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A Review on the Visible Light Active Titanium Dioxide Photocatalysts for Environmental Applications


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1 **A review on the visible light active titanium dioxide photocatalysts for**
2 **environmental applications***

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1 Abstract

2
3 Fujishima and Honda (1972) demonstrated the potential of titanium dioxide (TiO_2)
4 semiconductor materials to split water into hydrogen and oxygen in a photo-
5 electrochemical cell. Their work triggered the development of semiconductor
6 photocatalysis for a wide range of environmental and energy applications. One of the
7 most significant scientific and commercial advances to date has been the development of
8 visible light active (VLA) TiO_2 photocatalytic materials. In this review, a background on
9 TiO_2 structure, properties and electronic properties in photocatalysis is presented. The
10 development of different strategies to modify TiO_2 for the utilization of visible light,
11 including non metal and/or metal doping, dye sensitization and coupling semiconductors
12 are discussed. Emphasis is given to the origin of visible light absorption and the reactive
13 oxygen species generated, deduced by physicochemical and photoelectrochemical
14 methods. Various applications of VLA TiO_2 , in terms of environmental remediation and
15 in particular water treatment, disinfection and air purification, are illustrated.
16 Comprehensive studies on the photocatalytic degradation of contaminants of emerging
17 concern, including endocrine disrupting compounds, pharmaceuticals, pesticides,
18 cyanotoxins and volatile organic compounds, with VLA TiO_2 are discussed and
19 compared to conventional UV-activated TiO_2 nanomaterials. Recent advances in bacterial
20 disinfection using VLA TiO_2 are also reviewed. Issues concerning test protocols for real
21 visible light activity and photocatalytic efficiencies with different light sources have been
22 highlighted.

23
24
25 *Keywords: TiO_2 , visible, solar, water, treatment, air purification, disinfection, non-metal*
26 *doping, anatase, rutile, N- TiO_2 , metal doping, environmental application, reactive*
27 *oxygen species, photocatalysis, photocatalytic, EDCs, cyanotoxins, emerging pollutants.*
28

30 1. Titanium dioxide- an Introduction

31 1.1 TiO_2 structures and properties

32
33
34 Titanium dioxide (TiO_2) exists as three different polymorphs; anatase, rutile and brookite
35 [1]. The primary source and the most stable form of TiO_2 is rutile. All three polymorphs
36 can be readily synthesised in the laboratory and typically the metastable anatase and
37 brookite will transform to the thermodynamically stable rutile upon calcination at
38 temperatures exceeding ~ 600 °C [2]. In all three forms, titanium (Ti^{4+}) atoms are co-
39 ordinated to six oxygen (O^{2-}) atoms, forming TiO_6 octahedra [3]. Anatase is made up of
40 corner (vertice) sharing octahedra which form (001) planes (Figure 1a) resulting in a
41 tetragonal structure. In rutile the octahedra share edges at (001) planes to give a
42 tetragonal structure (Figure 1b), and in brookite both edges and corners are shared to give
43 an orthorhombic structure (Figure 1c) [2,4-7].

44
45 Titanium dioxide is typically an *n*-type semiconductor due to oxygen deficiency [8]. The
46 band gap is 3.2 eV for anatase, 3.0 eV for rutile, and ~ 3.2 eV for brookite [9-11]. Anatase

1 and rutile are the main polymorphs and their key properties are summarized in Table 1
2 [12-14]. TiO₂ is the most widely investigated photocatalyst due to high photo-activity,
3 low cost, low toxicity and good chemical and thermal stability [12,15,16]. In the past few
4 decades there have been several exciting breakthroughs with respect to titanium dioxide.
5 The first major advance was in 1972 when Fujishima and Honda reported the
6 photoelectrochemical splitting of water using a TiO₂ anode and a Pt counter electrode
7 [17]. Titanium dioxide photocatalysis was first used for the remediation of environmental
8 pollutants in 1977 when Frank and Bard reported the reduction of CN⁻ in water [18,19].
9 This led to a dramatic increase in the research in this area because of the potential for
10 water and air purification through utilization of “free” solar energy [12,14,20]. Other
11 significant breakthroughs included Wang *et al.* (1977), who reported TiO₂ surfaces with
12 excellent anti-fogging and self-cleaning abilities, attributed to the super hydrophilic
13 properties of the photoexcited TiO₂ surfaces [21] and use of nano titanium dioxide in an
14 efficient dye sensitized solar cell (DSSC), reported by Graetzel and O’Regan in 1991
15 [22].

16 1.2 Electronic processes in TiO₂ photocatalysis

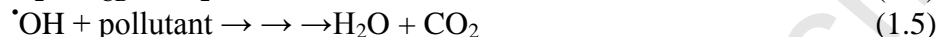
17
18 Photocatalysis is widely used to describe the process in which the acceleration of a
19 reaction occurs when a material, usually a semiconductor, interacts with light of
20 sufficient energy (or of a certain wavelength) to produce reactive oxidizing species
21 (ROS) which can lead to the photocatalytic transformation of a pollutant. It must be noted
22 that during the photocatalytic reaction, at least two events must occur simultaneously in
23 order for the successful production of reactive oxidizing species to occur. Typically, the
24 first involves the oxidation of dissociatively adsorbed H₂O by photogenerated holes, the
25 second involves reduction of an electron acceptor by photoexcited electrons; these
26 reactions lead to the production of a hydroxyl and superoxide radical anion, respectively
27 [23].

28 It is clear that photocatalysis implies photon-assisted generation of catalytically active
29 species rather than the action of light as a catalyst in a reaction [24,25]. If the initial
30 photoexcitation process occurs in an adsorbate molecule, which then interacts with the
31 ground state of the catalyst substrate, the process is referred to as a “catalyzed
32 photoreaction”, if, on the other hand, the initial photoexcitation takes place in the catalyst
33 substrate and the photoexcited catalyst then interacts with the ground state adsorbate
34 molecule, the process is a “sensitized photoreaction”. In most cases, heterogeneous
35 photocatalysis refers to semiconductor photocatalysis or semiconductor-sensitized
36 photoreactions [23].

37
38 In photocatalysis, light of energy greater than the band gap of the semiconductor, excites
39 an electron from the valence band to the conduction band (see Figure 2). In the case of
40 anatase TiO₂, the band gap is 3.2 eV, therefore UV light ($\lambda \leq 387$ nm) is required. The
41 absorption of a photon excites an electron to the conduction band (e^-_{CB}) generating a
42 positive hole in the valence band (h^+_{VB}) (Eq. 1.1).



1 Charge carriers can be trapped as Ti^{3+} and O^- defect sites in the TiO_2 lattice, or they can
 2 recombine, dissipating energy [26]. Alternatively, the charge carriers can migrate to the
 3 catalyst surface and initiate redox reactions with adsorbates [27]. Positive holes can
 4 oxidize OH^- or water at the surface to produce $\cdot OH$ radicals (Eq. 1.2) which, are
 5 extremely powerful oxidants (Table 2). The hydroxyl radicals can subsequently oxidize
 6 organic species with mineralization producing mineral salts, CO_2 and H_2O (Eq. 1.5) [28].



16
 17 Electrons in the conduction band can be rapidly trapped by molecular oxygen adsorbed
 18 on the titania particle, which is reduced to form superoxide radical anion ($O_2^{\cdot-}$) (Eq. 1.4)
 19 that may further react with H^+ to generate hydroperoxyl radical ($\cdot OOH$) (Eq. 1.6) and
 20 further electrochemical reduction yields H_2O_2 (Eq. 1.7) [29,30]. These reactive oxygen
 21 species may also contribute to the oxidative pathways such as the degradation of a
 22 pollutant (Eq. 1.8 and 1.9) [26,28,29].

23 1.3 Recombination

24
 25 Recombination of photogenerated charge carriers is the major limitation in
 26 semiconductor photocatalysis as it reduces the overall quantum efficiency [30]. When
 27 recombination occurs, the excited electron reverts to the valence band without reacting
 28 with adsorbed species (Eq. 1.2) [31] non-radiatively or radiatively, dissipating the energy
 29 as light or heat [6,32].

30
 31 Recombination may occur either on the surface or in the bulk and is in general facilitated
 32 by impurities, defects, or all factors which introduce bulk or surface imperfections into
 33 the crystal [30,33]. Serpone *et al.*, found that trapping excited electrons as Ti^{3+} species
 34 occurred on a time scale of ~ 30 ps and that about 90 % or more of the photogenerated
 35 electrons recombine within 10 ns [34]. Doping with ions [35-37], heterojunction coupling
 36 [38-40] and nanosized crystals [41,42] have all been reported to promote separation of
 37 the electron-hole pair, reducing recombination and therefore improve the photocatalytic
 38 activity. For example, the TiO_2 crystallites of Evonik (Degussa) P25 contain a
 39 combination of anatase ($\sim 80\%$) and rutile ($\sim 20\%$). The conduction band potential of
 40 rutile is more positive than that of anatase which means that the rutile phase may act as
 41 an electron sink for photogenerated electrons from the conduction band of the anatase
 42 phase. Many researchers attribute the high photocatalytic activity of this preparation to
 43 the intimate contact between two phases, enhancing separation of photogenerated
 44 electrons and holes, and resulting in reduced recombination [43].

45 46 1.4 Strategies for improving TiO_2 photoactivity

1
2 Various strategies have been adopted for improving the photocatalytic efficiency of TiO₂.
3 They can be summarized as either morphological modifications, such as increasing
4 surface area and porosity, or as chemical modifications, by incorporation of additional
5 components in the TiO₂ structure. Although visible light active (VLA) TiO₂
6 photocatalysts require chemical modifications, which will be reviewed in the next
7 section, their overall efficiencies have been significantly enhanced by controlling the
8 semiconductor morphology.

9
10 The most commonly used TiO₂ morphology is that of monodispersed nanoparticles
11 wherein the diameter is controlled to give benefits from the small crystallite size (high
12 surface area, reduced bulk recombination) without the detrimental effects associated with
13 very small particles (surface recombination, low crystallinity) [44]. One dimensional
14 (1D) titania nanostructures (nanotubes, nanorods, nanowires, nanobelts, nanoneedles)
15 have been also formed by hydrothermal synthesis but high emphasis was given in titania
16 self-assembled nanotubular films grown by electrochemical anodization on titanium
17 metal foils. Advantages of such structures is their tailored morphology, controlled
18 porosity, vectorial charge transfer [45,46] and low recombination at grain boundaries that
19 result in enhanced performance in photoinduced applications, mainly in photocatalysis
20 [45,47,48]. An interesting use of TiO₂ nanotubes in photocatalytic applications is the
21 growth of freestanding flow-through membranes [45].

22 23 **2. Development of Visible Light Active (VLA) Titania Photocatalysts**

24 25 *2.1 Non metal doping*

26 27 2.1.1 Nitrogen doping

28
29 Ultraviolet light makes up only 4-5 % of the solar spectrum, whereas approximately 40 %
30 of solar photons are in the visible region. A major drawback of pure TiO₂ is the large
31 band gap meaning it can only be activated upon irradiation with photons of light in the
32 UV domain ($\lambda \leq 387$ nm for anatase), limiting the practical efficiency for solar
33 applications [49-51]. Therefore, in order to enhance the solar efficiency of TiO₂ under
34 solar irradiation, it is necessary to modify the nanomaterial to facilitate visible light
35 absorption. Non-metal doping of TiO₂ has shown great promise in achieving visible light
36 active (VLA) photocatalysis, with nitrogen being the most promising dopant [52,53].

37
38 Nitrogen can be easily introduced in the TiO₂ structure, due to its comparable atomic size
39 with oxygen, small ionization energy and high stability. It was in 1986 when Sato
40 discovered that addition of NH₄OH in a titania sol, followed by calcination of the
41 precipitated powder, resulted in a material that exhibited a visible light response [54,55].
42 Later on, Asahi and co-workers explored for first time the visible light activity of N-
43 doped TiO₂ produced by sputter deposition of TiO₂ under an N₂/Ar atmosphere, followed
44 by annealing under N₂ [56]. Since then, there have been many reports dealing with
45 nitrogen doping of TiO₂. Significant efforts are being devoted to investigating the
46 structural, electronic and optical properties of N-doped TiO₂, understanding the

1 underlying mechanisms and improving the photocatalytic and self-cleaning efficiency
2 under visible and solar light [57-59]. Comprehensive reviews have been published which
3 summarize representative results of these studies [60,61]. Model pollutants that have
4 been reported to be effectively degraded by VLA photocatalyst include phenols,
5 methylene blue, methyl orange (although dyes have strong absorption in the visible
6 range) and rhodamine B, as well as several gaseous pollutants (e.g., volatile organic
7 compounds, nitrogen oxides).

8
9 For the efficient incorporation of nitrogen into TiO_2 either in the bulk or as a surface
10 dopant, both dry and wet preparation methods have been adopted. Physical techniques
11 such as sputtering [62-66] and ion implantation [67,68], rely on the direct treatment of
12 TiO_2 with energetic nitrogen ions. Gas phase reaction methods [69-71], atomic layer
13 deposition [72] and pulsed laser deposition [73] have been successfully applied to prepare
14 N- TiO_2 , as well. However, the most versatile technique for the synthesis of N- TiO_2
15 nanoparticles is the sol-gel method, which requires relatively simple equipment and
16 permits fine control of the material's nanostructure, morphology and porosity.
17 Simultaneous TiO_2 growth and N doping is achieved by hydrolysis of titanium alkoxide
18 precursors in the presence of nitrogen sources. Typical titanium salts (titanium
19 tetrachloride) and alkoxide precursors (including titanium tetra-isopropoxide, tetrabutyl
20 orthotitanate) have been used. Nitrogen containing precursors used include aliphatic
21 amines, nitrates, ammonium salts, ammonia and urea [74-76]. The synthesis route involves
22 several steps; however, the main characteristic is that precursor hydrolysis is usually
23 performed at room temperature. The precipitate is then dried to remove solvents,
24 pulverized and calcined at temperatures from 200 to 600°C.

25
26 One promising way to increase the nitrogen content in the TiO_2 lattice is to combine the
27 titanium precursors with a nitrogen-containing ligand, such as Ti^{4+} -bipyridine or Ti^{4+} -
28 amine complexes [77,78]. An alternative soft chemical route is based on the addition of
29 urea during the condensation of an alkoxide acidified solution, leading to interstitial
30 surface doping and shift of the absorption edge well into the visible spectral range (from
31 3.2 to 2.3 eV) [79]. An innovative sol-gel related technique for the preparation of
32 efficient visible-light active nanostructured TiO_2 is the templating sol-gel method,
33 utilizing titanium precursors combined with nitrogen-containing surfactants. Specifically,
34 successful synthesis of visible light activated N- TiO_2 has been achieved by a simple sol-
35 gel method employing dodecylammonium chloride (DDAC) as surfactant [80]. The
36 DDAC surfactant acts simultaneously as a pore templating material to tailor-design the
37 structural properties of TiO_2 (see Figure 3) as well as a nitrogen dopant to induce visible-
38 light photoactivity and unique reactivity and functionality for environmental applications
39 [81,82].

40
41 In a different approach N- TiO_2 , was synthesized via two successive steps: synthesis of
42 TiO_2 and then nitrogen doping using various nitrogen-containing chemicals (e.g. urea,
43 ethylamine, NH_3 or gaseous nitrogen) at high temperatures [53,83-85] or inductively
44 coupled plasma containing a wide range of nitrogen precursors [86]. In that case, the
45 nitrogen atoms predominantly resided on the TiO_2 surface. The origin of the visible-light

1 photocatalytic activity in these methods may arise from condensed aromatic s-triazine
2 compounds containing melem and melon units [74].

3
4 Although most reports on N-TiO₂ concern the anatase polymorphic phase, visible light
5 active N-TiO₂ with anatase-rutile mixed phase (Figure 4) has also been prepared by
6 tuning the parameters of the sol-gel synthesis. Such heterojunction photocatalysts seem to
7 effectively transfer photo-excited electrons from the conduction band of anatase to that of
8 rutile, favoring electron-hole separation and enhancing the visible light photocatalytic
9 activity. [87,88]. Etacheri *et al.*, have successfully developed nitrogen doped anatase-
10 rutile heterojunctions which were found to be nine times more photocatalytically active at
11 wavelengths higher than 450 nm (blue filter) in comparison with Evonik P25.

12
13 Most of the above methods have also been successfully applied for the doping of 1D
14 titania nanostructures with nitrogen. In this way, N-doped anatase titania nanobelts were
15 prepared via hydrothermal processing and subsequent heat treatment in NH₃ [89]. Similar
16 post-treatment was employed for doping anodized titania nanotubes [90], while high
17 energy ion implantation was found to be more efficient in introducing N atoms in the
18 TiO₂ lattice [91]. Nitrogen localized states have also been introduced into highly ordered
19 TiO₂ nanotubes via nitrogen plasma [92]. Visible light-active N-TiO₂ nanoarray films
20 have also been prepared on sacrificial anodized alumina liquid phase deposition with urea
21 mixed with (NH₄)₂TiF₆ aqueous solution [93]. Recently, surface N-doping on titania
22 nanowires, their lateral dimensions reaching the atomic scale, was achieved by the
23 introduction of amines during the condensation stage of the titania precursor [94]. Other
24 approaches for preparing doped TiO₂ nanotubes include employment of nitrogen sources
25 in the electrolyte solutions of electrochemical anodization [95] or in the initial solution of
26 hydrothermal growth [96,97].

27
28 Many results, up to now, describe nitrogen doping as substitutional element on the
29 oxygen lattice sites or at interstitial lattice sites. The two sites can be in principle
30 discriminated by X-ray photoelectron spectroscopy (XPS) relying on the distinct N1s
31 binding energies at 396 and 400 eV, respectively [52,70,98-100], although there is still
32 some debate concerning the attribution of the 400 eV peak to interstitial or molecularly
33 chemisorbed nitrogen [65,66]. Compared with the UV activity of undoped TiO₂, the
34 visible light activity of N-TiO₂ is rather low. There is also some conflict in the literature
35 concerning the preferred N sites, substitutional or interstitial, which induce the highest
36 photocatalytic action [70,84,100,101]. Independently of the origin of visible light
37 absorption in substitutional or interstitial nitrogen discrete energy states, the low
38 photocatalytic efficiency is mainly attributed to the limited photo-excitation of electrons
39 in such narrow states, the very low mobility of the corresponding photo-generated holes
40 [102] and the concomitant increase of the recombination rate due to the creation of
41 oxygen vacancies by doping [103].

42 43 2.1.2 Other non-metal doping (F, C, S)

44
45 Fluorine doping does not shift the TiO₂ band gap; however it improves the surface acidity
46 and causes formation of reduced Ti³⁺ ions due to the charge compensation between F⁻ and

1 Ti^{4+} . Thus, charge separation is promoted and the efficiency of photoinduced processes is
2 improved [104]. Insertion of fluorine into the TiO_2 crystal lattice has also been reported
3 to elevate the anatase to rutile phase transformation temperature. Padmanabhan *et al.*,
4 successfully modified titanium isopropoxide with trifluoroacetic acid carrying out a sol-
5 gel synthesis. The resulting material proved to be more photocatalytically active than
6 Evonik P25 while also retaining anatase at temperatures of up to 900 °C [105].

7
8 Carbon, phosphorous and sulphur as dopants have also shown positive results for visible
9 light activity in TiO_2 [49,50]. The non-metal dopants effectively narrow the band gap of
10 TiO_2 (< 3.2 eV) [51,106,107]. The change of lattice parameters, and the presence of trap
11 states within the conduction and valence bands from electronic perturbations, gives rise
12 to band gap narrowing [108]. Not only does this allow for visible light absorption but the
13 presence of trap sites within the TiO_2 bands increases the lifetime of photo-generated
14 charge carriers.

15
16 Successful insertion of sulfur into the TiO_2 lattice is far more difficult to achieve than
17 nitrogen, due to its larger ionic radius. Insertion of cationic sulfur (S^{6+}) is chemically
18 favourable over the ionic form (S^{2-}) lattice. Cationic (sulfur) and anionic (nitrogen) co-
19 doped with TiO_2 has also been synthesised from a single source, ammonium sulfate,
20 using a simple sol-gel technique [109]. Periyat *et al.*, successfully developed S-doped
21 TiO_2 through modification of titanium isopropoxide with sulphuric acid. They found that
22 formation of titanyl oxysulfate results in the retention of anatase at increased
23 temperatures (≥ 800 °C) and that the presence of sulfur causes increased visible light
24 photocatalytic activity of the synthesised materials. [110]. Recently, visible light-
25 activated sulfur doped TiO_2 films were successfully synthesized using a novel sol-gel
26 method based on the self-assembly technique with a nonionic surfactant to control
27 nanostructure and H_2SO_4 as an inorganic sulfur source [111]. Sulfur species distributed
28 uniformly throughout the films were identified both as S^{2-} ions related to anionic
29 substitutional doping of TiO_2 as well as $\text{S}^{6+}/\text{S}^{4+}$ cations, attributed mainly to the presence
30 of surface sulfate groups. A strong electron paramagnetic resonance (EPR) signal, whose
31 intensity correlated with the sulfur content and most importantly was markedly enhanced
32 under visible light irradiation, implied formation of localized energy states in the TiO_2
33 band gap due to anion doping and/or oxygen vacancies. Calcination at 350°C for 2 h
34 provided sulfur doped TiO_2 films with the highest sulfur content and BET surface area,
35 small crystallite size, high porosity, and large pore volume together with very smooth and
36 uniform surface. The corresponding mesoporous S- TiO_2 film was the most effective
37 photocatalyst for the degradation of microcystin-LR (MC-LR) under visible light
38 irradiation.

39 40 2.1.3 Non-metal co-doping

41
42 N-F co-doped TiO_2 has been explored in visible light photocatalysis [112,113] due to the
43 similar structural preferences of the two dopants. In addition, the combined structure
44 retains the advantages of N-doping in high visible light response and the F-doping
45 significant role in charge separation. Furthermore, synergetic effects of the co-doping
46 have been found. In fact, surface fluorination inhibits phase transformation from anatase

1 to rutile and removal of N-dopants during annealing [114]. In addition, it reduces the
2 energy cost of doping and also the amount of oxygen defects in the lattice, as a
3 consequence of the charge compensation between the nitrogen (p-dopant) and the
4 fluorine (n-dopant) impurities [115]. These effects stabilize the composite system and
5 effectively reduce the concomitant electron-hole recombination that hampers the
6 photocatalytic performance of singly doped N-TiO₂.

7
8 The synergistic approach of the N-F doping has been further exploited employing a
9 modified sol-gel technique based on a nitrogen precursor and a Zonyl FS-300 nonionic
10 fluorosurfactant as both fluorine source and pore template material to tailor-design the
11 structural properties of TiO₂ [116]. The obtained materials are active under visible light
12 illumination and have been used for the photocatalytic degradation of a variety of
13 pollutants in water. Very recently, these N-F doped titania materials were successfully
14 immobilized on glass substrates employing the dip-coating method with subsequent
15 drying under infrared lamp, followed by calcination at 400°C. The nanostructured titania
16 doped thin films preserve their visible light induced catalytic activity [117]. Furthermore,
17 comparative EPR measurements between the co-doped and reference samples identified
18 distinct N spin species in NF-TiO₂, with a high sensitivity to visible light irradiation. The
19 abundance of these paramagnetic centers verifies the formation of localized intra-gap
20 states in TiO₂ and implies synergistic effects between fluorine and nitrogen dopants
21 [117].

22
23 Significant improvement of the visible-light photoactivity of N-F co-doped titania films
24 has been observed by employing an inverse opal growth method, using a silica colloidal
25 crystal as a template for liquid phase deposition of NF-TiO₂. In this way, hierarchical
26 meso-macroporous structures are prepared which promote efficient and stable
27 photocatalysis via tuned morphology and photon multiple scattering effects [118].

28 29 2.1.4 Oxygen rich TiO₂ modification

30
31 Following another approach, recently the visible light active photocatalytic properties
32 have been achieved by the *in-situ* generation of oxygen through the thermal
33 decomposition of peroxo-titania complex [119]. Increased Ti-O-Ti bond strength and
34 upward shifting of the valence band (VB) maximum were responsible for the visible light
35 activity. The upward shifting of the VB maximum for oxygen rich titania is identified as
36 another crucial reason responsible for efficient visible light absorption. Typical band gap
37 structures of control and oxygen rich titania samples obtained are represented in Figure 5.

38 39 2.2 Metal Deposition

40 41 2.2.1. Noble metal and transition metal deposition.

42
43 Modifications of TiO₂ with transition metals such as Cr, Co, V and Fe have extended the
44 spectral response of TiO₂ well into the visible region also improving photocatalytic
45 activity [108,120-123]. However, transition metals may also act as recombination sites
46 for the photo induced charge carriers thus, lowering the quantum efficiency. Transition

1 metals have also been found to cause thermal instability to the anatase phase of TiO₂
2 [30]. Kang argues that despite the fact that a decrease in band gap energy has been
3 achieved by many groups through metal doping, photocatalytic activity has not been
4 remarkably enhanced because the metals introduced were not incorporated into the TiO₂
5 framework. In addition, metals remaining on the TiO₂ surface block reaction sites [124].
6 While Morikawa *et al.*, showed that doping TiO₂ with Cr was found to reduce
7 photocatalytic activity but Cr and V ion implanted TiO₂ showed higher photocatalytic
8 performances than bare TiO₂ did for the decomposition of NO under solar irradiation
9 [125]. Another technique involves modifying TiO₂ with transition metals such as Fe, Cu,
10 Co, Ni, Cr, V, Mn, Mo, Nb, W, Ru, Pt and Au [126-135]. The incorporation of transition
11 metals in the titania crystal lattice may result in the formation of new energy levels
12 between VB and CB, inducing a shift of light absorption towards the visible light region.
13 Photocatalytic activity usually depends on the nature and the amount of doping agent.
14 Possible limitations are photocorrosion and promoted charge recombination at metal sites
15 [127].

16
17 Deposition of noble metals like Ag, Au, Pt and Pd on the surface of TiO₂ enhances the
18 photocatalytic efficiency under visible light by acting as an electron trap, promoting
19 interfacial charge transfer and therefore delaying recombination of the electron-hole pair
20 [126,136-140]. Hwang *et al.*, showed that platinum deposits on TiO₂ trap photo-
21 generated electrons, and subsequently increase the photo-induced electron transfer rate at
22 the interface. Seery *et al.*, showed enhanced visible light photocatalysis with Ag modified
23 TiO₂ [141]. While Gunawan *et al.*, demonstrated the reversible photoswitching of nano
24 silver on TiO₂ where reduced silver on a TiO₂ support exposed to visible light (> 450 nm)
25 resulted in excitation and reverse electron flow from silver to the TiO₂ support, oxidising
26 silver ($\text{Ag}^0 \rightarrow \text{Ag}^+$) in the process [142]. The visible light responsiveness of TiO₂ was
27 accredited to the surface plasmon resonance of silver nanoparticles (Figure 6) [142,143].

28 29 2.3 Dye sensitization in photocatalysis

30
31 Dye photosensitization has been reported by different groups and to be one of the most
32 effective ways to extend the photoresponse of TiO₂ into the visible region [144-147].
33 Indeed these types of reactions are exploited in the well known dye sensitized solar cells
34 [22]. The mechanism of the dye sensitized photo-degradation of pollutants is based on the
35 absorption of visible light for exciting an electron from the highest occupied molecular
36 orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of a dye. The
37 excited dye molecule subsequently transfers electrons into the conduction band of TiO₂,
38 while the dye itself is converted to its cationic radical. The TiO₂ acts only as a mediator
39 for transferring electrons from the sensitizer to the substrate on the TiO₂ surface as
40 electron acceptors, and the valence band of TiO₂ remains unaffected. In this process, the
41 LUMO of the dye molecules should be more negative than the conduction band of TiO₂.
42 The injected electrons hop over quickly to the surface of titania where they are scavenged
43 by molecular oxygen to form superoxide radical $\text{O}_2^{\cdot-}$ and hydrogen peroxide radical
44 $\cdot\text{OOH}$. These reactive species can also disproportionate to give hydroxyl radical [148-
45 150]. In addition to the mentioned species, singlet oxygen may also be formed under
46 certain experimental conditions. Oxygen has two singlet excited states above the triplet

1 ground ones. Such relatively long live oxygen species may be produced by quenching of
2 the excited state of the photosensitizer by oxygen. The subsequent radical chain reactions
3 can lead to the degradation of the dye [150].

4
5 Knowledge of interfacial electron transfer between semiconductor and molecular
6 adsorbates is of fundamental interest and essential for applications of these materials
7 [151-154]. Ultrafast electron injection has been reported for many dye-sensitized TiO₂
8 systems. This injection depends on the nature of the sensitizer, the semiconductor, and
9 their interaction. Asbury *et al.*, observed very different electron injection times from
10 *femto* to *pico* second by changing the semiconductor under the same conditions [152].

11 12 2.4 Coupled semiconductors

13
14 Many efforts have been made in the synthesis of different coupled semiconductors such
15 as ZnO/TiO₂ [155], CdS/TiO₂ [156], and Bi₂S₃/TiO₂ [157]. The synthesized couples
16 significantly enhance the photocatalytic efficiency by decreasing the recombination rate
17 of the photogenerated electron-hole pairs and present potential applications in water
18 splitting, organic decomposition, and photovoltaic devices [158-160]. These composites
19 were also considered as promising materials to develop a high efficiency photocatalyst
20 activated with visible light. They can also compensate the disadvantages of the individual
21 components, and induce a synergistic effect such as an efficient charge separation and
22 improvement of photostability [160,161]. Therefore, visible light-driven coupled
23 photocatalysts that can decompose organic material are of great interest [159,162,163].

24
25 Analysis of the microstructure and phase composition of the coupled semiconductor of
26 BiFeO₃/TiO₂ revealed that a core-shell structure was formed [164]. This couple resulted
27 in extended photo-absorption bands into the visible which was dependent on the BiFeO₃
28 content. This couple was reported to be more effective for the photocatalytic degradation
29 of congo red dye under visible light irradiation, as compared to pure BiFeO₃ and TiO₂
30 powders. Sensitizing TiO₂ nanotube arrays with ZnFe₂O₄ was found to enhance
31 photoinduced charge separation and to extend the photoresponse from the UV to the
32 visible region, too [165].

33
34 Up until now, the main efforts have been devoted to the synthesis of various core-shell
35 nanocrystals. The prevalent view point is that it requires a lattice matching between shells
36 and core materials to achieve a better passivation and minimize structural defects [166-
37 169]. In addition, the coupling of a large band gap semiconductor with a smaller one,
38 which can be activated with visible light, is of great interest for the degradation of
39 organic pollutants using solar radiation. Blocking trap states by coating the particles with
40 thin layers of a wide band gap material can lead to a drastic enhancement of the
41 photostability [170-172]. For instance, CdS is a fascinating material with ideal band gap
42 energy for solar and visible light applications (2.4 eV). However, CdS is prone to photo-
43 anodic corrosion in aqueous environments. To overcome this stability problem and
44 improve the photoactivity, CdS has been combined with a wide band gap semiconductor,
45 such as ZnO and TiO₂ [159,173], and this coupling gives improved charge separation of
46 photogenerated electrons and holes (see Figure 7).

1
2 In addition to the flat band potential of the components, the photocatalytic performance
3 of the coupled semiconductors is also related to the geometry of the particles, the contact
4 surface between particles, and the particle size [174-175]. These parameters strongly
5 depend on the manner with which the couples are prepared. Various core/shell type
6 nanocrystals have been extensively studied using different methods. Synthesis methods
7 normally require high temperatures, long times, strict inert atmosphere protection and
8 complex multistep reaction process.

9
10 By applying ultrasound under specific conditions, there is the possibility of synthesizing
11 nano-composites in a short time, under mild conditions, in air, and without calcination
12 [156]. For example, TiO₂-coated nanoparticles with a core-shell structure have been
13 prepared with ultrasound treatment. The TiO₂ was found to be uniformly coated on the
14 surface of CdS and this led to an enlargement of the nanoparticles. In the absence of
15 ultrasound, the formation of large irregular aggregates was observed. The UV-Vis
16 absorbance spectra of the pure and composite semiconductors are shown in Figure 8
17 [156]. The absorption band of CdS nanoparticles was found at around 450-470 nm in
18 comparison with the bulk crystalline CdS which appeared at about 515 nm ($E_g = 2.4$ eV)
19 [176]. In the case of TiO₂, the onset absorption for nanoparticles prepared under
20 ultrasound was about 360 nm, while for the bulk it was about 385 nm ($E_g = 3.2$ eV)
21 [177]. It is found that modification of TiO₂ with CdS particles extends the optical
22 absorption spectrum into the visible region in comparison with that of pure TiO₂.
23 Increasing the amount of TiO₂ led to a further red-shift of the absorption band in
24 composite photocatalysts. The red shift of spectra are typical characteristics of core-shell
25 nano-crystals, originating from the efficient diminishing of the surface defects of core
26 nano-crystals after capping them with higher band gap shells [169]. This is in agreement
27 with the previous report by Kisch *et al.* that the band gap of CdS employed in composite
28 photocatalysts is shifted by an electronic semiconductor-support interaction [178,179].

29
30 The synthesized CdS/TiO₂ nano-composite system was applied for the removal of
31 Reactive Black 5 in aqueous solution, under different conditions, and employing visible
32 and solar light irradiation. The mechanism for the degradation that is proposed is based
33 on the reactions in Figure 9 [156]. In semiconductor core-shell structures electronic
34 interactions that occur at the heterojunction can trap photo-generated electrons at the
35 interface and improve the efficiency of the photocatalytic activity. The photo-generated
36 electrons and holes induce redox reactions according to the relative potentials of the
37 conduction and valence bands of the two semiconductors. Such core-shell nano-
38 composites may bring new insights into the design of highly efficient photocatalysts and
39 potential applications in technology.

40 41 2.5 Defect induced VLA photocatalysis

42
43 VLA titania can also be formed by introducing color centers inside the material [45, 57].
44 This defect induced doping can be produced either by heat treatment of TiO₂ in vacuum
45 or inert gas environments or by intercalation of small cations (H⁺, Li⁺, etc.) into the
46 lattice. In some cases, O₂ is released from the material and Ti³⁺ centers are formed. Very

1 recently, hydrogenation has been demonstrated as a very effective route to engineer the
2 surface of anatase TiO₂ nanoparticles with an amorphous layer which, instead of inducing
3 detrimental recombination effects, resulted in the marked extension of the optical
4 absorption to the infrared range and remarkable enhancement of solar-driven
5 photocatalytic activity [180].

6 7 **3. Oxidation chemistry, the reactive oxygen species generated and their subsequent** 8 **reaction pathways.**

9 10 *3.1. Reactive oxygen species and reaction pathways in VLA TiO₂ photocatalysis*

11
12 As a model, the reaction pathways of visible light-induced photocatalytic degradation of
13 acid orange 7 (AO7) in the presence of TiO₂ has been investigated [181], monitoring the
14 formation and the fate of intermediates and final products in solution and on the
15 photocatalyst surface as a function of irradiation time. It was observed that the intensity
16 of the chromophore band of AO7 reduced exponentially with time and disappeared after
17 about 60 h. The intensities of the absorbance peaks related to the naphthalene and
18 benzene rings in AO7 decreased with a slower rate compared to that of decolorization of
19 the solution during the first 60 h. After complete decolorization, the absorbance due to
20 the naphthalene and benzene rings remained constant. This observation confirmed that in
21 the absence of colored compounds on the photocatalyst surface, visible light cannot
22 effectively degrade fragments containing the benzene and naphthalene rings produced by
23 the cleavage of the dye molecule. It should be noted that AO7 solution was stable under
24 visible light without TiO₂, and that the TiO₂ suspension was unable to initiate the dye
25 degradation in the dark. Both visible light and TiO₂ particles were indispensable for the
26 degradation of AO7 in aqueous solution. During the irradiation of AO7-TiO₂ suspension
27 with visible light different intermediates such as compounds containing a naphthalene
28 ring, phthalic derivatives, aromatic acids, and aliphatic acids were identified. In addition,
29 the evolution of inorganic ions such as sulfate, nitrate, nitrite, and ammonium ions were
30 monitored during the irradiation by visible light.

31
32 By using appropriate quenchers, the formation of oxidative species such as singlet
33 oxygen, superoxide, and hydroperoxide radicals and their role in the degradation of the
34 dye molecules during illumination was studied [181]. It was observed that in the presence
35 of 1, 4-benzoquinone (BQ), which is a superoxide quencher and a good electron acceptor
36 [120], both photodegradation and formation of hydrogen peroxide were completely
37 suppressed. This indicates that the superoxide radical is an active oxidative intermediate.
38 Addition of sodium azide, which is a singlet oxygen quencher [182] and may also interact
39 with hydroxyl radical [183], initially did not significantly affect the degradation of AO7
40 but the inhibition became important after 40 min, indicating the delayed formation of
41 singlet oxygen and possibly hydroxyl radical species. Formation of hydrogen peroxide
42 was also suppressed in the presence of this inhibitor. Similar results were obtained by
43 addition of 1,4-diazabicyclo[2,2,2]-octane (DABCO) [184], which is also a singlet
44 oxygen quencher. The important point of the work in [181] is that when complete
45 decolorization of the solution was achieved, the formation of active oxidation species and
46 hydrogen peroxide stopped, the oxidation reactions ceased and the concentrations of

1 intermediates remained constant. This is because only in the presence of visible light
2 absorbing compounds, the formation of oxidizing species was possible.

3
4 In a visible light/sensitizer/TiO₂ system, oxygen is indispensable in order to generate
5 active oxygen radicals [185]. The role of dissolved oxygen and active species generated
6 in the photocatalytic degradation of phenol was investigated by using a polymer
7 sensitized TiO₂ under visible light [186]. The experimental results showed that the
8 photocatalytic degradation of phenol was almost stopped under nitrogen atmosphere.
9 Therefore, oxygen is very important in photocatalytic reactions induced by visible light
10 and it acts as an efficient electron scavenger. In this system, the degradation of phenol
11 gradually decreased by increasing sodium azide concentration. This indicated that singlet
12 oxygen was generated under visible light irradiation. Singlet oxygen can degrade phenol
13 directly to about 40 percent which is due to its high energy level (22.5 kcal mol⁻¹). In
14 addition, singlet oxygen can be measured by phosphorescence in near IR as a direct
15 method of detection. There is a range of different fluorescence or spin-trap probes for
16 indirect measurements of singlet oxygen and/or superoxide. The spin-trap 2,2,6,6-
17 tetramethyl-4-piperidone-*N*-oxide (TEMP) is generally used as a probe for singlet oxygen
18 in EPR studies. The reactions of TEMP with singlet oxygen yields a stable radical adduct
19 [187]. Another useful spin trap system is the 5,5 dimethylpyrrolineloxy (DMPO) [188-
20 190]. Monitoring intermediate 5,5 dimethylpyrrolineloxy (DMPO)-OH[•] radicals
21 formed in the suspension during illumination [186] is done by its characteristic 1:2:2:1
22 quartet EPR spectrum and provides evidence of hydroxyl radicals in the system. In
23 addition, some alcohols are commonly used as diagnostic tools for hydroxyl radical
24 mediated mechanisms [191,192]. The degradation of phenol by adding *i*-PrOH or MeOH
25 was decreased by about 60 percent which indicated that both of them seriously inhibited
26 the photocatalytic degradation of phenol [186]. This confirmed that hydroxyl radicals
27 were the predominant active species in this system, but did not probe the mechanism of
28 hydroxyl radical formation.

29 30 *3.2 Photoelectrochemical methods for determining visible light activity*

31
32 If the photocatalytic material is immobilized onto an electrically conducting supporting
33 substrate, one can use this electrode in a photoelectrochemical cell to measure properties
34 including the band gap energy, flat band potential, dopant density, kinetics of hole and
35 electron transfer, and the energies of dopant levels. If one examines the current-potential
36 response under potentiometric control, for an n-type semiconductor e.g. TiO₂, in the dark
37 no significant anodic (positive) current is observed because there are essentially no holes
38 in the valence band. When irradiated with light equal to the band gap energy, electrons
39 are promoted to the conduction band, leaving positive holes in the valence band, and an
40 increase is observed in the anodic current at potentials more positive than the flat band
41 potential E_{fb} . The difference between the current observed in the light and that in the dark
42 is called the photocurrent (J_{ph}) and it is a measure of the hole-transfer rate at the SC-
43 electrolyte interface. At the flat band potential, no net current is observed as all charge
44 carriers recombine. For a p-type semiconductor, the situation is reversed and an increase
45 in cathodic current is observed under band gap irradiation for potentials more negative
46 than E_{fb} . If a monochromator is used along with a polychromatic source e.g. xenon, to

1 irradiate the electrode one can determine the spectral photocurrent response and the
2 incident photon to current conversion efficiency (IPCE).

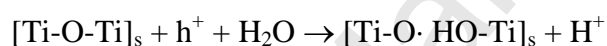
$$\text{IPCE} = \frac{J_{\text{ph}}}{I_0 F}$$

4
5
6 where J_{ph} is the photocurrent density (A cm^{-2}), I_0 is the incident light flux (moles of
7 photons $\text{s}^{-1} \text{cm}^{-2}$) and F is Faraday's constant (C mol^{-1}). For an n-type semiconductor, this
8 is the quantum efficiency for hole-transfer to the electrolyte. The maximum wavelength
9 at which photocurrent is observed will correlate to the band gap energy for the material.
10 Therefore, the visible light activity can be confirmed by simply using a light source with
11 the desired emission spectrum to excite the electrode while monitoring the current as a
12 function of applied potential. For example, Hamilton *et al.*, [193] compared the spectral
13 IPCE response between TiO_2 and WO_3 for the photooxidation of water (Figure 10). WO_3
14 shows some activity in the visible with onset potential for anodic current positive relative
15 to that observed for TiO_2 .

16
17 In detailed work concerning the photoelectrochemical investigation of metal ion doped
18 TiO_2 , Hamilton *et al* found that in all cases doping resulted in a decrease of the
19 photocurrent response under solar simulated illumination [194]. However, a sub-band
20 gap response (visible light activity) was observed for some samples. The sub-band gap
21 photocurrent was potential dependent and could be correlated to oxygen vacancy states
22 below the conduction band. The primary band-gap photocurrent response was decreased
23 by the addition of metal ion dopants, which act as charge-carrier recombination centres,
24 and the sub-band gap photocurrent was only a very small fraction of the band-gap
25 photocurrent.

26
27 Nakamura *et al.*, used photoelectrochemical methods to investigate the mechanism of
28 visible light activity for N-doped TiO_2 powder prepared by both wet and dry methods
29 [195]. The powder was immobilised on FTO glass by spin coating of a colloidal
30 suspension (N-doped TiO_2 /water/acetylacetone/ HNO_3 /Triton-X 100) followed by
31 sintering at 400°C . Photocurrents for undoped and N-doped TiO_2 film electrodes were
32 measured as a function of wavelength, using a 350 W xenon lamp and a monochromator.
33 The N-doped TiO_2 films gave a measurable IPCE% beginning around 525 nm (increasing
34 with decreasing wavelength), whereas the undoped TiO_2 began to show a small IPCE%
35 around 425 nm. To probe the mechanism further, they measured the IPCE% in the
36 presence of different reductants (hole acceptors). Their basic theory was that those
37 species with an oxidation potential more negative than the N-2p level can be oxidised by
38 holes in this inter-band gap state (0.75 eV above the valence band) thus giving rise to an
39 increase in the measured IPCE%, while those species with an oxidation potential more
40 positive than the N-2p level cannot be oxidised by this state and therefore, no increase in
41 IPCE% will be observed. They found that all reductants used caused an increase in the
42 UV IPCE%, however, only I⁻ and hydroquinone gave an increase in the visible IPCE%
43 (Figure 11). Doping with N will give rise to a (occupied) mid-gap (N-2p) level slightly
44 above the top of the (O-2p) valence band and visible-light illumination will generate
45 holes in the mid-gap level, whereas UV illumination will generate holes in the (O-2p)

1 valence band. The differences in the IPCE enhancement between UV and visible
2 illumination can be attributed to differences in the reactivity of these holes (Figure 12).
3 The measurement of the photocurrent should distinguish the above two oxidation
4 processes because the photocurrent largely increases if a direct reaction with
5 photogenerated holes occurs, whereas it there should be no difference observed if an
6 indirect reaction via the intermediates of water photooxidation occurs. Nakamura *et al.*,
7 suggested that an increase in IPCE is not observed with the addition of SCN^- or Br^-
8 because large reorganisation energies are required for the electron transfer reactions.
9 Therefore, simply assuming the photocurrent (or reactivity) is only related to the redox
10 potential of the reductant (hole acceptor) is not adequate for explaining visible light
11 activity. Furthermore, photocurrent was observed under visible light irradiation for the
12 photo-oxidation of water (no hole acceptor present) and the redox potential for the
13 ($\cdot\text{OH}/\text{H}_2\text{O}$) is more positive than the mid-gap N-2p level. Nakamura *et al.* reported that
14 water photooxidation on n-TiO₂ (rutile) is not initiated by the oxidation of the surface OH
15 group (Ti-OHs) with photogenerated holes (h^+), but rather initiated by a nucleophilic
16 attack of an H₂O molecule (Lewis base) to a surface hole (Lewis acid), accompanied by
17 bond breaking.



19
20
21 The latter will not have any direct relation with the redox potential such as $E_{\text{eq}}(\cdot\text{OH}/\text{H}_2\text{O})$
22 but will have a strong relation with the basicity of H₂O or the energy of an intermediate
23 radical $[\text{Ti-O}\cdot\text{HO-Ti}]_s$ that is roughly giving the activation energy for the reaction. They
24 concluded that the observed photocurrent in the presence of reductants strongly depends
25 on the reaction mechanism of oxidation and more knowledge is needed concerning the
26 mechanism.

27
28 Beranek and Kisch reported the photoelectrochemical response of N-doped TiO₂
29 prepared by heating anodized titanium sheets and urea to 400°C [196]. The resulting
30 material consisted of a nitrogen-rich surface layer on the top of a nitrogen-poor core. The
31 TiO₂-N thin films exhibit photocurrents in the visible up to 700 nm due to the presence
32 of occupied nitrogen-centered surface states above the valence band edge (Figure 13).
33 The photocurrent transients significantly differed from those observed for undoped TiO₂
34 films and this could be explained by increased electron-hole recombination in TiO₂-N
35 through these surface states. The addition of iodide partially suppressed the
36 recombination due to hole scavenging. The flat band potential was determined by open
37 circuit photopotential measurements and was anodically shifted by +0.2 V to -0.35 V
38 (NHE) for TiO₂-N as compared to the undoped TiO₂.

39
40 Photoelectrochemical measurements can contribute significantly to the understanding of
41 the mechanisms involved in the visible light activity of doped TiO₂ and other
42 photocatalytic materials and can be combined with direct measuring the spectral
43 dependence of the quantum efficiency for different pollutants [197]. More research is
44 required to fully elucidate the mechanisms involved.

45 46 **4. Environmental Applications of VLA TiO₂**

4.1 Water treatment and air purification with VLA photocatalysis

Conventional TiO₂ has been extensively studied for water treatment and air purification and it is well known to be an effective system to treat several hazardous compounds in contaminated water and air. Some focus is given nowadays to VLA TiO₂-based photocatalysis and its application towards remediation of regulated and emerging contaminants of concern.

Senthilnatan and Philip reported the degradation of lindane, an organochlorine pesticide, under visible light with different TiO₂ photocatalyst [198]. N-doped TiO₂, synthesized with different nitrogen containing organic compounds in a modified sol-gel method, showed better photocatalytic activity compared to other metal ions-doped TiO₂ and Evonik P25-TiO₂. Several phenoxyacid herbicides (i.e., mecopop, clopyralid) were photocatalytically transformed employing Fe-, N-doped anatase and rutile TiO₂ as well as undoped anatase and rutile TiO₂ under visible light irradiation [199]. Degradation rates of all pesticides employed were higher with N-doped anatase TiO₂ and the difference in photoreactivity was directly related to the molecular structure of the herbicide and its interaction with the radical species produced. 2,4-dichlorophenoxyacetic acid (2,4-D) is a widely used herbicide and found in surface and ground water from agricultural runoffs. Ag/TiO₂ photocatalyst, hydrothermally synthesized with template-assisted methods, effectively degraded 2,4-D under visible light [200]. Increasing Ag content diminished the photoreactivity of TiO₂ under the conditions tested. Also, increase in Ag concentration also increase the amount of brookite phase formed, affecting this the photoresponse of Ag/TiO₂.

The diverse group of substances, which are commonly detected at low concentration in the aqueous media and often are difficult to quantitatively remove from the water by conventional water treatment processes, can produce important damages in human health and in the aquatic environment, even at low concentrations. Some of these contaminants can have endocrine disruption effects in humans and aquatic organisms and the consequences of their exposure to organisms can go from developmental problems to reproduction disorders. Wang and Lim developed several nitrogen and carbon doped TiO₂ via solvothermal method for the degradation of bisphenol-A under visible light-emitting diodes. The use of alternative visible light, such as light-emitting diodes, LEDs, provides several advantages, including energy efficiency, flexibility and extended lifetime [201]. All the synthesized CN-TiO₂ photocatalysts exhibited higher removal efficiencies for bisphenol-A than reference materials. In all cases, the highest extend of removal and mineralization was with emitting white light followed by blue, green and yellow light, in agreement with the adsorption edge of the doped TiO₂ materials. Neutral pH seems to be favorable for the degradation of this EDC in water. The presence of inorganic ions in the water matrix had different effects towards the degradation of bisphenol-A. Chloride, nitrate and sulfate ions partially inhibited the photocatalytic process while silica and bicarbonate scavenged to a greater extend the degradation of bisphenol-A under the conditions tested. In a related study, nitrogen-doped TiO₂ hollow spheres (NHS), prepared through ammonia treatment of monodispersed polystyrene

1 spheres in a titania sol followed by heat treatment, were evaluated for the photocatalytic
2 degradation of bisphenol-A under different light emitting LEDs [202]. NHS exhibited
3 higher performance towards the degradation of bisphenol-A compared to undoped TiO₂
4 hollow spheres and TiO₂ powder. Nevertheless, the degree of degradation of bisphenol-A
5 decreased from blue LED ($\lambda=465$ nm) to yellow LED ($\lambda=589$ nm) light, which is in
6 agreement with Wang and Ling. Several intermediates detected were found to be reported
7 previously with UV-irradiated TiO₂, thus following similar degradation pathways.
8 Composite materials, such as nitrogen-doped TiO₂ supported on activated carbon (N-
9 TiO₂/AC), have also been tested and proven to have a dual effect on the adsorption and
10 photocatalytic degradation of bisphenol-A under solar light [203]. Even though the
11 maximum adsorption capacity for bisphenol-A was reduced for N-TiO₂/AC compared to
12 virgin AC at pH 3.0, higher photodegradation efficiencies were found for N-TiO₂/AC
13 than with N-TiO₂ and undoped TiO₂ only at different excitation wavelengths.

14
15 Visible light active TiO₂ photocatalysts have also been employed for the photocatalytic
16 degradation of cyanotoxins, in particular, the hepatotoxin microcystin-LR (MC-LR). MC-
17 LR is a contaminant of emerging concern, highly toxic and frequently found cyanotoxin
18 in surface waters. N-TiO₂ photocatalyst, described in section 2.1 as a one step process
19 synthesis with DDAC as pore template and nitrogen dopant, efficiently degraded MC-LR
20 under visible light. N-TiO₂ calcined at 350°C showed the highest MC-LR degradation
21 efficiency and an increase in calcination temperature resulted in a decrease of the
22 photocatalytic activity of N-TiO₂ towards the removal of MC-LR. N-F co-doped TiO₂
23 nanoparticles synthesized from a modified sol-gel method were also applied for the
24 degradation of MC-LR. Synergistic effects were observed with co-doped material,
25 specifically in the photocatalytic improvement of MC-LR degradation at wavelengths >
26 420 nm, compared to nitrogen and fluorine only doped TiO₂ and undoped TiO₂. A pH
27 dependence was observed in the initial degradation rates of MC-LR where acidic
28 conditions (pH 3.0) were favorable compare to higher pH values [116]. When
29 immobilizing NF-TiO₂ on glass substrate, different fluorosurfactant molar ratios in the sol
30 were tested and the efficiency of the synthesized photocatalytic films was evaluated for
31 MC-LR removal. When increasing the fluorosurfactant ratio, higher MC-LR degradation
32 rates were observed at pH 3.0 [117]. This is due to the effective doping of nitrogen and
33 fluorine and the physicochemical improvements obtained with different surfactants
34 loadings in the sol. Rhodium doped TiO₂, at high photocatalyst concentration, was shown
35 to completely remove MC-LR under visible light conditions [204]. Much less active
36 visible light photocatalyst for MC-LR degradation were TiO₂-Pt(IV) and carbon doped
37 TiO₂ [204].

38
39 Volatile organic compounds (VOCs) are hazardous air pollutants that can be emitted into
40 the atmosphere by a wide variety of industrial processes and cause adverse effects on the
41 human nervous system, via breathing. A bifunctional photocatalyst, obtained from
42 nitrogen-doped and platinum-modified TiO₂ (Pt/TiO_{2-x}N_x), was proven effective for the
43 decomposition of benzene and other persistent VOCs under visible light irradiation in a
44 H₂-O₂ atmosphere [205]. The doping of nitrogen and the incorporation of platinum
45 played an important role in the enhancement of the visible light photocatalytic activity,
46 mainly on the interfacial electron transfer at the surface of the photocatalyst. Ethyl

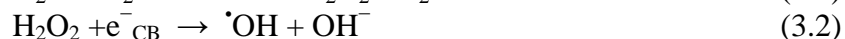
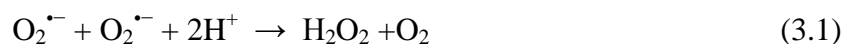
1 benzene and *o,m,p*-xylenes were removed by employing N-TiO₂ at indoor air levels in an
2 annular reactor even under typical humidified environments found indoor. Both low
3 stream flow rates and low hydraulic diameter in the reactor are beneficial for higher
4 degradation efficiencies. Composite N-TiO₂/zeolite was investigated for the removal of
5 toluene from waste gas. High porosity and effective visible light activation of the
6 composite material gave a synergistic effect on the photocatalytic degradation of toluene
7 compared to bare TiO₂/zeolite [206]. This process was coupled to a biological treatment
8 for further mineralization of toluene.

11 4.2 Water disinfection with VLA photocatalysis

13 Over the past ten years solar activated photocatalytic disinfection of water has received
14 significant attention with research focus moving from laboratory studies to pilot
15 experimentation [207]. Visible light-active (VLA) doped TiO₂ has also been investigated
16 for a range of disinfection applications, including water purification. Twenty years after
17 Matsunaga *et al.*, published the first paper detailing with photocatalytic disinfection using
18 a range of organisms and TiO₂/Pt particles [208], Yu *et al.*, described disinfection of the
19 Gram positive bacterium *Micrococcus lylae* using sulfur-doped titanium dioxide exposed
20 to 100 W tungsten halogen lamp fitted with a glass filter to remove wavelengths less than
21 420 nm [209]. They reported 96.7% reduction in viable organisms following 1 hour
22 treatment in a slurry reactor containing 0.2 mg/mL S-doped-TiO₂ (1.96 At %), prepared
23 via a copolymer sol-gel method. ESR measurements, using DMPO, confirmed the
24 formation of hydroxyl radicals which were described as the reactive oxygen species
25 responsible for the observed disinfection. Early work with N-doped TiO₂, using
26 *Escherichia coli* (*E. coli*) as the target organism, reported superior photocatalytic activity
27 in comparison to Evonik P25 under solar light exposure [210]. Li *et al.*, reported
28 enhanced disinfection of *E. coli* when VLA TiON was co-doped with carbon [211]. They
29 attributed the additional biocidal effect to increased visible light absorption.

31 Mitoraj *et al.*, describe VLA photocatalytic inactivation of a range of organisms,
32 including Gram negative and Gram positive bacteria (*E. coli*, *Staphylococcus aureus* and
33 *Enterococcus faecalis*) and fungi (*Candida albicans*, *Aspergillus niger*), using carbon-
34 doped TiO₂ and TiO₂ modified with platinum(IV) chloride complexes in both suspension
35 and immobilized reactor configurations [212]. The order of disinfection followed that
36 commonly observed, whereby organisms with more significant cell wall structures
37 proved more resistant to the biocidal species produced by photocatalysis: *E. coli* > *S.*
38 *aureus* = *E. faecalis*. *C. albicans* and *A. niger* were much more resistant than the bacterial
39 organisms examined. *E. coli* inactivation has also been reported using S-doped TiO₂
40 films, produced via atmospheric pressure chemical vapor deposition, upon excitation with
41 fluorescent light sources commonly found in indoor healthcare environments [213]. A
42 palladium-modified nitrogen-doped titanium oxide (TiON/PdO) photocatalytic fiber was
43 used for the disinfection of MS2 phage by Li *et al.* [214]. Under dark conditions,
44 significant virus adsorption was measured (95.4–96.7%) and upon subsequent
45 illumination of the samples with visible light (> 400 nm) for 1 hour additional virus
46 removal of 94.5–98.2% was achieved (the overall virus removal was 3.5-log from an

1 initial concentration of $\sim 1 \times 10^8$ plaque forming units). EPR measurements were used to
 2 confirm the presence of $\cdot\text{OH}$ radicals. It was suggested that $\cdot\text{OH}$ radicals were formed via
 3 a reduction mechanism involving dissolved oxygen (Eq. 3.1 and 3.2).



6
 7
 8 Wu *et al.*, produced titanium dioxide nanoparticles co-doped with N and Ag and
 9 investigated the efficiency of photocatalytic inactivation of *E. coli* under visible light
 10 irradiation ($\lambda > 400$ nm) [215]. A 5-log inactivation was observed after ca. 30 min
 11 irradiation, although disinfection was observed in the dark controls due to the biocidal
 12 properties of Ag ions. ESR studies demonstrated a significant increase in $\cdot\text{OH}$ production
 13 on the Ag, N-doped TiO_2 . Interactions between the ROS and *E. coli* resulted in physical
 14 damage to the outer membrane of the bacterial cell, structural changes within the plasma
 15 membrane were also observed. Similar structural and internal damage was suggested to
 16 be responsible for the inactivation in *Pseudomonas aeruginosa* when exposed to sunlight
 17 in the presence of Zr doped TiO_2 [216].

18
 19 Some of the most comprehensive studies on VLA TiO_2 disinfection have been
 20 undertaken by the Pulgarin group at EPFL, Switzerland. Commercial titania powders
 21 (Tayca TKP101, TKP102 and Evonik P25) were mechanically mixed with thiourea and
 22 urea to produce S-doped, N-doped and S, N co-doped VLA TiO_2 powders [217-220].
 23 Various thermal treatments produced both interstitial and substitutional N-doping and
 24 cationic and anionic S-doped Tayca powders; thiourea treated P25 exhibited low level
 25 interstitial N-doping and anionic S-doping. Suspension reactor studies using *E. coli*
 26 showed that the doped Tayca materials were slightly less active than the non-doped
 27 powders during UV excitation, however, under visible light excitation (400-500 nm) the
 28 N, S co-doped powders outperformed the undoped powders, with those annealed at
 29 400°C resulting in 4-log *E. coli* inactivation following 75 min treatment [216]. The
 30 authors concluded that the nature of the doping (substitutional or interstitial N-doping and
 31 cationic or anionic S doping), surface hydroxylation and the particle size play important
 32 roles in the generation of biocidal ROS. In experiments with N, S co-doped Evonik P25,
 33 a 4-log *E. coli* inactivation was observed following 90 min exposure to visible light ($\lambda =$
 34 $400\text{-}500$ nm) [217]. The authors proposed that upon UVA excitation the $\cdot\text{OH}$ radical is
 35 the most potent ROS, however; under visible excitation a range of ROS could be
 36 produced through reduction of molecular oxygen by conduction band electrons
 37 (superoxide radical anion, hydrogen peroxide and hydroxyl radicals), with singlet oxygen
 38 likely to be produced by the reaction of superoxide radical anion with localised N and S
 39 mid band-gap states [217]. Further mechanistic studies using N, S co-doped Tayca titania
 40 with phenol and dichloroacetate (DCA) as model probes, demonstrated complete *E. coli*
 41 disinfection but only partial phenol oxidation and no degradation of DCA under visible
 42 excitation [218]. Subsequent ESR experiments confirmed the production of both singlet
 43 oxygen and superoxide radical anion.

44
 45 More recently, Rengifo-Herrera and Pulgarin investigated the use of N, S co-doped
 46 titania for disinfection under solar simulated exposure [221]. Using the photocatalyst in

1 suspension, *E. coli* inactivation was observed with all doped and un-doped materials,
 2 however, the most efficient catalyst was undoped Evonik P25. Although the production
 3 of singlet oxygen and superoxide radical anion may contribute to the biocidal activity
 4 observed in N, S co-doped P25, under solar excitation the main species responsible for *E.*
 5 *coli* inactivation was the hydroxyl radical produced by the UV excitation of the parent
 6 material (Figure 14). This finding clearly demonstrates that production of VLA
 7 photocatalytic materials for disinfection applications requires careful consideration of the
 8 ROS being generated and detailed experiments to show potential efficacy of new VLA
 9 materials.

10 11 **5. Assessment of VLA photocatalyst materials**

12 13 *5.1 Standardization of test methods*

14 Many researchers working in the field of photocatalysis are frustrated by the difficulty
 15 posed when attempting to compare results published by different laboratories. Long ago
 16 it was proposed that the extent of the difference in the photocatalytic experimental
 17 systems used could be identified if each group reported the initial rate of a standard test
 18 pollutant [222-225]. In the establishment of a standard test system, one of the most
 19 important factors is the determination of quantum yield or quantum efficiency. The
 20 overall quantum yield for a photoreaction (Φ_{overall}) is defined as follows [23],
 21

$$22 \quad \Phi_{\text{overall}} = \text{rate of reaction} / \text{rate of absorption of radiation} \quad (5.1)$$

23 In heterogeneous semiconductor photocatalysis, the Φ_{overall} is very difficult to measure
 24 due to the problems distinguishing between absorption, scattering and transmission of
 25 photons. A more practical term, the photonic efficiency (ξ), sometimes referred to as
 26 Φ_{apparent} , has been suggested:
 27

$$28 \quad \xi = \text{rate of reaction} / \text{incident monochromatic light intensity} \quad (5.2)$$

29 where the rate of absorption of radiation is simply replaced by the light intensity incident
 30 upon the reactor (or just inside the front window of the photoreactor). It is much simpler
 31 to determine the photonic efficiency than the true quantum yield. In addition the photonic
 32 efficiency is also a more practical quantity in terms of the process efficiency as the
 33 fraction of light scattered or reflected by semiconductor dispersion (or immobilized film)
 34 may be 13%-76% of the incident light intensity. Thus the difference between Φ_{overall} and
 35 ξ may be significant. In research and practical applications, polychromatic light sources
 36 will be employed, and therefore one must replace ξ with the Formal Quantum Efficiency
 37 (FQE);
 38

$$39 \quad \text{FQE} = \text{rate of reaction} / \text{incident light intensity} \quad (5.3)$$

40 For multi-electron photocatalytic degradation processes, the FQE will be much less than
 41 unity; unless a chain reaction is in operation. Therefore, it is most important that
 42 researchers specifically report their methods of quantum efficiency determination.
 43
 44
 45
 46

1
2 The solar spectrum contains only a small fraction of UV (4-5%) and this somewhat limits
3 the application of wide band (UV absorbing) semiconductors, e.g. TiO₂, for solar energy
4 driven water treatment. Even with good solar irradiance, the maximum solar efficiency
5 achievable can only be 5%. The apparent quantum efficiency for the degradation of
6 organic compounds in water is usually reported to be around 1 % with UV irradiation,
7 under optimum experimental conditions. Therefore, one can only reasonably expect an
8 overall solar efficiency of around 0.05% for photocatalytic water treatment employing a
9 UV band gap semiconductor.

10
11 A number of test systems have been proposed to assess the relative photocatalytic
12 efficiency for the degradation of organic pollutants in water. For example, Mills *et al.*
13 [225], suggested phenol / Evonik P25 / O₂ or 4-chlorophenol / Evonik P25 / O₂. In such a
14 standard system, the experimental parameters would be defined, e.g. [4-chlorophenol] =
15 10⁻³ mol dm⁻³, [TiO₂] = 500 mg dm⁻³, [O₂] = 1.3 x 10⁻³ mol dm⁻³ (P_{O₂} = 1 atm), pH 2, T =
16 30°C. A comparison of the rate of the photocatalytic reaction under test with that
17 obtained for the standard test system would provide some idea of the efficiency of the
18 former process and allow some degree of comparison of results between groups. Other
19 researchers [222-226] have suggested the use of relative photonic efficiencies (ξ_r), where
20 both (initial) destruction rates of the tested pollutant and phenol as a model one with
21 common molecular structure are obtained under exactly the same conditions.

$$\xi_r = \text{rate of disappearance of substrate} / \text{rate of disappearance of phenol} \quad (5.4)$$

22
23
24
25 However, Ryu and Choi reported that the photocatalytic activities can be represented in
26 many different ways, and even the relative activity order among the tested photocatalysts
27 depends on what substrate is used [227]. They tested eight samples of TiO₂ (suspension
28 reactor) and each showed the best activity for at least one test-substrate. This highly
29 substrate-specific activity of TiO₂ photocatalysts hinders the relative comparison of
30 different catalyst materials. They proposed that a multi-activity assessment should be
31 used for comparison of photocatalytic activity, i.e. four substrates should be examined:
32 phenol, dichloroacetic acid (DCA), tetramethyl ammonium (TMA), and trichloroethylene
33 (TCE) to take the substrate-specificity into account. They represent the aromatic, anionic,
34 cationic, and chlorohydrocarbon compounds, respectively, which are distinctly different
35 in their molecular properties and structure.

36
37 The problems relating to the measurement of photocatalytic efficiency is further
38 complicated when researchers attempt to compare the activities of 'visible light active'
39 materials. Although visible light activity is in itself of fundamental interest, the test
40 regime should consider the proposed application of the material. For example, if the
41 application is purely a visible light driven process e.g. self-cleaning surfaces for indoor
42 applications, then a visible light source should be utilized for the test protocol. However,
43 if the application is towards a solar driven process then simulated solar light or ideally
44 real sun should be utilized for the test protocol. Many researchers investigate visible light
45 activity by using a polychromatic source, e.g. xenon, and cutting out the UV component
46 with a filter. That is important when determining the visible only activity; however, it is

1 important the experiments are also conducted with light which corresponds to the solar
2 spectrum, including ca. 5% UVA. When the UV activity of the material is good, this may
3 outweigh any contribution from a relatively small visible light activity, hence the
4 importance of photonic efficiency or FQE.

5
6 Doping of TiO₂ may give rise to a color change in the material as a result of the
7 absorption of visible light however; an increase in visible absorption, in principle, does
8 not guarantee visible light induced activity. Photocatalytic reactions proceed through
9 redox reactions by photogenerated positive holes and photoexcited electrons. No activity
10 may be observed if, for example, all of these species recombined. Various photocatalytic
11 test systems with different model pollutants/substrates have been reported. Dyes are
12 commonly used as model pollutants, partly because their concentration can be easily
13 monitored using visible spectrophotometry; however, because the dyes also absorb light
14 in the visible range, the influence of this photo-absorption by dyes should be excluded for
15 evaluation of the real photocatalytic activity of materials. According to Herrmann [228],
16 a real photocatalytic activity test can be erroneously claimed if a non-catalytic side-
17 reaction or an artefact occurs. Dye decolorization tests can represent the most “subtle
18 pseudo-photocatalytic” systems, hiding the actual non-catalytic nature of the reaction
19 involved. An example of this dye sensitised phenomenon was reported with the apparent
20 photocatalytic “disappearance” of indigo carmine dye [229]. The indigo carmine was
21 totally destroyed by UV-irradiated titania; however, its colour also disappeared when
22 using visible light but the corresponding total organic carbon (TOC) remained intact.
23 The loss of colour actually corresponded to a limited transfer of electrons from the photo-
24 excited indigo (absorbing in the visible) to the TiO₂ conduction band. This ‘dye
25 sensitization’ phenomenon is well known and exploited in the ‘Gratzel’ dye sensitized
26 photovoltaic cell [22]. A dye which has been used widely as a test substrate for
27 photocatalytic activity is methylene blue. Indeed the degradation of methylene blue is a
28 recommended test for photocatalytic activity in the ISO/CD10678 [230]. Yan *et al.*,
29 reported on the use of methylene blue as a test substrate to evaluate the VLA for S-TiO₂
30 [231]. Two model photocatalysts were used, i.e. homemade S-TiO₂ and a commercial
31 sample (Nippon Aerosil P-25) as a reference. Their results showed that a photo-induced
32 reaction by methylene blue photo-absorption may produce results that could be mistaken
33 to be evidence of visible-light photocatalytic activity. They suggested that dyes other than
34 methylene blue should also be examined for their suitability as a probe molecule. Yan *et al.*,
35 used monochromatic light to determine the action spectrum enabling them to
36 discriminate the origin of photoresponse by checking the wavelength dependence.
37 However, most researchers simply use optical cut-off filters that transmit light above a
38 certain wavelength. Yan *et al.*, recommend the use of model organic substrates which do
39 not absorb in the spectral region being used for excitation.

40
41 To complicate matters further, the photoreactor to be used in test reaction must be
42 appropriate. It is good practice to compare any novel material with a relatively well
43 established photocatalyst material, e.g. Evonik P25 [232]. The test system should utilize
44 the catalyst in the same form - suspension or immobilized. Where suspension systems are
45 employed, the catalyst must be well dispersed and an analysis of the particle size
46 distribution should be undertaken. The optimum loading for each catalyst should also be

1 determined. Where an immobilized catalyst system is employed, one must ensure that the
2 reaction is not mass transfer limited otherwise the rate of degradation will simply be
3 reflecting the mass transfer characteristics of the reactor. A high flow or a stirred tank
4 system may be employed in an attempt to determine the intrinsic kinetics of the
5 photocatalytic system [233].

6
7 Analysis of the literature concerning the development of visible light active
8 photocatalytic materials for the destruction of organic pollutants in water shows that,
9 while there has been enormous effort towards synthesis and characterisation of VLA
10 materials, more attention has been paid to the photocatalysis test protocols. In the
11 absence of a widely accepted standard test protocol, researchers should ensure the
12 following, where possible: 1) the light source is appropriate with respect to the
13 application and the emission spectrum is quantitatively determined, 2) more than one test
14 substrate is used e.g. multi-activity assessment proposed by Ryu and Choi [227], and
15 substrates absorbing light within the emission spectrum of the light source are avoided
16 [230], 3) the reactor is well characterized i.e. for suspension systems the particle size
17 distribution is determined, 4) the photoreactor is appropriate and well characterized in
18 terms of mass transfer; and 5) the photonic efficiencies or FQEs are reported along with
19 the emission spectrum of the illumination source. Research and development for solar
20 driven water treatment should utilize experiments under simulated or real solar
21 irradiation, not just visible light sources.

22 23 *5.2 Challenges in commercializing VLA photocatalysts*

24
25 Some VLA TiO₂ photocatalytic products, like Kronos® VLP products, have already
26 appeared in the market. Apart from the need for improvement on the photocatalytic
27 efficiency, deactivation of TiO₂ photocatalysts over time has proven to be an inherent
28 obstacle of the material that needs to be considered when commercializing VLA
29 photocatalysts., in general [234]. Deactivation occurs when partially oxidized
30 intermediates block the active catalytic sites on the photocatalyst [235]. Gas phase
31 deactivation is more predominant than the aqueous phase, because in the aqueous phase,
32 water assists in the removal of reaction intermediates from the photocatalyst surface
33 [236]. The photocatalytic degradation of many organic compounds also generates
34 unwanted by-products, which may be harmful to human health [23]. Certain elements and
35 functional groups contained in organic molecules have been found to strongly hinder the
36 photocatalytic ability of TiO₂ through deactivation. Peral and Ollis found that N or Si
37 containing molecules may cause irreversible deactivation through the deposition of
38 species that inhibit photoactive sites on the catalyst surface [237]. Carboxylic acids
39 formed from alcohol degradation are also believed to strongly be adsorbed to the active
40 sites of a catalyst and cause deactivation [23]. Strongly adsorbed intermediate species
41 appear to commonly cause deactivation of a photocatalyst and it is certainly an area
42 where further improvement is essential before TiO₂ can be considered a viable option for
43 continuous photocatalytic applications.

44
45 Several researchers have been studying regeneration methods for the TiO₂ photocatalyst.
46 Potential regeneration methods investigated include; thermal treatment (< 400 °C) in air

1 [238], sonication with water and methanol [239], irradiating the catalyst under UV light
2 while passing humid air over the surface [240] and exposing the catalyst to air rich with
3 H₂O₂, both with and without UV light [236].
4

5 **Conclusions**

6

7 In this review, titanium dioxide is introduced as a promising semiconductor photocatalyst
8 due to its physical, structural and optical properties under UV light. In order to be photo-
9 excited under visible light and aim at solar-driven TiO₂ photocatalysis, several synthesis
10 methods have been successfully applied to achieve VLA TiO₂ photocatalysts. Non metal
11 doping, in particular nitrogen doping, can be incorporated as substitutional or interstitial
12 state in the TiO₂ lattice. Other non metals including carbon, fluorine and sulphur for
13 doping and co-doping with nitrogen have been also investigated and shown visible light
14 photo-induced activity. A variety of synthesis methods for noble metal and transition
15 metal deposition, dye sensitization and coupling semiconductors have also extended the
16 optical response of TiO₂ into the visible region. The reactive oxygen species generated
17 with VLA TiO₂ under visible light indicate a different mechanism of photoactivation
18 compared to UV light. The photocatalytic inactivation of a range of microorganisms has
19 been explored using VLA TiO₂. High log reductions were observed for common
20 microorganisms, like *E.coli*, with metal and non-metal doped TiO₂ under visible and
21 solar light. Moreover, the application of VLA TiO₂ for the removal of persistent and
22 contaminants of emerging concern in water treatment and air purification has been
23 effective compared to conventional TiO₂ under visible light. Therefore, these results are
24 promising for further development of sustainable environmental remediation
25 technologies, based on photocatalytic advanced oxidation processes driven by solar light
26 as a renewable source of energy. Nevertheless, an effective assessment of VLA
27 nanomaterials is needed to address several issues regarding test protocols, ensure true
28 photocatalytic activity, and explore future commercialization of the material.
29

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31

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1 **Figure Captions**

2
3 **Figure 1.** Crystalline structures of titanium dioxide (a) rutile, (b) anatase, (c) brookite
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5 <http://staff.aist.go.jp/nomura-k/english/itsecgallary-e.htm>) Copyright (2002)).
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7 **Figure 2.** Schematic of TiO₂ photocatalytic mechanism.
8

9 **Figure 3.** Templating sol-gel method utilizing nitrogen containing surfactants as both
10 nitrogen source and pore template material. (Reprinted with permission from H. Choi, M.
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14 **Figure 4.** Electron transfer mechanism in N-doped anatase rutile heterojunction.
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18 **Figure 5.** Mechanism of band gap narrowing by oxygen excess. Number 2 and 16 in
19 H₂O₂-TiO₂ was used to identified two different modified titania samples. (Reprinted with
20 permission from V. Etacheri, M. K. Seery, S. J. Hinder, S. C. Pillai, *Adv. Funct. Mater.*
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23 **Figure 6.** Mechanism for light absorption of silver supported in TiO₂. (Adapted with
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27 **Figure 7.** TEM and mechanistic image of the interface between CdS nanowires and TiO₂
28 nanoparticles. TiO₂ provide sites for collecting the photoelectrons generated from CdS
29 nanowires, enabling thereby an efficient electron-hole separation. (Reprinted with
30 permission from S.J. Jum, G.K. Hyun, A.J. Upendra, W.J. Ji, S.L. Jae, *Int. J. Hydrogen*
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33 **Figure 8.** The UV-vis absorbance spectra of pure and composite semiconductors.
34 (Reprinted with permission from N. Ghows, M.H. Entezari, *Ultrason. Sonochem.*, 18
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37 **Figure 9.** Proposed mechanism that shows the interaction of one species from the core
38 with one species from the shell for the removal of RB5 by nanocomposite CdS/TiO₂.
39 (Reprinted with permission from N. Ghows, M.H. Entezari, *Journal of Hazardous*
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42 **Figure 10.** %IPCE as a function of wavelength for the photooxidation of water on TiO₂
43 (red) and WO₃ (blue) (Adapted with permission from J.W. J. Hamilton, J. A. Byrne, P. S.
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45 185479. Copyright (2008) Hindawi Publishing Corporation).
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1 **Figure 11.** Effect of the addition of 0.5 mM I⁻, H₂Q, SCN⁻, and Br⁻ on IPCE vs λ in the
2 (a) UV- and (b) visible-light regions for N-doped TiO₂. The supporting electrolyte was
3 0.1 M HClO₄ and the electrode potential was 0.5 V vs Ag/AgCl (Reprinted with
4 permission from R. Nakamura, T. Tanaka, Y. Nakato, *J. Phys. Chem. B* 108 (2004)
5 10617-10620. Copyright (2004) American Chemical Society).

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7 **Figure 12.** Energy levels for N-doped TiO₂ (anatase) relative to reported equilibrium
8 redox potentials for one-electron-transfer redox couples (Reprinted with permission from
9 R. Nakamura, T. Tanaka, Y. Nakato, *J. Phys. Chem. B* 108 (2004) 10617-10620.
10 Copyright (2004) American Chemical Society).

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12 **Figure 13.** IPCE spectra (a) and (IPCE $h\nu$)^{1/2} vs $h\nu$ plots (b) for TiO₂ and TiO₂-N
13 recorded in LiClO₄ (0.1 M) + KI (0.1 M) (Reprinted with permission from R. Beranek
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17 **Figure 14.** Proposed bacterial disinfection mechanism during solar excitation of N, S co-
18 doped TiO₂. (Adapted with permission from J. A. Rengifo-Herrera, C. Pulgarin, *Sol.*
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22 **Table Captions**

23
24 **Table 1.** Physical and structural properties of anatase and rutile TiO₂.

25
26 **Table 2.** Oxidation potentials of various oxidants relative to NHE.

27

Table 1.

Property	Anatase	Rutile
Molecular Weight (g/mol)	79.88	79.88
Melting point (°C)	1825	1825
Boiling Point (°C)	2500 ~ 3000	2500 ~ 3000
Light absorption (nm)	< 390	< 415
Mohr's Hardness	5.5	6.5 – 7.0
Refractive index	2.55	2.75
Dielectric constant	31	114
Crystal structure	Tetragonal	Tetragonal
Lattice constants (Å)	a = 3.78 c = 9.52	a = 4.59 c = 2.96
Density (g/cm ³)	3.79	4.13
Ti–O bond length (Å)	1.94 (4) 1.97 (2)	1.95 (4) 1.98 (2)

Table 2.

Oxidant	Oxidation Potential (V)
•OH (hydroxyl radical)	2.80
O ₃ (Ozone)	2.07
H ₂ O ₂ (hydrogen peroxide)	1.77
HClO (hypochlorous acid)	1.49
Cl ⁻ (chlorine)	1.36

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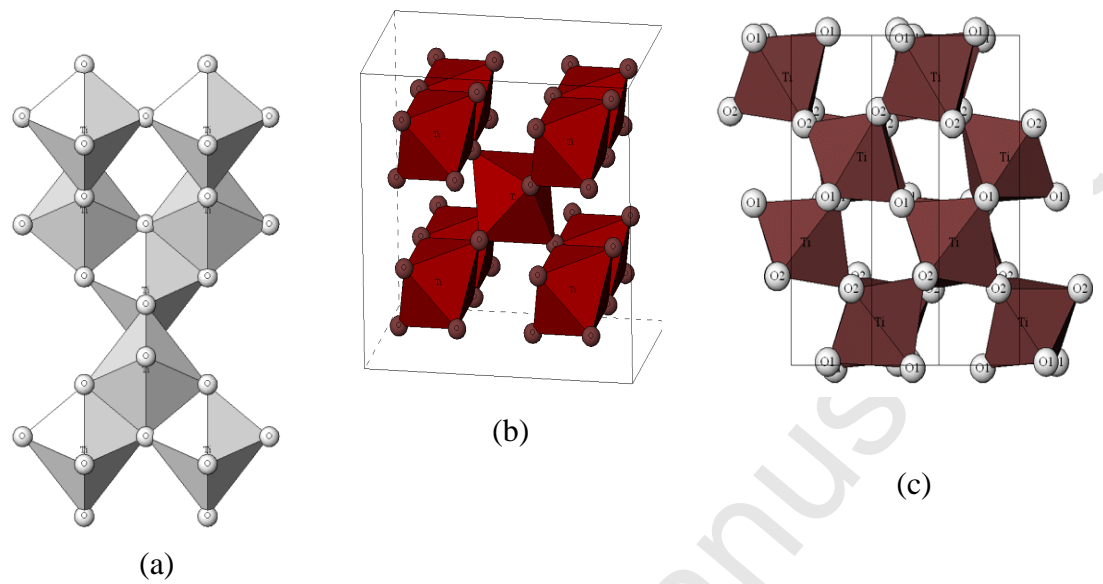


Figure 1.

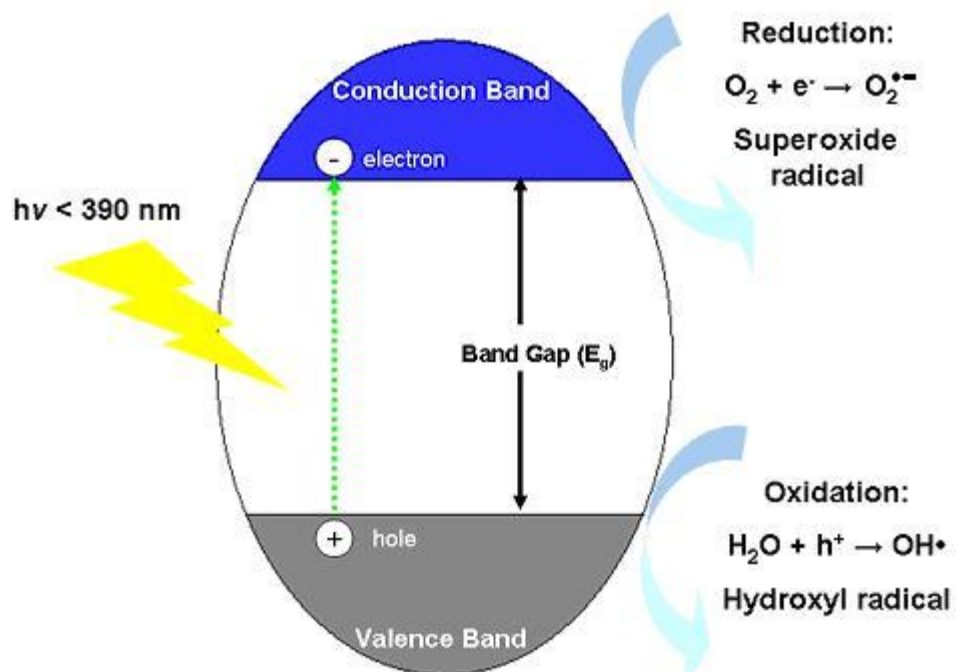


Figure 2.

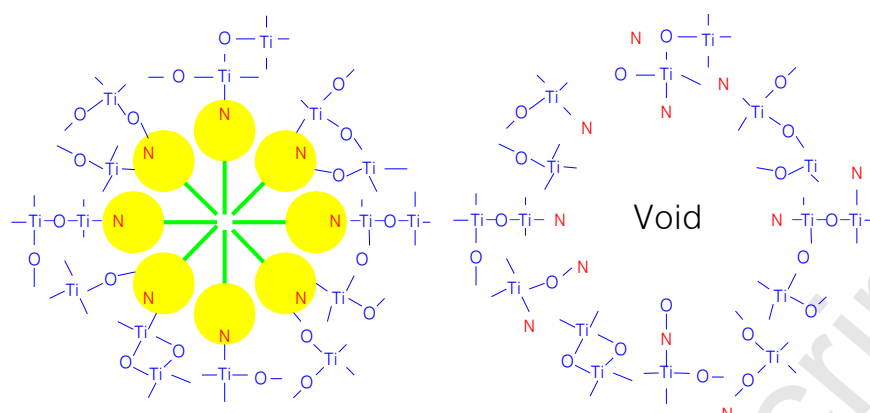


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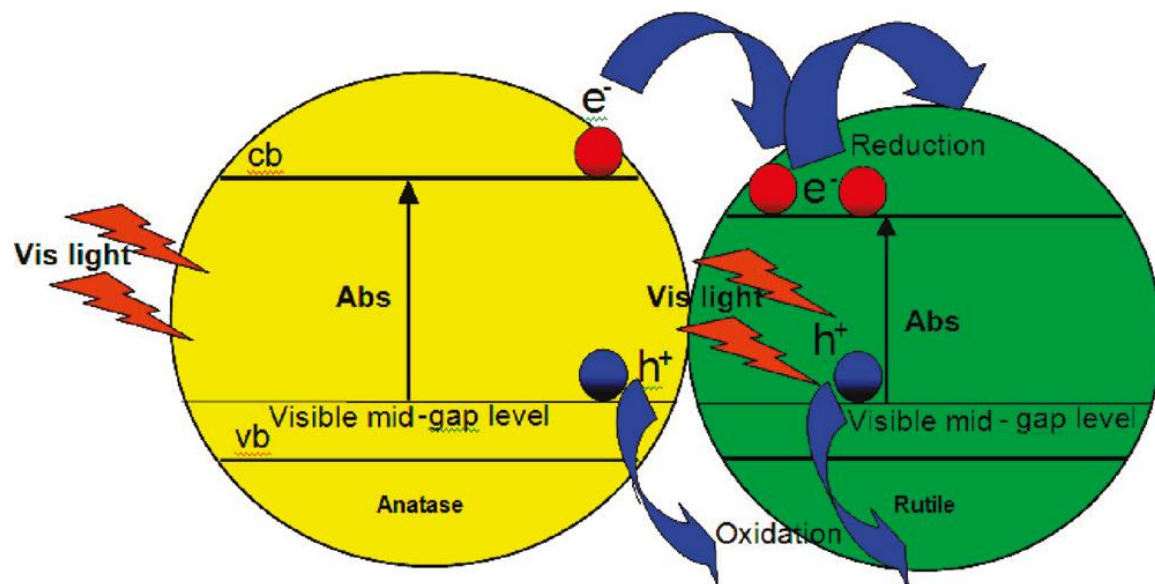


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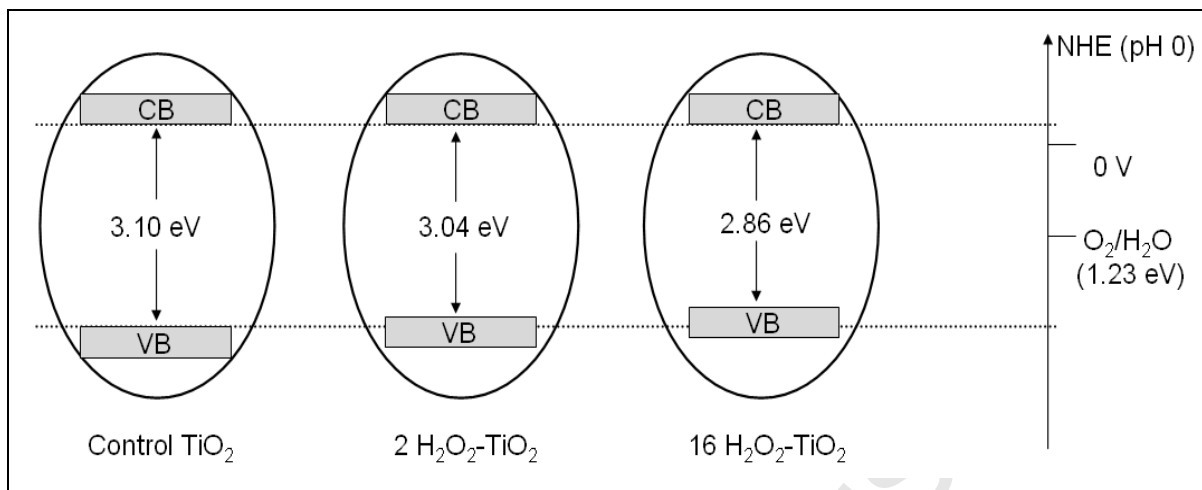


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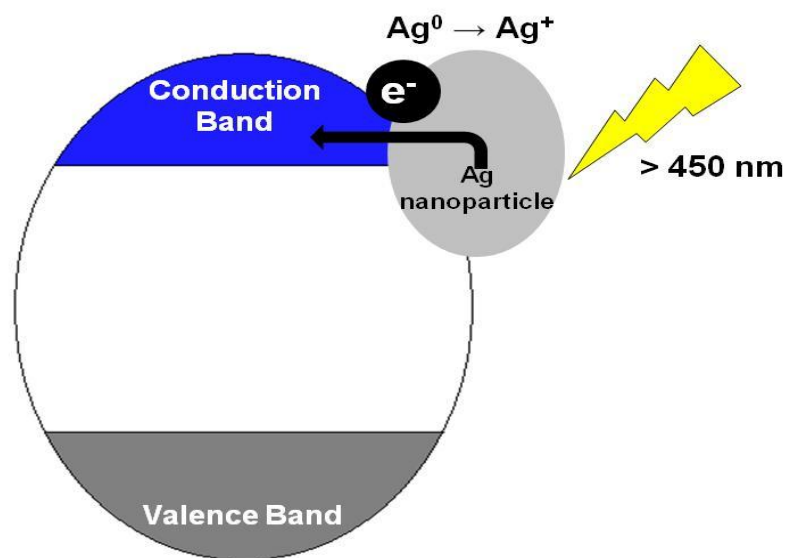


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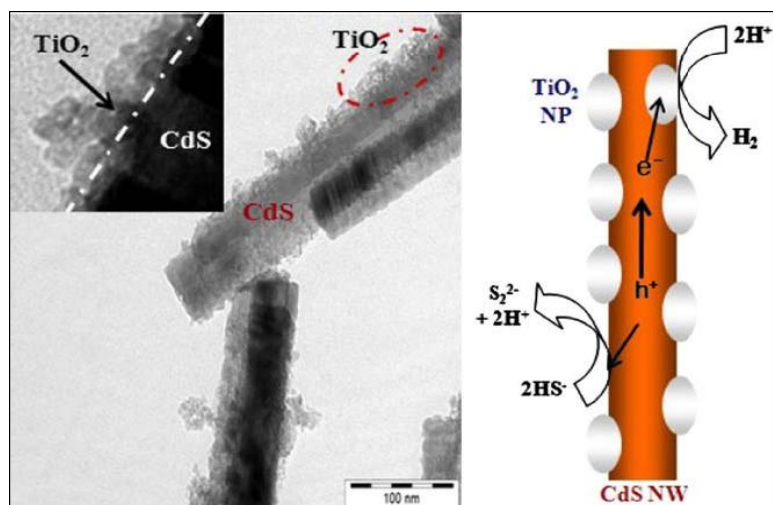


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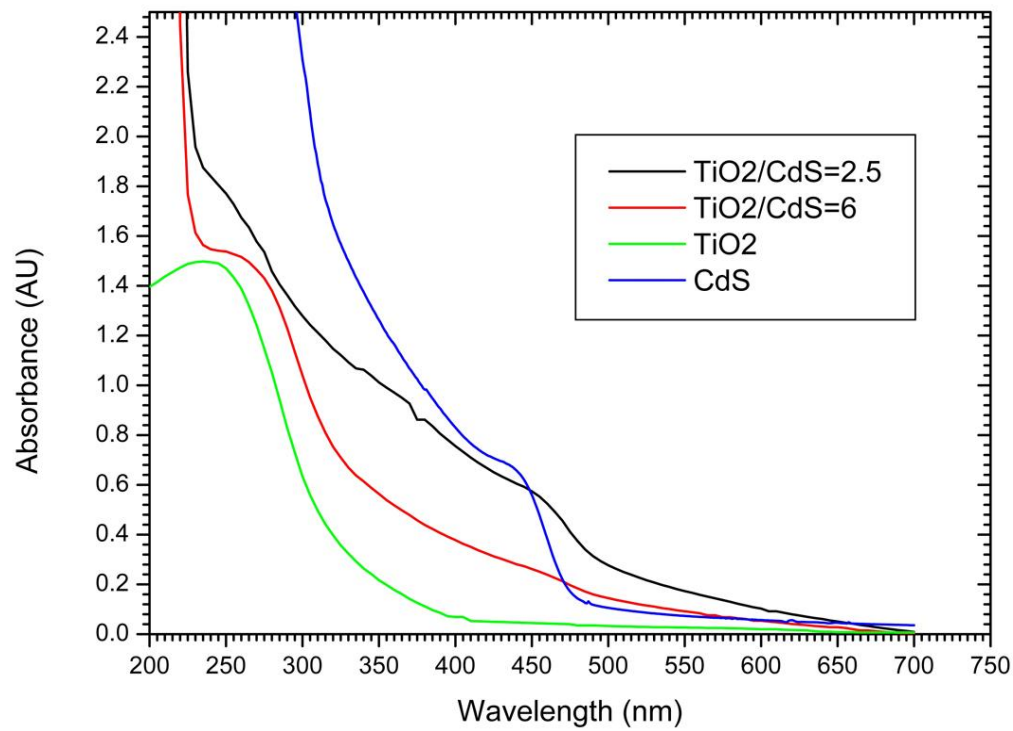


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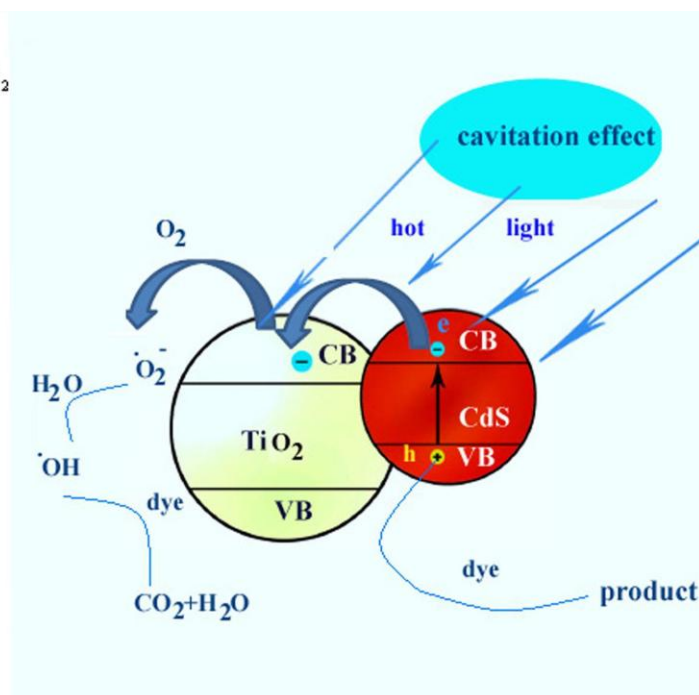
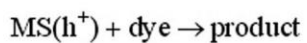
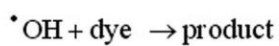
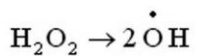
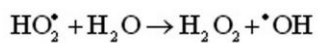
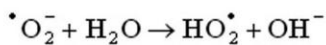
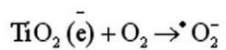
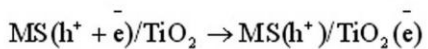
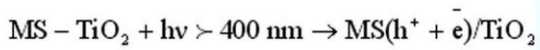


Figure 9.

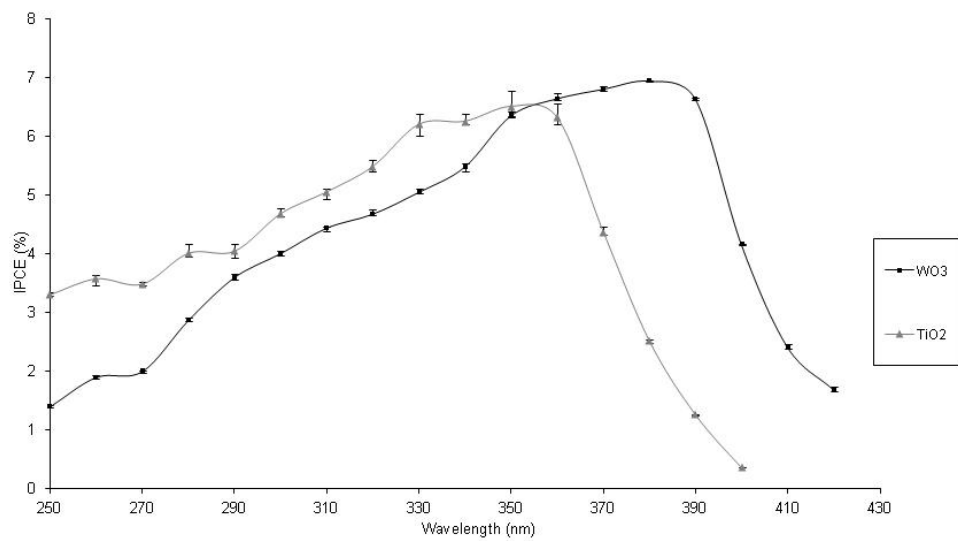


Figure 10.

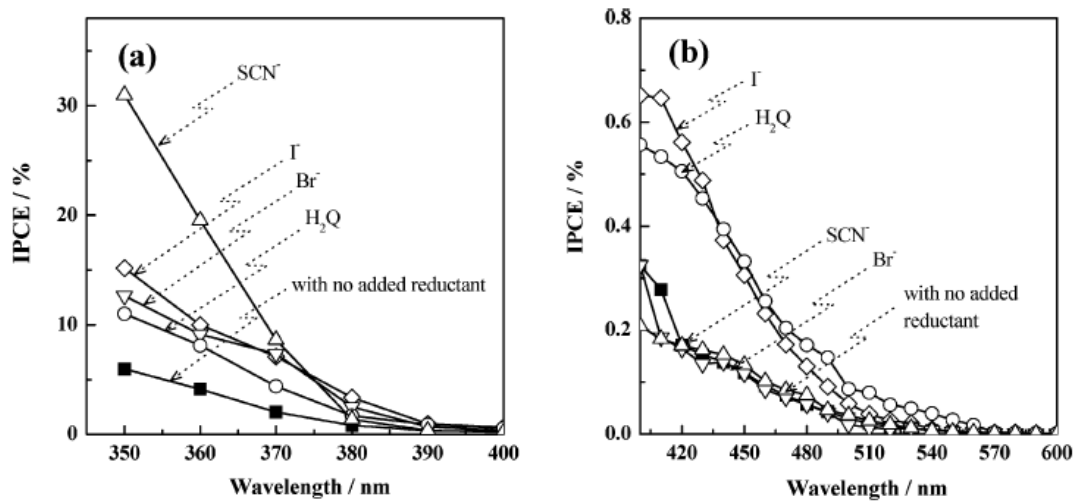


Figure 11.

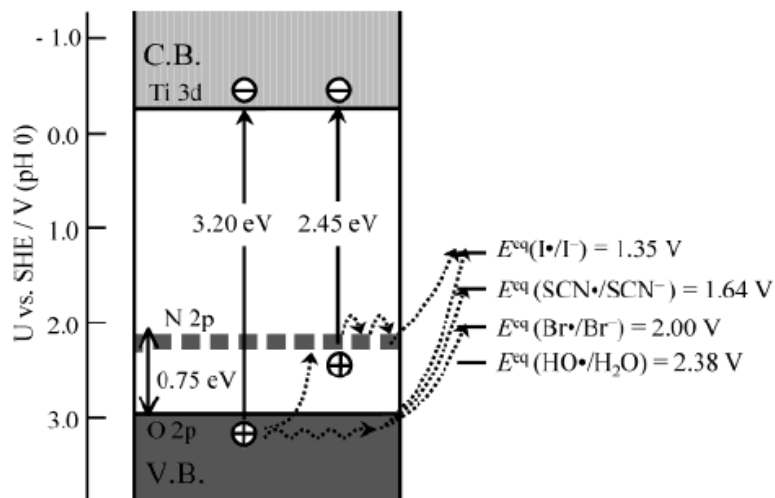


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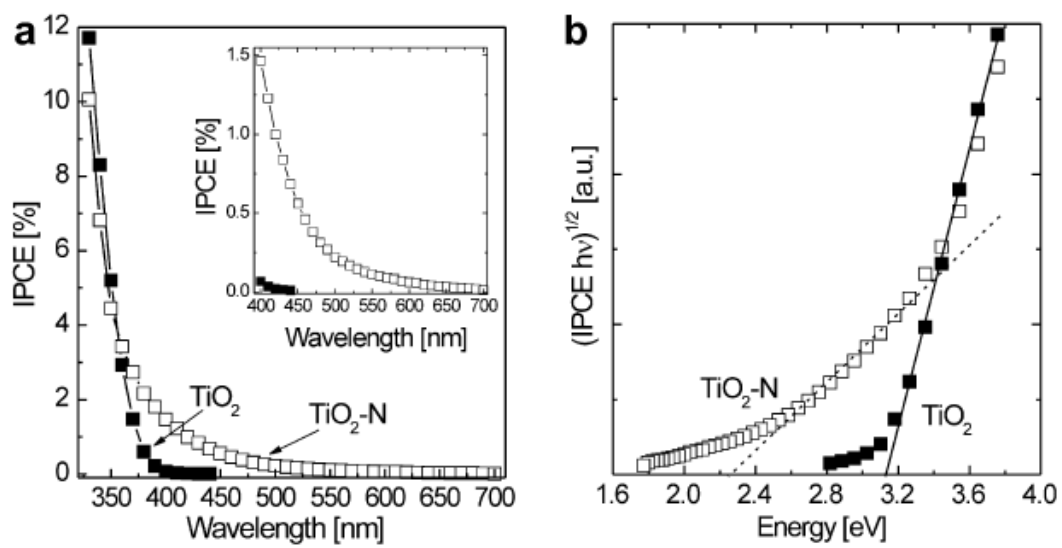


Figure 13.

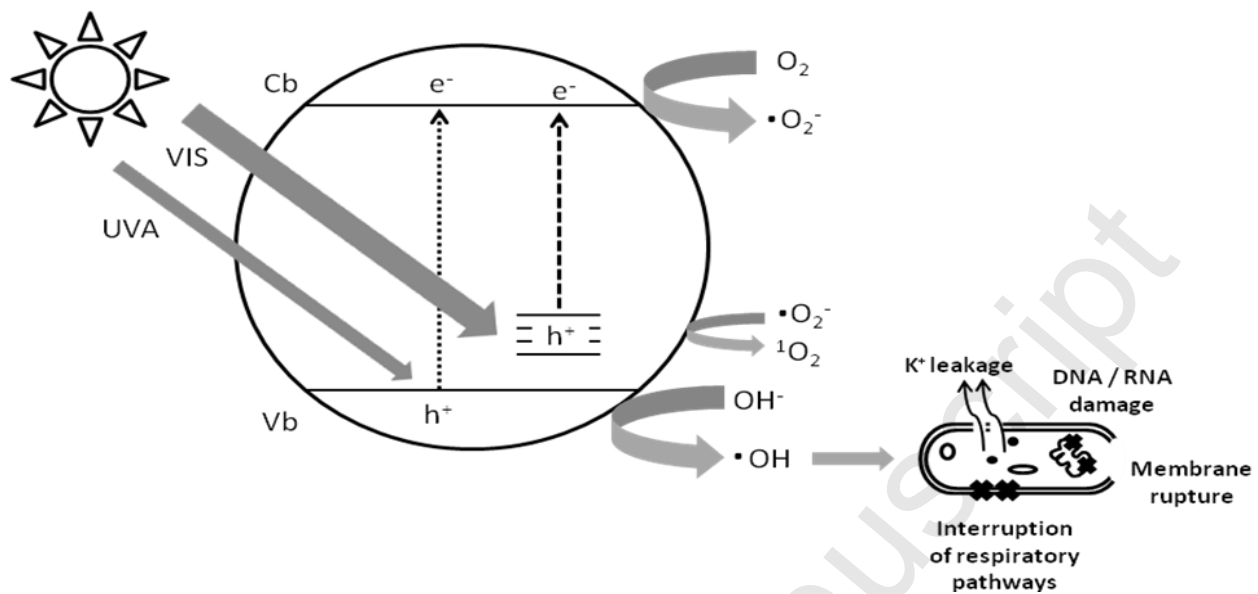
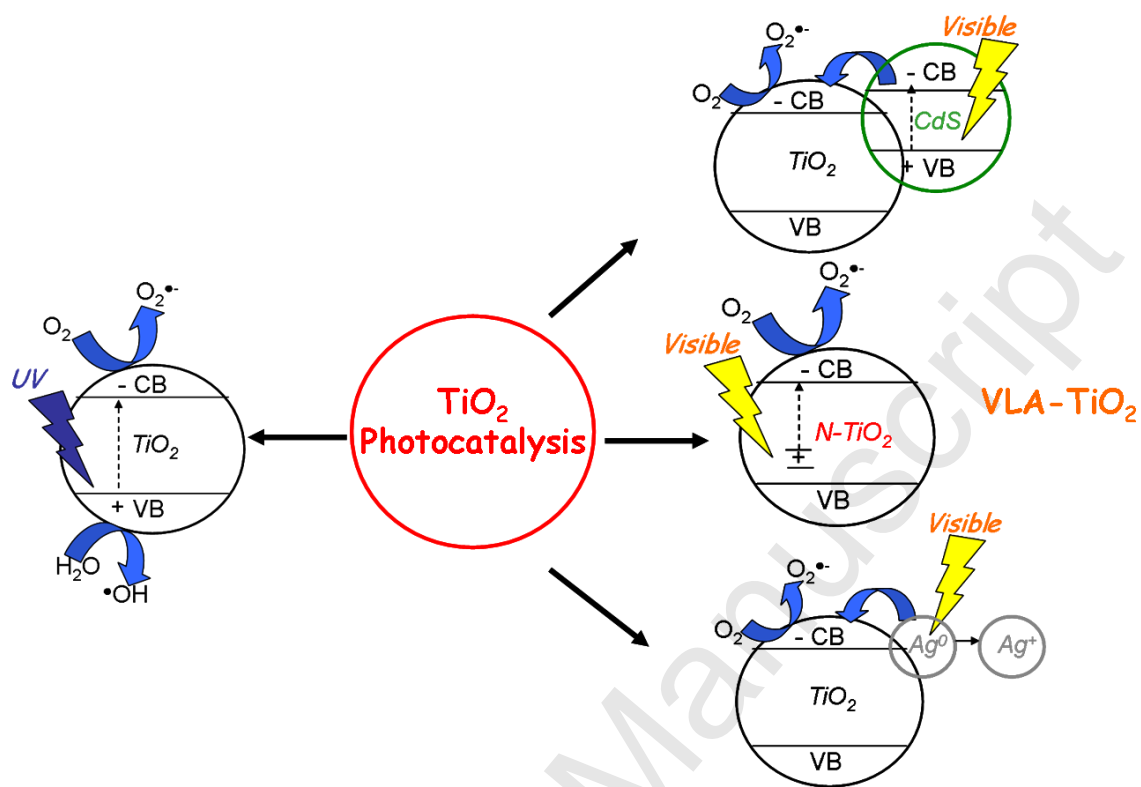


Figure 14.



Research Highlights

>VLA-TiO₂ include non metal, metal doping, dye sensitized and coupling semiconductors>Physicochemical/photoelectrochemical methods to deduce VLA-TiO₂ reaction mechanisms>Examination of VLA-TiO₂ for water treatment, disinfection and air purification.

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