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Rapid Microwave Synthesis of Mesoporous TiO₂ for Electrochromic Displays

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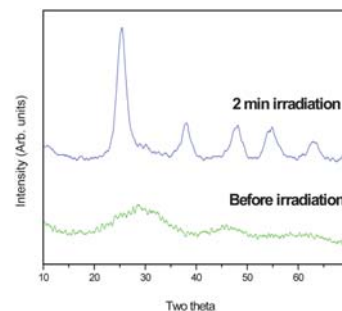
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Rapid microwave synthesis of mesoporous TiO₂ for electrochromic displays

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A straightforward and industrially viable synthesis for mesoporous nanocrystalline titania in electrochromic displays has been achieved using titanium butoxide, deionised water and butanol at a low microwave power intensity (300 W, 2 min) irradiation.



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Rapid microwave synthesis of mesoporous TiO₂ for electrochromic displays†

Pradeepan Periyat,^{ab} Nigel Leyland,^c Declan E. McCormack,^{*b} John Colreavy,^a David Corr^c and Suresh C. Pillai^{*a}

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The fabrication of paper quality electrochromic displays based on the viologen modified TiO₂ electrodes (Vi²⁺/TiO₂) requires a cost-effective, energy efficient and rapid synthesis of mesoporous TiO₂ with high yield in short reaction time. A straightforward and industrially viable process for the preparation of mesoporous nanocrystalline titania (meso-nc-TiO₂) for NanoChromics™ display device applications by the use of microwave synthesis is presented here. Spherical aggregates of meso-nc-TiO₂ were rapidly achieved using titanium butoxide, deionised water and common alcohols (isopropanol, ethanol and butanol) at comparatively low microwave power intensity (300 W) for 2 min irradiation. The material has been characterised by a range of different techniques such as XRD, Raman spectroscopy, SEM and BET surface area analysis. These materials possess surface areas up to 240 m² g⁻¹, which is significantly higher than similar traditional sol-gel or commercial samples. This meso-nc-TiO₂ prepared was used as the working electrode for an electrochromic display device with Sb doped SnO₂ as the counter electrode material on an ITO coated conducting glass. A working prototype of a NanoChromics™ display was successfully fabricated using this approach.

1 Introduction

Nanocrystalline titania has found various applications in diverse fields such as photocatalysis, photovoltaics and gas sensors.^{1–4} A recent utilisation of nanocrystalline anatase titania is in electrochromic display devices, which exhibit a reversible colour change upon reduction or oxidation of a redox chromophore by the application of an electrical potential.^{5–7} Previous fabrication of such electrochromic systems was achieved by incorporating the chromophore in a polymeric film deposited on a transparent conducting oxide.⁸ However this film had a tendency to peel from the transparent conducting oxide and the redox chromophores are not in direct contact with the conducting substrate.^{8,9} Hence the rates of colouration and de-colouration (bleaching) are limited by the extent of diffusion charges to and from the chromophore into the conducting substrate.^{8,9} As a result, devices based on this method suffer from very long switching times (of the order of several seconds), even for small area devices. The current processing technology developed by NTERA for fabrication of nanomaterial based display devices involves the preparation of mesoporous TiO₂ by screen printing a solvent based paste of commercial titania precursors and then baking at a higher temperature (500 °C) to induce crystallisation in titania and to burn off the organic components. In addition to this,

organic pore-formers were added before the calcination step to induce mesoporosity. This method negatively impacts on several aspects of the production process through increased production cost, loss of substrate electrical function, decreased optical quality, and glass warping due to softening. Hence there is a strong requirement to develop a cost effective and eco-friendly method to synthesise mesoporous TiO₂, to develop formulations with enhanced reliability and reduced production costs in display device manufacture.

Microwave irradiation is becoming an increasingly popular method to synthesise biological, organic, inorganic, and polymer nanostructured materials, in particular in the synthesis of nanoparticles.^{10–12} In this work, microwave technology was adopted for the low temperature preparation of mesoporous titania. The advantage of this technique is that it is very rapid and no further heat treatment is required for sample production. Moreover it leads to enhanced structural and morphological properties for the nanomaterials.¹¹ Unlike the conventional annealing process, the microwave technique offers a clean, cost-effective, energy efficient, eco-friendly, rapid and convenient method of heating, which results in higher yields in shorter reaction times.^{10–12} In this paper the development of a simple, rapid and industrially viable low temperature synthesis method for mesoporous titania using microwave technology is presented. The major objective of this research was to develop novel material formulations and process methods using a microwave assisted technology to enhance reliability and to reduce production costs of NTERA's current processing technology through refining NTERA's existing processing formulation. Such materials are processable at a lower temperature using microwave energy. The innovative aspects of this project were the formulation of materials with novel processes and the use of advanced printing processes such that high temperatures can be avoided to produce mesoporosity and the production costs

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† Electronic supplementary information (ESI) available: Fig. S1: TEM pictures of microwave TiO₂ synthesised using butanol at 300 W for 5 min. See DOI: 10.1039/b924341k

1 significantly reduced. Hence the overall technology using
a solvent based paste of commercial titania and then baking at
higher temperatures (500 °C) to induce crystallisation and meso-
porosity in titania can be replaced by using the as-synthesized
5 microwave TiO₂. In addition to this, the surface area of the
current commercial material before calcination was 50 m² g⁻¹ but
the newly developed microwave mesoporous materials possessed
a surface area up to 240 m² g⁻¹. Spherical aggregates of these
mesoporous nanocrystalline titania powder were synthesised at
10 a comparatively low microwave power intensity (300 W) for
2 min irradiation and its screen printing onto a indium tin oxide
(ITO) conducting glass substrate resulted in an electrode that was
incorporated into a prototype of an electrochromic display
device.

2 Experimental

2.1 TiO₂ sample preparation

15 The reagents used in this study were titanium butoxide (Aldrich,
97%) and various alcohols namely isopropanol, ethanol and
butanol. In a typical experiment a 0.4 M titanium butoxide
(27.2 g) solution was prepared in 200 mL butanol. The above
solution was stirred for 10 min and 57.6 mL deionised water
20 (8 molar times) was slowly added in small quantities to allow
hydrolysis. Stirring was continued for a further 30 min. The
white precipitate obtained was subjected to microwave irradiation
power of 300 and 600 W in a Teflon[®] bomb for different time
intervals using a C-MARS microwave with an adjustable power
25 minimum of 300 W and a maximum of 1200 W. The pressure was
released after five minutes of cooling and these samples were used
for further analysis. The XRD patterns were obtained with
a Siemens D 500 X-ray diffractometer in the range, 2θ = 10–70°
using Cu-Kα radiation. The crystal size of the samples was
30 calculated by using the Scherrer equation below.¹³

$$\phi = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

35 Where, φ = crystallite size, λ = X-ray wavelength, θ = Bragg
angle, β = full width at half maximum.

40 Raman spectra measurements were taken using an S. A. (Jobin
Yvon) Labram 1B instrument. A helium–neon laser (514 nm)
was used as the laser source. BET (Brunauer, Emmett and Teller)
surface area measurements and pore size analysis were carried
out for nitrogen adsorption using a Quantachrome Nova 4200
45 surface area analyser. The measurements were performed at
liquid nitrogen temperature after degassing the powder samples
for 2 h at 200 °C. Scanning electron micrographs were obtained
using a Hitachi S-4300 microscope with an accelerating voltage
of 5 kV.

2.2 Electrochromic device fabrication

50 The microwave synthesized titania was used to fabricate
a nanochromic display device. The ink was formulated using
microwave treated titania, terpineol and a cellulose binder. The
average solid loading was 32 wt%. The films were white, with
a smooth marbled appearance having an average film thickness
55 of 6.3 μm and they showed good resistance to damage or
delamination when immersed in a dye. Films were screen-printed

1 onto ITO-coated glass, sintered at 500 °C and dyed in a solution
of phosphonic acid-modified viologen dye. After dyeing, the
electrodes were assembled into display units, with a counter
electrode comprising porous antimony-doped tin oxide over-
coated with a porous white reflector containing a proprietary
5 lithium salt solution electrolyte according to NTERA's standard
practice.

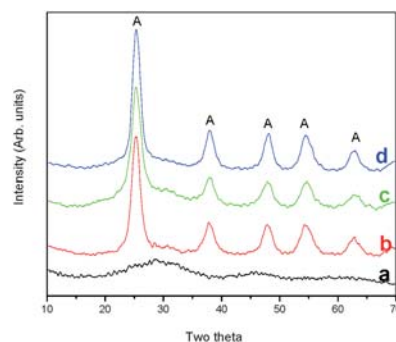
3 Results and discussion

3.1 X-Ray diffraction (XRD)

10 Fig. 1 shows XRD spectra of titania synthesised using the
microwave method. Before microwave irradiation, the sample
exhibited completely amorphous characteristics (Fig. 1a). After
5 min irradiation at 300 W, the crystalline titania was obtained
(Fig. 1b). These results were repeatable for all solvents indicating
15 that crystalline anatase titania can be prepared by using various
alcohols at a comparatively low microwave power (300 W)
within 5 min reaction time. Table 1 shows the crystallite size of
as-synthesised titanium dioxide calculated using the Scherrer
equation.¹³ The crystallite sizes calculated are in the nanometre
20 range and a small increase in size was observed when the
microwave power was increased for all solvents. Further crystalline
anatase titania formation was controlled with respect to
time by using butanol as a model solvent for 300 W power
irradiation (Fig. 2). For this purpose the prepared samples were
25 treated at a microwave power of 300 W for different time
intervals. Lower time periods (less than two minutes) showed
only amorphous or semicrystalline titania, however as time
progressed the crystallinity improved and crystalline titanium
dioxide was obtained after 2 min irradiation.

3.2 Raman studies

35 The Raman spectra of the microwave treated samples are shown
in Fig. 3. The four peaks shown by each sample are due to the
anatase phase. The anatase peaks were identified at values of 144,
395, 514 and 639 cm⁻¹.¹⁴ These results also show that after
microwave treatment the amorphous material transformed fully
40 into crystalline anatase titania and confirmed the XRD results
presented in the previous section.



55 Fig. 1 XRD pattern of the titania samples (a) before irradiation, and
titania synthesised using (b) isopropanol (c) butanol (d) ethanol at 300 W
for 5 min irradiation (A = anatase).

Table 1 Crystallite size of titania synthesised using different microwave power and solvent. All samples were irradiated for 5 min

Solvent	Crystallite size/nm	
	300 W	600 W
Butanol	4.1	6.0
Isopropanol	5.4	6.9
Ethanol	5.7	6.9

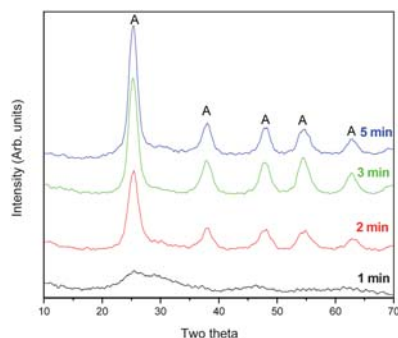


Fig. 2 XRD study of anatase formation with respect to time using butanol solvent at 300 W power (A = anatase).

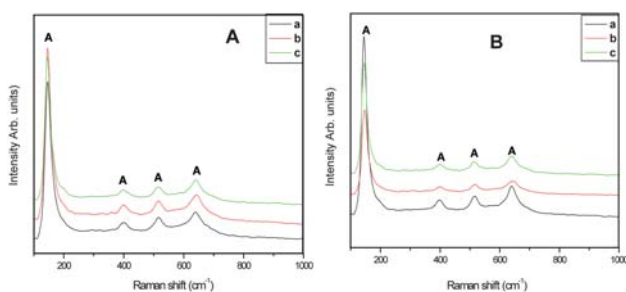


Fig. 3 Raman spectra of titania synthesised using microwave power (A) 300 W for 5 min (B) 600 W for 5 min using solvent (a) isopropanol (b) butanol (c) ethanol.

3.3 Scanning electron microscopy (SEM)

Scanning electron micrographs of the titania sample prepared using the microwave method are shown in Fig. 4. The microwave irradiation method generated spherical aggregates of titania, however the particle size of the aggregate varies with solvent. The TiO₂ preparation using butanol led to aggregates having uniform

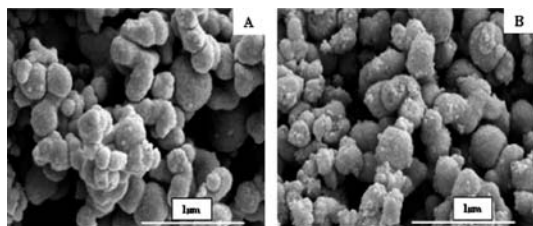


Fig. 4 SEM images of titania synthesised (A) 300 W for 5 min (B) 600 W for 5 min using butanol.

distribution when it is subjected to a microwave power of 300 W for 5 min (Fig. 4A). When the microwave power was increased to 600 W (Fig. 4B) for the same solvent, the size of the spherical aggregates is more or less similar. It is believed that the spherical morphology of the titania obtained here will assist the adsorption of a large number of viologen molecules on the TiO₂ surface. This should positively contribute towards the improvement in the quality of electrochromic device fabrication. TEM analysis has also been carried out to investigate the texture and morphology of the powders. However the powders were aggregated to a great extent after the microwave treatment (ESI†).

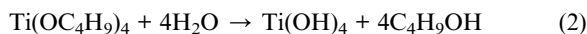
3.4 BET surface area analysis

The surface area, pore volume and pore size of all microwave synthesised samples using solvents isopropanol, butanol and ethanol were measured using a BET surface area analyzer. It can be seen from Table 2 that the microwave synthesized titania samples show very high surface area. The N₂ adsorption and desorption isotherm were shown in Fig. 5. The adsorption and desorption isotherms of all samples show type IV behaviour with the typical hysteresis loop. This hysteresis is characteristic of mesoporous materials.¹⁵ The mesoporous nature of the samples is also evident from the adsorption and desorption pore size measurement using the BJH method (Table 2). It has been observed that there is no significant difference in the surface area values when the power is increased to 600 W.

3.5 Microwave synthesis of TiO₂

The reactivity of titanium metal alkoxide precursor is very high compared to other metal alkoxides, such as silicon alkoxide because of the variable oxidation capability of the transition metal.^{16,17} The presence of vacant *d*-orbitals in a transition metal enables it to increase its co-ordination number and in the case of titanium metal ion precursor, it can increase the co-ordination number from 4 to 6.¹⁸ The titanium butoxide reacts with water, undergoes hydrolysis and condensation reaction to form amorphous TiO₂ particles, which can be represented in eqn (2) (hydrolysis) and eqn (3) (condensation).

Hydrolysis:



Condensation:



During this precipitation reaction (which leads to the formation of crystalline titanium dioxide after microwave treatment) primary particles nucleate initially from the solution and these primary particles aggregate to form secondary particles. The secondary agglomerates formed in this study results in spherical aggregates of nano sized crystalline titania. The size and morphology of TiO₂ has great importance and significance in developing a high surface area electrode to adsorb large quantities of electrochromic viologen molecules.⁷ The SEM images (Fig. 4) clearly show that the butanol led to spherical shaped particles. The particle growth after the nucleation of primary particles can be affected by the solvents used during the

Table 2 BET Surface area and pore size measurements. All samples were irradiated for 5 min (error $\pm 5\%$)

Solvent	Power/W	BET surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	BJH desorption pore size/nm
Isopropanol	300	239	0.258	2.0
	600	194	0.295	2.3
Butanol	300	242	0.359	2.3
	600	230	0.443	2.8
Ethanol	300	212	0.263	2.0
	600	206	0.266	2.3

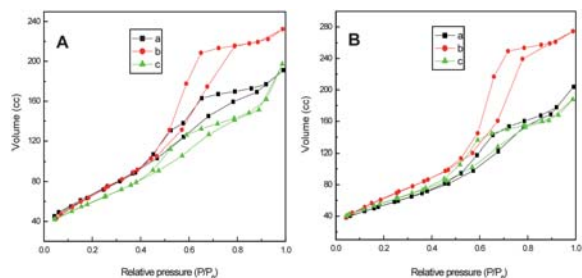
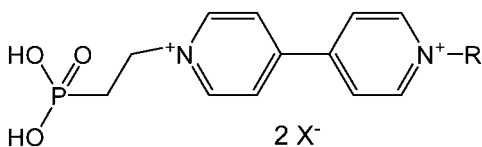


Fig. 5 Type IV isotherm of the titania synthesised using microwave power (A) 300 W for 5 min (B) 600 W for 5 min using solvents (a) isopropanol (b) butanol (c) ethanol.

microwave treatment possibly due to their difference in dielectric constants.^{12,19} The dielectric constant of butanol, isopropanol and ethanol are 17.8, 18.3 and 24.3 respectively.²⁰ These solvents interact strongly with microwave power and form the spherical aggregates of crystalline mesoporous nanotitania at comparatively low microwave power, 300 W for 5 min irradiation. More studies are underway on the detailed investigation into the mechanism and kinetics of the formation of these spherical particles using low microwave power in short reaction time and the role of the solvent in maintaining the spherical shape of the particles.

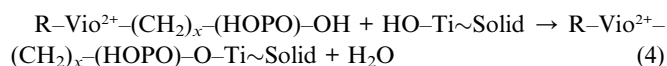
3.6 Interaction of electrochromic viologen dye with a TiO₂ electrode

The electrochromic species used in this work was the viologen (Vio²⁺) having a structure shown below.



It can undergo one-electron reduction into the strongly coloured Vio^{•+} radical ion. Further reduction produces a pale yellow neutral species Vio⁰.⁷ Viologens are known to be unstable in basic conditions, both in aqueous^{21,22} and organic²³ environments. It is therefore important that the titanium dioxide synthesis should take place in an acidic/neutral environment or at a surface that can be easily neutralized/acidified afterwards. The microwave synthesis route using the alcohol solvents discussed here yielded a weakly acidic product. Thus it provides a benign environment for the adsorbed viologen as described below. Control of the bonding behaviour between the titanium dioxide

surface and the viologen molecule strongly influences both the efficiency of electron transfer between the dye and oxide substrate and the durability of the device. Phosphonic acids have been established as being among the best anchoring groups for dye molecules to metal oxides.²⁴ A particular advantage of the phosphonic acid moiety as a ligand is the stability of the titania to phosphonic acid bond over a wide range of electronic potentials. This leads to very stable bonding in electronic devices utilizing dye-sensitized TiO₂ films, including electrochromic displays⁵ and dye-sensitized solar cells.²⁵ The -OH group present in the microwave synthesised TiO₂ forms an 'ester-like P-O-Ti bond' by the reaction with phosphonic acid group as shown in eqn (4) below.^{7,26}



This mesoporous TiO₂ electrode was incorporated into a test display device as indicated in Fig. 6. The viologen modified with TiO₂ shows colour upon application of an electrical potential. The application of the electric potential causes the accumulation of electrons in the conduction band of TiO₂ semiconductor electrode ejected from the valence band. Subsequently electrons transfer from the conduction band to adsorbed viologen causing its reduction which alters the colour. The display units were evaluated by cyclic voltammetry, in which the antimony-doped tin oxide layer was used as a combined reference and counter electrode. Cyclic voltammetry confirmed the reversibility of the display device switching behaviour (Fig. 7). Three potential sweeps of 0 V to 650 mV at a scan rate of 10 mV s⁻¹ were performed and the third sweep was presented in Fig. 7. The oxidative and reductive waves have almost equal area, within the

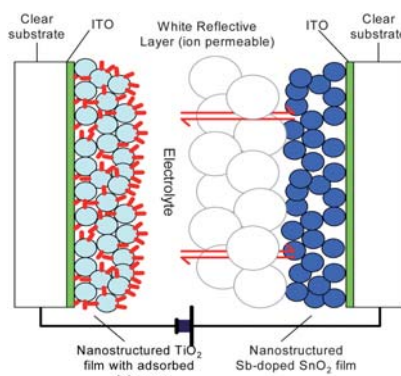


Fig. 6 Diagrammatic representation⁷ of device cross-section of the NanoChromics™ display constructed at NTERA.

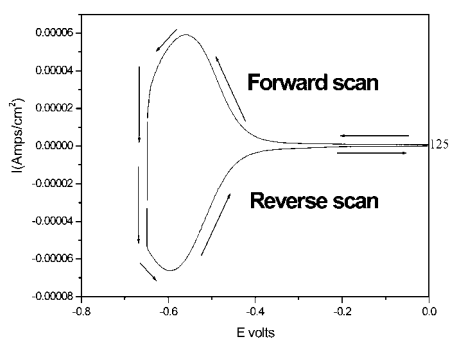


Fig. 7 Cyclic voltammograms of the film prepared by using microwave synthesised titanium dioxide.

resolution of the instrument, showing full reversibility of charge transfer. The specific charge on the pixels of each display fabricated using the microwave titania when coloured at 650 mV was 1.01 mC cm^{-2} . Displays were also evaluated using a suite of optical characterisation measurements, including reflectance measurement in the bleached and coloured states, from which a good contrast ratio was obtained and the degree of optical bleaching indicates the good reversibility of the viologen reduction in this environment. The overall reflectance in the bleached state was 68.4%. The dyed titanium dioxide pixels in the display were a pale grey colour, yielding a shadowed image in the bleached state. The contrast of the pixels expressed as the ratio of the background reflectance to that of the pixels was 1.08. The contrast ratio re-measured after applying a potential of 650 mV for three seconds, was 2.31. The displays showed a small degree of incomplete bleaching, with a contrast ratio of 1.08 after the application of a short circuit, equating to retention of 0.46% of the colour seen in the charged state. This retained colour was detected by the CCD camera used for reflectance measurements (Fig. 8).

4 Conclusions

Mesoporous nanocrystalline titania was successfully synthesised for the development of nanomaterial based electrochromic display devices using a simple microwave method. SEM studies showed that spherical aggregates of mesoporous nanosized titanium dioxide were formed using the titanium butoxide and various alcohols such as isopropanol, ethanol and butanol. XRD studies showed that crystalline nanotitania was obtained at a very low microwave power 300 W after as little as 2 min irradiation. In addition to that, these materials possess surface area as high as $240 \text{ m}^2 \text{ g}^{-1}$. This microwave technique offers a clean, cost-

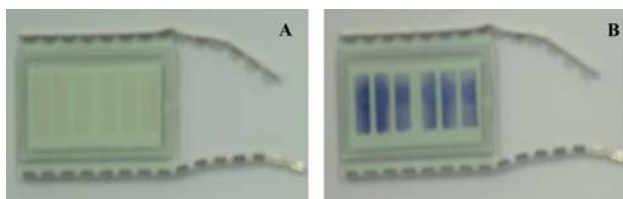


Fig. 8 Electrochromic display device fabricated using the mesoporous titania synthesised by microwave method.

effective, energy efficient, rapid and convenient method resulting in higher yields of TiO_2 in shorter reaction times. In the second part of the work, films were fabricated onto ITO coated glass using the as-synthesised titania and it was successfully used as an electrode for a simple display device. A cyclic voltammetry study of the films showed the oxidative and reductive curves have almost equal area showing full reversibility of charge transfer and thereby confirming the reversibility of the display device switching behaviour. The specific charge on the pixels of each display fabricated was 1.01 mC cm^{-2} . Finally, a working prototype of an electrochromic display device was successfully fabricated using this approach.

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