Photochemical preparation of CdS hollow microspheres at room temperature and their use in visible-light photocatalysis

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ARTICLE INFO

ABSTRACT

CdS hollow microspheres have been successfully prepared by a photochemical preparation technology at room temperature, using polystyrene latex particles as templates, $CdSO_4$ as cadmium source and $Na_2S_2O_3$ as both sulphur source and photo-initiator. The process involved the deposition of CdS nanoparticles on the surface of polystyrene latex particles under the irradiation of an 8 W UV lamp and the subsequent removal of the latex particles by dispersing in dichloromethane. Photochemical reactions at the sphere/solution interface should be responsible for the formation of hollow spheres. The as-prepared products were characterized by X-ray diffraction, transmission electron microscopy and scanning electron microscopy. Such hollow spheres could be used in photocatalysis and showed high photocatalytic activities in photodegradation of methyl blue (MB) in the presence of H_2O_2. The method is green, simple, universal and can be extended to prepare other sulphide and oxide hollow spheres.

1. Introduction

Cadmium sulfide (CdS), an important semiconductor with a band gap of 2.42 eV at room temperature, has attracted considerable interest in photocatalysis [1–3], light-emitting diodes [4], solar cells [5], and some other optoelectronic applications [6,7]. In order to be more suitable applications or acquire the enhanced properties, many CdS micro- or nanostructures with different morphologies have been synthesized and applied [8–10]. CdS hollow microspheres, as an important microstructure for many areas of technology [11], have been studied by some groups. They could be fabricated by template-free methods involving employments of surfactants [12], hydrothermal treatments [1,13], long-time aging [14] and treatments in vacuum [15]. The crystalline phase, shell thickness and chemical compositions of the final phase could not be easily controlled. Although the removal of the template core by calcinations or solvent dissolution could lead to the formation of defects and the cracking of hollow spheres, giving opened and truncated spherical voids, the template strategy remains the only way to generate hollow spheres with easy control of shell thickness, crystalline phase and diameter. Miniemulsion droplets [16,17], $EO_{20}PO_{70}EO_{20}$ (P123) [18], chitosan [19], poly-(styrene–acrylic acid) latex spheres [20,21] and hollow latex cage [22] have ever been used as templates to fabricate CdS hollow spheres. However, most of them need special treatments at certain temperature, composition designs of precursors or modifications of latex spheres. Preparation of hollow spheres in a simple precursor solution at room temperature remains a challenge.

Herein, we introduce a new photochemical route to synthesize CdS hollow microspheres. Over the past few years, ultraviolet (UV) light irradiation techniques have emerged as a green [16] and effective way of controlling the morphology of noble metals and some semiconductors at room temperature, such as gold [23,24], silver [25], CdS [26–28], CdSe [29], HgS [30] and SnO_2 [31], etc. But no any report on the photochemical preparation of hollow microspheres has been found. In this paper, taking polystyrene latex spheres without any modification as templates, and $CdSO_4$ and $Na_2S_2O_3$ solution as precursor, CdS hollow microspheres could be formed under the irradiation of UV light at the room temperature. Interestingly, the as-prepared CdS hollow microspheres showed high photocatalytic activities in photodegradation of MB in the presence of H_2O_2 under the irradiation of UV–visible light.

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2. Experimental

2.1. Preparation of CdS hollow microspheres

In a typical synthesis, as shown in Scheme 1, 100 ml solution composed of 0.0125 M $CdSO_4$ and 0.075 M $Na_2S_2O_3$ in a beaker was used as precursor. And then 1 g polystyrene latex spheres (PSs) prepared in our laboratory [32] were put into it to be used as templates. Subsequently, the beaker was placed under a tube-type UV lamp (Philips, 245 nm, 8 W, 0.734 mW cm^{-2}) (Scheme 1a) in a box. The solution containing the latex spheres was kept stirring. PSs were suspended in the solution (Scheme 1b). When the lamp was turned on, photochemical reactions preferably occurred at the surface of PSs in the solution (Scheme 1c). Twenty four hours later, yellow particles had formed inside the solution. The particles were collected by a centrifugal separator and washed 3–5 times with deionized water, and then coated on the glass. Finally, the glass was immersed in dichloromethane to remove the polystyrene latex spheres and CdS hollow microspheres were hence obtained (Scheme 1d).

2.2. Characterization

After washed drastically more than five times in a centrifugal machine, the compositions and the phase structures were investigated by the X-ray powder diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). Morphologies and sizes of the samples were characterized by the scanning electron microscope (SEM) (JSM-6330F). For further insight into the microstructure of the samples, transmission electron microscope (TEM) and high resolution transmission electron microscope HRTEM (JEM-2010HR) observations were employed.

2.3. Photocatalysis

The photocatalytic degradation of MB was carried out in an aqueous solution at ambient temperature. Briefly, 0.01 g of CdS hollow microspheres and 1 ml 3% H_2O_2 was dispersed in 100 ml of 3×10^{-5} mol/l MB solution. The mixture was put into a beaker with magnetic stirring. A 150 W halogen tungsten lamp was used for the visible light source. It was put a side of the beaker with a distance of 20 cm. Of about 5 ml solution were then taken out every 20 min and centrifuged immediately to separate any suspended solid. The transparent solution was analyzed by a UV–vis spectrometer, and the absorbance was measured at a wavelength of 665 nm, corresponding to the maximum absorption. The absorbance of the target is proportional to its concentration in the solution. To record the real photocatalytic activity of catalyst, the measured solution and the centrifuged particles were

poured back into the original beaker to maintain a consistent total amount of an MB in the solution.

3. Results and discussion

Fig. 1a shows the SEM images of the PS spheres. Although they have a wide size distribution (1.2–2.5 μm), they can still be used as templates to prepare the hollow microspheres. The PS spheres were chosen as the templates, because the spheres could be easily prepared with a photo-initiated dispersion polymerization process at room temperature, as we reported before [32]. In addition, the PS spheres were easily and quickly to be removed by dichloromethane. Obviously, such choice could effectively simplify the fabrication procedure. Other polymer microspheres were not easily fabricated at room temperature or a careful design must be employed. Silica spheres can also be used as templates, but they must be removed by HF or heated NaOH solution. CdS would be dissolved in HF solution [33]. When NaOH solution was employed [34], it must be heated (usually at 60 °C) and a long time (about 24 h) soaking was required. The morphologies of sulfides or oxides would be destroyed more or less.

After the mixture of PSs and precursor solution was irradiated 24 h by the UV lamp, the product could be collected and washed fully for further characterization. Fig. 1b shows the XRD pattern of the obtained yellow particles. Two characteristic peaks appear at 26.53° and 43.95°, which correspond to the (1 1 1) and (2 2 0) crystal faces of CdS (JCPDS no. 75-1546), respectively. SEM image (Fig. 1c) shows the product is composed of CdS hollow microspheres with diameters of 1.50–3.0 μm. Such size distribution was caused by the polystyrene spheres used as templates. The SEM image of the broken microspheres shows their hollow features (see Fig. 1d). The walls of the hollow spheres are composed of nanoparticles with sizes of $\sim$80 nm and the wall thickness is also around 80 nm.

TEM and HRTEM images are shown in Fig. 2. The hollow structure with a wall thickness of $\sim$80 nm can be clearly discerned (Fig. 2a and b). The aggregated nanoparticles in the walls form many pores. A HRTEM image of a region of the square seal (Fig. 2b) is shown in Fig. 2c. The lattice fringe allows identification of the crystallographic spacing of CdS. According to the Fourier transform of the full image (inset of Fig. 2c), nearly all fringe distances calculated are $d = 0.34$ nm, matching the (1 1 1) crystallographic plane of CdS. The adjacent fringes with the same orientation constitute nanoclusters, and different CdS nanoclusters are closely connected to each other. This further reveals that the wall of the hollow sphere is almost entirely composed of polycrystalline CdS. The polycrystalline character would result in the weak intensity of X-ray diffraction peaks (Fig. 1b) and the production of voids in the CdS nanoparticles.
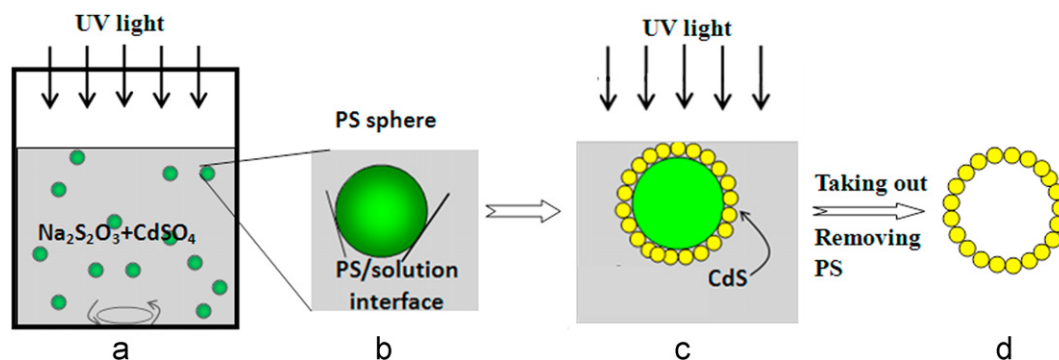
Scheme 1. Photochemical route for preparation of CdS hollow microspheres using PS spheres as templates. (a) UV light irradiates the precursor solution containing PS spheres; (b) state of a PS sphere before the photochemical reaction occurs; (c) formation of a CdS/PS composite microsphere; and (d) CdS hollow microsphere.
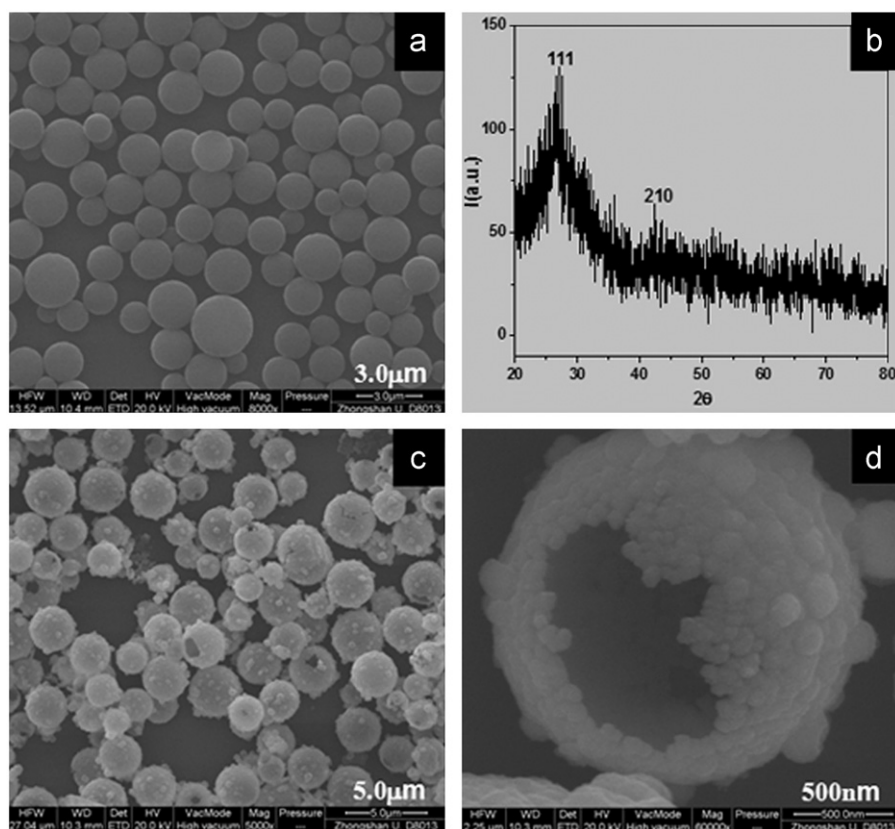
Fig. 1. (a) SEM image of PS spheres used as templates; (b) XRD pattern of CdS hollow microspheres; (c) SEM image of CdS hollow microspheres; and (d) an amplified SEM image of a CdS hollow microsphere.
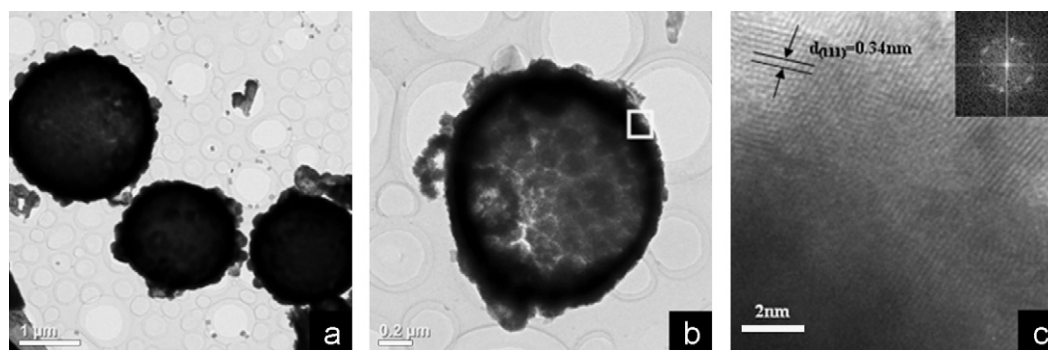

Fig. 2. (a) TEM image of the CdS hollow microspheres; (b) an amplified TEM image; and (c) HRTEM image of the rectangle region in (b).
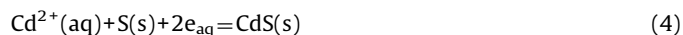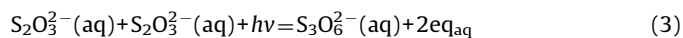
Fig. 3 shows the N$_2$ adsorption–desorption isotherm and the pore-size distribution (inset) of CdS hollow microspheres. The isotherm is identified as type IV, which is characteristic of mesoporous materials. Brunauer–Emmett–Teller (BET) specific surface area of the sample is about 4.34 m^2 g^{-1}, calculated from N$_2$ isotherms at −196.6 °C. The pore-size distribution obtained from the isotherm indicates most of the nanopores in the sample are smaller than 20.0 nm. Some pores should be formed by the aggregation of nanoparticles in the walls of hollow spheres and the others (smaller than 5.0 nm) might derive from the natural void existing in the polycrystalline nanoparticles.

We propose a mechanism for the formation of CdS hollow microspheres. When UV irradiates the precursor, a series of photochemical reactions would occur at the interface as follows.

S$_2$O$_3^{2-}$ ions were used as the source of sulfur, because they can adsorb photons and dissociate to provide sulfur under the irradiation [35]

$$S_2O_3^{2-}(aq)+h\nu=S(s)+S_2O_3^{2-}(aq) \tag{1}$$
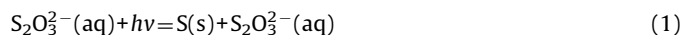
S$_2$O$_3^{2-}$ ions also provide aquated electrons, which then reacts with Cd^{2+} to form CdS:

$$2S_2O_3^{2-}(aq)+h\nu=S_4O_6^{2-}(aq)+2eq_{aq} \tag{2}$$

$$S_2O_3^{2-}(aq)+S_2O_3^{2-}(aq)+h\nu=S_3O_6^{2-}(aq)+2eq_{aq} \tag{3}$$

$$Cd^{2+}(aq)+S(s)+2e_{aq}=CdS(s) \tag{4}$$

Though the reduction potential of S(s) ($E_{S/S^{2-}}^{\Theta}=-0.445V$ vs. SHE) is lower than zero, the aquated electrons is a powerful
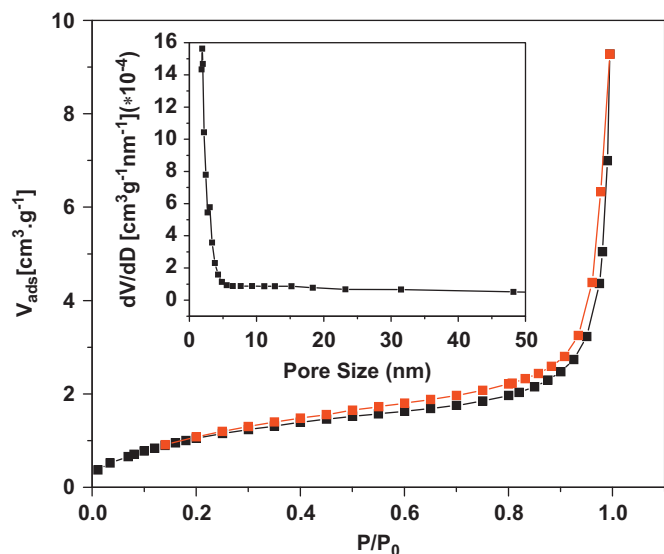
Fig. 3. Nitrogen adsorption–desorption isotherm and pore-size distribution (inset) plot for the CdS hollow microspheres.

reductant [36] and it can still lead to the reaction (4) occurred. For the same reason, Cd^{2+} ($E^{\Theta}_{Cd^{2+}/Cd} = -0.4022 V$ vs. SHE) can also be directly reduced to metallic cadmium at the same time

$$Cd^{2+}(aq) + 2e_{aq} = Cd(s) \qquad (5)$$

And then, the S(s) would react with metallic cadmium

$$S(s) + Cd(s) = CdS(s) \qquad (6)$$

Gibbs free energy, $\Delta_r G^{\Theta}_m$, of reaction (6) can be calculated as

$$\Delta_r G^{\Theta}_m = -440.70 - 0.15T(kJ\,mol^{-1}) < 0$$

Obviously, it is a thermodynamically favored reaction. Therefore, CdS could form by the two mechanisms (reactions (4) and (6)).

In general, crystal nuclei form preferentially in interfaces, for example solid/solution interface and gas/solution interface [28,37]. There would form a solid/solution interface when PS spheres were put into the precursor solution, as shown in Scheme 1b. When irradiated by the UV light, CdS nuclei would be concentrated on the surface of polystyrene latex spheres, according to Eqs. (4) and (6) (Scheme 1c). If the rate of formation of crystal nuclei is suitably high, nuclei could be homogenously deposited on the surface of polystyrene latex spheres (Scheme 1d). Each nucleus absorbs the corresponding ions and grows gradually. Finally, a shell composed of small particles was formed around the polystyrene latex spheres in the solution. After the photochemical reaction was finished, the product was washed by dichloromethane in order to remove polystyrene spheres templates and obtain the CdS hollow microspheres.

To demonstrate the potential applicability of the present CdS hollow microspheres in photocatalysis, we investigated its visible-light photocatalytic activity in photodegradation of MB. The characteristic absorption of MB at 665 nm was chosen as the monitored parameter for the photocatalytic degradation process. A 150 W halogen tungsten lamp was used as the light source for degradation of 100 ml 3×10^{-5} mol/l MB solution. As shown in Fig. 4, when CdS hollow spheres alone were used as the catalyst, the degradation efficiency only reached 38.2% in 3 h. To improve the efficiency, 1 ml 3% H_2O_2 was added into the MB solution. When the mixed solution containing CdS hollow spheres was kept in dark, 16.8% MB molecular could disappear because of the adsorption of CdS. Under the irradiation of the halogen tungsten
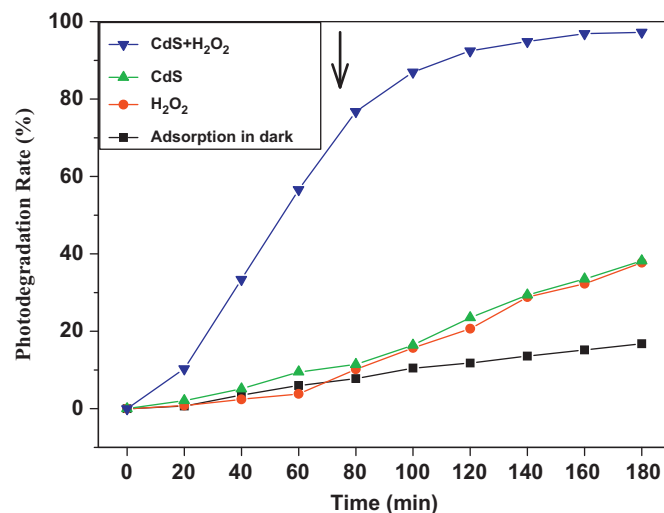

Fig. 4. The photocatalytic performance of CdS hollow microspheres irradiated by a 150 W halogen tungsten lamp for degrading MB solution.

lamp, the degradation efficiency could be sharply increased to 97.3%, while the mixed solution without CdS only reached to 37.7%. Obviously, CdS hollow microspheres possess higher photocatalytic activities in the presence of H_2O_2. The enhancement could be explained that the H_2O_2 acted as an electron acceptor [38] under the irradiation of visible light to lower the electron–hole recombination, and hence increase the efficiency of hole utilization for photocatalytic oxidation of the MB molecular. In addition, the CdS hollow microspheres could be used in photodegradation of other organic pollutants.

4. Conclusion

In summary, we have developed a novel photochemical route to prepared CdS hollow microspheres at room temperature, using polystyrene latex spheres as templates and low-power UV light as light source. These hollow microspheres exhibited high visible-light photocatalytic activities in photodegradation of MB in the presence of H_2O_2. This method is universal and offers a new route for the preparation of hollow spheres. ZnS, CuS, SnO_2 and Cu_2O hollow spheres could also have been prepared by the method. These structured materials might be effectively used in some optoelectron-related fields, for example photocatalytic and photovoltaic devices.

References

[1] G.F. Lin, J.W. Zheng, R. Xu, J. Phys. Chem. C 112 (2008) 7363–7370.
[2] X. Zong, H.J. Yan, G.P. Wu, G.J. Ma, F.Y. Wen, L. Wang, C. Li, J. Am. Chem. Soc. 130 (2008) 7176–7177.
[3] H.B. Yin, Y. Wada, T. Kitamura, S. Yanagida, Environ. Sci. Technol. 35 (2001) 227–231.
[4] J.S. Steckel, J.P. Zimmer, S. Coe-Sullivan, N.E. Stott, V. Bulovic, M.G. Bawendi, Angew. Chem.—Int. Ed. 43 (2004) 2154–2158.
[5] A. Aguilera, V. Jayaraman, S. Sanagapalli, R.S. Singh, V. Jayaraman, K. Sampson, V.P. Singh, Sol. Energy Mater. Sol. Cells 90 (2006) 713–726.
[6] K.J. Wu, K.C. Chu, C.Y. Chao, Y.F. Chen, C.W. Lai, C.C. Kang, C.Y. Chen, P.T. Chou, Nano Lett. 7 (2007) 1908–1913.

[7] B.L. Cao, Y. Jiang, C. Wang, W.H. Wang, L.Z. Wang, M. Niu, W.J. Zhang, Y.Q. Li, S.T. Lee, Adv. Funct. Mater. 17 (2007) 1501–1506.

[8] Y.D. Li, H.W. Liao, Y. Ding, Y.T. Qian, L. Yang, G.E. Zhou, Chem. Mater. 10 (1998) 2301–2303.

[9] F. Gao, Q.Y. Lu, S.H. Xie, D.Y. Zhao, Adv. Mater. 14 (2002) 1537.

[10] J.H. Warner, S. Djouahra, R.D. Tilley, Nanotechnology 17 (2006) 3035–3038.

[11] X.W. Lou, L.A. Archer, Z.C. Yang, Adv. Mater. 20 (2008) 3987–4019.

[12] Z.H. Dai, J. Zhang, J.C. Bao, X.H. Huang, X.Y. Mo, J. Mater. Chem. (2007) 1087–1093.

[13] X.P. Li, Y.A Gao, L. Yu, L.Q. Zheng, J. Solid State Chem. 183 (2010) 1423–1432.

[14] M.W. Shao, D.B. Wang, B. Hu, G.H. Yu, Y.T. Qian, J. Cryst. Growth 249 (2003) 549–552.

[15] X.C. Jiang, Y. Xie, J. Lu, L.Y. Zhu, W. He, X.M. Liu, Can. J. Chem. 80 (2002) 263–268.

[16] W. Lu, M. Chen, L.M. Wu, J. Colloid Interface Sci. 324 (2008) 220–224.

[17] J.X. Huang, Y. Xie, B. Li, Y. Liu, Y.T. Qian, S.Y. Zhang, Adv. Mater. 11 (2000) 808–811.

[18] Y.R. Ma, L.M. Qi, J.M. Ma, H.M. Cheng, W. Shen, Langmuir 19 (2003) 9079–9085.

[19] S.M. Wang, Q.S. Wang, Q.L. Wan, J. Cryst. Growth 310 (2008) 2439–2443.

[20] C.X. Song, G.H. Gu, Y.S. Lin, H. Wang, Y. Guo, X. Fu, Z.S. Hu, Mater. Res. Bull. 38 (2003) 917–924.

[21] X. Fu, L. Lin, D.B. Wang, Z.S. Hu, C.X. Song, Colloids Surf. A: Physicochem. Eng. Aspects 262 (2005) 216–219.

[22] M. Yang, J. Ma, Z. Niu, X. Dong, H. Xu, Z. Meng, Z. Jin, Y. Lu, Z. Hu, Z. Yang, Adv. Funct. Mater. 15 (2005) 1523–1528.

[23] A. Housni, M. Ahmed, S.Y. Liu, R. Narain, J. Phys. Chem. C 112 (2008) 12282–12290.

[24] F. Kim, J.H. Song, P.D. Yang, J Am. Chem. Soc. 124 (2002) 14316–14317.

[25] B. Pietrobon, V. Kitaev, Chem. Mater. 20 (2008) 5186–5190.

[26] S. Kundu, H. Liang, Adv. Mater. 20 (2006) 826–830.

[27] M. Marandi, N. Taghavinia, A.I. Zad, S.M. Mahdavi, Nanotechnology 16 (2005) 334–338.

[28] Y.Y. Huang, F.Q. Sun, H.J. Wang, Y. He, L.S. Li, Z.X. Huang, Q.S. Wu, J.C. Yu, J. Mater. Chem. 19 (2009) 6901–6906.

[29] W.B. Zhao, J.J. Zhu, H.Y. Chen, Scr. Mater. 50 (2004) 1169–1173.

[30] T. Ren, S. Xu, W.B. Zhao, J.J. Zhu, J. Photochem. Photobiol. A—Chem. 173 (2005) 93–98.

[31] H.J. Wang, F.Q. Sun, Y. Zhang, L.S. Li, H.Y. Chen, Q.S. Wu, J.C. Yu, J. Mater. Chem. 20 (2010) 5641–5645.

[32] Z.X. Huang, F.Q. Sun, S.H. Liang, H.J. Wang, G. Shi, L.J. Tao, J.X. Tan, Macromol. Chem. Phys. 211 (2010) 1868–1878.

[33] J.E.G.J. Wijnhoven, S.J.M. Zevenhuizen, M.A. Hendriks, D. Vanmaekelbergh, J.J. Kelly, W.L. Vos, Adv. Mater. 12 (2000) 888–890.

[34] S. Kuai, S. Badilescu, R. Bruning, X.F. Hu, V.V. Truong, Adv. Mater. 15 (2003) 73–75.

[35] L. Dogliotti, E. Hayon, J. Phys. Chem. 72 (1968) 1800–1807.

[36] J. Butler, A. Henglein, Radiat. Phys. Chem. 15 (1980) 603–612.

[37] F.Q. Sun, J.C. Yu, Angew. Chem. Int. Ed. 46 (2007) 773–777.

[38] P.X. Lei, C.C. Chen, J. Yang, W.H. Ma, J.C. Zhao, L. Zang, Environ. Sci. Technol. 39 (2005) 8466–8474.