

Sol–gel hydrothermal synthesis of bismuth–TiO₂ nanocubes for dye-sensitized solar cell

M.N. An'amt^{a,*}, S. Radiman^a, N.M. Huang^{b,*}, M.A. Yarmo^c,
N.P. Ariyanto^d, H.N. Lim^e, M.R. Muhamad^b

^a School of Applied Physics, Faculty of Science & Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia

^b Low Dimensional Materials Research Centre, Block A, Physics Building, University of Malaya, 50603 Kuala Lumpur, Malaysia

^c School of Chemical Science and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia

^d Department of Electrical, Electronic & Systems Engineering, Faculty of Engineering and Build Environment,
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia

^e Faculty of Engineering, Nottingham University, Jalan Broga, 43500 Semenyih, Selangor, Malaysia

Received 11 March 2010; received in revised form 12 April 2010; accepted 14 May 2010

Available online 30 June 2010

Abstract

Bismuth–TiO₂ nanocubes were synthesized via a facile sol–gel hydrothermal method with titanium tetraisopropoxide as the precursor. The influence of the bismuth on the size, morphology, crystallinity and optical behavior of TiO₂ nanocubes were investigated. The samples were characterized by X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), field emission scanning electron microscopy (FESEM) and UV–visible spectroscopy (UV–vis). Photovoltaic behavior of dye-sensitized solar cells (DSSCs) fabricated using Bi–TiO₂ nanocubes was studied. The DSSCs had an open-circuit voltage (V_{oc}) of 590 mV, a short-circuit current density (J_{sc}) of 7.71 mA/cm², and the conversion efficiency (η) of 2.11% under AM 1.5 illumination, a 77% increment as compared to pure TiO₂ nanocubes. © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Sol–gel processing; B. Nanocomposites; D. TiO₂

1. Introduction

Titanium dioxide (TiO₂) is a wide band-gap semiconductor with energy of 3.0–3.2 eV. It is widely used in applications such as hydrogen production [1,2], gas sensors [3,4], photocatalytic activities [5,6], dye-sensitized solar cells and photoelectrochemical cells because of its relative high efficiency and high stability. However, due to its wide band gap energy, TiO₂ is active only under near-ultraviolet irradiation. Therefore, numerous researches have been carried out over the last 20 years to develop modified TiO₂ so that they are active under visible light irradiation ($\lambda > 400$ nm). One of the most studied methods is by doping the TiO₂ materials with metal ions (iron [7,8], nickel [9,10], vanadium [11,12], and chromium [13,14]) or nonmetallic elements (nitrogen [15,16], sulfur [17,18] and carbon [19,20]).

Among these doping methods, doping with transitional metals is one of the most efficient methods. Researches have been carried out to dope bismuth into TiO₂ to enhance the photocatalytic activities in these systems [21–24]. However, to the knowledge of the authors, there is no known report on the study of bismuth–TiO₂ nanomaterials for dye-sensitized solar cell (DSSC) application.

It has been reported that the metal/TiO₂ nanostructures will enhance the efficiency of DSSCs. Metals compounded on semiconductor materials increase charge-collection efficiency due to a much slower electron-hole recombination, giving rise to longer electron lifetime, which will result in an increasing interfacial electron-transfer process [25–27]. Metal–TiO₂ nanocomposites make an attractive research field by modifying the structure of the working electrode to improve the performance of solar energy conversion [28,29]. In DSSCs, the photoelectric conversion occurs by electron injection from photo-excited dye into the conduction band of TiO₂ and later the dye is regenerated by I^-/I_3^- through diffusion of electrons to the counter electrode [30,31]. Electron transport happens in

* Corresponding authors. Tel.: +60 38 9214256; fax: +60 38 9269470.

E-mail addresses: anamt_1003@yahoo.com (M.N. An'amt),
huangnayming@gmail.com (N.M. Huang).

the space charge region at nanocrystalline surface, which separates the photo-generated electron–hole and prevents charge recombination at the electrode–electrolyte interface. Decrease in probability of electron–hole recombination induces a large amount of electron–hole on the nanocrystalline surface, resulting in higher efficiency of solar energy conversion. Therefore, it is assumed that metal–TiO₂ nanocomposites could enhance the efficiency of DSSCs because of electron-transfer kinetics at the crystal surface and low probability of electron–hole recombination.

Hydrothermal approach has been used extensively for the synthesis of ceramic materials which takes advantage of a direct preparation at low crystallization temperatures [32–34]. In this work, we utilized Ti⁴⁺ aqueous solution to synthesis cube-like Bi–TiO₂ via sol–gel hydrothermal method. The Bi–TiO₂ nanocomposites formed were fabricated into DSSCs. To the best of our knowledge, this is the first report on the synthesis of Bi–TiO₂ nanocomposites for DSSCs application.

2. Experimental

2.1. Synthesis of TiO₂ and Bi–TiO₂ nanocubes

TiO₂ nanocrystals were synthesized using the modified sol–gel hydrothermal approach as reported previously [35]. In a typical synthesis route, 30 ml titanium tetraisopropoxide (TTIP) was added to 27 ml of triethanolamine (TEA) under constant magnetic stirring. Deionized water (18.2 MΩ cm resistivity) was added to obtain 200 ml of clear Ti⁴⁺ aqueous solution. Then, 30 ml of the Ti⁴⁺ solution was mixed with 30 ml of 0.1 M ethylenediamine. The mixed solution was then poured into a Teflon-lined autoclave and put inside the furnace at 100 °C for 24 h for gelation process. Then, the crystallization was completed by heating up the autoclave to 180 °C for 24 h. The hydrothermal crystallization time was varied for 24, 48 and 72 h at the same temperature with samples denoted as TiO₂-24, TiO₂-48 and TiO₂-72, respectively. Bi–TiO₂ nanocrystals were synthesized via the same procedure mentioned above with hydrothermal crystallization time of 72 h. The only difference was by adding 0.3 mmol Bi(NO₃)₃·5H₂O into the TTIP and TEA mixture during the initial stage of the synthesis process. All the samples were recovered by washing with deionized water followed by centrifugation for three times and dried at 60 °C in an oven overnight.

2.2. Fabrication of dye-sensitized solar cells (DSSCs)

In order to fabricate the DSSC, TiO₂ film electrode was made by the doctor blade technique on an indium tin oxide, ITO conductive glass (15 Ω cm resistivity). After drying in air and sintered at 450 °C for 30 min, the resulting film were immersed in an ethanol solution of 0.3 mM N₃ dye for about 16 h. The dye-adsorbed electrode was assembled into a sandwich-type cell with a counter electrode (platinum-sputtered ITO glass) and a spacer in the middle for ease of electrolyte solution injection. A drop of electrolyte solution (Iodolyte MPN-100, Solaronix) was introduced into the clamped electrodes using

syringe. An active area typically 0.2 cm² was employed to measure the cell performance.

2.3. Characterization and DSSCs conversion efficiency measurement

The morphology and size of the samples were examined by a Philips CM12 transmission electron microscopy (TEM) operated at 100 kV. Measurement of the average diameter of the samples was carried out using an I-Solution-DT (version 6.5, IMT) image analysis software. A field emission scanning electron microscope, FESEM was used to examine the morphology of the sample and elemental analysis of the Bi–TiO₂ sample was carried out by energy dispersive analysis (EDX). The crystallinity of the samples were characterized by a Philip X-ray diffractometer (XRD) at a scanning rate of 0.02° s^{−1} with Cu Kα radiation and λ = 1.5418 Å. The optical properties were analyzed using a PerkinElmer Lamda-35 UV–vis spectrometer (UV–vis). The photovoltaic activities of the TiO₂ samples were measured by a Gamry Potentiostat Series G-300 under a xenon lamp, simulated solar illumination with Air Mass 1.5G filter (AM 1.5, 100 mW/cm²).

3. Results and discussion

From Fig. 1, it was shown that the crystalline phase of the TiO₂ nanocrystals formed is anatase phase. There are no other peaks showing impurities or other TiO₂ phases like rutile or brookite present in the sample. The crystallinity and crystallite size increased as the hydrothermal treatment time increased based on the intensities of characteristic XRD peaks. All the peaks corresponded to the anatase phase of TiO₂ with 2θ = 25.3°, 36.9°, 37.8°, 36.6°, 48.0°, 53.8° and 55.0° attributed to [1 0 1], [1 0 3], [0 0 4], [1 1 2], [2 0 0], [1 0 5] and [2 1 1]

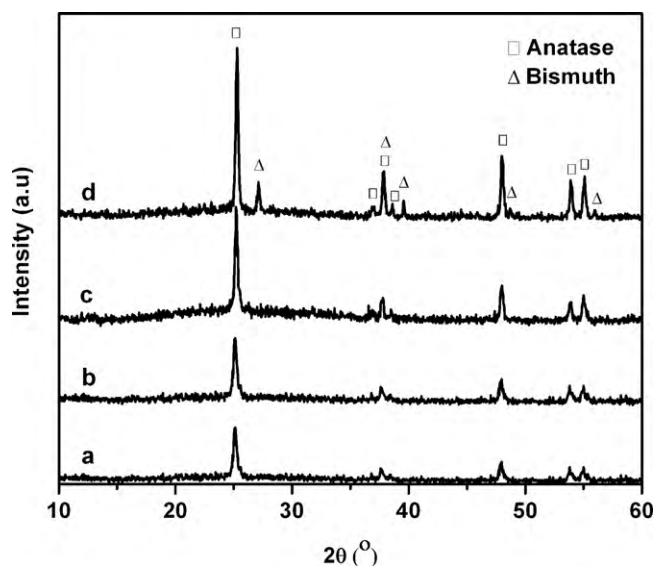


Fig. 1. XRD patterns of the TiO₂ nanocubes (a) TiO₂-24, (b) TiO₂-48, (c) TiO₂-72 and (d) Bi–TiO₂ prepared under different experimental conditions. The TiO₂ anatase peaks are labeled as square shape while the triangle shape denote peaks attributed to the Bi element.

plane, respectively (JCPDS 84-1285). When examining the diffraction peaks of Bi–TiO₂, it is clearly shown that there are other peaks besides the anatase phase. These peaks are indexed to the rhombohedral phase of bismuth with $2\theta = 27.1^\circ$, 37.8° , 39.6° , 48.7° and 56.0° corresponding to [0 1 2], [1 0 4], [1 1 0], [2 0 2] and [0 2 4] plane, respectively (JCPDS 005-0519). It has been reported that the doping of bismuth into TiO₂ crystal structure can be observed from the shifting of 1 0 1 diffraction peak at $2\theta = 25.5^\circ$ [23]. For Bi doped sample, there will be a shift to lower angle because the ionic radius of Bi³⁺ (0.103 nm) is larger than that of Ti⁴⁺ (0.061 nm), the distance of nearest-neighbor crystalline plane becomes wider after Bi³⁺ ions replace Ti⁴⁺ ions in TiO₂. However, we do not observe this shifting phenomenon in our work; instead there is a slight shift towards the higher angle for Bi–TiO₂ sample. The slight shift towards the higher angle may be contributed by the mixed crystalline phases of anatase and bismuth metal. The inclusion of bismuth also increased the crystallinity of the TiO₂ nanocube crystals as can be seen from the intensity of the peaks. In general, the increase in the crystallinity of anatase TiO₂ is favorable to enhance the photovoltaic activity of TiO₂.

TEM micrographs in Fig. 2 show the morphologies of TiO₂ and Bi–TiO₂ nanocubes. The TiO₂ produced have cube-like shaped for all the different hydrothermal crystallization times and bismuth inclusion. As shown in Fig. 2(a–c), TiO₂-24, TiO₂-48 and TiO₂-72 have average sizes of 66 ± 18 , 69 ± 11 and 75.2 ± 17 nm, respectively. This suggests that longer hydrothermal treatment allows particles to grow larger. While, Bi–TiO₂ nanocubes has the largest average particle size (92.3 ± 17 nm) as shown in Fig. 2(d). In comparison to the pure TiO₂ nanocubes, the Bi–TiO₂ nanocubes have higher reaction rate which contributed to the larger particle size produced. Fig. 3(a) shows a FESEM image of three-dimensional Bi–TiO₂ nanocubes which is in accordance to the observation from TEM while the atomic percentages of bismuth, titanium and oxygen were analyzed by EDX as shown in Fig. 3(b). For EDX, several areas on the individual nanocubes were selected for the analysis. It was found that the average atomic ratio for Ti:O is 32.4:65.1 which agrees well with the formation of TiO₂. The atomic percentage for bismuth is 1.5 wt.%. The EDX and XRD results have confirmed the existence of bismuth element on the surface of TiO₂ nanocubes instead of the doping of Bi³⁺.

UV–vis absorption spectra for TiO₂-72 and Bi–TiO₂ were measured to study the effect of bismuth on optical property of TiO₂ nanocubes (Fig. 4). Undeniably, introduction of bismuth has modified the absorption characteristics of the TiO₂ nanocubes. It is obvious that the absorption range for Bi–TiO₂ have red shifted to longer wavelength which falls in the visible range as compared to TiO₂-72. This means that the Bi–TiO₂ sample can enlarge the wavelength response range and hence, enhances the solar light photovoltaic activity. This is crucial for TiO₂ material as the absorption region for TiO₂ falls in the UV zone which only consists of 5% in the solar light. The formation of Bi–TiO₂ nanocomposites intrinsically narrows the band-gap transition of TiO₂ which has the same effect as the reported Ag–TiO₂ nanocomposites [26,36,37].

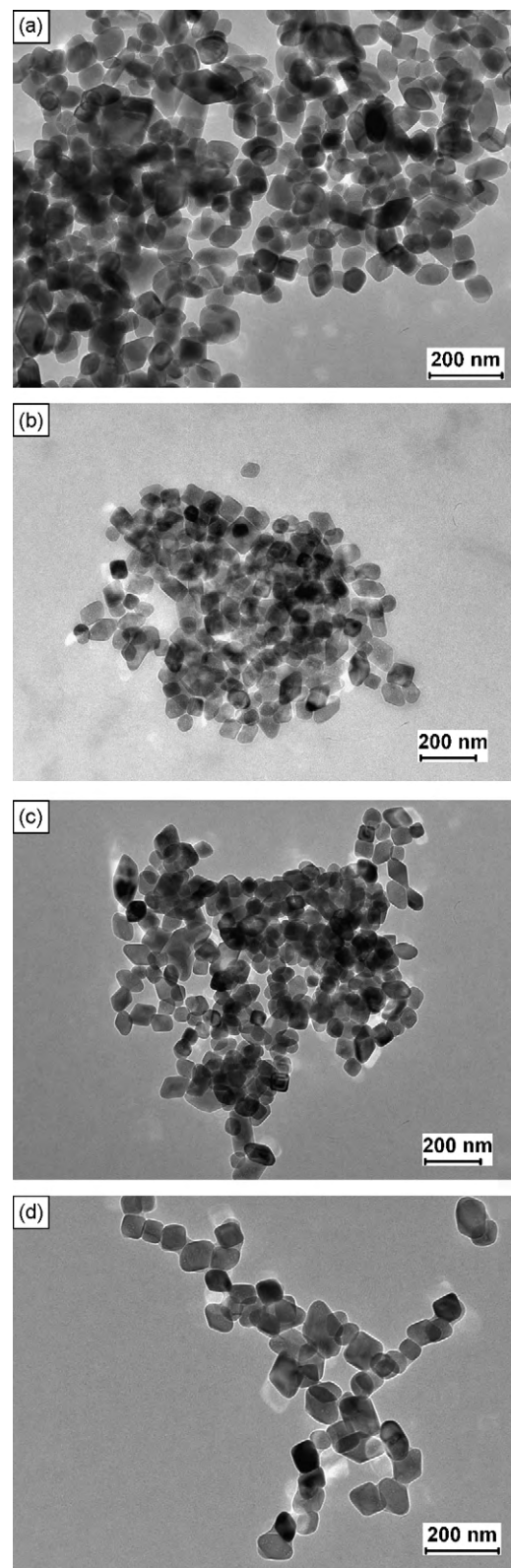


Fig. 2. TEM images of TiO₂ nanocubes (a) TiO₂-24, (b) TiO₂-48, (c) TiO₂-72 and (d) Bi–TiO₂ synthesized by the sol–gel hydrothermal method.

The photocurrent density–voltage characteristics (*J*–*V* curve) were studied under standard solar simulated light AM 1.5. From the analysis of the *J*–*V* curves, critical parameters of the cell's operation were obtained such as (a) open-circuit

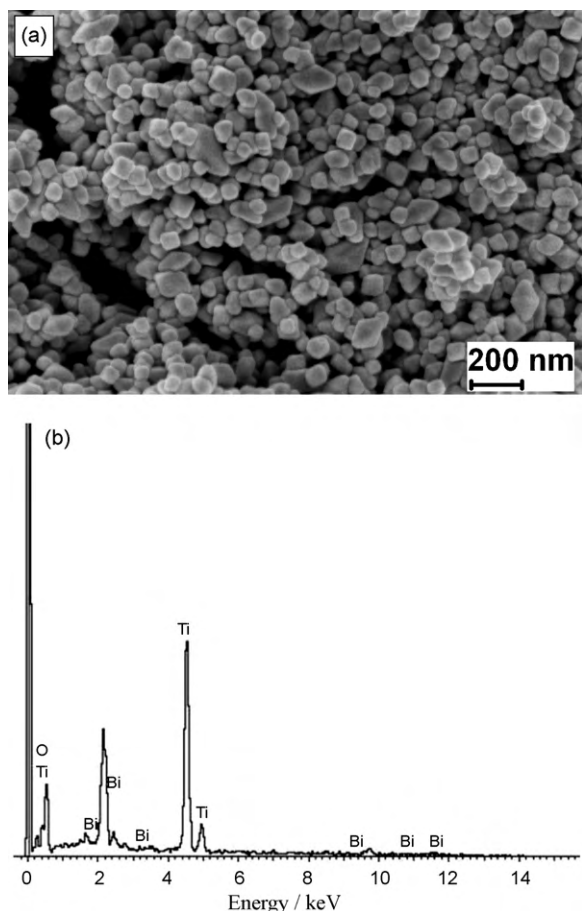


Fig. 3. FESEM image of cube-like Bi-TiO₂ (a) and EDX spectra of Bi-TiO₂ (b).

photovoltage V_{oc} , (b) the short-circuit photocurrent density J_{sc} , fill factor (FF) calculated using Eq. (1) and the cells overall energy conversion efficiency (η) estimated by Eq. (2). The parameters were shown in Table 1.

$$FF = \frac{V_{max} J_{max}}{V_{oc} J_{sc}} \quad (1)$$

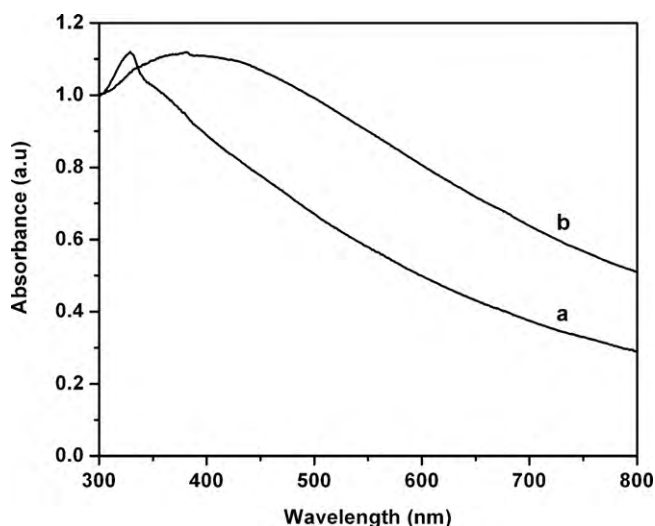


Fig. 4. UV-vis absorption spectra for (a) TiO₂-72 and (b) Bi-TiO₂ nanocubes.

Table 1

The critical parameters for open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and cell efficiency (η) analyzed from curves J - V .

Electrode	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
Bi-TiO ₂	0.59	7.71	0.46	2.11
TiO ₂ -72	0.57	5.52	0.38	1.19
TiO ₂ -48	0.57	3.12	0.62	1.10
TiO ₂ -24	0.56	2.40	0.63	0.84

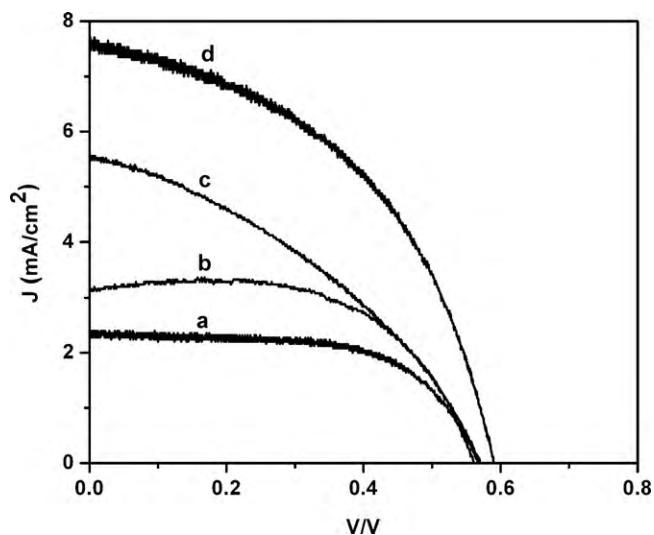


Fig. 5. Photocurrent density-voltage (J - V) curves for dye-sensitized solar cells using (a) TiO₂-24, (b) TiO₂-48, (c) TiO₂-72 and (d) Bi-TiO₂ nanocubes.

$$\eta = \frac{V_{oc} J_{sc} FF}{I_s} \quad (2)$$

where V_{max} and J_{max} are voltage and current density for maximum power output, respectively while I_s is the intensity of the incident light (mW/cm²).

From the J - V curves results as shown in Fig. 5, a short-circuit photocurrent density (J_{sc}) of 7.71 mA/cm², an open-circuit photovoltage (V_{oc}) of 0.59 V and the conversion efficiency (η) of 2.11% for Bi-TiO₂ electrode were obtained. In comparison, J_{sc} , V_{oc} , and η were 5.52 mA/cm², 0.57 V, and 1.19%, respectively, for TiO₂-72 electrode. There is about 39% increase in J_{sc} and 77% increase in conversion efficiency for Bi-TiO₂ electrode compared to TiO₂-72 electrode, whereas η and V_{oc} for Bi-TiO₂ electrode are nearly the same as TiO₂-72 electrode. In this case, we have improved J_{sc} significantly without sacrificing V_{oc} , indicating that Bi-TiO₂ is better than TiO₂ for DSSCs with the same technique. For TiO₂-48 and TiO₂-24 electrodes, the J_{sc} and η values were lower than TiO₂-72 which is due to the shorter hydrothermal crystallization time as longer crystallization time resulted in higher crystallinity of the anatase phase formed. It has been reported that anatase phase with higher crystallinity resulted in lower probability of electron-hole recombination as the electron transport is faster in these anatase layer [16,17]. Furthermore, modification of the TiO₂ nanocubes' surface with bismuth has increased the charge transport and suppressed the electrons in TiO₂ to recombine

with the dye and redox species, and hence gives rise to the high DSSCs performance.

4. Conclusion

We report a facile sol–gel hydrothermal process to prepare Bi–TiO₂ nanocubes that demonstrated much higher dye-sensitized solar cell conversion efficiency than pure TiO₂. The enhanced DSSCs conversion efficiency for the Bi–TiO₂ sample is due to the formation of bismuth/TiO₂ nanocomposites and the higher crystallinity of the TiO₂ formed.

Acknowledgments

This work is supported by the UKM-OUP-NBT-27-138/2008 grant and UMRG grant RG096/10AFR. The author would like to thank Ms. Su and Mr. Hasnul from the Electron Microcopy Unit, UKM for their assistance in carrying out the EM characterization.

References

- [1] W.S. Hong, J.H. Park, G.Y. Han, Optimization of conditions for hydrogen production from anodized TiO₂ nanotube-based photoelectrochemical cells, *Journal of Nanoscience and Nanotechnology* 9 (2009) 7293–7297.
- [2] S. Sato, J.M. White, Photodecomposition of water over Pt/TiO₂ catalysts, *Chemical Physics Letters* 72 (1980) 83–86.
- [3] C.-H. Han, D.-W. Hong, S.-D. Han, J. Gwak, K.C. Singh, Catalytic combustion type hydrogen gas sensor using TiO₂ and UV-LED, *Sensors and Actuators B: Chemical* 125 (2007) 224–228.
- [4] J.A. Park, J. Moon, S.J. Lee, S.H. Kim, T. Zyung, H.Y. Chu, Structure and CO gas sensing properties of electrospun TiO₂ nanofibers, *Materials Letters* 64 (2010) 255–257.
- [5] L.J. Chen, J.T. Tian, H. Qiu, Y.S. Yin, X. Wang, J.H. Dai, P.W. Wu, A.P. Wang, L. Chu, Preparation of TiO₂ nanofilm via sol–gel process and its photocatalytic activity for degradation of methyl orange, *Ceramic International* 35 (2009) 3275–3280.
- [6] T. Yazawa, F. Machida, N. Kubo, T. Jin, Photocatalytic activity of transparent porous glass supported TiO₂, *Ceramic International* 35 (2009) 3321–3325.
- [7] S. Nahar, K. Hasegawa, S. Kagaya, Photocatalytic degradation of phenol by visible light-responsive iron-doped TiO₂ and spontaneous sedimentation of the TiO₂ particles, *Chemosphere* 65 (2006) 1976–1982.
- [8] X.W. Zhang, L.C. Lei, One step preparation of visible-light responsive Fe–TiO₂ coating photocatalysts by MOCVD, *Materials Letters* 62 (2008) 895–897.
- [9] D.H. Kim, K.S. Lee, Y.S. Kim, Y.C. Chung, S.J. Kim, Photocatalytic activity of Ni 8 wt%-doped TiO₂ photocatalyst synthesized by mechanical alloying under visible light, *Journal of the American Ceramic Society* 89 (2006) 515–518.
- [10] R. Niishiro, H. Kato, A. Kudo, Nickel and either tantalum or niobium-codoped TiO₂ and SrTiO₃ photocatalysts with visible-light response for H₂ or O₂ evolution from aqueous solutions, *Physical Chemistry Chemical Physics* 7 (2005) 2241–2245.
- [11] S. Klosek, D. Raftery, Visible light driven V-doped TiO₂ photocatalyst and its photooxidation of ethanol, *The Journal of Physical Chemistry B* 105 (2001) 2815–2819.
- [12] J.C.S. Wu, C.H. Chen, A visible-light response vanadium-doped titania nanocatalyst by sol–gel method, *Journal of Photochemistry and Photobiology A: Chemistry* 163 (2004) 509–515.
- [13] S.K. Biswas, A. Pathak, N.K. Pramanik, D. Dhak, P. Pramanik, Codoped Cr and W rutile nanosized powders obtained by pyrolysis of triethanolamine complexes, *Ceramic International* 34 (2008) 1875–1883.
- [14] C.C. Pan, J.C.S. Wu, Visible-light response Cr-doped TiO₂–xN_x photocatalysts, *Materials Chemistry and Physics* 100 (2006) 102–107.
- [15] J.L. Gole, J.D. Stout, C. Burda, Y.B. Lou, X.B. Chen, Highly efficient formation of visible light tunable TiO₂–xN_x photocatalysts and their transformation at the nanoscale, *Journal of Physical Chemistry B* 108 (2004) 1230–1240.
- [16] M. Mrowetz, W. Balcerski, A.J. Colussi, M.R. Hoffmann, Oxidative power of nitrogen-doped TiO₂ photocatalysts under visible illumination, *The Journal of Physical Chemistry B* 108 (2004) 17269–17273.
- [17] Y.M. Liu, J.Z. Liu, Y.L. Lin, Y.F. Zhang, Y. Wei, Simple fabrication and photocatalytic activity of S-doped TiO₂ under low power LED visible light irradiation, *Ceramic International* 35 (2009) 3061–3065.
- [18] Y. Wang, Y. Wang, Y. Meng, H. Ding, Y. Shan, X. Zhao, X. Tang, A highly efficient visible-light-activated photocatalyst based on bismuth- and sulfur-codoped TiO₂, *The Journal of Physical Chemistry C* 112 (2008) 6620–6626.
- [19] T. Tachikawa, S. Tojo, K. Kawai, M. Endo, M. Fujitsuka, T. Ohno, K. Nishijima, Z. Miyamoto, T. Majima, Photocatalytic oxidation reactivity of holes in the sulfur- and carbon-doped TiO₂ powders studied by time-resolved diffuse reflectance spectroscopy, *The Journal of Physical Chemistry B* 108 (2004) 19299–19306.
- [20] X. Yang, C. Cao, K. Hohn, L. Erickson, R. Maghirang, D. Hamal, K. Klabunde, Highly visible-light active C- and V-doped TiO₂ for degradation of acetaldehyde, *Journal of Catalysis* 252 (2007) 296–302.
- [21] J. Wang, L. Jing, L. Xue, Y. Qu, H. Fu, Enhanced activity of bismuth-compounded TiO₂ nanoparticles for photocatalytically degrading rhodamine B solution, *Journal of Hazardous Materials* 160 (2008) 208–212.
- [22] S. Rengaraj, X.Z. Li, Enhanced photocatalytic reduction reaction over Bi³⁺–TiO₂ nanoparticles in presence of formic acid as a hole scavenger, *Chemosphere* 66 (2007) 930–938.
- [23] T. Ji, F. Yang, Y. Lv, J. Zhou, J. Sun, Synthesis and visible-light photocatalytic activity of Bi-doped TiO₂ nanobelts, *Materials Letters* 63 (2009) 2044–2046.
- [24] J. Yu, S. Liu, Z. Xiu, W. Yu, G. Feng, Combustion synthesis and photocatalytic activities of Bi³⁺-doped TiO₂ nanocrystals, *Journal of Alloys and Compounds* 461 (2008) L17–L19.
- [25] A. Sclafani, J.-M. Herrmann, Influence of metallic silver and of platinum-silver bimetallic deposits on the photocatalytic activity of titania (anatase and rutile) in organic and aqueous media, *Journal of Photochemistry and Photobiology A: Chemistry* 113 (1998) 181–188.
- [26] M. Seery, K.R. George, P. Floris, S.C. Pillai, Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis, *Journal of Photochemistry and Photobiology A: Chemistry* 189 (2007) 258–263.
- [27] N. Sobana, M. Muruganadham, M. Swaminathan, Nano-Ag particles doped TiO₂ for efficient photodegradation of direct azo dyes, *Journal of Molecular Catalysis A: Chemical* 258 (2006) 124–132.
- [28] C.-S. Chou, R.-Y. Yang, C.-K. Yeh, Y.-J. Lin, Preparation of TiO₂/nanometal composite particles and their applications in dye-sensitized solar cells, *Powder Technology* 194 (2009) 95–105.
- [29] Z. Liu, K. Pan, M. Liu, M. Wang, Q. Lü, J. Li, Y. Bai, T. Li, Al₂O₃-coated SnO₂/TiO₂ composite electrode for the dye-sensitized solar cell, *Electrochimica Acta* 50 (2005) 2583–2589.
- [30] M. Grätzel, Dye-sensitized solar cells, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 4 (2003) 145–153.
- [31] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films, *Nature* 353 (1991) 737–740.
- [32] D.S. Kim, S.-Y. Kwak, The hydrothermal synthesis of mesoporous TiO₂ with high crystallinity, thermal stability, large surface area, and enhanced photocatalytic activity, *Applied Catalysis A: General* 323 (2007) 110–118.
- [33] H. Yan, X.-H. Zhang, J.-M. Wu, L.-Q. Wei, X.-G. Liu, B.-S. Xu, The use of CTAB to improve the crystallinity and dispersibility of ultrafine magnesium hydroxide by hydrothermal route, *Powder Technology* 188 (2008) 128–132.
- [34] B. Bayati, A.A. Babaluo, R. Karimi, Hydrothermal synthesis of nanostructure NaA zeolite: the effect of synthesis parameters on zeolite seed size and crystallinity, *Journal of the European Ceramic Society* 28 (2008) 2653–2657.

- [35] T. Sugimoto, X. Zhou, A. Muramatsu, Synthesis of uniform anatase TiO₂ nanoparticles by gel–sol method. 4. Shape control, *Journal of Colloid and Interface Science* 259 (2003) 53–61.
- [36] H.M. Sung-Suh, J.R. Choi, H.J. Hah, S.M. Koo, Y.C. Bae, Comparison of Ag deposition effects on the photocatalytic activity of nanoparticulate TiO₂ under visible and UV light irradiation, *Journal of Photochemistry and Photobiology A: Chemistry* 163 (2004) 37–44.
- [37] J. Wang, H. Zhao, X. Liu, X. Li, P. Xu, X. Han, Formation of Ag nanoparticles on water-soluble anatase TiO₂ clusters and the activation of photocatalysis, *Catalysis Communications* 10 (2009) 1052–1056.