



# Chemical synthesis of highly size-confined triethylamine-capped TiO<sub>2</sub> nanoparticles and its dye-sensitized solar cell performance

T PRAKASH<sup>1,\*</sup>, M NAVANEETHAN<sup>2</sup>, J ARCHANA<sup>3</sup>, S PONNUSAMY<sup>4</sup>,  
C MUTHAMIZHCHELVAN<sup>4</sup> and Y HAYAKAWA<sup>2</sup>

<sup>1</sup>Department of S & H, QIS Institute of Technology, Ongole, Prakasam 523 272, India

<sup>2</sup>Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8011, Japan

<sup>3</sup>SRM Research Institute, Department of Physics & Nanotechnology, SRM University, Kattankulathur, Kancheepuram 603203, India

<sup>4</sup>Department of Physics & Nanotechnology, SRM University, Kattankulathur, Kancheepuram 603203, India

\*Author for correspondence (t.praakash.phy@gmail.com)

MS received 1 May 2017; accepted 11 September 2017; published online 23 March 2018

**Abstract.** TiO<sub>2</sub> nanoparticles were synthesized by a facile wet chemical synthesis using triethylamine (TEA) as a surface passivating agent. The role of TEA on the formation and functional properties of TiO<sub>2</sub> nanoparticles were investigated. Particle agglomeration was restricted and nanoparticle size was limited to 5 nm by passivating the amine molecule. Photoanodes were fabricated by spray deposition method using synthesized TiO<sub>2</sub> nanoparticles. The efficiency of 5.91% was obtained by the dye-sensitized solar cells.

**Keywords.** Nanostructures; semiconductors; chemical synthesis; electron microscopy.

## 1. Introduction

The physical and chemical properties of TiO<sub>2</sub> are dependent on their size, morphology and crystal structure. Titanium dioxide exists in three crystalline forms: anatase, rutile and brookite. Among these, anatase is considered as one of the most promising phase for photocatalysis and solar energy conversion applications, because of their least recombination rate [1,2]. It is well known that dimensionality (nanorods, nanowires, nanotubes, etc.) and crystalline quality of the anatase TiO<sub>2</sub> nanostructures have played an important role in the dye-sensitized solar cells (DSSCs) to achieve the higher conversion efficiency [3–5]. Several methods were developed to synthesize TiO<sub>2</sub> nanostructures such as micelle and inverse micelle methods, direct oxidation method, chemical vapour deposition, physical vapour deposition, electrodeposition, sonochemical method, microwave method and wet chemical method [26].

Among these, wet chemical method is found to be the easiest and promising method for the preparation of TiO<sub>2</sub> nanoparticles due to their simplicity, low cost and possibility of large scale synthesis [6–9]. Till now, a few research works were reported on the synthesis of size-confined TiO<sub>2</sub> nanoparticles using an organic ligand as capping agent. For example, Wang *et al* [10] grew hexylamine-capped TiO<sub>2</sub> nanoparticles with an average size of 3.9 nm. Kim *et al* [11] synthesized oleic acid-capped TiO<sub>2</sub> nanoparticles with an average size of 3–5 nm. Wu *et al* [12] synthesized stearic acid-capped TiO<sub>2</sub> nanoparticles with an average size of

6–8 nm by sol–gel method and Misra and Liu [13] reported resorcinarene-capped TiO<sub>2</sub> nanoparticles with an average size of 5 nm by a wet chemical method. Recently, amine molecules were attracted as a capping agent to the synthesis of size-confined oxide nanocrystals owing to their chemisorption nature, which exists by virtue of their lone pair electrons on the nitrogen atoms [14].

In the previous reports, triethylamine (TEA) was used as a capping ligand for the synthesis of monodispersed CdS and PbS nanoparticles with a smaller size [15,16]. Hence, TEA was selected as a capping agent to synthesize the size-confined TiO<sub>2</sub> nanoparticles using wet chemical process. In the present research, we report a facile synthesis of highly size-confined anatase TiO<sub>2</sub> nanoparticles using titanium (IV) isopropoxide solution as a titania source and TEA as a capping agent. The functional properties and DSSCs performance were studied.

## 2. Materials and methods

### 2.1 Preparation of anatase TiO<sub>2</sub> nanoparticles

All the chemicals were purchased from Wako chemicals (Japan) and used without further purification. The synthesis of TiO<sub>2</sub> nanoparticles as follows: 0.5 ml TEA was added slowly to 40 ml ethanol under vigorous stirring for 5 min at room temperature. A white precipitate was obtained, while drop-wise addition of 4 ml titanium isopropoxide (TIP) into

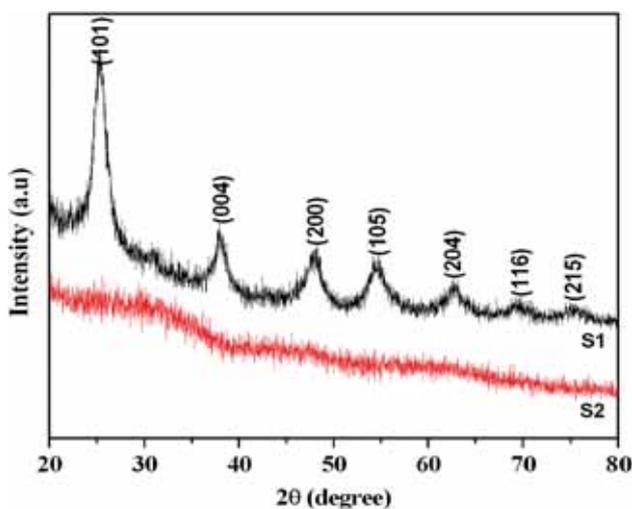
the parent solution under vigorous stirring (490 rpm) at room temperature, and the final ratio of TIP, TEA and ethanol was 4: 0.5: 40. After 12 h, the precipitates were separated by centrifugation and washed with water for several times. Finally, a precipitate was dried at 100°C for 12 h using hot air oven and stored at room temperature for further studies. The uncapped TiO<sub>2</sub> particles were synthesized by the method used for TEA-capped TiO<sub>2</sub> nanoparticles without using TEA. TEA-capped and uncapped TiO<sub>2</sub> nanoparticles were marked as S1 and S2, respectively.

## 2.2 Solar cell fabrication

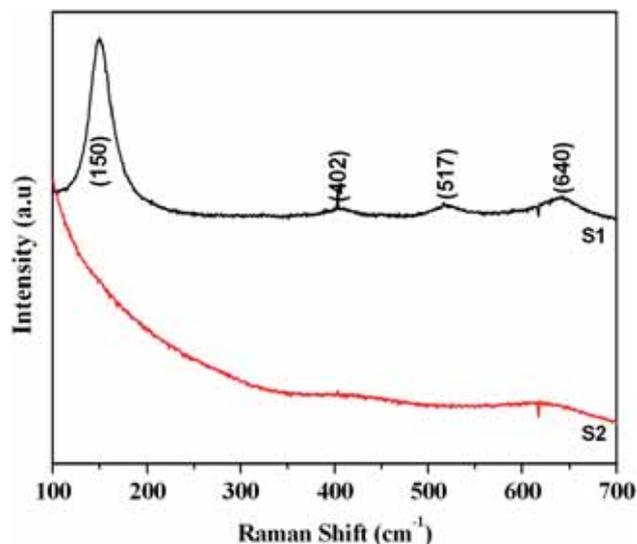
Two grams of TiO<sub>2</sub> nanoparticles and 50 ml ethanol were grounded in a mortar for a few minutes to form colloidal suspensions. Thereafter, five drops of triton-X were added into the solution as an organic binder. Fluorine-doped tin oxide (FTO) substrates were cleaned ultrasonically using a mixture of acetone and ethanol for 30 min at room temperature. To fabricate the photoanode, TiO<sub>2</sub> nanoparticles suspension in ethanolic solution was sprayed over the FTO substrate at a substrate temperature of 150°C by spray-deposition method and annealed at 530°C for 2 h. Photoanodes were immersed in ethanolic solution with 0.03 M di-tetrabutylammonium cis-bis (isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) (N-719). The dye-sensitized photoanode and Pt-coated counter electrode were clamped using clips. Finally, an iodide-based redox electrolyte was filled between the electrodes via capillary action.

## 2.3 Characterization of anatase TiO<sub>2</sub>

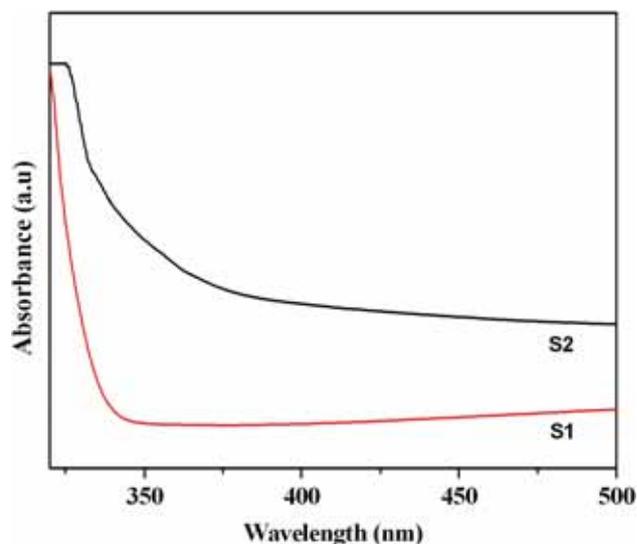
Powder XRD patterns were recorded using a Rigaku (Japan) X-ray diffractometer (XRD) (RINT-2200) with CuK $\alpha$



**Figure 1.** Powder XRD patterns of TEA-capped (S1) and uncapped (S2) TiO<sub>2</sub> nanoparticles.



**Figure 2.** Raman spectra of TEA-capped (S1) and uncapped (S2) TiO<sub>2</sub> nanoparticles.

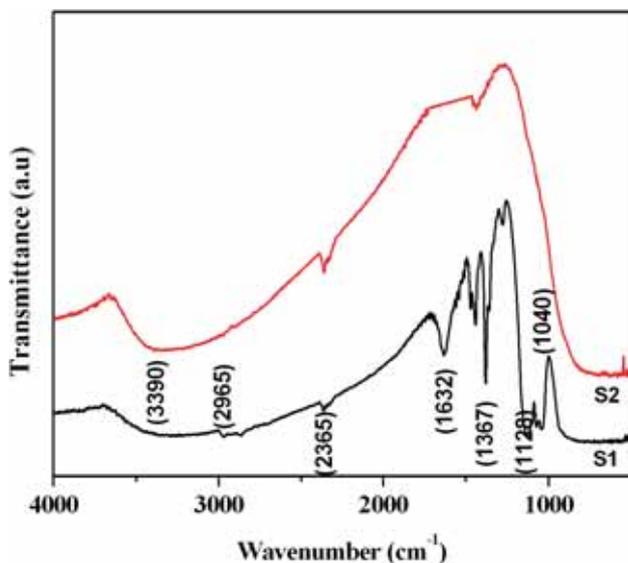


**Figure 3.** UV spectra of TEA-capped (S1) and uncapped (S2) TiO<sub>2</sub> nanoparticles.

radiation at 0.02° s<sup>-1</sup> step interval. Fourier transform infrared (FTIR) spectra were obtained from JEOL JIR-WINSPEC 50 spectrometer. UV-visible absorption analyses were performed using a Shimadzu (Japan) 3100 PC spectrophotometer with ethanol as dispersing medium. Raman spectra were obtained using a JASCO NR 1800 Raman spectrophotometer equipped with Nd:YAG laser. Field emission scanning electron microscope (FESEM) images were recorded using a JEOL JSM 6320F. Transmission electron microscope (TEM) images were recorded using a JEOL JEM 2100F at an accelerating voltage of 200 kV.

### 3. Results and discussion

The phase purity of the synthesized products was identified by powder XRD measurement. Powder XRD patterns were recorded for TEA-capped and uncapped  $\text{TiO}_2$  nanoparticles as shown in figure 1. All the observed diffraction peaks were indexed as anatase crystal structure of  $\text{TiO}_2$  (JCPDS 89-4921) for TEA-capped  $\text{TiO}_2$  nanoparticles [17–19]. But,

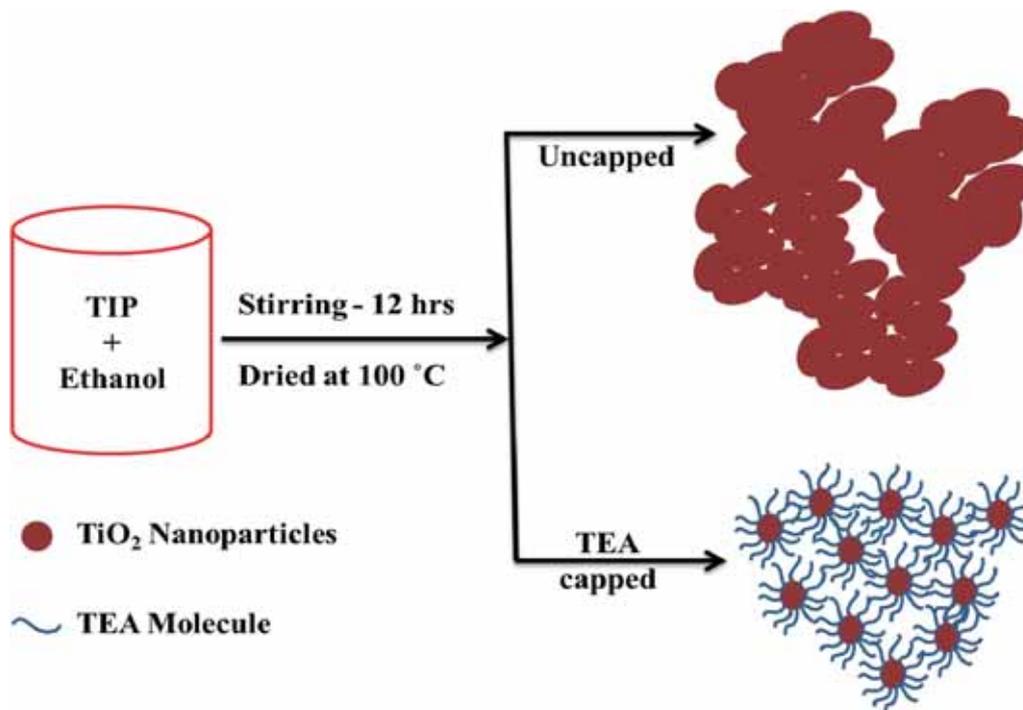


**Figure 4.** FTIR spectra of TEA-capped (S1) and uncapped (S2)  $\text{TiO}_2$  nanoparticles.

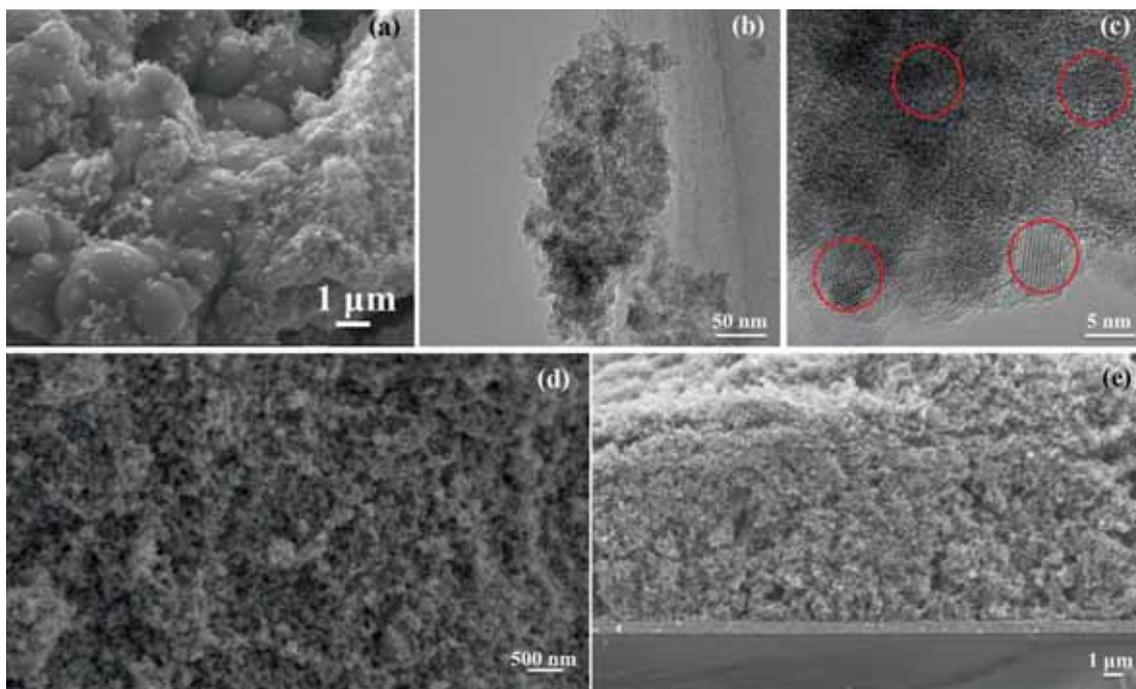
detectable diffraction peaks were not observed in uncapped  $\text{TiO}_2$  nanoparticles, which indicate the amorphous nature of the sample. The amorphous nature of uncapped  $\text{TiO}_2$  nanoparticles is due to the formation of hydrated  $\text{TiO}_2$ . Highly crystalline and anatase phase  $\text{TiO}_2$  nanoparticles were formed by the addition of TEA into the ethanol solution of titanium isopropoxide results from large coordination bonding of TEA ligands sitting on Ti atoms. The uncapped  $\text{TiO}_2$  particles were synthesized using same preparation procedure without using TEA. If stirred for overnight, then we can get nanoparticles. But reaction parameter might be changed, hence, maintained same reaction time.

Raman spectra were recorded to investigate the crystalline phase purity of the synthesized products as represented in figure 2. The Raman spectrum of uncapped sample (S2) does not show any clear spectral peak, which represents the formation of amorphous hydrated  $\text{TiO}_2$  nanoparticles. On the contrary, TEA-capped  $\text{TiO}_2$  nanoparticles (S1) shows the bands at  $150\text{ cm}^{-1}$  (very strong),  $402\text{ cm}^{-1}$  (weak),  $517\text{ cm}^{-1}$  (weak) and  $640\text{ cm}^{-1}$  (medium). The bands observed at  $150\text{ cm}^{-1}$  ( $E_g$ ),  $402\text{ cm}^{-1}$  ( $B_{1g}$ ),  $517\text{ cm}^{-1}$  ( $A_{1g} + B_{1g}$ ) and  $640\text{ cm}^{-1}$  ( $E_g$ ) were consistent with the bands observed from the previous report for anatase  $\text{TiO}_2$  [20–22].

UV-visible absorption spectra of uncapped (S2) and TEA-capped (S1)  $\text{TiO}_2$  nanoparticles are illustrated in figure 3. The absorption edges of the uncapped (S2) and TEA-capped (S1) nanoparticles were 360 and 336 nm, respectively, and exhibited a blue shift from 360 to 336 nm arises from particle size reduction [23]. The surface capping of the  $\text{TiO}_2$



**Figure 5.** Formation mechanism of TEA-capped and uncapped  $\text{TiO}_2$  nanoparticles.

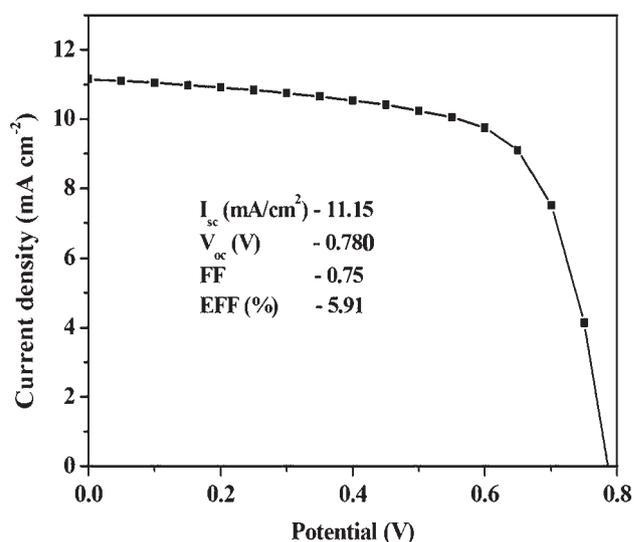


**Figure 6.** (a) FESEM images of uncapped TiO<sub>2</sub> nanoparticles, (b and c) TEM images of TEA-capped TiO<sub>2</sub> nanoparticles, (d and e) the top and cross-sectional view of annealed photoanode of sample S2.

nanoparticles by TEA was confirmed by FTIR studies. Figure 4 shows the FTIR spectra of uncapped (S2) and TEA-capped (S1) TiO<sub>2</sub> nanoparticles. The peak at 1040 cm<sup>-1</sup> attributed to C–N stretching vibration of TEA molecule. The peaks at 1128, 1367 and 1632 cm<sup>-1</sup> corresponded to N–H vibrations of TEA molecule [24]. It clearly demonstrated the surface capping of TEA molecule on the surface of TiO<sub>2</sub> nanoparticles.

The schematic representation to the formation of TiO<sub>2</sub> nanoparticles is shown in figure 5. Formation of TEA-capped TiO<sub>2</sub> nanoparticle is as follows: lone pair of electrons in the nitrogen atom of TEA was attached to the surface of the TiO<sub>2</sub> nanoparticles due to the affinity of the nitrogen with Ti<sup>4+</sup>. The nitrogen atom forms a coordinate bond with the surface of TiO<sub>2</sub>, because of its chemisorption properties. In addition to that the longer stirring time and alcoholysis of TEA in the ethanol brings the formation of nanoparticles.

FESEM image of uncapped TiO<sub>2</sub> shows the spherical shape with an agglomeration in the range of 2 μm (figure 6a). TEM image of TEA-capped TiO<sub>2</sub> nanoparticles presented in figure 6b, a spherical shape was observed with an average size of 5 nm. The clear distinguished lattice fringes were observed from HRTEM images represent a high crystalline quality of the nanoparticles (figure 6c). Photoanode was prepared by using spray pyrolysis technique for TEA-capped TiO<sub>2</sub> nanoparticles. The top and cross-sectional FESEM views of the photoanode are shown in figure 6d and e, respectively. Clearly, they show that the pores adsorb enough dye molecules on the TiO<sub>2</sub> nanoparticles. DSSCs works under a complicated



**Figure 7.** *I*–*V* curve of TEA-capped TiO<sub>2</sub> nanoparticles.

system involving several processes such as light absorption, charge separation and injection, transport of injected electron and electrolyte diffusion. The charge collection and electron transport in DSSCs are highly dependent on the morphology, surface area, porosity and size of TiO<sub>2</sub>.

DSSCs were fabricated using nanocrystalline TiO<sub>2</sub> particles. However, 5.91% conversion efficiency, with the open

circuit photovoltage of 780 mV, the shortcircuit photocurrent of  $11.15 \text{ mA cm}^{-2}$  and the fill factor 0.75, were obtained with the nanocrystalline  $\text{TiO}_2$  film of  $20 \mu\text{m}$  in thickness fabricated at  $530^\circ\text{C}$  (figure 7). However, higher efficiency is difficult to be achieved with only the nanocrystalline  $\text{TiO}_2$  film composed of these very small nanoparticles and the sensitizer dye of N719 due to the low light harvest in the red region. It is suggested that the  $\text{TiO}_2$  photoelectrode morphology, nanoparticles, mixture of nanoparticles and light-scattering particles on the conductive glass at a desirable sequence and thickness, is essential and necessary for high efficiency [25]. However, the small nanocrystals adsorbed much more sensitizer will be a notable item for improvement of DSSC performance. With N719 dye, it is very easy to get efficiency of  $\sim 7\text{--}9\%$  when focussed only on the efficiency. But their way of preparation is also important. Synthesizing nanoparticles with some different techniques requires high-cost equipments. But in this research work,  $\text{TiO}_2$  nanoparticles were synthesized by simple preparation procedure with low-cost equipments. Already published research work was carried out by hydrothermal method. In this research work, synthesized TEA-capped  $\text{TiO}_2$  nanoparticles were prepared by using simple chemical preparation procedure.

#### 4. Conclusions

We have clearly demonstrated the synthesis of  $\text{TiO}_2$  nanoparticles at room temperature with the use of TEA as a capping ligand. Fabrication of photoanode can be easily achieved by using the spray deposition method. XRD and Raman studies confirm the formation of anatase  $\text{TiO}_2$  nanoparticles. TEM and HRTEM reveal the size confinement of  $\text{TiO}_2$  nanoparticles with an average size of 5 nm. FTIR spectra confirmed the surface passivation of TEA on  $\text{TiO}_2$ . This low-cost synthesis method shows good performance and successfully attributed to the control growth of  $\text{TiO}_2$  nanoparticles with tuning the size.

#### References

- [1] Zeman P and Takabayashi S 2002 *J. Vac. Sci. A* **20** 388
- [2] Deb S K 2005 *Sol. Energy Mater. Sol. Cells* **88** 1
- [3] Jiu J, Isoda S, Wang F and Adachi M 2006 *J. Phys. Chem. B* **110** 2087
- [4] Park J H, Lee T W and Kang M G 2008 *Chem. Commun.* **7** 2867
- [5] Kang S H, Choi S H, Kang M S, Kim J Y, Kim H S, Hyeon T *et al* 2008 *Adv. Mater.* **20** 54
- [6] Wang X, Zhaung J, Peng Q and Li Y D 2005 *Nature* **437** 121
- [7] Wu M, Lin G, Chen D, Wang G, He D, Feng S *et al* 2002 *Chem. Mater.* **14** 1974
- [8] Yanagisawa K and Ovenstone J 1999 *J. Phys. Chem. B* **103** 7781
- [9] Coronado R D, Gattorno R G, Pesqueira E M E, Cab C, Coss R and Oskam G 2008 *Nanotechnology* **19** 145605
- [10] Wang Y, Zhang S and Wu X 2004 *Nanotechnology* **15** 1162
- [11] Kim E Y, Choi H and Wang C M 2010 *J. Mater. Sci.* **45** 3895
- [12] Wu X, Wang D and Yang S 2000 *J. Colloid Interf. Sci.* **222** 37
- [13] Misra T K and Liu C Y 2007 *J. Colloid Interf. Sci.* **310** 178
- [14] Navaneethan M, Archana J, Arivanandhan M and Hayakawa Y 2012 *Chem. Eng. J.* **213** 70
- [15] Nisha K D, Navaneethan M, Ponnusamy S and Muthamizhchelvan C 2009 *J. Alloys Compd.* **486** 844
- [16] Navaneethan M, Nisha K D, Ponnusamy S and Muthamizhchelvan C 2009 *Mater. Chem. Phys.* **117** 443
- [17] Peng F, Cai L, Yu H, Wang H and Yang J 2008 *J. Solid State Chem.* **181** 130
- [18] Kosowska B, Mozia S, Morawski A W, Grzmil B, Janus M and Kalucki K 2005 *Sol. Energy Mater. Sol. Cells* **88** 269
- [19] Li H, Li J and Huo Y 2006 *J. Phys. Chem. B* **110** 1559
- [20] Swamy V, Kuznetsov A, Dubrovinsky L S, Caruso R A, Shchukin D G and Muddle B C 2005 *Phys. Rev. B* **71** 184302
- [21] Lottici P P, Bersani D, Braghini M and Montenero A 1993 *J. Mater. Sci.* **28** 177
- [22] Balachandran U and Eror N G 1982 *J. Solid State Chem.* **42** 276
- [23] Kim E Y, Choi H and Wang C M 2010 *J. Mater. Sci.* **45** 3895
- [24] Zhang R and Gao L 2002 *Key Eng. Mater.* **224** 573
- [25] Wang Z, Kawauchi H, Kashima T and Arakawa H 2004 *Coord. Chem. Rev.* **248** 1381
- [26] Chen X and Mao S S 2007 *Chem. Rev.* **107** 2891