geometric area of 4 mm diameter, and 15 ± 4 µm thickness. The counter electrode consisted of a graphite film, and a silver pseudo-reference electrode was also part of the three-electrode system. However, in order to avoid any interference due to the instability of the reference electrode (Ag- as the pseudo-reference electrode), an external reference electrode was utilised instead (Hg/Hg₂Cl₂, KCl (sat’d) – saturated calomel electrode (SCE)). Screen-printed electrochemical sensors were purchased from Methohm-DropSens, model DRP-110 with dimensions: 3.4 x 1.0 x 0.05 cm (Length x Width x Height) (no information was available though on SPCE composition [36]). Scanning electron microscopy (SEM) images were obtained using a Hitachi SU 6600 FESEM model. An acceleration voltage of 5 kV was employed. A Labquest2 digital pH meter was utilised together with a calibrated pH electrode
to measure the pH of solutions. A Gallenkamp (from Fistreem International Ltd) vacuum oven was used under 1 atm for further treatment of the sensors.

6.2.3 - Methodology

6.2.3.1 – Preparation of the modified electrode (SPCE-CeO₂)

All SPCEs were exposed to an electrochemical pre-treatment (EP), in an attempt to remove impurities and thus improve their electroactivity, and also to alter the WE surface wettability (hydrophobicity/hydrophilicity). Each SPCE utilised was subject to an anodic treatment. A potential of +1.4 V (vs. SCE) was applied for 300s in 0.05 M phosphate buffer solution (pH 7.2), after which it was rinsed with deionised water. Such pre-treatment has been reported previously [4,20,21]. For example, it has been reported by Moreno et al. that the EP can introduce new electrochemically active sites by removing impurities on the SPCE active electrode surface [21].

A suspension of the nanoceria annealed at 900°C produced in chapter 2 was prepared by adding 0.5 mg of NPs in 1 mL of ultrapure water. The temperature of 900°C was chosen based on the optimisation carried out in chapter 3. After the SPCE pre-treatment, 5 µL of this suspension was drop cast directly on the WE surface by a micropipette and the sensor was exposed to a heat treatment in a vacuum (7.6 torr) oven for 1h at 100°C, thus completing the preparation of the modified SPCE-CeO₂. This vacuum heat treatment (VHT) was necessary in order to allow the NPs to strongly adhere to the WE surface thus avoiding dislodgement during the subsequent electrochemical analysis. All experiments were carried out at room temperature (20–23°C) using a fresh electrode for each analysis and all solutions were stirred for 60s with
an equilibration time of 30s between each consecutive analysis. A summary of the procedure is shown in the flowchart in figure 6.2.

Figure 6.2 (a) Illustration of the EP performed at SPCE. A potential of +1.4 V (vs. SCE) was applied for 300s in 0.05 M phosphate buffer solution (pH 7.2) (b) CeO2 annealed at 900ºC produced in chapter 2 was prepared by adding 0.5 mg of NPs in 1 mL of ultrapure water. 5 µL of this suspension was drop cast directly on the WE surface (c) thermal treatment in a vacuum (7.6 torr) oven for 1h at 100ºC, thus completing the preparation of the modified SPCE-CeO2.

6.2.3.2 – Square wave voltammetry (SWV)

For analytical purposes, square wave voltammetry is usually the ideal method for analysis as it suppresses the background (non-Faradaic or capacitive) current effectively and has higher sensitivity compared to other electrochemical techniques [22]. In this approach, the effective scan rate is controlled by three variables: the square wave frequency (f), the potential step height (E_{step}) and the pulse height (E_{pulse}). This method offers an increase in peak height and enables much faster scan rates into the Vs^{-1} range to be employed and removes double layer charging [23]. Figure 6.3 shows the SWV waveform that consists of a square wave
superimposed on a staircase. The currents at the end of the forward and reverse pulses are both recorded as a function of staircase potential. The difference between them, the net current, is larger than either of its two-element parts in the region of the peak which is centred on the half-wave potential [22].

Figure 6.3 Square wave voltammetry. waveform showing the summation of a staircase and a square wave. Adapted from Ref [22].
All scans were performed at an initial potential of 0 V (vs. SCE) to a final potential that varied from +1 V to +1.5 V (vs. SCE) depending on the compound to be analysed. Sensitivity was set at 1µA. In this work, the square-wave parameters were optimised to increase the sensitivity and to enhance the quality of the signal (e.g. to improve the signal-to-noise ratio).

6.2.3.3 – Acquisition and presentation of voltammetric data

All results obtained by square wave voltammetry are presented after a baseline-correction using the “moving average” algorithm (peak width = 0.03 V) included in the Autolab GPES software (version 4.9.007). This method is very effective when peaks appear as shoulders on steep flanks. After baseline correction, individual peaks can be seen more clearly.

This mathematical treatment improves the imaging and identification of the peaks above the baseline without the introduction of artefacts, although the peak current is in some cases decreased (<10%) compared to that of the untreated curve [24]. In the quantitative voltammetric analysis, the peak height (the maximum current with respect to the baseline) is the most widely used parameter to determine concentrations. This parameter will, therefore, be utilised for further calculation [21].

6.3 – Results & Discussion

6.3.1.1 – Surface characterisation

Scanning electron microscopic images of the sensor surfaces were used to compare the morphological features of the WE surface of the screen-printed electrode, before and after adding the CeO₂. The SEM image of a bare SPCE, Fig. 6.4 (a) indicated a porous, highly faceted and structure of rough appearance. In contrast, the relatively smooth surface roughness
observed for the drop cast in Fig 6.4 (b) was possibly due to the solvent affecting the binder and thus causing the smoother surface. The nanoparticles cannot be seen in this image due to the high roughness of the WE surface, allowing the smaller ceria NPs to fall within trenches and gaps with the graphite structure. Similar results have also been reported by Kadara et al. where by a comparison between different electrochemical platforms was carried out [4].

Figure 6.4 (a) Scanning electron micrographs of untreated carbon-based working electrodes (b) and after drop-casting with CeO₂ NPs annealed at 900°C and VHT at 100°C for 1h.

6.3.1.2 – Cyclic voltammetry characterisation of the modified electrode

In order to determine and compare the electrochemically active surface area (EASA) of the SPCE-CeO₂, and SPCE, a CV conducted at 0.05 V s⁻¹ scan rate was carried out in a solution of 5 mM K₄Fe(CN)₆ in 0.1 M KCl. The electrochemical reaction of K₄Fe(CN)₆ , which diffuses to the electrode surface, is described according to the following equation for a quasi-reversible electron transfer process, Randles–Ševčik (RS) equation [22]:
\[ I_p = 299000 \ n^{3/2} \ \alpha^{1/2} \ \sqrt{A \ D \ C} \nu^{1/2} \]  

(6.1)

where \( I_p \), \( n \), \( \alpha \), \( A \), \( D \), \( C \), \( \nu \) are peak current in amps, \( n \) is the number of electrons transferred (\( n = 1 \) for \([\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4+}\)), \( \alpha \) is the transfer coefficient (usually assumed to be close to 0.5), electrochemically active surface area (cm\(^2\)), diffusion coefficient (cm\(^2\)s\(^{-1}\)), concentration of ferrocyanide (mol/cm\(^3\)) and scan rate (Vs\(^{-1}\)), respectively. The diffusion coefficient of potassium ferrocyanide is \( 6.3 \times 10^{-6} \) cm\(^2\)s\(^{-1}\) at 25º C [25]. It should be noted that, in the literature there is a misinterpretation of results. In that the reversible RS equation is used rather than the quasi reversible RS [26-28]. The adequate way to confirm this is in understanding the reversibility of the reaction and to measure the peak potentials for forward and reverse scans and find out the peak separations \( \Delta E > 57 \) mV [22], as previously discussed in chapter 5.

A typical C.V is shown in figure 6.5, obtained at a scan rate of 0.05 Vs\(^{-1}\) and the anodic peak current resultant was used to calculate the EASA using the Randles–Ševcik (equation 6.1). The original carbon surface of SPCE (bare) is characterised by a content of edge graphite particles and a rough surface as can be seen in Fig 6.4. However, for the modified SPCE-CeO\(_2\) it seems that it is smoother and perhaps the nanoceria made the WE surface more conductive. Such a statement can be confirmed with a better current response recorded in the voltammogram for SPCE-CeO\(_2\).
Figure 6.5 Typical cyclic voltammogram recorded in 5 mM potassium ferrocyanide in 0.1 M KCl supporting electrolyte at an SPCE (bare) (dashed line) SPCE-CeO₂ (solid line) and a scan rate of 0.05 Vs⁻¹.

The effective area of a bare SPCE and SPCE-CeO₂ was evaluated in order to compare the EASA for both electrodes. It has been reported that the active areas WE of SPCE from DropSens are exposed edge plane-like sites/defects formed during its fabrication, and such changes can affect the roughness of the electrode surface [29,41]. Table 6.1 indicates the real electrochemical surface area of SPCE-CeO₂ and SPCE.
Table 6.1 Real electrochemical and geometrical surface area of the SPCE-CeO$_2$ and SPCE.

<table>
<thead>
<tr>
<th></th>
<th>A real (cm$^2$)</th>
<th>Geometrical surface area WE (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPCE</td>
<td>0.0361</td>
<td>0.1256</td>
</tr>
<tr>
<td>SPCE-CeO$_2$</td>
<td>0.0833</td>
<td>0.1256</td>
</tr>
</tbody>
</table>

It can be observed that the geometrical area of the SPCE is 3.5 times greater than the EASA. Such a result confirms that not all the exposed edge plane-like graphite flakes in the WE surface area are electrochemically active. Furthermore, the results obtained show that SPCE/SPCE-CeO$_2$ exhibited a higher electrochemical area, than the bare SPCE suggesting, that the surface roughness varies between the two electrodes. In this case, the SPCE-CeO$_2$ is roughly nanostructured and displays isolated nanoceria in between sites/defects of the graphite. It has also been reported by Bolado et al, that the increase in the MWCNT-COOH-modified SPCE electrochemical area compared to the bare SPCE was greater, due to the ordered ensemble of carbon nanotubes [26]. In their work, it was found an increase in the electrochemical area of SPCE in around 50% while in this study it was found to be 43%. Considering that in this work the CeO$_2$ NPs has a spherical shape, as shown in chapter 2 and in Bolado et al. [26] work the nanostructure is shaped of nanotubes, the results found in table 6.1 are encouraging, as it is a simple fabrication process as previously described in section 6.2.3.1.
The surface rate constant was also calculated and the values of kinetic parameter $k^0$ for the redox couples can be calculated using equation 6.2. The parameter $\Psi$ is expressed as, and was previously discussed in chapter 5 [30]:

$$\Psi = \frac{k^0}{[\pi D_0v (F/RT)]^{1/2}}$$  \hfill (6.2)

Using the cyclic voltammogram of 5 mM K4[Fe(CN)6] in 0.1 M KCl at the SPCE-CeO2 electrode with the scan rate of 0.05 Vs$^{-1}$ as shown in Figure 6.5. The measured value of $\Delta E_p$ was 360 mV which corresponds to $2.0 \times 10^{-2}$ of the dimensionless rate parameter $\Psi$, as previously discussed in chapter 5 (Table 5.2). Then, the $k^0$ value at 278 K can be estimated to be $8.8 \times 10^{-4}$ cms$^{-1}$ using $D_0 = 6.3 \times 10^{-6}$ cm$^2$s$^{-1}$ [25] and $v = 0.05$ Vs$^{-1}$ according to Eq 6.2. The value of kinetic parameter $k_0$ indicates that the electron transfer rate at the WE of the SPCE is slower when compared to the G.C and carbon cloths used in chapter 5, possible reason for such behaviour could be that the SPCE does not efficiently promote electron transfer.

6.3.1.3 – Square-Wave voltammetric optimisation of detection of Acetaminophen.

As previously discussed, SWV was chosen as the voltammetric technique. Prior to this study, preliminary results for differential pulse voltammetry (DPV) were obtained. However, a comparison between DPV vs. SWV showed a much greater current response for SWV, as can be seen in Fig 6.6. Such a finding can be explained by the more severe pulse usually applied for SWV than DPV. Therefore, the pulses can be shorter than in DPV and the square wave frequency can be higher. Instead of the effective sweep rates of 1–10 mVs$^{-1}$ of DPV, scan rates of 1 Vs$^{-1}$ or even larger can be employed [22]. It should be noted that most of the studies reported for the determination of ACOP used the DPV technique [31, 32].
Figure 6.6 Plot showing square wave voltammograms vs. differential pulse voltammogram of 50 µM ACOP in BRB pH 7 using the SPCE-CeO₂ as the WE, CE carbon ink and the external SCE as RE. SWV conducted from 0 to 1 V. SWV conditions: $E_{step}=10$ and 20 mV, $E_{pulse}=25$ mV and $f=10$ Hz. DPV conditions: $E_{step}=10$ and 20 mV, $E_{pulse}=25$ mV and scan rate = 0.05 V⁻¹.

A plot of background current of the BRB pH 7 (blank) after the EP treatment of an SPCE-CeO₂ is shown in Fig 6.7. The parameters used in the SWV were a frequency of 10 Hz, potential step height of 10 mV and a pulse height of 25 mV [23]. In this work, these conditions were optimised in order to improve the sensitivity and quality of the signal of the compounds to be
analysed. The high overpotential for oxygen evolution (above +1.0 V) invariably leads to a high background current, which could adversely affect the baseline correction at higher potentials. Such high background currents have also been observed at high potentials for other SPCE [3, 32].

Figure 6.7 Voltammogram showing the background current of BRB (pH=7) as a function of potential. SWV conditions: f=10 Hz, $E_{\text{step}} = 10$ mV and $E_{\text{pulse}} = 25$ mV. The SPCE-CeO$_2$ is the WE. Scan conducted from 0 to 1.5 V at a rate of 0.05 Vs$^{-1}$. 

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Acetaminophen (ACOP) was chosen as the compound to be used for the optimisation of the voltammetric response, due to the number of existing reports of its electrochemical characterisation and determination [17,18,31]. The SWV parameters $f$, $\Delta E$ and $E_{\text{pulse}}$ were varied experimentally in order to find out the major influences on peak currents. Figure 6.8 shows the experimental current profile obtained for 50 $\mu$M of ACOP in BRB (pH=7), as a function of frequency.

**Figure 6.8** Square wave voltammograms of 50 $\mu$M ACOP in BRB pH 7 using the SPCE-CeO$_2$ as the WE. CE carbon ink and the external SCE as RE. SWV conducted from 0 to 1 V. SWV conditions: $E_{\text{step}}=10$ mV, $E_{\text{pulse}}=25$ mV and $f$ was varied from 8 to 40 Hz.
It can be seen that, as $f$ increases, the peak current increases, along with a shift in the peak position. At higher frequencies, noise and peak distortion were more pronounced, which can adversely affect the signal measured. However, a strong sharp signal was obtained at 0.43 V for the highest frequency of 40 Hz. The $f$ of 40 Hz was then selected for use with the other parameters $E_{\text{step}}$ and $E_{\text{pulse}}$.

**Figure 6.9** Results from an SWV of 50 $\mu$M ACOP in BRB pH 7 using the SPCE- CeO$_2$ as the WE. CE carbon ink and the external SCE as RE. Conducted from 0 to 1 V. SWV conditions: $E_{\text{pulse}} = 25$ mV, $f=40$ Hz and $E_{\text{step}}$ was varied from 10 to 40 mV.
The voltammograms obtained for different $E_{\text{step}}$ values are presented in Figure 6.9. It can be seen that the variation of $E_{\text{step}}$ has only a small effect on the peak current (from 3.8 $\mu$A to 4.4 $\mu$A. For $E_{\text{step}}$ of 20 mV, a well-defined peak was obtained, and a higher peak current was also generated. As $E_{\text{step}}$ increased the peaks broadens, resulting in a decrease in selectivity and signal quality.

![Figure 6.10](image)

**Figure 6.10** Square wave voltammograms of 50 $\mu$M ACOP in BRB pH 7 using the SPCE-CeO$_2$ as the WE. CE carbon ink and the external SCE as RE. Conducted from 0 to 1 V. SWV conditions: $f=40$ Hz, $E_{\text{step}}=20$ mV and $E_{\text{pulse}}$ was varied from 10 to 25 mV.
Figure 6.10 shows that the increase in pulse height results in increased peak current, possibly due to the greater driving force provided for oxidation (as expected). The pulse height that showed the best compromise between signal quality and sensitivity was 25 mV. Therefore the optimum settings for SPCE-CeO$_2$ were found to be a square wave frequency of 40 Hz, $E_{\text{step}}$ of 20 mV, and $E_{\text{pulse}}$ of 25 mV. Table 6.2 shows a comparison of the SWV optimisation parameters for ACOP using different modified electrodes:

**Table 6.2 SWV optimisation parameters for ACOP found in the literature**

<table>
<thead>
<tr>
<th>Method</th>
<th>Frequency (Hz)</th>
<th>$E_{\text{step}}$ (mV)</th>
<th>$E_{\text{pulse}}$ (mV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDDE</td>
<td>60</td>
<td>20</td>
<td>25</td>
<td>[37]</td>
</tr>
<tr>
<td>FAP-CPE</td>
<td>30</td>
<td>10</td>
<td>20</td>
<td>[38]</td>
</tr>
<tr>
<td>(Fluoroapatite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FZ-G/GCE</td>
<td>15</td>
<td>5</td>
<td>25</td>
<td>[33]</td>
</tr>
<tr>
<td>(Fe doped zeolite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPCE-CeO$_2$</td>
<td>40</td>
<td>20</td>
<td>25</td>
<td>This work</td>
</tr>
</tbody>
</table>

As can be observed in Table 6.2 the parameters used in the optimisation of SWV conditions by other authors are similar to the parameters used in this work.

6.3.1.3.1 – Optimisation of volumes of CeO$_2$ suspension.

In order to determine the optimum volume of the suspension of CeO$_2$ NPs to be drop cast onto the WE area of the SPCE, five replicates of varying volumes were carried out: 5, 10 and 15 µL. In this investigation the optimised parameters of SWV were utilised and 50 µM of
ACOP in BRB pH 7. The five replicates were performed using different SPCE-CeO$_2$ electrode samples. As can be seen in Fig 6.11 a volume of 5 µL showed the best performance and the highest sensitivity most likely due to the lower thickness of the layer formed on the WE area. For larger volumes of 10 and 15 µL, the layer was too thick to enable a more effective electron transfer, consequently making it less conductive.

**Figure 6.11** 50 µM ACOP in BRB pH 7 using the SPCE- CeO$_2$ as the WE. CE carbon ink and the external SCE as RE. SWV conditions: f=40 Hz, $E_{\text{step}} = 20$ mV and $E_{\text{pulse}} = 25$ mV.
6.3.1.3.2 Electrochemical determination of acetaminophen, caffeine and aspirin in Excedrin® tablet.

Excedrin® is a common pharmaceutical medication used as a headache pain reliever and is typically found in the form of tablets. It consists of a combination of acetaminophen (250 mg), aspirin (250 mg) and caffeine (65 mg) in a single tablet. An Excedrin® tablet was weighed and ground to a fine powder using a mortar and pestle used to prepare the solution. This solution was made of approximately 32 mM of ACOP, 28 mM of ASA and 6.6 mM of CAF in BRB (pH=7), based on the Excedrin® composition. There are a number of reports for the simultaneous, electrochemical determination of these species [3, 31, 32]. Notable is a study by Khairy et al. who reported the simultaneous determination of acetaminophen, caffeine and codeine (instead of ASA) using a modified fabricated in house screen-printed electrode coated with a mixture of graphite/CeO₂ NPs using DPV studies. In their study, the DPV response (Ip) was 2.5 µA while in this work using SWV it was found to be 4 µA [32]. However, to the author's knowledge, no comparison between a bare homemade and commercial screen-printed electrode with the modified SPCE or any indication of the real effect of the coating on the sensitivity has been reported. Furthermore, the purpose of this study is to compare the sensitivity of the SPCE-CeO₂ with and without vacuum heat treatment as previously mentioned earlier in the methodology section (6.2.3.1).
Current (µA) vs. Potential (V) vs. SCE

(a)

- SPCE-CeO₂ - After bg correction
- SPCE-CeO₂ - Before bg correction
Figure 6.12 (a) Square wave voltammograms of an Excedrin ® solution in BRB pH 7, of SPCE- CeO₂ before (solid line) and after (dashed line) background correction (b) Comparison of SPCE- CeO₂ with and no vacuum heat treatment and SPCE (bare) with and no vacuum treatment. Using the SPCE- CeO₂ as the WE. CE carbon ink and the external SCE as RE. (b) Cycled positively from 0 to 1.6 V. SWV conditions: f=40 Hz, E_{step}= 20 mV and E_{pulse}= 25 mV.

Figure 6.12 (a) shows the SPCE-CeO₂ before and after the moving average background correction. As can be observed from figure 6.7 a background with high current can be seen.
above +1 V for the voltammogram of BRB pH 7. It is evident this characteristic of SPCE and the influence in ASA and CAF peaks, where by the background masks the real peak height of the compound of interest. It should be noted that there is no mention of how the background was corrected and the effect of the high potential peaks in the work reported by Khairy et al [32].

As can be seen in Fig 6.12 (b), three distinctive peaks were found in both unmodified and modified SPCE. The peak potentials of ACOP, ASA and CAF were found to be 0.53 V, 1.0 V and 1.44 V (vs. SCE) respectively for SPCE-CeO2 with VHT; for the SPCE-CeO2 no VHT 0.57 V, 1.0 V and 1.51 V (vs. SCE) respectively; while on SPCE (bare) with VHT it was 0.50 V, 1.01 V and 1.44 V (vs. SCE) respectively; on SPCE (bare) no VHT it was 0.57 V, 0.99 V and 1.45 V (vs. SCE). A small shift towards a more negative potential can be observed for ACOP and CAF for SPCE-CeO2 and SPCE (bare) with VHT. Such behaviour may be due to disruption of the polymer/binder leading to more exposed electroactive C surfaces leading to better electrochemical activity [33].

The SPCE (bare) shows higher sensitivity (more conductive) compared to SPCE-CeO2 before the vacuum treatment. However, when the modified electrode was subjected to the VHT an enhancement in the peak current was achieved, and it was not observed for the SPCE (bare) with VHT. It is possible that CeO2 NPs may have better adhered in the pores throughout the graphite after VHT due to the combination with the binder, thus preventing them from being washed out during the exposure to the electrolyte during analysis.

The improvement of the reactivity of SPCE-CeO2 after VHT could also possibly be explained by an increase of oxygen vacancies on the CeO2 surface. Such behaviour can change
the concentration and recombination ratio of Ce$^{4+}$ and Ce$^{3+}$ species. It was reported by Choudhury et al. that annealing (100º C) of CeO$_2$ NPs under vacuum introduces Ce$^{3+}$ and oxygen vacancies in the lattice sites, and surface on grain boundaries. Such an effect improves the photocatalytic activity of CeO$_2$ in the degradation of dyes [34].

The intention was to develop an effective electrochemical technique for the analytical simultaneous determination of ACOP, ASA and CAF in this work. However, it was found that as the concentration of one these molecules increased, and the concentration of the other two compounds was kept constant, there was also a change in the oxidation peak height as indicated in the figure 6.13.
Figure 6.13 Square wave voltammograms of a solution of 100 µM of ACOP, 100 µM of ASA and 100 µM of CAF in BRB pH 7 using the SPCE- CeO₂ as the WE. CE carbon ink and the external SCE as RE. Conducted from 0.0 to 1.6 V. SWV conditions: f=40 Hz, E_{step} = 20 mV and E_{pulse}= 25 mV. With the increase in CAF concentration. The solid line represents the initial concentration, dashed line the first addition of 100 µM of CAF and the dotted line the second addition of 100 µM of CAF.

Figure 6.13 displays the SWV voltammogram of a solution of 100 µM of ACOP, 100 µM of ASA and 100 µM of CAF with consecutive additions of 100 µM of CAF, while the concentration of ACOP and ASA were kept constant. As can be seen in this figure, the
oxidation peak of ACOP and ASA also slightly diminished compared to CAF, although it was less pronounced for ACOP compared to ASA. The possible reason for this is that the oxidation process of caffeine is poorly defined and in competition with oxygen evolution and the high overpotential for oxygen evolution reaction (OER) (above of +1.0 V). This oxidation reaction occurs, generating oxygen gas and releasing electrons to the anode and leads to a high background current, as can be seen in Fig. 6.7. When the baseline correction (the moving average) in this high potential region is performed there is an interference with the peak height, which is as a result of the high background current. Similar phenomena have been reported elsewhere [3, 32]. However, there is no mention in these reports of how the baseline was corrected in order to calculate the peak current. Additionally, a small change in the voltammetric response for the compounds with constant concentration is often seen in these studies [3, 32]. However, in these studies, the LOD was still determined, for the simultaneous determination of the three molecules, which is probably not entirely appropriate, since the determination of compounds above +0.8 V are not reliable.

Another aspect to be taken into consideration is the oxidation reactions of ACOP, ASA and CAF on the electrode surface. It is possible that the oxidation of ACOP is predominant in this system and its oxidation products may be adsorbed on the electrode surface and thus affecting the ASA peak. This could change the local pH at the WE electrode surface and hence interfere with the determination of the other species at higher potential values. The $pK_a$ values for ACOP, ASA and CAF are 9.5, 3.5 and 14 respectively [3]. This means that at BRB (pH=7) the ASA is almost completely ionised whereas both ACOP and CAF are in their unionised
forms. Additionally, Wudarska et al. reported a decrease in current after consecutive scans of ASA and it could correspond to the electrooxidation of an ASA adsorbed form [35].

The scheme presented in 6.1 shows the oxidation reaction products of these three molecules. These were N-acetyl-p-quinone imine for ACOP [Scheme 6.1, (1)], which involved two proton and two-electron transfers, and 3,6-dioxocyclohexa-1,4-dienecarboxylate (a) or 5,6-dioxocyclohexa-1,3-dienecarboxylate (b) for ASA [Scheme 6.1, (2)], which involved two-electron and one proton transfers. The reaction of CAF [Scheme 6.1, (3)] involved four electrons and four protons, sequentially forming uric acid (c), and the 4,5-diol analogue of uric acid (d), which rapidly fragmented [3].
Scheme 6.1 Electrochemical oxidation mechanism of ACOP (1), ASA (2) and CAF (3) molecules [3].
6.4 – Conclusions

The SPCE-CeO₂ approach shows many advantages over other sensors reported in the literature; notably a simple fabrication process, and hence the possibility of large scale-production, low-cost, portability (with a small battery-powered potentiostat), and the potential for use over wide concentration ranges of ACOP, ASA and CAF. A comparison of the real electrochemical area between the SPCE (bare) and SPCE-CeO₂ was carried out and it was found that the area of SPCE-CeO₂ increased 43% compared to the SPCE. The use of square wave voltammetry as the electrochemical technique showed a greater response than differential pulse voltammetry. The main advantage of SWV over any other analytical technique is that the analysis can be carried out in a shorter time (seconds). Consequently, this method is worth consideration for both the individual and the simultaneous determination of all three molecules at trace levels in clinical and quality control laboratories. However, as any analytical technique, there are limitations, as for electrochemical technique the limitation is the specificity, such technique cannot identify compounds it's only able to detect it at a range of concentrations.

The main advantage of this electrochemical sensor is that it can be used portably, utilising a catalyst that is relatively inexpensive and abundant as discussed in chapter 2. In order to improve the electrode conductivity and consequently the real electrochemical area, the modification in the morphology of CeO₂ NP could be beneficial, as for example the synthesis of CeO₂ nanorods or nanotubes. The development of a biodegradable base for the carbon screen-printed could also be incorporated since the electrochemical sensor could be used as disposable material. This modification could improve the environmental credentials of the system and make it more feasible for the field monitoring of selected organic contaminants.
6.5 - References


CHAPTER 7

ELECTROOXIDATION OF DICLOFENAC
Chapter 7 - Electrooxidation of Diclofenac

7.1 – Introduction

To date, there have not been any reports on the electrooxidation of diclofenac (DCF) using a CeO$_2$ NP modified electrode (SPCE-CeO$_2$). This chapter follows the same experimental section in chapter 6.

7.1.1 – DCF for electroanalysis

Diclofenac 2-[(2,6-dichlorophenyl)amino] benzene acetic acid sodium salt is well known as a non-steroidal anti-inflammatory drug (commonly abbreviated as an NSAIDs) and is often used as an analgesic [1]. Due to its widespread use, diclofenac waste can be found in seawater, rivers and lakes, as discussed previously in chapter 3 [1-5]. Diclofenac and its degradation products, dispensed on their own, might be toxic at high levels. However, when accumulated in aquatic and terrestrial organisms, some adverse side-effects can occur such as allergies and toxicity, particularly if combined with other molecules [6]. Since DCF can be electrochemically oxidised, it can also be determined by electrochemical techniques [7-11]. As previously discussed in chapter 6 (section 6.1.2) electrochemical methodologies are an interesting alternative due to their low cost, rapid response and potential portability [9]. Furthermore, the colour or turbidity of the sample is not a problem when using these techniques, whereas it could be an inconvenience for spectroscopic based analysis. Additionally, the fact that there is no need to use expensive organic solvents or columns, as would be required for chromatography analysis. There are a number of publications reporting electrochemical sensors for DCF detection that use square wave voltammetry (SWV) [3,4,12],
electrochemical impedance spectroscopy (EIS) [7] or differential pulse voltammetry (DPV) [1,2]. Thus, the development of an electrochemical method for the detection of diclofenac and its degradation products along with many other pharmaceutical substances in-situ is important for environmental monitoring reasons.

7.2 – Experimental

7.2.1 – Materials

- Acetic Acid 99.5 % (CH₃COOH) (Fisher)
- Boric Acid 99% (H₃BO₃) (Acros)
- Cerium dioxide NPs <25 nm dispersion in 10 wt% in H₂O (Sigma)
- Hydrochloric acid 37% (HCl) (Fisher)
- Phosphoric acid 98% (H₃PO₄) (Fisher)
- Sodium diclofenac Analytical grade (DCF)(Sigma)
- Sodium hydroxide pellets (NaOH)(Acros)
- Synthesized Cerium dioxide NPs (Described in chapter 2)

7.2.2 – Equipment

- Autolab PGSTAT 12 (three-electrode one compartment configuration)
- (Hg/Hg₂Cl₂, KCl (sat’d) – saturated calomel electrode (SCE))
- Screen-printed carbon electrode (SPCE) model DRP-110 (DROPSENS)
- Labquest2 digital pH meter
- Gallenkamp (from Fistreem international) vacuum oven
7.2.3 - Methodology

7.2.3.1 – Preparation of the modified electrode (SPCE-CeO₂)

All SPCEs were exposed to an electrochemical pre-treatment (EP), in an attempt to remove impurities and thus improve their electroactivity, and also to alter the WE surface wettability (hydrophobicity/hydrophilicity). Each SPCE utilised was subject to an anodic treatment as discussed in chapter 6. A suspension of the nanoceria produced in chapter 2 was prepared by adding 0.5 mg of NPs in 1 mL of ultrapure water. After the SPCE pre-treatment, 5 µL of this suspension were drop cast directly on the WE surface by a micropipette and the sensor was exposed to a thermal treatment in a vacuum (7.6 torr) oven for 1h at 100ºC, thus completing the preparation of the modified SPCE-CeO₂.

7.2.3.2 – Square wave voltammetry (SWV)

For analytical purposes, square wave voltammetry is usually the ideal method for analysis as it suppresses the background current (non-faradaic or capacitive) effectively and has higher sensitivity compared to other electrochemical techniques, as reported in chapter 6.

7.2.3.3 – Acquisition and presentation of voltammetric data

All results obtained by square wave voltammetry are presented after a baseline-correction using the “moving average” algorithm (peak width = 0.03 V) included in GPES software (version 4.9.007). This method is very effective when peaks appear as shoulders on steep flanks. After baseline correction, individual peaks can be seen more clearly.
7.3 – Results & Discussion

7.3.1 – Electrooxidation of Diclofenac (DCF)

The electrochemical behaviour of DCF at the surface of the modified screen-printed electrode was investigated initially utilising the cyclic voltammetry technique. The CV was obtained in 100 µM DCF solution in 0.1 M BRB at pH 7 in the potential range from −0.4 to 0.8 V (vs SCE) and a scan rate of 0.05 Vs⁻¹, and is shown in Fig 7.1. A comparison was made between bare-SPCE (a) and the modified screen-printed electrode (a), with the CVs displayed in Figure 7.1. The formation of an anodic peak (Ia) with the highest current at 0.60 V (vs. SCE), which is related to the oxidation of the anionic form of DCF [9]. As the potential scan was reversed, a cathodic peak (IIc) was observed at 0.26 V (vs. SCE). Aguilar-Lira et al. reported that this peak corresponds to the reduction of 2-(2-hydroxyphenyl) acetic acid to 1-hydroxy-2-(hydroxyphenyl) ethanoate [10]. During the second sweep, one new anodic peak (IIa) appears at 0.34 V (vs. SCE). This could be related to the oxidation of 1-hydroxy-2-(hydroxyphenyl) ethanoate (previously formed) to 2-(2-hydroxyphenyl) acetic acid indicating that peaks IIc and IIa are related to the same REDOX process [10].

The voltammogram in Fig 7.1 (a) confirms the higher peak current for the modified electrode, which is likely due to the incorporation of CeO₂ nanoparticles increasing the electrochemically active surface area of the working electrode and also enhancing the electrocatalytic activity of the CeO₂ sensor for electrooxidation of the DCF molecule. DCF is irreversibly oxidised and thus there is no reverse peak associated with peak Ia. Such behaviour has also been reported elsewhere [1-5,12]. Since the first anodic peak (Ia) had the highest
current intensity (6.7 µA) and was the one with better definition, it was chosen as an analytical signal for DCF quantification.

Figure 7.1  Cyclic voltammograms (CVs) of 100 µM of DCF solution in BRB (pH 7) at (a) Modified SPCE-CeO₂ (solid line) and (b) Bare- SPCE (dashed line). The potential ranged from −0.4 to 0.8 V (vs SCE) at a scan rate of 0.05 Vs⁻¹. The SPCE- CeO₂ is the WE. CE carbon ink and the external SCE as RE.
7.3.2 – Effect of Scan rate

In order to better understand the nature of the reaction and the role of the potential sweep rate on the oxidation peak current ($I_p$) of DCF, CVs were performed at various selected scan rates in the range $0.05 – 1.5 \text{Vs}^{-1}$. As shown in Fig 7.2, the anodic peak current increases with increasing scan rate and a slight shift in the oxidation peak potentials ($E_p$) occurs towards more positive values. The absence of a reverse peak for peak Ia is observed, which indicates that the electron transfer reaction is irreversible and is an electrochemical mechanism [12].

![Cyclic voltammograms of DCF at SPCE-CeO$_2$ at different scan rates from 0.05 to 1.5 V/s in BRB (pH=7) and [DCF] = 100 µM. The SPCE-CeO$_2$ is the WE. CE carbon ink and the external SCE as RE.](image)

**Figure 7.2** Cyclic voltammograms of DCF at SPCE-CeO$_2$ at different scan rates from 0.05 to 1.5 V/s in BRB (pH=7) and [DCF] = 100 µM. The SPCE-CeO$_2$ is the WE. CE carbon ink and the external SCE as RE.
A linear relationship was observed between the anodic peak current (with background correction) and the scan rate ($I_p$ vs. $\nu$). This indicates that the DCF oxidation on the screen-printed electrode process is adsorption controlled. However, when $I_p$ vs. $\nu^{1/2}$ was plotted, a non-linear relationship was observed. Such behaviour could be due to the porous carbon WE from SPCE and a change in the mass transport regime may occur. It should be noted that there is also a contribution of the oxidation product of diclofenac (IIc) which is electrochemically active. Such behaviour has also been observed elsewhere [9-11,13]. Costa-Rama et al. reported that there are regions exposed to the bulk solution in which planar diffusion operates and a region in which “thin layer” diffusion effects occur for carbon-based WE [11].

![Graph showing linear relationship between $I_p$ and $\nu$. The equation of the line is $y = 10.06X + 2.02$ with $R^2 = 0.98881$.]
Figure 7.3 (a) The plot of $I_p$ vs. $v$ (b) $I_p$ vs. $v^{1/2}$ with background correction for the oxidation of DCF at SPCE-CeO$_2$.

7.3.3 – Optimisation of response for DCF determination

In order to investigate the effect of the annealing temperature of the CeO$_2$ NP on the electrochemical behaviour of DCF, SWV was recorded and the peak current was used to compare results. As was shown in chapter 2, the annealing temperature of CeO$_2$ NP plays a key role in CeO$_2$ photocatalytic activity. The nanosised CeO$_2$ NPs produced after annealing at 900°C showed the highest degradation efficiency of DCF among the prepared nanoparticles,
which has also been discussed earlier in chapter 3. The same effect was also observed in their electrochemical behaviour. The NPs annealed at 900°C showed the highest anodic peak current for 100 μM of DCF in BRB pH 7. Hence, 900°C was selected as an optimum annealing temperature value with enhanced sensitivity.

**Figure 7.4** Current response of DCF 100 μM in BRB pH 7 under CeO₂ NP at 100°, 300°, 600° and 900°C. The SPCE- CeO₂ is the WE. CE carbon ink and the external SCE as RE. SWV conditions: f=40 Hz, E_{step} = 20 mV and E_{pulse}= 25 mV. Duplicate measurements.
Figure 7.5 Graph showing a comparison of the optimum CeO\(_2\) NP 900ºC- SPCE, Bare-SPCE and commercial CeO\(_2\)NP–900º-Sigma-SPCE. The SPCE- CeO\(_2\) is the WE. CE carbon ink and the external SCE as RE. SWV performed under optimum conditions. Analysis conditions: \(f=40\) Hz, \(E_{\text{step}} = 20\) mV and \(E_{\text{pulse}} = 25\) mV. SWV performed in BRB (pH = 7), \([\text{DCF}] = 100\ \mu\text{M}\).

Figure 7.5 displays a comparison of the sensitivities of CeO\(_2\) NP 900ºC- SPCE, Bare-SPCE and the commercial CeO\(_2\)NP-900º-Sigma-SPCE. As can be observed, the peak potential of bare (0.63 V vs. SCE) and Sigma sample (0.57 V vs. SCE) were both shifted towards a more positive value compared to the modified SPCE (0.54 V vs. SCE). A decrease in the peak potential indicates that CeO\(_2\) NP 900ºC- SPCE operated as a promoter for the electrochemical...
reaction, substantially accelerating the rate of electron transfer, such behaviour has also been observed when the WE/GC was coated with gold NP/multi-walled carbon nanotubes [13]. The peak current was found to be 3.9 µA, 6.3 µA and 6.5 µA for Bare-SPCE, commercial CeO\textsubscript{2} NP-900º-Sigma-SPCE and CeO\textsubscript{2} NP 900ºC- SPCE, respectively. The possible reason for this enhanced current response for CeO\textsubscript{2} NP 900ºC- SPCE is that the vacuum treatment provided a higher variation in the concentration of oxygen vacancies, as discussed previously. In chapter 3, the CeO\textsubscript{2} NPs annealed at 900ºC also showed higher photoactivity. Therefore, CeO\textsubscript{2} NP 900ºC- SPCE showed higher sensitivity and quicker response compared to the bare SPCE and commercial CeO\textsubscript{2}.

7.3.4 – Effect of pH

One of the variables that can affect the shape of voltammograms is the pH of the solution, and it happens due to the characteristic oxidation of the molecule and more noticeably the peak position. The peak shift towards more negative or positive potential values could be ascribed to the reaction mechanism and stability at the different pH values [8]. The electrochemical behaviour of DCF in solutions of pH 2, 7 and 10 using BRB was studied, and the results are shown in Figure 7.6 (a), (b) and (c) respectively. The pH was adjusted with either 0.2 M HCl or 2 M NaOH. The peak current of DCF decreased in more basic and neutral media, showing a higher response at acidic pH, which indicates the involvement of the proton in the electrochemical reaction [14].

The \( E_p \) shifted to a more positive value at pH 2 (\( E_p = 0.81 \text{ V vs. SCE} \)) and more negative values at pH 10 (\( E_p = 0.51 \text{ V vs. SCE} \)) and \( E_p = 0.57 \text{ V vs. SCE} \) for neutral pH. Such a shift in \( E_p \) towards more positive values with a decrease in pH has also been reported elsewhere [1-
It can also be observed that at pH 2 the DCF has a higher current response ($I_p = 11 \ \mu A$) and a lower response at pH 10 ($I_p = 2.5 \ \mu A$), possibly due to the deprotonation of this species, and at neutral media ($I_p = 6.5 \ \mu A$).

**Figure 7.6** Square wave voltammograms of 100 µM DCF in BRB at different pH.(a) 2 (b) 7 on top in the left and right side respectively and (c) 10 in the bottom. The SPCE- CeO$_2$ is the WE, carbon ink CE and an external SCE as a RE. SWV was performed under the optimum parameters of: $f=40$ Hz, $E_{step} = 20$ mV and $E_{pulse}= 25$ mV. SWV performed in BRB (pH = 7), [DCF] = 100 µM
It has been reported that DCF possesses a $\text{pK}_a$ value of 4.15 [8]. Changes in the pH can lead to two species; the neutral and the anionic species. In Fig 7.7 it can be observed that where for pHs lower than 4.15 are the neutral species or carboxylic acid whereas at pH 4.15 the anionic species dominate. Therefore, pH 7 was selected as an optimum pH, where the DCF anionic species predominates.

**Figure 7.7** Plot showing the pH distribution of the species fraction ratio of DCF versus pH ($\text{pK}_a = 4.2$).
7.3.5 – *Analytical performance*

The SWV method was utilised for the determination of different concentrations of DCF solutions, using the modified SPCE-CeO$_2$ under the optimised experimental conditions. The current values are obtained by automatically subtracting the background current. Figure 7.8 shows that the peak current increases with successive additions of DCF.

![Figure 7.8](image)

**Figure 7.8** Square wave voltammetry of DCF at different concentrations in the range 0.1-100 µM. The SPCE-CeO$_2$ is the WE. CE carbon ink and the external SCE as RE. SWV was performed under the optimum parameters. Analysis conditions: $f=40$ Hz, $E_{step} = 20$ mV and $E_{pulse} = 25$ mV. SWV performed in BRB (pH = 7).
The determination of the limit of detection (LOD) and limit of quantification (LOQ) of the proposed modified electrode, which is defined as the concentration of the sample yielding a signal equal to the blank signal three times (LOD) and 10 times (LOQ) its standard deviation was obtained [7]. The calibration curve is linear in the concentration range of 0.4 – 25.6 µM with the regression equation: \( I_p = 0.05787 \, C + 0.05132 \), with a correlation coefficient \((R)^2\) of 0.98208. The LOD and LOQ based on 3s/m and 10s/m respectively, where s is the standard deviation of the peak currents (three runs) and m is the slope of calibration curve [7] was estimated to be 0.4 µM for LOD and 0.12 µM for LOQ and the sensitivity of 0.058 µA/µM. This indicated that DCF can be estimated in the given concentration range (0.4 – 25.6 µM).

**Figure 7.9** Linear dependence of the anodic peak current as a function of DCF concentration in the range of 0.1-25.6 µM.
The analytical conditions of a range of different modified electrodes using a variety of materials as the WE and a variety of nanoparticles for the determination of DCF are compared in Table 7.1. It should be noted that LOD is commonly used in most of the studies rather than LOQ, and therefore only LOD will be compared in the Table. As can be observed in this Table, the LOD value that was obtained for the sensor fabricated in this work is either lower than or similar to those reported for other electrochemical sensors. However, this comparison strictly should only be carried out with regard to sensitivity and simplicity. Also, the difference in background correction procedure used and the number of data points utilised varies widely, as reported in Table 7.1. It is well known that the background correction can have a huge effect on the current response and peaks detected. However, it is rarely dealt with in the literature and consequently, comparison of LOD should not be directly undertaken without taking this into account.
Table 7.1 Comparison of the analytical conditions of different modified electrodes for the determination of Diclofenac.

<table>
<thead>
<tr>
<th>Method</th>
<th>Technique</th>
<th>Linear range (µmolL⁻¹)</th>
<th>Detection limit (µmolL⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-PtNPs/f-MWCNTs/AuE</td>
<td>DPV</td>
<td>0.5–1000</td>
<td>0.3</td>
<td>[1]</td>
</tr>
<tr>
<td>MWCNTs/Cu(OH)₂NPs/IL/GCE</td>
<td>DPV</td>
<td>0.18-119</td>
<td>0.04</td>
<td>[2]</td>
</tr>
<tr>
<td>MWCNT-COOH/GCE</td>
<td>SWV</td>
<td>40-670</td>
<td>13</td>
<td>[3]</td>
</tr>
<tr>
<td>Vinilferrocene multiwall</td>
<td>SWV</td>
<td>5-600</td>
<td>2</td>
<td>[4]</td>
</tr>
<tr>
<td>Reduced graphene oxide (rGO) and Co(OH)₂ nano-flakes rGO/CHNF/CPE</td>
<td>CV</td>
<td>3.7-140</td>
<td>0.05</td>
<td>[5]</td>
</tr>
<tr>
<td>CeO₂-SPCE</td>
<td>SWV</td>
<td>0.1-25.6</td>
<td>0.4</td>
<td>This work</td>
</tr>
</tbody>
</table>

It should be pointed out that in the reports cited in Table 7.1, no mention is made of how the background correction is carried out. Furthermore, the number of data points (not the range of concentration) selected to obtain the regression equation (and hence determine the LOD) is
not the same within existing reports. However, in the majority of studies of electrochemical sensors typically the number of data points varies from 3 to 10 [1-5, 15-16]. In the table above the number of data points selected for all studies was 6 or 7, and in this work, it was 7 as can be seen in Figure 7.9.

In order to show how the number of data points selected for LOD determination can affect the results, Figure 7.10 shows an identical plot to Figure 7.9 however, only the three lowest concentration points are plotted. These are representative of low DCF concentration.

![Graph](image)

**Figure 7.10** Linear dependence of the anodic peak current as a function of DCF concentration in the low range of 0.1-1.6 µM.
In this case, the calibration curve is linear in the concentration range of 0.1 – 1.6 µM with the regression equation: \( I_p = 0.05787C + 0.01323 \), with a higher correlation coefficient \((R)^2\) of 0.99635. The LOD was found to be 0.1 µM and the sensitivity was 0.058 µA/µM. Notably, there was an improvement in the correlation coefficient from 0.98184 using 7 data points to 0.99635 for 3 data points and a decrease in the LOD value. Therefore the comparison of the sensitivity of different modified electrodes cannot be performed without taking these factors into consideration. However, electrochemical sensors can also be compared in terms of cost-effectiveness and simplicity. This makes the SPCE-CeO₂ an attractive viable analytical option for the determination of diclofenac as it avoids time-consuming and complex preparation methods which are required for many alternative techniques. Additionally, the high cost of some electrode materials such as (BDDE, AuE), the difficulty of in-field application, and the requirement for polishing to create a fresh electrode surface can be circumvented using the method presented in this work.

7.3.6 - Stability and reproducibility of the modified electrode

The long term stability of the CeO₂-SPCE was evaluated by measuring the voltammetric current response of a fixed concentration of DCF (100 µM) after the modified electrode was stored for 2 weeks in a refrigerator at 4ºC and the peak current was measured every week. A relative standard deviation (R.S.D) of about 15% was observed, which indicates a limitation of this technique.

The repeatability of the modified electrode was also investigated. The precision of the method was evaluated by repeating five sequential measurements in the same solution containing 100 µM of DCF using the same CeO₂-SPCE. The R.S.D was found to be 8.5%,
indicating that CeO$_2$-SPCE is more suitable as a disposable electrode. There was a lack of repeatability for consecutive analysis using the same sensor, where by a decrease of the signal was observed. The higher R.S.D. obtained could be due to the strong adsorption of the reaction products which then can block the WE surface and decrease the number of available reaction sites at the modified electrode. This effect has been reported by Yang et al. [16].

The reproducibility of the modified sensor was evaluated by using five independent electrodes and checking the current response of a 100 µM DCF solution. Here, the R.S.D. value obtained was 2.7%, indicating excellent reproducibility of the method. However, it has been observed by Kadara et al. that the DropSens sensor shows an inherently high surface roughness, thus affecting its reproducibility, due to the variance of the EASA between different electrodes [17]. This method improves the DropSens electrode’s capability to perform electrochemical transformation.

7.3.7 – Oxidation products of DCF analysis

In chapter 3 the photodegradation of 10 mg/L of DCF using 1 g/L of CeO$_2$ annealed at 900° C as the catalyst, under solar simulation was studied. The analysis of the degradation products formed after 3h of irradiation was carried out through LC-MS. In order to compare and use the electrochemical technique to identify these degradation products, SWV was utilised. Fig 7.11 (a) and (b) shows the voltammograms of a standard solution of 10 mg/L of DFC before and after background correction respectively. And Fig 7.11 (c) and (d) shows the same solution after 3h of irradiation of solar simulation before and after background correction respectively. It should be pointed out that CeO$_2$ was utilised as the catalyst both to degrade DCF molecule and to detect it on the SPCE- CeO$_2$. 

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As observed in Fig 7.1, the cyclic voltammogram showed an irreversible peak (Ia) at 0.57 V (vs SCE) and a reversible couple peak (IIa and IIc with Ip= 0.32V and 0.23 V (vs SCE) respectively), corresponding to the redox process of the oxidation of 1-hydroxy-2-(hydroxyphenyl) ethanoate (previously formed) to 2-(2-hydroxyphenyl) acetic acid, as reported by Aguilar-Lira et al. [10]. However, in their study this identification was just an assumption, since there is no mention of how the products were identified.

Figure 7.11 Square wave voltammograms of DCF 10 mg/L (a) without background correction and (b) with background correction. And (c) the same solution of DCF (10 mg/L) after photodegradation under solar simulator for 3h without background correction and (d) with background correction. Using the SPCE- CeO2 as the WE, carbon ink CE and an external SCE
as a RE. SWV analysis conditions: f=40 Hz, E_{step} = 20 mV and E_{pulse} = 25 mV. SWV performed in BRB (pH = 7).

As can be seen in Fig 7.11, it is necessary to carry out background correction in order to reveal the true magnitude of the peaks. It can be noted that the DCF peak current decreased almost to half of its initial concentration (from 6.0 µA to 3.5 µA), confirming that the DCF molecule was degraded. There are a number of mechanisms proposed for this in the literature. It is often described that the mechanism of this reaction is a reversible process of $2e^- , 2H^+$ as reported by Goyal et al., whereby 5-OH diclofenac is formed [12]. In these studies, the DCF oxidation process begins with the protonated molecule. However, at pH 7 the predominant DCF species would be the deprotonated molecule, as shown in Fig 7.7, and such a mechanism is also reported by Cid-Cerón et al. [9].

Scheme 7.1 displays the proposed oxidation mechanism for this reaction. Here, DCF (peak 2) reacts with water and after the DCF molecule loses one electron and one proton, the nitrogen resonates between the creation of a double bond and formation of a radical, which may be able to react with the medium thus producing the irreversible DCF rupture into two products peak 1 and 3. These molecules were identified as 1) 8-Chloro-9-H-Carbazole and 3) 2(8-Chloro-9-H-Carbazol-1-yl) acetic acid though LC-MS analysis, as discussed previously in chapter 3. The degradation products identified contrast with what has been found in the literature [9-13,18,19] as previously discussed. Cid-Cerón et al. carried out a spectro-electrochemical study recording simultaneously the UV-vis absorption spectra of DCF after different potentiostatic electrolysis periods (at 640 mV) [9]. In their study, it was reported that
the DCF degradation occurred through the nitrogen atom, producing the fragments 2,6 dichloroaniline and 2- (2 hydroxypropyl-2-enyl) phenol [9]. However, these products were not specifically identified in their analysis. However, 2,6 dichloroaniline has been identified as the degradation product of DCF through ozone and UV/H₂O₂ treatments by other authors using GC-MS analysis [18,19]. These results indicate that different products of oxidation can be obtained when the reaction is carried out by electrochemical or photocatalysis methods.

Scheme 7.1 Electrochemical and chemical mechanisms proposed for the DCF photocatalytic oxidation in BRB at pH 7, using SPCE-CeO₂.

It should be mentioned that the structures shown for the products of photodegradation of DCF can only be considered as proposals, and further characterisation needs to be carried
out, such as fragmentation of these molecules using LC-MS/MS, as described in chapter 3. Considering that these structures could also have similar molecular mass and in the electrochemical determination these molecules could also overlay at the same $I_p$, this technique offers an inexpensive and simple way to rapidly quantify DCF degradation and its oxidation products.

7.4 – Conclusions

The SPCE-CeO$_2$ approach shows many advantages over other sensors reported in the literature; notably, a simple fabrication process, the possibility of large scale-production, low-cost, portability, and the potential for use over wide concentration ranges of DCF. Consequently, this method is worth consideration for both individual and simultaneous determination of DCF at trace levels in clinical and quality control laboratories. A LOD of 0.4 $\mu$molL$^{-1}$ and sensitivity of 0.058 $\mu$A/$\mu$M in the range of 0.1-25.6 $\mu$molL$^{-1}$ were determined for DCF. The fabricated electrodes demonstrated superior reproducibility, with R.S.D. of 2.7% even with a primitive casting of CeO$_2$ on the electrode surface.

The main advantage of this electrochemical sensor is that it can be used portably, utilising a catalyst that is relatively inexpensive and abundant, as discussed in chapter 2. The electroanalysis of pharmaceutical compounds could be carried on-site and a pre-analysis of the oxidation products produced from the photodegradation of DCF. Also, the decrease of diclofenac concentration in wastewater treatment after exposure to solar light can be performed using CeO$_2$ as the semiconducting nanoparticles. In order to improve the signal amplification, the use of nanomaterials with nanotubes or nanofibres morphology could be used on the electrode surface thus leading to enhanced sensitivity. Additionally, the modification of the
sensor base, using another material that can be biodegradable is worth consideration as it could reduce the waste generated by using currently available conductive supports.

7.5 – References


CHAPTER 8

CONCLUSIONS AND FUTURE WORK
Chapter 8 – Conclusions and Future Work

As previously described in chapter 1 (section 1.2), it is important to utilise processes that are sustainable, with the aim to reduce energy and minimise the use and generation of harmful materials. This work targets different applications of CeO₂ to achieve some of the principles of green chemistry and they are listed as follows.

8.1 – Cerium dioxide synthesis and characterisation.

Chapter 2 of this work described a facile way to synthesise cerium dioxide NPs. A new method was developed for the fabrication of CeO₂ NPs by using frozen NH₄(OH) cubes as a precipitating agent to precipitate Ce(OH)₄ from cerium nitrate, resulting in a greater yield of nanoparticles compared to the standard method. This was achieved along with an experimental design strategy to evaluate the best parameters and conditions for the methodology.

CeO₂ NPs were produced with a mean size of 35 nm. The direct bandgap was found to be 3.23 eV for CeO₂ NPs annealed at 900°C, using the Tauc plot principle. The EDS and Raman results analysis confirmed the CeO₂ composition and face centre cubic structure respectively. The BET specific surface area scaled with increased crystallite size as the annealing temperature increased. XPS measurement estimated the concentration of cerium states in the synthesized sample, where Ce³⁺/Ce⁴⁺ ratio was found to be 59.44% for Ce³⁺ and 40.87% for Ce⁴⁺.

Future studies should focus on the effects of doping on the ionic composition (Ce³⁺/Ce⁴⁺), size and morphological characteristics that could change the properties of nanoceria and consequently its behaviour. Furthermore, this would contribute to help gain better
understanding of the mechanism of action of nanoceria in various applications such as photocatalysis, in PEFC devices, in resistive switching memory, as a mediator in sensor electrodes amongst other applications.

Understanding the composition of CeO$_2$ in terms of the ratio of Ce$^{3+}$ and Ce$^{4+}$ is of great interest in the field of CeO$_2$ NP synthesis. This is important in order to gain insights into the influence of nanoceria states after doping and their influence on the photodegradation efficiency of organic pollutants in wastewaters. While some encouraging results were achieved with the development of a simple and cost-effective synthesis of CeO$_2$ NPs, the “Frozen NH$_4$(OH) cubes method” showed promising results with a higher yield compared to the standard method. Perhaps in order to improve this yield, further the shape of the frozen cubes could be modified in order to increase their surface area. Overall it is essential to explore and improve nanoceria photocatalytic and catalytic activity for a variety of different applications.

8.2 – Photocatalysis of organic pollutants.

Water has become highly contaminated with toxic compounds, making water pollution an immediate and important challenge in the world. As was mentioned in Chapter 3, many variables are known to affect the kinetics of the photocatalytic process such as reactor design type, irradiation arrangement, light source, the reaction of solution conditions, and the catalyst’s properties. The goal of this chapter was to evaluate if CeO$_2$ could degrade MO and DCF. It was observed that the suspension of the nanoceria produced in chapter 1, was efficient in the photocatalysis of MO reaching a 100% of degradation efficiency in 85 min and 56% for DCF in 3h under solar irradiance. However, there are many factors that still have to be optimised and evaluated for performance improvement.
The well-known variables that affect a photocatalytic process should be studied in more detail, such as the optimisation of the experimental set-up and development of an improved photoreactor. The comments mentioned in the previous section for the future work that needs to be performed on “Cerium dioxide synthesis and characterization” should be considered as the catalyst properties such as redox states, size and morphology directly influence the photocatalytic process.

Another challenge observed for this process is the post-treatment catalyst recovery. The suspension of NPs should be removed eventually and it would be important at the industrial scale as it would add to the capital and operating cost of the treatment process. Another way to avoid this issue would be to coat CeO$_2$ NPs on a membrane or to produce an insoluble film. This would facilitate the post-treatment recovery of CeO$_2$ NP photocatalyst.

An important feature often neglected in past research in this area is the identity of the intermediates formed during the photocatalytic reaction of CeO$_2$. This is needed in order to identify properly a possible reaction scheme. In this work, the products of DCF degradation were identified and a degradation pathway was proposed; however, further experiments should be carried out, such as a second fragmentation (LC-MS/MS) in order to confirm the degradation scheme. It is important to clarify such transformation pathways because the intermediate compounds might be more toxic to the environment than the parent compound. Therefore, it is important to study the environmental behaviour of pharmaceuticals overall in wastewater treatments.
8.3 – A Novel Mechanism for a facile memristor-type device based on CeO$_2$ and TiO$_2$.

In this study, a resistive-switching device of very simple construction was demonstrated. A novel p-n junction model based on concepts associated with point defects is proposed. This is markedly different from the widely published models, which normally rely on the movement of oxygen vacancies and/or formation of conductive filaments during such a device’s operation.

The devices fabricated with both TiO$_2$ (Degussa P25) and CeO$_2$ NPs exhibited steady constant currents upon the imposition of potential steps, (both anodic and cathodic) indicating non-ionic movement. This result further supports the notion that the charge is carried by electrons and holes, rather than by ions in a defective semiconductor oxide solid-state electrolyte. The thin interlayer may be considered part of an electrolytic cell which functions upon the application of potential in an electrical field of the order of 10$^7$ V/m.

In order to demonstrate how a single device can fit different conduction models, an attempt was made to explain the conduction mechanism using a range of common conduction models: Schottky, Poole-Frenkel emission, and SCLC. A good fit was obtained for the SCLC which is in agreement with the formation of a p-n junction. However, the conduction mechanisms cannot be described by a single model due to the inherent complexity of ReRAM. This type of behaviour may involve the operation of many different models. EIS modelling could also be recommended to support the physical understanding of the resistive switching mechanisms. This remains a challenge due to the lack of direct characterisation technologies available to investigate such thin layers in-situ.
8.4 –Photoanode Development for the photoelectrochemical fuel cell.

There is an evident benefit of carrying out the electrochemical synthesis of CeO$_2$ NPs directly on to conductive carbon-based materials including cloths. It is a relative facile method for fabrication of anodes, compared with other methods of catalyst deposition because it does not require any thermal treatment. Unfortunately, the CeO$_2$ synthesised in chapter 2 was not the best choice for the immobilisation on carbon cloth as it tended to slough off following immersion in a model wastewater solution.

The photoanode development chapter presented preliminary results in terms of the photocurrent generated and the behaviour of carbon cloths as a photoanode coated with cerium dioxide, which has not been reported in the literature. A direct comparison with the well-known TiO$_2$ NPs was carried out in order to validate the performance of the novel PEFC configuration. It showed an enhanced current density compared to more complex photoanode fabrications involving multi-step methods. It is recommended that future work could include optimising the photoelectrochemical synthesis in terms of being able to control the CeO$_2$ coating’s thickness along the carbon fibres, as it has a direct effect on the photo-electrocatalytic process.

Photoelectrochemical fuel cells have experienced rapid development in the past few years due to the progress in nanomaterials. Future work arising from this project could involve the exploration of the use of various options for conductive supports (such as Vulcan XC 72, ITO, graphene, titanium /nickel mesh), using a variety of synthetic methods, including hydrothermal/ solvothermal techniques to fabricate electrodes. Different processing techniques should also be investigated.
The development of a synthetic method to produce nanotube or nanorod structures of cerium dioxide onto the conductive support is a promising pathway as that morphology is effective for fuel cell applications due to the light absorption and direct electrical pathways into the electrode. The addition of other compounds such as Cadmium Selenide (CdSe) quantum dots and Graphene oxide (GO) may also enhance the light absorption of the visible light region of the solar spectrum. To summarise, future work could focus on the development of novel, cost-effective and highly visible-light-active materials-CeO2 catalyst for PEFC degradation of organic pollutants and the attainment of higher conversion efficiency.

The novel PEFC design could also be improved in order to avoid the evaporation of the electrolyte/fuel operation. Perhaps the use of a quartz plate on the top of the cell or the use of flow-through cell could overcome this issue. A heat sink placed in between the light source could also possibly be beneficial. In order to improve the resistance of the cell different ratios of anode/cathode could also contribute to cell performance. A larger cathode would enhance the oxygen reduction reaction and consequently increase the rate of resultant photoanode oxidation reaction, ultimately leading to improved pollutant degradation and higher PEFC power output.

8.5 – Electroanalysis of pharmaceutical compounds

The SPCE-CeO2 sensor approach described in chapter 6 showed many advantages over other commonly used analytical techniques reported in the literature. These electrochemical sensors involve a simple fabrication process, offer the possibility of use in the field with a portable small battery-powered potentiostat, use low-cost materials, are essentially solvent-free
(e.g utilise green chemistry) and offer the potential for use over wide concentration ranges of many pharmaceutical compounds such as ACOP, ASA and CAF.

The real electrochemical area between the SPCE (bare) and SPCE-CeO₂ was compared and it was found that the Electrochemically Active Surface Area (EASA) of SPCE-CeO₂ increased 43% compared to the bare commercial SPCE, resulting in enhanced currents and improved sensor sensitivity. The use of SWV as the electrochemical detection technique also showed a greater response than the more often used DPV method. One of the main advantages of SWV over most other analytical techniques currently employed is that the analysis can be carried out in a far shorter time (seconds) and is far less costly. Consequently, this method is worth consideration for both the individual and the simultaneous determination of other compounds, which could be carried out on-site, since it has the advantages of portability and good sensitivity and does not involve the use of gases and organic solvents as used in many other techniques.

Future work could involve the exploration of the use of various heat treatments to enhance the sensor’s performance by altering the CeO₂ material’s Ce³⁺/Ce⁴⁺ ratios which can have a marked influence on it’s catalytic and electrical properties.

8.6 – Electrooxidation of Diclofenac

The detection of DCF, which is a compound of increasing concern in wastewaters throughout the world, was carried out using the SPCE-CeO₂ sensor electrodes. The LOD was found to be 0.4 μmol L⁻¹, LOQ of 0.12 μmol L⁻¹ and with a sensitivity of 0.058 μA/μM in the range of 0.1-25.6 μmol L⁻¹. The fabricated electrodes demonstrated superior reproducibility,
with an R.S.D. of 2.7%. The pre-analysis of the oxidation products produced from the photodegradation of DCF was performed using the SWV method. It is also worthwhile recommending that further investigations of this method could prove beneficial for determining levels of other organic contaminants, ultimately as a potential portable (field) analytical technique.

In order to improve the electrode conductivity and consequently the real electrochemical surface area, modification of the morphology of CeO$_2$ could be beneficial, such as the synthesis of CeO$_2$ nanorods or nanotubes. Moreover, the development of a biodegradable base for the carbon screen-printed electrode could also be incorporated into the modified sensor since the electrochemical sensor is most likely to be used as once-off disposable material. This modification could further improve the environmental credentials of the system and make it more feasible for the field monitoring of selected organic contaminants. Research leading to higher electrical conductivity of the conductive base layer on SPCEs would be useful through the use of highly conductive materials incorporated in lower non-conductive polymer support compounds.

8. 7 Final Comments

CeO$_2$ is an interesting material but remains poorly understood. More work along the lines described above is needed to better understand its operation and to inform its use in a variety of technologically important areas in both environmental and energy fields.
Appendix I - Brunauer, Emmett and Teller (BET) data

The data are treated according to the Brunauer, Emmett and Teller (BET) adsorption isotherm equation:

\[
\frac{1}{X[(P_0/P) - 1]} = \frac{1}{X_m C} + \frac{C - 1}{X_m C} \left( \frac{P}{P_0} \right)
\]

The BET Equation, uses the information from the isotherm to determine the surface area of the sample, where \( X \) is the weight of nitrogen adsorbed at a given relative pressure \((P/P_0)\), \( X_m \) is monolayer capacity, which is the volume of gas adsorbed at standard temperature and pressure (STP), and \( C \) is constant. STP is defined as 273 K and 1 atm.

Figure 1- BET surface area plot for CeO₂ NP annealed at 300ºC.
Figure 2- BET surface area plot for CeO$_2$ NP annealed at 600ºC.

Figure 3- BET surface area plot for CeO$_2$ NP annealed at 900ºC.
Appendix II – Summary of the Kröger-Vink Defect Notation.

The Kröger–Vink notation is principally used to describe point defects in crystals. The main points are as follows:

1. Empty positions that are normally occupied by atoms are called vacancies and are indicated by the symbol V (italic) to differentiate it from the chemical symbol for the element vanadium, V (roman). The atom which is absent from the normally occupied site is specified by the normal chemical symbol for the element, written as a subscript. Thus in SrTiO$_3$, the symbol V$_{Sr}$ would represent a strontium atom vacancy.

2. A substituent atom is given its normal chemical symbol, and the site occupied is written as a subscript, using the chemical symbol for the atom normally present. Thus, a Ba substituent on a Sr site in SrTiO$_3$ is written as Ba$_{Sr}$.

3. Positions in a crystal not normally occupied by an atom, called interstitial positions, are denoted by the subscript i. For example, O$_i$ would represent an interstitial oxygen atom in La$_2$CuO$_{4+\delta}$.

4. Associated lattice defects are indicated by enclosing the components of such a cluster in parentheses.

5. The charge on defect is taken as an effective charge, which is the charge that the defect has with respect to the charge that would be present at the same site in a perfect crystal. The superscript ′ is used for each unit of an effective negative charge, and the superscript • is used for each unit of an effective positive charge. Thus a La substituent on a Sr site in SrTiO$_3$ would...
have an effective charge of +1 and be written La′Sr. The charge balance would be maintained by the creation of a Ti^{3+} cation in place of a Ti^{4+} cation, written Ti′_Ti.

6. Electrons and holes that are free to move through the matrix are denoted by the symbols e′ and h′.

7. When an atom or an ion occupies an interstitial site, the effective charge is the same as its real charge. For example, O_i would represent an interstitial O^{2−} anion in La_2CuO_4+δ.

8. A defect that has no effective charge can be given the (optional) superscript x to emphasis this state. The main features of the notation are summarised in Table 1. It is useful to note that the nomenclature is not structured sensitive so that the same terminology can be used across the whole spectrum of perovskite and perovskite-related phases [1].

Table 1 – The Kröger–Vink notation for defects in crystals.

<table>
<thead>
<tr>
<th>Defect type</th>
<th>Notation</th>
<th>Defect type</th>
<th>Notation</th>
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<tbody>
<tr>
<td>Metal vacancy at metal (M) site</td>
<td>V_M</td>
<td>Non-metal vacancy at metal (M) site</td>
<td>V_y</td>
</tr>
<tr>
<td>Impurity metal (A) at metal (M) site</td>
<td>A_M</td>
<td>Impurity non-metal (Z) at metal (M) site</td>
<td>Z_y</td>
</tr>
<tr>
<td>Interstitial metal (M)</td>
<td>M_i</td>
<td>Interstitial non-metal (Y)</td>
<td>Y_i</td>
</tr>
<tr>
<td>Neutral metal (M) vacancy</td>
<td>V_M^*</td>
<td>Neutral non-metal (Y) vacancy</td>
<td>V_y</td>
</tr>
<tr>
<td>Metal (M) vacancy with negative effective charge</td>
<td>V_M^-</td>
<td>Non-metal (Y) vacancy with negative effective charge</td>
<td></td>
</tr>
<tr>
<td>Interstitial metal (M) with n positive effective charges</td>
<td>M_x^n</td>
<td>Interstitial non-metal (Y) with n positive effective charges</td>
<td></td>
</tr>
<tr>
<td>Free electron</td>
<td>e'</td>
<td>Free hole</td>
<td>h'</td>
</tr>
<tr>
<td>Neutral associated defects (vacancy pair)</td>
<td>(V_M V_y)</td>
<td>Associated defects with positive effective charge</td>
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References
Appendix III - Solartron – EIS Calibration: Dummy Cell Randles Circuit Bode Plots

<table>
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<th>Error</th>
<th>Error %</th>
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Appendix IV – Publications, presentation and modules attended.

Publications

- “Fabrication of CeO\textsubscript{2} nanostructures Memristor”, R.C.Carvalho, A.J.Betts, J.F.Cassidy (Submitted).
- “Photodegradation of Sodium diclofenac using novel CeO\textsubscript{2} nanoparticles”, R.C.Carvalho, A.J.Betts, J.F.Cassidy (In preparation)
- Detection of sodium diclofenac and its photodegradation products using novel CeO\textsubscript{2} nanoparticles based screen-printed-electrode”, R.C.Carvalho, A.J.Betts, J.F.Cassidy (In preparation)

Conferences Presentations

- “Environmental Remediation of water by novel CeO\textsubscript{2} nanoparticle photoelectrocatalysts”. R.C.Carvalho, A.J.Betts, J.F.Cassidy, poster presented at 68\textsuperscript{th} Irish Universities Colloquium, University College Cork, (27\textsuperscript{th} -28\textsuperscript{th} June 2016)
- “Environmental Remediation of water by novel CeO\textsubscript{2} nanoparticle photoelectrocatalysts”. R.C.Carvalho, A.J.Betts, J.F.Cassidy, poster presented at Food and water conference, DIT opening Grangegorman (25\textsuperscript{th} June – 2016).
• “A Simple TiO₂ Memristor-based on Nanoparticles”. R.C.Carvalho, A.J.Betts, J.F.Cassidy, poster presented at 69th Irish Universities Colloquium, Dublin City University, (22nd -23rd June 2017)

• “Environmental Remediation of water by novel CeO₂ nanoparticle photoelectrocatalysts”. R.C.C.Carvalho, A.J.Betts, J.F.Cassidy, poster presented at Nanotech in France, (28th - 30th June 2017)

• ‘The use of CeO₂ as an electrochemical sensor for the simultaneous determination of caffeine, paracetamol and aspirin”. R.C.Carvalho, A.J.Betts, J.F.Cassidy, oral presentation presented at Aimes ECS meeting in Mexico, (28th - 5th October 2018) – Travel Grant Award from Royal Society of Chemistry.

• “A Simple TiO₂ Memristor-based on Nanoparticles”. R.C.Carvalho, A.J.Betts, J.F.Cassidy, oral presentation presented at Chemistry talks, University College Dublin, (28th June 2019)


• “Electroanalysis of pharmaceutical compounds” R.C.Carvalho, A.J.Betts, J.F.Cassidy, oral presentation presented at Euro Analysis 2019 in Istambul, (1st - 5th September)
Modules Attended

- Writing in Science and Engineering (UL) – 5 ECTS (2016)
- Applied Modelling in Environmental, Food and Health (DIT) - 5 ECTS – (2016-2017)
- Teaching for higher education. (ITT) – 5 ECTS (2017)
- Agriculture and Food Research & Development (Teagasc Food Research Centre) – 5 ECTS (2017)
- Introduction to Statistics (DIT) – 5 ECTS (2018)