OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 6, June 2010, p. 803 – 807

# One-pot synthesis of uniform $TiO_2$ nanorods and monodisperse $TiO_2$ microspheres and their light scattering properties

HEQUAN WANG[a*], YONGCAI WANG[a,c], WENXIA ZHAO[b], CHAOLUN LIANG[b], YONG. LIU[c], HAI WANG[c] HAIBO LI[a]

[a]*Institute of Mechanical and Electrical Engineering, Shenyang Institute of Aeronautical Engineering, Shenyang 110136, China*

[b]*Instrumental Analysis and Research center, Sun Yat-sen University, Guangzhou 510275, China*

[c]*School of Physics and Engineering, Institute for Solar Energy Systems, State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-sen University, Guangzhou 510275, China*

The large-scale highly ordered $TiO_2$ nanorods and monodisperse $TiO_2$ microspheres were synthesized via a facile hydrothermal route. Under the same conditions, the $TiO_2$ nanorod arrays were directly obtained on the fluorine-doped tin oxide (FTO) substrate, while the monodisperse $TiO_2$ microspheres were obtained at the bottom of Teflon-lined autoclave without the FTO substrate. The as-prepared $TiO_2$ microspheres are found to be composed of radial single-crystal rutile $TiO_2$ nanorods. The FTO substrate plays a crucial role in the oriented growth of nanorod arrays. Accordingly, a possible mechanism for the formation of $TiO_2$ nanorod arrays and $TiO_2$ microspheres was proposed. The light scattering properties of $TiO_2$ nanorod arrays and $TiO_2$ microspheres were characterized by the UV-Vis spectrometry. The superior light scattering properties of $TiO_2$ microspheres makes them promising materials for applications in the solar cells.

(Received April 09, 2010; accepted June 16, 2010)

*Keywords*: Titanium oxide, Nanorods, Microsphere, Scattering properties

## 1. Introduction

As an important p-type versatile oxide semiconductor, titania has been widely utilized in photonic crystals [1, 2], photovoltaic cells [3, 4], photocatalysis [2, 5, 6], energy conversion and storage [7], and electrochemical sensing [8-11]. These practical applications of titania often varied considerably with its morphology and texture, tunable size, phase, as well as crystallographic orientation bearing specific functional characteristics. Recently, one-dimensional titania-based nanomaterials including nanowires [12-14] or nanorods [15], nanotubes [16-19], nanoflowers [20] and other hierarchical structures [21, 22], have gained considerable attention due to their promising applications in photovoltaic cells, such as dye-sensitized solar cells (DSSCs) [23-25], a promising alternative to silicon solar cells in the future. Among these one-dimensional $TiO_2$ nanomaterials, such as nanotubes and nanowires or nanorods have potential to increase the photovoltaic performance of DSSCs owing to their surface area for dye loading and reduced grain boundaries where charge recombination occurs [26].

To date, some light-scattering $TiO_2$ nanostructures have been reported in order to further improve the energy conversion efficiency of DSSCs [27]. These morphologies of $TiO_2$ nanostructures are often microspheres composed of many nanoparticles. Thus, these light scattering $TiO_2$ nanostructures not only have practical light scattering ability, but also have large surface area for dye adsorption. Compared with the nanoparticles, nanorods show superior electron transfer ability. Similar to composite $TiO_2$ microspheres made of nanoparticles, the synthesis of $TiO_2$ microspheres composed of nanorods were also been successfully prepared via a simple hydrothermal method [28, 29]. However, relatively few studies reported the synthesis and light scattering properties of $TiO_2$ microspheres by a nonpolar solvent/hydrophilic solid substrate interfacial reaction under hydrothermal conditions.

In this work, we report the synthesis of monodisperse $TiO_2$ microspheres via a nonpolar solvent/hydrophilic solid substrate interfacial reaction under mild hydrothermal conditions and investigate their light scattering properties. Additionally, the proposed method can also selectively prepare highly ordered rutile $TiO_2$ single-crystal nanorod arrays on fluorine-doped tin oxide (FTO) glass substrate.

## 2. Experimental section

### 2.1 Chemicals

Titanium Tetrabutoxide, HCl (wt37%) and Toluene were purchased from Guangzhou reagent Co., Ltd, China. Toluene was used as the nonpolar solvent (Shang Hai ShenXiang chemical Reagent CO . Ltd ). FTO glass was purchased from Nippon Sheet Glass Co., Ltd.

### 2.2 Synthesis of $TiO_2$ microspheres and $TiO_2$ nanorod arrays

The monodisperse $TiO_2$ microspheres were synthesized by the modified method for $TiO_2$ nanorods described in the literature [30]. In a typical synthesis, 2 mL of titanium tetrabutoxide, 0.5 mL of titanium tetrachloride, and 1 mL HCl (37wt%) were mixed with 10 mL of toluene. Then the resulting mixtures were sealed within a Teflon-lined stainless steel autoclave (50 mL) and heated at 150 for 20 h. After the reaction, the $TiO_2$ microspheres samples were obtained after centrifugation, washing with ethanol, and finally drying in air for further characterization. For the formation of $TiO_2$ nanorod arrays, a FTO substrate was placed against the wall of the autoclave with the conducting side facing down. Other synthesis conditions are the same as in the above described hydrothermal process.

### 2.3 Characterization

Powder X-ray diffraction (XRD; SHIMADZU XRD-6000) was used to determine the crystalline phase of $TiO_2$ microspheres and nanorods. The morphologies and dimensions of the as-synthesized $TiO_2$ microspheres and nanorods were observed by field-emission scanning electron microscopy (FESEM, LEO 1550 VP) equipped with EDS. TEM images and selected area electron diffraction (SAED) patterns of the resulting $TiO_2$ microspheres were obtained on a JEM-100 CX transmission electron microscope operating at 200 KV. To investigate the geometry influence on solar light scattering, diffuse reflection was measured in the 400-800 nm wavelength range on Model U-4100 spectrophotometer (HITACHI) with integrating sphere as accessory.

## 3. Results and discussion

### 3.1 Formation of $TiO_2$ nanorod arrays

Fig. 1 shows the typical SEM images of $TiO_2$ nanorod arrays on the FTO substrate. Fig. 1a and b are top-view images of $TiO_2$ nanorod arrays at low and high magnification, respectively. It can be seen that the $TiO_2$ nanorod arrays are highly uniform and densely packed with flat tetragonal crystallographic planes. Fig. 1c is a cross-sectional view of $TiO_2$ nanorod arrays.

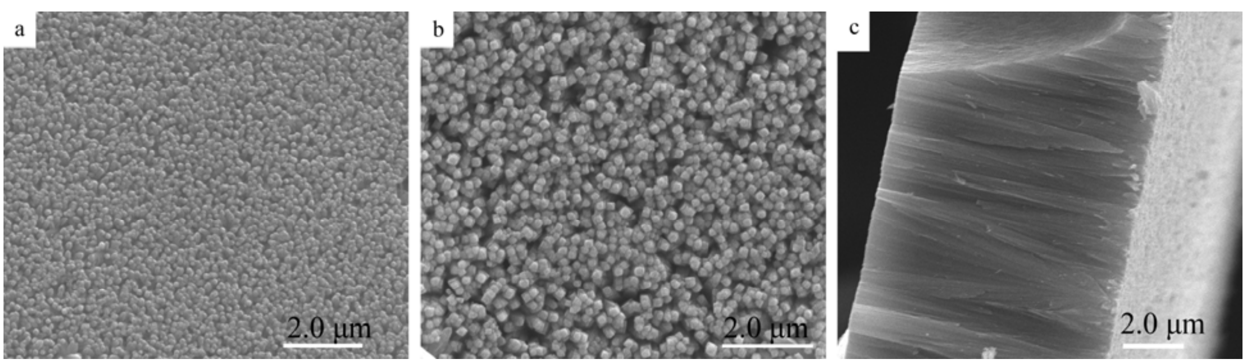


*Fig. 1. FESEM images of $TiO_2$ nanorod arrays on FTO coated glass at 150 ℃ for 20h. (a) top-view images at low magnification; (b) top-view images at high magnification; (c) cross-sectional FESEM image of the $TiO_2$ nanorods, mechanically peeled off the FTO coated glass.*

The diameter of the $TiO_2$ nanorods is ca. 20-30 nm and the thickness of $TiO_2$ film composed of nanorods is ca. 8 µm. The XRD pattern of the obtained nanorods is shown in Fig. 2. The XRD pattern shows that the $TiO_2$ nanorod deposited on FTO substrate has tetragonal rutile structure (JCPDS No.65-0191).

Compared to the powder diffraction pattern, the (002) diffraction is was significantly enhanced, showing that the $TiO_2$ nanorod arrays are well crystallized and grow perpendicularly to the FTO substrate.

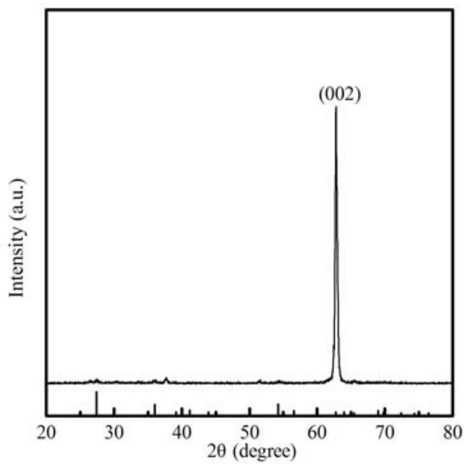


*Fig. 2. XRD pattern of $TiO_2$ nanorod arrays coated on FTO glass.*

### 3.2 Formation of $TiO_2$ microspheres

It is remarkable that large-scale uniform $TiO_2$ microspheres composed of many radial $TiO_2$ nanorods can be readily obtained at the bottom of the Teflon-lined autoclave without FTO substrate, as shown in Fig. 3.

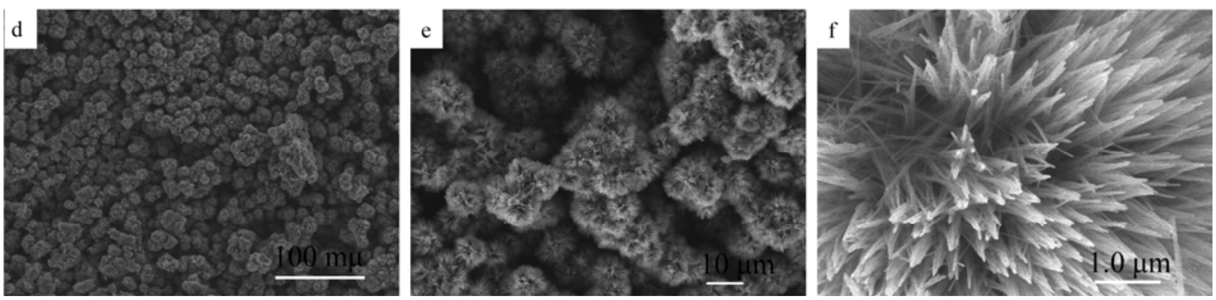


*Fig. 3. FESEM images of $TiO_2$ microspheres composed of nanorods 150 ℃ for 20 h. (a) top-view images at low magnification; (b) and (c) top-view images at high magnification.*

The corresponding XRD pattern points out that the $TiO_2$ microspheres has rutile structure (Fig. 4).

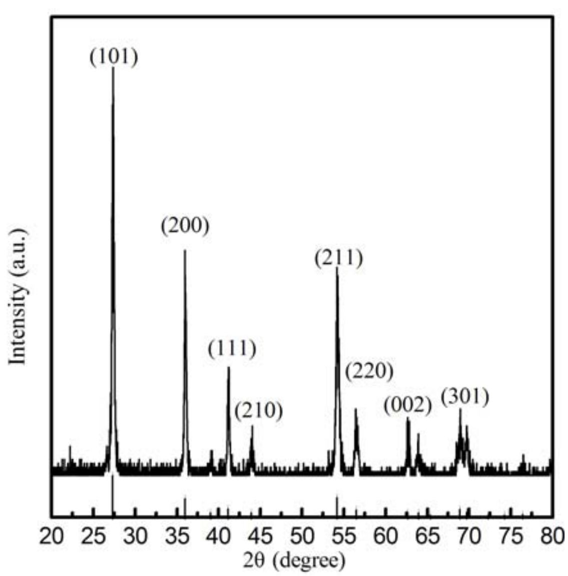


*Fig. 4. The corresponding XRD pattern of $TiO_2$ microspheres without FTO substrate.*

### 3.3 Possible mechanism for the formation of highly ordered $TiO_2$ nanorods and $TiO_2$ microspheres

On the basis of the above research results, we proposed a possible growth mechanism of $TiO_2$ nanorods with FTO substrate and $TiO_2$ microspheres without FTO substrate, as schematically shown in Fig. 5. In the presence of FTO substrate, at the beginning, $Ti^{4+}$ precursors can hydrolyze with water at the interface of water/FTO substrate, resulting in the formation of a nucleus. With the $Ti^{4+}$ precursor continuous hydrolysis, the nuclei finally grew into $TiO_2$ nanorod arrays on the FTO substrate. Here, it is important to mention that HCl in the solution has played a crucial role throughout the synthesis process. Firstly, the low pH value of the reaction solution delays the hydrolysis of $Ti^{4+}$ precursor with water. Secondly, a $Cl^-$ ion can selectively adsorb on different crystal planes, ensuring anisotropic growth in the [001] direction [31]. Compared to the FTO substrate, the interface of water/FTO substrate between the nuclei and substrate can not be formed without the FTO substrate. Therefore, the nuclei were randomly formed at the bottom of the Teflon-lined autoclave. With the continuous reaction, the nuclei grow into $TiO_2$ nanorods and finally formed $TiO_2$ microspheres.

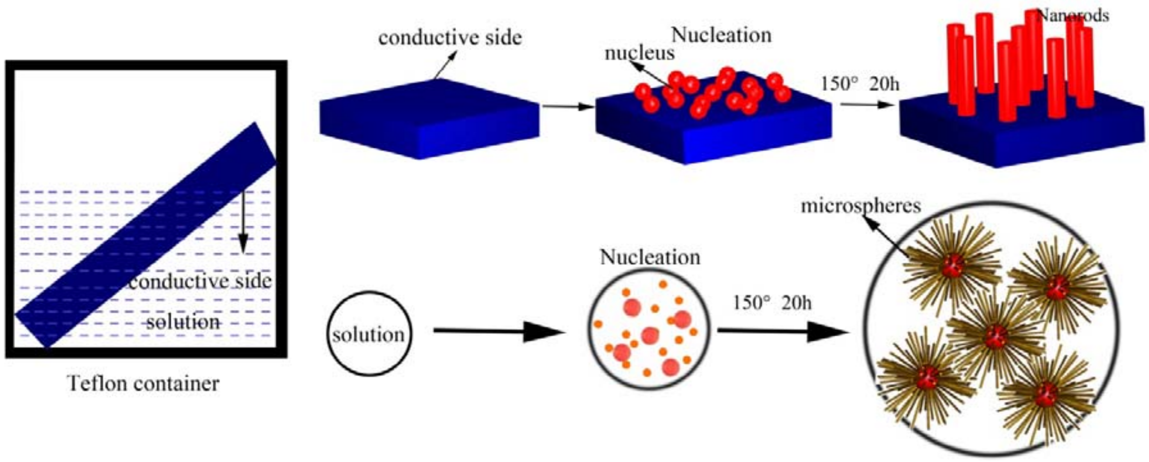


*Fig. 5. Schematic illustration of the formation of highly ordered $TiO_2$ nanorod arrays on the FTO substrate and uniform $TiO_2$ microspheres .*

### 3.4 Light scattering properties of $TiO_2$ nanorods and $TiO_2$ microspheres

To explore the potential application of $TiO_2$ nanomaterials, the light scattering properties of $TiO_2$ nanorods and microspheres were measured. Fig. 6 shows the UV-vis reflectance spectra of highly ordered $TiO_2$ nanorods and monodisperse $TiO_2$ microspheres. The reflectance of monodisperse $TiO_2$ microspheres is 39% in the wavelength range 400-800 nm, which is almost up to two times higher than that (22.0%) of highly ordered $TiO_2$ nanorods, indicating that the monodisperse $TiO_2$ microsphere have a higher light scattering properties than the highly ordered $TiO_2$ nanorods. The superior light scattering properties of monodisperse $TiO_2$ microspheres is expected to be applied dye-sensitized solar cells.

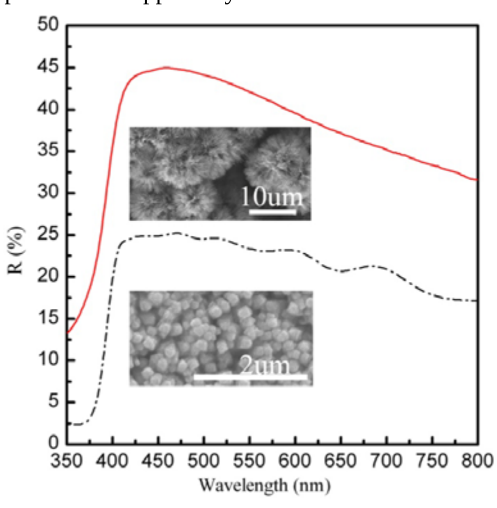


*Fig. 6. The UV-Vis reflectance spectra of highly ordered $TiO_2$ nanorods and monodisperse $TiO_2$ microspheres.*

## 4. Conclusions

In conclusion, a facile hydrothermal method was selectively developed to prepare $TiO_2$ microspheres without FTO substrates and highly ordered single-crystal rutile $TiO_2$ nanorods on FTO substrates. The diameters of the $TiO_2$ microspheres were around 6 μm, and the $TiO_2$ microspheres are built from small single-crystal nanorods with diameters of 20-30 nm. The FTO substrate is believed to play a crucial role in the synthesis of uniform $TiO_2$ microspheres. The small lattice mismatch between the $TiO_2$ nanorods and FTO substrate drives the nucleation and growth of the $TiO_2$ nanorods. More importantly, the experiments have demonstrated a strong improvement of light scattering by the $TiO_2$ microspheres thin films, providing promising applications as light-scattering layers in different types of nanostructured solar cells including organic, hybrid and dye-sensitized solar cells.

### Acknowledgements

The authors greatly acknowledge the support of the Natural Science Foundation Project of Liaoning Province (Grant No. 20072013) for this research.

## References

[1] Y. Z. Zheng, X. Tao, L. X. Wang, H. Xu, Q. Hou, W. L. Zhou , J. F. Chen, Chem Mater. **22**, 928(2010).
[2] G. Subramania, Y . J .Lee, A. J. Fischer, D. D. Koleske, Adv Mater. **22**, 487 (2010).
[3] Y. T. Lin, T. W. Zeng, W. Z. Lai, C. W. Chen, Y. Y. Lin, Y. S. Chang , W. F. Su, nanotechnology **17**, 5781 (2006).

[4] A. Kukrek, D. Wang, Y. Hou, R. Zong, R. Thummel, Inorg Chem. **45**, 10131 (2006).
[5] F. Di. Fonzo, C. S.Casari, V. Russo, A. L. Bassi, C. E. Bottani, Nanotechnology **20**, 1 (2009).
[6] T. Ochiai, K. Nakata, T. Murakami, A. Fujishima, Y. Y. Yao, D. A.Tryk , Y. Kubota, Water Res. **44**, 904 (2010).
[7] M. T. Brumbach, T. M. Alam, P. G., Kotula, B. B. McKenzie, B. C. Bunker, ACS Appl. Mater Interfaces **2**,778.
[8] I. Hanzu, T. Djenizian , P. Knauth , J Phys Chem **C113**, 20568 (2009).
[9] J. Y. Park, A. M.Azad, S. J. Song, E. D. Wachsman, J. Am. Ceram. Soc. **93**, 742 (2010).
[10] E. Topoglidis, C. J. Campbell, A. E. G. Cass, J. R. Durrant, Langmuir **17**,7899 (2001).
[11] H. P. Wu, T. L.Cheng, W. L.Tseng, Langmuir **23**, 7880 (2007).
[12] D. L. Morgan, H. W. Liu, R. L. Frost E. R. Waclawik, J. Phys. Chem. **C114**, 101 (2010).
[13] N. Fu, Y. Q.Wu, Z. L. Jin , G.. X. Lu, Langmuir **26**, 447 (2010).
[14] H. M. Zhang, P. R. Liu, H. J. Wang, H. Yu, S. Q. Zhang, H. Y. Zhu , H. J. Zhao, Langmuir **26**, 1574 (2010).
[15] T. A. Kandiel, R.Dillert, A. Feldhoff, D. W. Bahnemann, J. Phys. Chem. **C114**, 4909 (2010).
[16] Y. Liu, H. Wang, M. Li, R. J. Hong, Q. H. Ye, J. M. Zheng, H. Shen, Appl. Phys. Lett, Article **95**, 3 (2009).
[17] L. X. Yang, S. L. Luo, R. H. Liu, Q. Y. Cai, Y. Xiao, S. H. Liu, F. Su, L. F. Wen, J. Phys. Chem. **C114**, 4783 (2010).
[18] X. J. Feng, T. J. La Tempa, J. I. Basham, G.. K. Mor, O. K.Varghese, C. A. Grimes, Nano Lett. **10**, 948 (2010).
[19] Z. Y. Liu, M. Misra, Nanotechnology **21**, 2010.
[20] J. M. Wu, B. Qi, J. Phys. Chem. **C111**, 666 (2007).
[21] S. H. Zhou, Z. Ma, G. A. Baker, A. J. Rondinone, Q. Zhu, H. M. Luo, Z. L. Wu, S. Dai, Langmuir **25**, 7229 (2009).
[22] R. Ostermann, D. Li, Y. D.Yin, J. T. McCann, Y . N. Xia, Nano Lett. **6**, 1297(2006).
[23] C. Y. Lee, J. T. Hupp, Langmuir **26**, 3760 (2010).
[24] P. Wang, S. M. Zakeeruddin, J. E. Moser, T. Sekiguchi, M. Gratzel, Nat. Mater. **2**, 402 (2003).
[25] M. K. Wang, S. J. Moon, M. F. Xu, K. Chittibabu, P. Wang, N. L. Cevey-Ha, R. Humphry-Baker, S. M. Zakeeruddin, M. Gratzel, Small **6,** 319 (2010).
[26] M. Y. Song , Y. R. Ahn, S. M. Jo, D. Y. Kim, J. P. Ahn, Applied Physics Letters **87**, 113113 (2005).
[27] Hyung-Jun Koo, Yong Joo Kim, Yoon Hee Lee, Wan In Lee, Kyungkon KimNam-Gyu Park, Adv. Mater, **20**, 195 (2008).
[28] J. Q. Luo, L. Gao, Journal of Alloys and Compounds **487**, 763 (2009).
[29] Y. B. Zhang, X. J. Feng, L. Jiang, Sci China Ser B-Chem. **50**, 175 (2007).
[30] X. J. Feng , K. Shankar, O. K. Varghese, M. Paulose, T. J. Latempa , C. A. Grimes, Nano Lett. **8**, 3781 (2008).
[31] M. Adachi, Y. Murata, J .Takao, J. T. Jiu, M. Sakamoto, F. M. Wang , J. Am. Chem. Soc **126**, 14943 (2004).

*Corresponding author: neuwhq@163.com