DOI: 10.1002/chem.201000264

Sonochemical Preparation of Hierarchical ZnO Hollow Spheres for Efficient Dye-Sensitized Solar Cells

Chun-Xiu He,[a, b] Bing-Xin Lei,[a] Yu-Fen Wang,[a] Cheng-Yong Su,[a] Yue-Ping Fang,[b] and Dai-Bin Kuang*[a]

Abstract: Hierarchical ZnO hollow spheres (400–500 nm in diameter) consisting of ZnO nanoparticles with a diameter of approximately 15 nm have been successfully prepared by a facile and rapid sonochemical process. The formation of hierarchical ZnO hollow spheres is attributed to the oriented attachment and subsequent Ostwald ripening process according to time-dependent experiments. The as-prepared ZnO hollow spheres are used as a photoanode in dye-sensitized solar cells and exhibit a highly efficient power conversion efficiency of 4.33 %, with a short-circuit current density of 9.56 mA cm^{-2}, an open-circuit voltage of 730 mV, and a fill factor of 0.62 under AM 1.5 G one sun (100 mW cm^{-2}) illumination. Moreover, the photovoltaic performance (4.33 %) using the hierarchical ZnO hollow spheres is 38.8 % better than that of a ZnO nanoparticle photoelectrode (3.12 %), which is mainly attributed to the efficient light scattering for the former.

Keywords: dye-sensitized solar cells · hollow spheres · nanoparticles · sonochemistry · zinc oxide

Introduction

Recently, nanostructured hollow spheres have attracted considerable attention because of their low density, high surface area, and hollow geometrical shapes, which make them of interest in many potential applications such as lithium-ion batteries,[1,2] drug-delivery carriers,[3] and optoelectronic devices.[4] Among metal oxides, the wide band gap semiconductor ZnO with a hollow structure is of special interest owing to its various applications in light-emitting diodes,[5] piezo-nanogenerators,[6] sensors,[7,8] and catalysts.[9] Several approaches, such as the hard template method,[10] the template-free hydrothermal method,[11] thermal evaporation, and vapour–transport method[12] have been successfully reported for the fabrication of ZnO hollow spheres. However, all these reported methods need either high temperature, high pressure, or are time-consuming. Therefore, it is highly desirable to develop a simple and rapid synthesis method for the preparation of nanostructured hollow materials with controlled size and morphology.

Sonochemistry is a very interesting method for the synthesis of novel nanostructured materials.[13,14] The method is based on acoustic cavitation, namely the formation, growth, and implosive collapse of bubbles in a liquid. During cavitation, bubble collapse generates localized hot spots with transient high temperatures of about 5000 K, pressures of about 1800 atm, and heating and cooling rates in excess of 10^{10} K s^{-1}.[15,16] Herein, we report a controllable sonochemical route for the fabrication of hierarchical ZnO hollow spheres consisting of crystalline nanoparticles.

Recently, dye-sensitized solar cells (DSSCs) have been attracted tremendous scientific and industrial interest owing to their low cost and respectable photovoltaic performance.[17] ZnO is an important photoanode material in the applications of DSSCs because of its wide band gap (3.37 eV) and high electron mobility (115–155 cm^2 V^{-1} s^{-1}). Hierarchical bifunctional TiO_2 or ZnO submicron spheres comprising nanoparticles have been successfully prepared and exhibit superior photovoltaic performance in DSSCs applications.[18–20] However, so far, no hollow ZnO spheres have been applied in DSSCs. Hierarchical hollow spheres consisting of nanoparticles possess both dye adsorption properties (10–20 nm particles) and light scattering effects (hollow sphere: a few hundreds of nanometers in size),

---

[a] C.-X. He, B.-X. Lei, Y.-F. Wang, C.-Y. Su, D.-B. Kuang
MOE Key Laboratory of Bioinorganic and Synthetic Chemistry
State Key Laboratory of Optoelectronic Materials and Technologies
School of Chemistry and Chemical Engineering
Sun Yat-Sen University, Guangzhou 510275 (P. R. China)
Fax: (+86) 20-84113015
E-mail: kuangdb@mail.sysu.edu.cn

[b] C.-X. He, Y.-P. Fang
School of Chemistry and Chemical Engineering
Guangxi Normal University, Guilin 541004 (P. R. China)

which might be an ideal structure for the enhancement of the photovoltaic performance in DSSCs. Therefore, herein we report for the first time the fabrication of ZnO hollow spheres (400–500 nm in size) consisting of nanoparticles (ca. 15 nm in size) by a facile sonochemical method and investigate their photovoltaic performance in DSSCs.

Hierarchical ZnO hollow spheres were synthesized by irradiating a solution containing $Zn(CH_3COO)_2$ (1.098 g), dimethyl sulfoxide (DMSO, 47.5 mL), and water (2.5 mL) with a high-intensity ultrasound horn (Shanghai shengxi. Co., China, FS-300, 1 cm diameter; Ti-horn, 20 kHz, 300 $W cm^{-2}$). The main advantages of the present synthesis procedure are that it is simple, rapid (<1 h), and template-free, can be carried out at low temperature, and thus has a low energy cost, and displays excellent reproducibility. The as-prepared ZnO hollow spheres were characterized in detail by using XRD, SEM, TEM, and the possible growth mechanism of the hollow spheres was proposed. DSSCs based on the as-prepared ZnO hollow spheres and commercial ruthenium dye (N719) exhibit a power conversion efficiency of 4.33 % under simulated AM 1.5 G one sun illumination.

Results and Discussion

Characterization of ZnO hollow spheres: Figure 1 shows the X-ray powder diffraction (XRD) patterns of as-prepared products after ultrasound irradiation for different periods of time; the patterns reveal crystalline ZnO with a wurtzite (JCPDS No. 36-1451) structure. The size of ZnO nanocrystals prepared, as estimated from the full width at half maximum of the (100) peak using the Debye–Scherrer equation, was 10–15 nm.

The morphology of the as-prepared products was characterized by SEM and TEM. Figure 2 a shows the SEM image of the ZnO sample prepared by ultrasound irradiation for 30 min; uniform spheres (400–500 nm in diameter) with a hollow structure are clearly visible. The high-magnification SEM image (inset in Figure 2 a) indicates that the hollow ZnO spheres are composed of nanoparticles that are about 15 nm in diameter, which is agreement with the above XRD results. The hollow structure was further characterized by TEM (Figure 2 b); the center portion of the sphere is lighter than the edge, clearly confirming the hollow interiors of the unique ZnO spheres. The TEM image of a single hollow ZnO sphere confirms that the shell is composed of ZnO nanoparticles approximately 15 nm in particle size (Figure 2 c). The corresponding high-resolution TEM (HRTEM) image (Figure 2 d) clearly shows that the lattice fringe distance is about 0.28 nm, which coincides with the (110) planes of ZnO in the wurtzite phase. The fast Fourier-transform patterns (inset in Figure 2 d) of the ZnO nanoparticles reveal the single-crystal nature. It is worth noting that the hierarchical hollow ZnO spheres consisting of single-crystalline nanoparticles were easily obtained by the present mild and rapid sonochemical route without high temperature, high pressure, or a template.

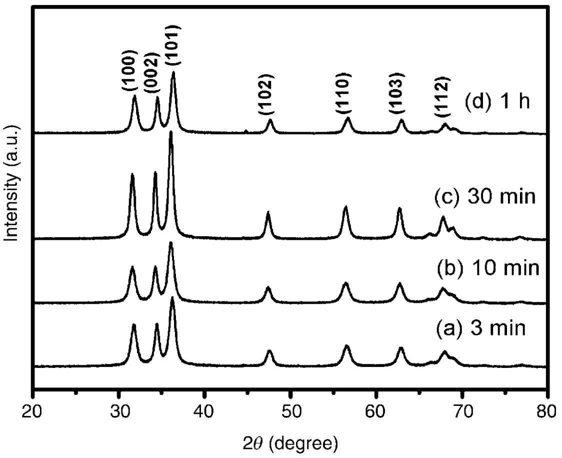


Figure 1. XRD patterns of ZnO samples prepared by ultrasound irradiation for 3 min (a), 10 min (b), 30 min (c), 60 min (d).

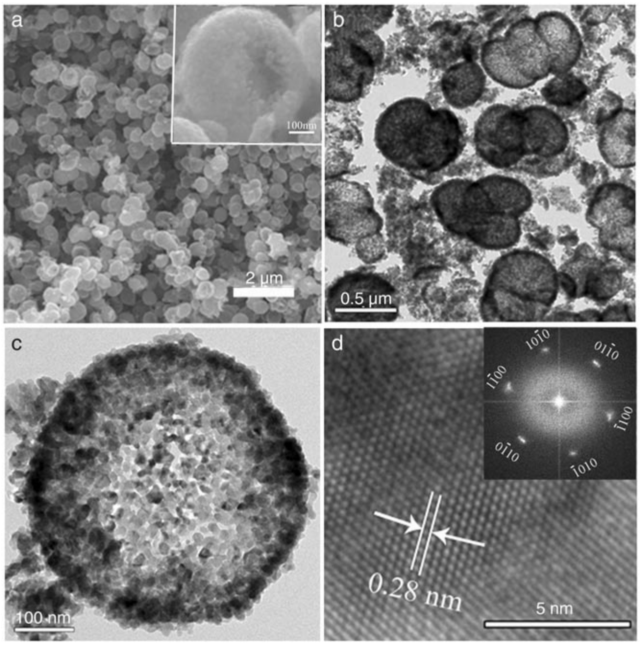


Figure 2. SEM (a) and TEM images (b–d) of hierarchical ZnO hollow spheres prepared after ultrasound irradiation for 30 min. See text for details.

To investigate the growth process of the hierarchical ZnO hollow spheres, time-dependent experiments were performed and the SEM images are shown in Figure 3. Hierarchical ZnO solid spheres (200-250 nm) consisting of nanoparticles approximately 10 nm in diameter (SEM images, Figure 3 a, b) were obtained for an ultrasound irradiation time of 3 min; this was confirmed in the TEM images (inset in Figure 3 b). When the ultrasound irradiation time was prolonged to 10 min (Figure 3 c, d), the ZnO solid spheres became hollow spheres, and the diameter of ZnO hollow spheres and nanoparticles increased to 400–500 nm and approximately 15 nm, respectively. Increasing the period of ultrasound irradiation to 30 min (see Figures 2a and b) and

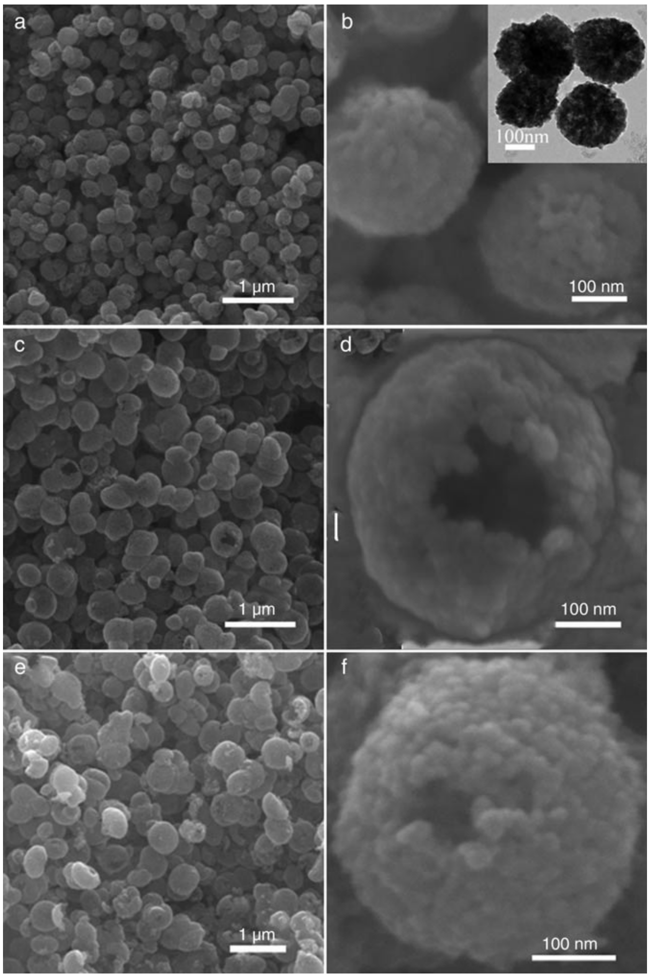
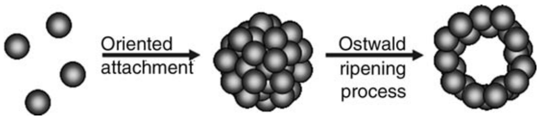


Figure 3. SEM images of the as-prepared ZnO samples prepared after ultrasound irradiation for 3 min (a, b), 10 min (c, d), and 60 min (e, f). Inset in Figure 3b is the TEM image.

then to 60 min (see Figure 3e and f), did not lead to a further increase in the size of the ZnO hollow spheres or the nanoparticles.

According to the SEM observations, a possible growth process for the ZnO hollow spheres is illustrated in Scheme 1. DMSO is a weak basic nonvolatile organic solvent and that can slowly release OH^- ions during the ultrasound irradiation; these ions react with Zn^{2+} to form ZnO nanoparticles. At the beginning of the ultrasound irradiation, the local high temperature results in the nucleation and the subsequent growth of ZnO to form nanoparticles. The ZnO nanoparticles preferentially aggregate and self-assemble into metastable spheres by the well known growth mechanism of "oriented attachment" to minimize the total surface energy.[21] On prolonging the ultrasound irradiation (from 10 min to 1 h), the metastable ZnO spheres consisting of nanoparticles adopt a hollow structure at the expense of small nanoparticles by an Ostwald ripening process.[22] The proposed formation process of ZnO hollow spheres was verified by SEM and TEM observations. Moreover, to our knowledge, this is the first report on the sonochemical synthesis of hierarchical hollow ZnO spheres consisting of nanoparticles of 10–15 nm in diameter.



Scheme 1. Schematic presentation of the formation of hierarchical ZnO hollow spheres during the sonochemical process.

Photovoltaic performance: Recently, hierarchical TiO_2 or ZnO solid spheres have shown improved power conversion efficiency in photovoltaic devices.[18–20] However, there are no reports of ZnO hollow spheres being used for DSSC applications. Herein, the as-prepared hierarchical ZnO hollow spheres consisting of nanoparticles were further used as photoanode in DSSCs. Figure 4a shows typical current density versus voltage curves of DSSCs based on different thicknesses of hierarchical ZnO hollow spheres, which were illuminated under AM 1.5 G simulated sunlight with a power density of $100\,mW\,cm^{-2}$. The detailed photovoltaic parameters such as the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), and the overall energy conversion efficiencies (η) for the cells are summarized in Table 1. As shown in Figure 4 and Table 1, the photovoltaic parameters of the DSSCs are largely dependent on the film thickness. The J_{sc} increases from $6.90\,mA\,cm^{-2}$ to $9.56\,mA\,cm^{-2}$ as the film thickness increases from 4.4 μm to 9.1 μm, and then decreases to $7.77\,mA\,cm^{-2}$ as film thickness further to 18.1 μm. Similar results were also observed for DSSCs based on TiO_2 nanoparticle films of different thicknesses.[23] The open-circuit voltage decreases with the increasing film thickness from 4.4 to 18.1 μm, which can be attributed to the larger amounts of defects and recombination for thicker films.[23] The fill factor only changes very slightly between 0.61 and 0.64 for different film thicknesses. Finally, the highest photovoltaic performance can be obtained for

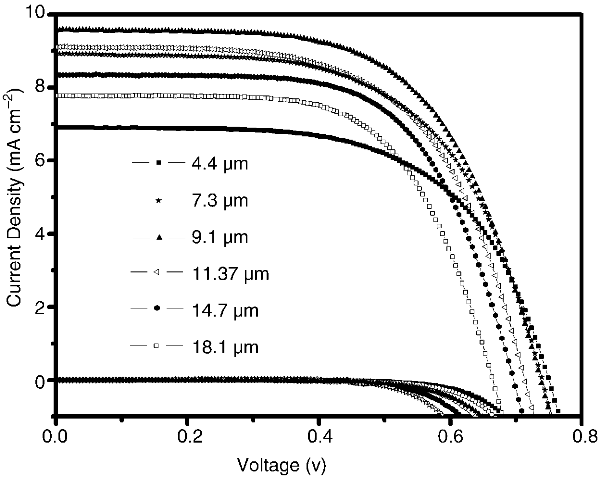


Figure 4. Current–voltage curves of DSSCs based on hierarchical ZnO hollow spheres as a function of film thicknesses under AM 1.5 G one sun ($100\,mW\,cm^{-2}$) illumination.

Table 1. Detailed photovoltaic parameters of solar cells based on hierarchical ZnO hollow spheres with different thicknesses under AM 1.5 G one sun (100 mW cm^{-2}) illumination.

Film thickness [μm]	V_{oc} [mV]	J_{sc} [mA cm^{-2}]	*FF*	η [%]
4.4	750	6.90	0.61	3.16
7.3	740	8.93	0.62	4.12
9.1	730	9.56	0.62	4.33
11.4	710	9.11	0.63	4.1
14.7	690	8.79	0.64	3.86
18.1	660	7.77	0.64	3.27
9.0[a]	650	7.82	0.61	3.12

[a] DSSC based on a ZnO nanoparticle (15 nm) film with a film thickness of 9.0 μm.

the hierarchical ZnO hollow sphere film with a thickness of 9.1 μm; the associated values of J_{sc}, V_{oc}, *FF*, and η are 9.56 mA cm^{-2}, 730 mV, 0.62, and 4.33 %, respectively.

For comparison, ZnO nanoparticles of 15 nm were also synthesized based on a modified method, and these were used as photoanode for DSSC applications. As shown in Table 1, a current density of 7.82 mA cm^{-2}, an open-circuit voltage of 650 mV, and a power conversion of 3.12 % were achieved for the DSSCs based on a 9.0 μm thick ZnO nanoparticle film. Hence, the photovoltaic performance (4.33 %) for the hierarchical ZnO hollow spheres is 38.8 % better than that of the photoelectrode based on nanoparticles (3.12 %). It is well known that the amounts of adsorbed dye on ZnO photoelectrodes significantly influence the photocurrent and hence the power conversion efficiency. Here, the amounts of dyes adsorbed on the ZnO films were obtained by measuring the UV/Vis absorption spectra of solutions containing dyes detached from the ZnO film in H_2O (3 mL) with 0.1 M NaOH. It was found that the amount of dye (9.78×10^{-8} mol cm^{-2}) adsorbed on the photoelectrode based on ZnO nanoparticles is higher than that of the hierarchical ZnO hollow spheres (6.81×10^{-8} mol cm^{-2}). Hence, the lower photocurrent and power conversion efficiency for the ZnO nanoparticles compared to the hierarchical ZnO hollow spheres can probably be attributed to the efficient light scattering effect of the latter.[24] Since the size of the ZnO hollow spheres is comparable to the wavelength of visible light, it potentially has excellent light scattering, and is further characterized by the UV/Vis diffuse reflectance spectra. Figure 5 presents the UV/Vis diffuse reflectance spectra of hierarchical ZnO hollow spheres and ZnO nanoparticle films with and without dye adsorption. As shown in Figure 5 a, for the bare ZnO films (without dye adsorption), the reflectance of films of hierarchical ZnO hollow spheres is much higher than that of films of ZnO nanoparticles, revealing the former has a higher light-scattering ability than the latter, which is in agreement with previous results.[19,20] Furthermore, for the dye/ZnO film, the reflectance of the two kinds of films decreases at short wavelengths (400–600 nm) due to the light absorption by the dye molecules. The dye-adsorbed hierarchical ZnO hollow sphere films show a higher reflectance than the dye-adsorbed ZnO nanoparticle films in the long wavelength region (600–800 nm) because of the light scattering from submicron spheres. Hence, the reason why DSSCs based on hierarchical ZnO hollow spheres exhibit superior photocurrent and photovoltaic performance compared to the ZnO nanoparticle films, is mainly attributed to the efficient light scattering for the former.

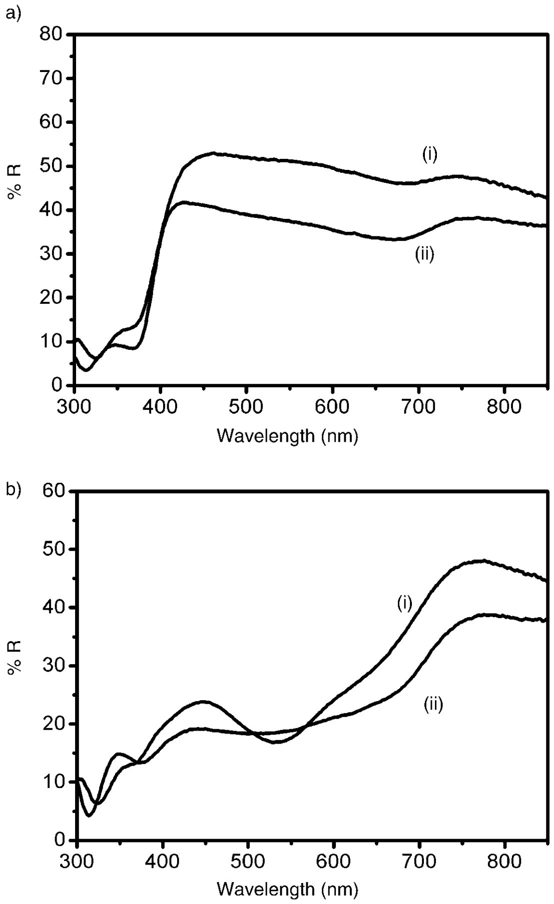


Figure 5. Diffuse reflectance spectra of the hierarchical ZnO hollow spheres film (i) and ZnO nanoparticle films (ii) without (a) and with adsorbed N719 dye (b).

Conclusion

In summary, we have developed a rapid sonochemical route for the fabrication of hierarchical ZnO hollow spheres (400–500 nm in diameter) consisting of approximately 15 nm nanoparticles. According to SEM observations of samples irradiated with a high-intensity ultrasound horn for different periods, the growth mechanism of ZnO hollow spheres can be attributed to oriented attachment followed by an Ostwald ripening process. Dye-sensitized solar cells based on photoanode materials from the prepared hierarchical ZnO hollow spheres exhibit a power conversion efficiency of 4.33 %, with a short-circuit current density of 9.56 mA cm^{-2}, an open-circuit voltage of 730 mV, and a fill factor of 0.62.

Superior photocurrent and power conversion efficiency for the hierarchical ZnO hollow spheres compared to the ZnO nanoparticles is a consequence of better light scattering for the former, which is confirmed by the UV/Vis reflectance spectra.

Experimental Section

Materials: All reagents used were of analytical purity and were used without further purification. $Zn(CH_3COO_2)\cdot 2H_2O$ and dimethyl sulfoxide (DMSO) were purchased from Tianjin Chemical Reagents Ltd. Co. of China. *cis*-Bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) bis-tetrabutylammonium (N719 dye) was obtained from Solaronix. Acetonitrile (99.6 %) and *tert*-butyl alcohol (>99 %) were purchased from Sigma–Aldrich.

Fabrication of hierarchical ZnO hollow spheres: $Zn(CH_3COO_2)\cdot 2H_2O$ (1.098 g, 0.005 mol) was dissolved in a DMSO–water mixture (47.5 mL : 2.5 mL) with stirring. This gave a clear solution at room temperature. The solution was exposed to high-intensity ultrasound irradiation for 30 min using 8 s pulses with a 2 s interval between the pulses. Ultrasound irradiation was performed using a high-intensity ultrasonic probe (Shanghaishengxi. Co., China, FS-300, 1 cm diameter; Ti-horn, 20 kHz, 300 $W\,cm^{-2}$) immersed in the reaction solution. ZnO products were collected by centrifugation, thoroughly washed with water and ethanol in sequence, and finally dried in air at 60 °C. The final products were collected for characterization.

Synthesis of ZnO nanoparticles: The synthesis of ZnO nanoparticles (15 nm in size) was performed according to method described in reference [25]. In brief, $Zn(CH_3COO_2)\cdot 2H_2O$ (0.1 $mol\,L^{-1}$) and lithium hydroxide monohydrate ($LiOH\cdot H_2O$, 0.14 $mol\,L^{-1}$) were dissolved in ethanol (500 mL) under vigorous stirring at room temperature. After ultrasonic treatment of the mixture for approximately 10 min, distilled water (10 mL) was added and the solution was stirred for 30 min at 60 °C. Then the ZnO nanoparticles were collected and annealed at 300 °C for 1 h. TEM images revealed the ZnO nanoparticles were approximately 15 nm in size (data not shown).

Characterization: The surface morphologies of the as-prepared ZnO hollow spheres were observed by thermal field emission environment scanning electron microscopy (FE-SEM, FEI, Quanta 400), and transmission electron microscopy (TEM, JEM-2010HR). The compositions and structures of the products were analyzed by X-ray diffraction (XRD, D8 ADVANCE X-ray diffractometer, $Cu_{K\alpha}$ radiation $\lambda = 0.15418$ nm) with a scanning rate of $10°\,min^{-1}$ in the 2θ range from 20 to 80°. The thickness of the ZnO films was measured by using a profilometer (Ambios, XP-1).

Fabrication of devices: To prepare the working electrode of the dye-sensitized solar cells, ethyl cellulose and terpineol were added to a solution of the ZnO spheres in ethanol. After about 30 min a viscous paste was obtained, then the resulting slurry was coated on an FTO glass (2.3 mm, 15 Ω/square, Nippon Sheet Glass, Japan) using a screen-printing method. The ZnO film thickness is dependent on the repeating times of the screen printing process. The deposited ZnO film was heated at 500 °C for 3 h. After heat treatment, the ZnO film was immersed in a 0.5 mM N719 dye solution in ethanol, and kept for 2 h at room temperature. Pt counter electrodes were prepared on the FTO glasses by using a 5 mM H_2PtCl_6 solution in 2-propanol, followed by heating at 400 °C for 15 min in air. The electrolyte solution is composed of 0.6 M PMII, 0.03 M I_2, 0.05 M LiI, 0.1 M guanidinium thiocyanate (GuSCN), and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile and valeronitrile (85:15 v/v). The active area of dye-coated ZnO film was 0.15 cm^2. The current–voltage characteristics were measured by using a Keithley 2400 source meter under simulated AM 1.5 G one sun (100 $mW\,cm^{-2}$) illumination provided by a solar simulator (69920, 1 kW Xe with an optical filter, Oriel). And the light intensity was adjusted with a NREL-cabibrated Si solar cell. To measure the amount of dye adsorbed on the ZnO film, the dye/ZnO film was immersed in a 0.1 M NaOH aqueous solution (3 mL) and UV/Vis absorption spectra of the desorbed-dye solution were measured by using a UV-vis-NIR spectrophotometer (UV-3150).

Acknowledgements

We thank the Natural Science Foundations of China (Grant Nos. 20873183, U0934003), the Natural Science Foundations of Guangdong Province (Grant Nos. 8151027501000030) and the Sun Yat-Sen University for financial support.

[1] H. M. Liu, Y. G. Wang, K. X. Wang, E. Hosono, H. S. Zhou, *J. Mater. Chem.* **2009**, *19*, 2835.

[2] W. M. Zhang, J. S. Hu, Y. G. Guo, S. F. Zheng, L. S. Zhong, W. G. Song, L. J. Wan, *Adv. Mater.* **2008**, *20*, 1160.

[3] J. H. Park, S. Y. Jung, R. Kim, N. G. Park, J. Kim, S. S. Lee, *J. Power Sources* **2009**, *194*, 574.

[4] H. J. Koo, Y. J. Kim, Y. H. Lee, W. I. Lee, K. Kim, N. G. Park, *Adv. Mater.* **2008**, *20*, 195.

[5] H. H. Guo, Z. H. Lin, Z. F. Feng, L. L. Lin, J. Z. Zhou, *J. Phys. Chem. C* **2009**, *113*, 12546.

[6] Y. Xi, J. H. Song, S. Xu, R. S. Yang, Z. Y. Gao, C. G. Hu, Z. L. Wang, *J. Mater. Chem.* **2009**, *19*, 9260.

[7] H. Zhang, J. B. Wu, C. X. Zhai, N. Du, X. Y. Ma, D. Yang, *Nanotechnology* **2007**, *18*, 455604.

[8] X. Hu, J. Gong, L. Zhang, J. C. Yu, *Adv. Mater.* **2008**, *20*, 4845.

[9] H. B. Zeng, W. P. Cai, P. S. Liu, X. X. Xu, H. J. Zhou, C. Klingshirn, H. Kalt, *Acs Nano* **2008**, *2*, 1661.

[10] Z. W. Deng, M. Chen, G. X. Gu, L. M. Wu, *J. Phys. Chem. B* **2008**, *112*, 16.

[11] Z. Q. Li, Y. Xie, Y. J. Xiong, R. Zhang, *New J. Chem.* **2003**, *27*, 1518.

[12] Z. J. Gu, M. P. Paranthaman, J. Xu, Z. W. Pan, *Acs Nano* **2009**, *3*, 273.

[13] S. Bhattacharyya, A. Gedanken, *Microporous Mesoporous Mater.* **2008**, *110*, 553.

[14] H. S. Park, B. G. Choi, S. H. Yang, W. H. Shin, J. K. Kang, D. Jung, W. H. Hong, *Small* **2009**, *5*, 1754.

[15] K. S. Suslick, *Science* **1990**, *247*, 1439.

[16] E. B. Flint, K. S. Suslick, *Science* **1991**, *253*, 1397.

[17] B. O′Regan, M. Gratzel, *Nature* **1991**, *353*, 737.

[18] Y. J. Kim, M. H. Lee, H. J. Kim, G. Lim, Y. S. Choi, N. G. Park, K. Kim, W. I. Lee, *Adv. Mater.* **2009**, *21*, 3668.

[19] T. P. Chou, Q. F. Zhang, G. E. Fryxell, G. Z. Cao, *Adv. Mater.* **2007**, *19*, 2588.

[20] Q. F. Zhang, T. P. Chou, B. Russo, S. A. Jenekhe, G. Cao, *Adv. Funct. Mater.* **2008**, *18*, 1654.

[21] R. L. Penn, J. F. Banfield, *Science* **1998**, *281*, 969.

[22] J. Li, H. C. Zeng, *J. Am. Chem. Soc.* **2007**, *129*, 15839.

[23] D. B. Kuang, S. Ito, B. Wenger, C. Klein, J. E. Moser, R. Humphry-Baker, S. M. Zakeeruddin, M. Gratzel, *J. Am. Chem. Soc.* **2006**, *128*, 4146.

[24] Q. F. Zhang, T. R. Chou, B. Russo, S. A. Jenekhe, G. Z. Cao, *Angew. Chem.* **2004**, *116*, 6056; *Angew. Chem. Int. Ed.* **2004**, *43*, 5930.

[25] H. H. Wang, C. S. Xie, *J. Phys. Chem. Solids* **2008**, *69*, 2440.

Received: January 30, 2010