

Preparation of mesoporous cadmium sulfide nanoparticles with moderate pore size

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Received 3 October 2006; received in revised form 11 December 2006; accepted 18 December 2006

Available online 27 December 2006

Abstract

The preparation of cadmium sulfide nanoparticles that have a moderate pore size is reported. This preparation method involves a hydrothermal process that produces a precursor mixture and a following acid treatment of the precursor to get the porous material. The majority of the particles have a pore size close to 20 nm, which complements and fills in the gap between the existing cadmium sulfide materials, which usually have a pore size either less than 10 nm or are well above 100 nm.

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Keywords: Cadmium sulfide; Semiconductor; Mesoporous materials; Hydrothermal process

1. Introduction

II–VI semiconductor nanomaterials are important for optoelectronic applications as light-emitting diodes and transistors [1–4], and for photocatalytic applications that may employ visible light as a radiation source [5–7]. Because the properties and applications of the materials are dependent upon microstructures of the materials, many attempts have been made to prepare the materials in different morphologies and structures, such as nanorods and nanowires [8–10]. Typically, for the II–VI semiconductor CdS, it has been made into matrix materials in form of nanometer particles and even sub-nanometer pillars [11], or coated by another agent [12], so yielded composite materials of the metal sulfide.

Porous materials are important owing to their large surface area and special interfacial properties. The preparation of CdS with porous features has become a special research interest. For instance, CdS film with an ordering

nanohole array structure was produced by a two-step replication process using porous Al₂O₃ as a template, the average size of the holes was 200 nm [13]. Mesoporous CdS was produced using porous SBA-15 silica as a template; the average pore size was about 3.7 nm [14]. Furthermore, pearl-necklace porous CdS nanofibers were fabricated using organogelator as a template [15], the pore size, which was not specified in the literature, but measured a few nanometers on the images presented. The CdS materials with porous features have also been prepared using some soft templates. For instance, mesoporous CdS was produced in the presence of lyotropic liquid crystal as the template, the pore size of the CdS was 2–3 nm [16,17]. Similar mesoporous CdS was produced using hexagonal liquid crystal as the template, having a slightly larger pore size, which was 7–8 nm [18]. It is noted that the pore size of such CdS material is either as large as hundreds of nanometers, or as small as less than 10 nm, which leaves a wide gap between the pore sizes of available mesoporous CdS materials. In addition, the previous preparation of porous CdS has usually employed a special ordering template, either a hard one or a soft one, at the beginning of the preparation. Recently, porous CdS aerogel with a pore size of 19–20 nm was prepared by a strategy that

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involves oxidative aggregation of metal chalcogenide nanoparticle building blocks followed by supercritical solvent removal [19]. In this paper, we report a different preparation method, which does not use a template at beginning of the preparation, rather, a sacrificial template is involved during the preparation, to produce CdS nanoparticles with a similar moderate pore size, which further fills in the gap between those achieved by the previous preparation.

2. Experimental

The reactants to the CdS material include ZnCl_2 , $\text{NaHS} \cdot x\text{H}_2\text{O}$, NaOH , and CdCl_2 , which are all analytical reagents. In the preparation, 20 mmol ZnCl_2 , 30 mmol $\text{NaHS} \cdot x\text{H}_2\text{O}$ and 30 mmol NaOH was dissolved in deionized water, without adding any template to the solution. Mixing the above chemicals in 80 ml deionized water lead to a white solid suspension immediately. After 11.6 mmol CdCl_2 was added into the suspension and stirred for 1 h at ambient temperature, a yellowish solid was generated. The solid was then separated, half of which was desiccated by natural evaporation, and the rest was dispersed into 60 ml deionized water and transferred to a 80-ml autoclave, heated in an oven at 150°C for 4 h. The autoclaved solid was soaked in 25 ml 2 M HCl solution under ultrasonic condition below 60°C , which produced a red-yellow solid finally. The solid was washed by deionized water repeatedly and desiccated by natural evaporation.

The solid samples were identified by X-ray diffraction (XRD), conducted on a Shimadzu XRD-6000 diffractometer, the X-ray wavelength was 1.5418 \AA . Transmission electron microscopy (TEM) of the particles was carried out on a Philips CM 12 electron microscope operating at an accelerating voltage of 120 kV; energy dispersive X-ray spectroscopy (EDXS) of typical samples was carried out on the same electron microscope. Nitrogen adsorption/desorption isotherms of representative samples were obtained on a Quantachrome Autosorb-1 surface area and pore size analyser; the samples were degassed at 120°C overnight prior to measurement. UV–Visible absorption spectra of typical sample were recorded on a Varian Cary 5E UV–Vis–NIR spectrophotometer, where barium sulfate was used as a reference.

3. Results and discussion

The yellowish solid produced from the reactants at room temperature is composed of both crystalline and amorphous components. As shown in Fig. 1a, there are no diffraction peaks of metal sulfide, the sharp diffraction peaks refer to $\text{Zn}_5(\text{OH})_5\text{Cl}_2 \cdot \text{H}_2\text{O}$ crystals, whereas the blunt hump in the range of $25\text{--}30^\circ$ refers to amorphous species, presumably some metal sulfides. After the powders were treated by a hydrothermal process at 150°C , $\text{Zn}_5(\text{OH})_5\text{Cl}_2 \cdot \text{H}_2\text{O}$ became almost disappeared while ZnO crystals were produced, indicated in Fig. 1b. The

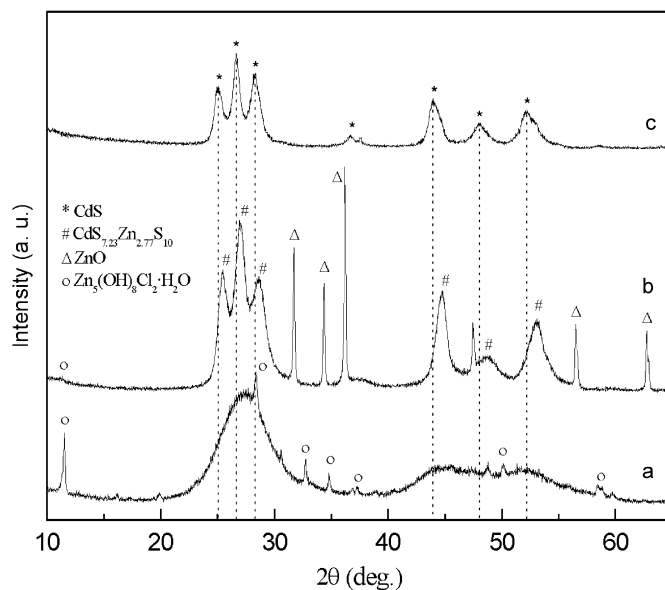


Fig. 1. XRD patterns of the solids produced (a) at room temperature, (b) after autoclaved but not acid-soaked, and (c) after autoclaved and acid-soaked.

conversion from $\text{Zn}_5(\text{OH})_5\text{Cl}_2 \cdot \text{H}_2\text{O}$ to ZnO is demonstrated by the experiment that refluxing the solution of $\text{Zn}_5(\text{OH})_5\text{Cl}_2 \cdot \text{H}_2\text{O}$ at 120°C produced ZnO [20]. Meanwhile, the amorphous phase disappeared, instead, $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ crystals were produced. The calculated lattice parameters for $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ are $a = 4.053$, and $c = 6.621 \text{ \AA}$. These data are close to those reported in literature, where $a = 4.042$, and $c = 6.588 \text{ \AA}$ (JCPDS PDF-2 Database #40-836). Because the main diffraction peaks of $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ are in the same angle range to that of the amorphous phase in Fig. 1a, it is believed that the amorphous phase is just $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$, nevertheless it became well crystallized during the hydrothermal process. After the powders composed of $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$, ZnO and $\text{Zn}_5(\text{OH})_5\text{Cl}_2 \cdot \text{H}_2\text{O}$ were soaked in dilute hydrochloric acid, the ZnO and $\text{Zn}_5(\text{OH})_5\text{Cl}_2 \cdot \text{H}_2\text{O}$ was dissolved in the acid solution. Moreover, $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ was transformed to CdS, demonstrated by Fig. 1c. The calculated lattice parameters for the sample are $a = 4.117$, and $c = 6.702 \text{ \AA}$, also close to the reported data of hexagonal CdS, where $a = 4.140$, and $c = 6.719 \text{ \AA}$ (JCPDS PDF-2 Database #41-1049).

Notably, the calculated lattice parameters of CdS are slightly but systematically larger than those of $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$. It is known that a cadmium cation has a larger radius than a zinc cation, when the $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ is transformed into CdS, the lattice parameters will become larger, and accordingly, the diffractions peaks shift to lower angles. The dashed lines plotted in Fig. 1 highlight the shift, which is still recognizable, although the total shift is not significant. Seen from a different angle, the differences in the peak positions between the samples shown in Fig. 1b and c unambiguously demonstrate a

phase change, which in this case represents the change from $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ to CdS.

A hydrothermal process conducted at a moderate temperature (above 120 °C) helps to improve the crystallinity of the metal sulfide, which could be produced in amorphous form at room temperature. Fig. 2a shows EDXS of the sample produced at room temperature without being autoclaved and acid-soaked. It demonstrates that there are Cd, Zn and S in the sample, besides Cu that is ascribed to the copper grid used to support the sample. This further demonstrates that the metal sulfide, $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$, is formed at room temperature although in an amorphous form. After the autoclaved sample was washed by dilute acid, zinc components were almost removed, nevertheless some of the zinc still retained in

the final product, as revealed by Fig. 2b. Ideally the zinc components should be completely removed from the samples by the acid washing. In practice, however, some aggregated large particles could prevent the acid from accessing all the zinc components, as a consequence, traces of zinc could be contained in the final powders. The residue of zinc species in the sample is insignificant and/or amorphous, hence not detected by XRD in Fig. 1c. The traces of Zn in the final product may also explain why the calculated lattice parameters of the produced CdS are slightly smaller than the data for the pure CdS reported in literature. In addition, EDXS of the CdS samples revealed traces of Cl, which could be ascribed to the chloride reactants and the washing agent hydrochloric acid. Traces of Cl could be trapped in the samples and not thoroughly removed after washing by deionized water.

Because the reaction between CdCl_2 and the white solid produced from ZnCl_2 , $\text{NaHS} \cdot x\text{H}_2\text{O}$ and NaOH at room temperature is a liquid–solid reaction, the $\text{Cd}_{7.23}\text{Zn}_{2.7}\text{S}_{10}$ would only be formed on the surface of the solid during the hydrothermal process, thus, $\text{Zn}_5(\text{OH})_5\text{Cl}_2 \cdot \text{H}_2\text{O} / \text{Cd}_{7.23}\text{Zn}_{2.7}\text{S}_{10}$ and $\text{ZnO} / \text{Cd}_{7.23}\text{Zn}_{2.7}\text{S}_{10}$ core-shell structures could be formed. When the powders was washed by dilute acid, $\text{Zn}_5(\text{OH})_5\text{Cl}_2 \cdot \text{H}_2\text{O}$ and ZnO would be removed by the acid. Meanwhile, the zinc component in the $\text{Cd}_{7.23}\text{Zn}_{2.7}\text{S}_{10}$ would also be removed. As a consequence, the remainder would be CdS shells or frames, in other words, the final product would be porous CdS. In this work the leaching of the readily dissolvable components from the powders to produce porous metal sulfide is analogous to the selective leaching of a sacrificial phase from dense bulk composites to prepare porous transition metal oxide materials [21].

The porosity of the CdS was demonstrated by SEM images shown in Fig. 3. The CdS nanoparticles look aggregated and foam-like, the contrast between the edge and the inner part of the particles reveals there are many voids, and the CdS nanoparticles are apparently porous. Pore sizes of the particles are measured from TEM images of the sample, the histogram showing the pore size distribution is also included in Fig. 3. The size of the pores ranges from 5 to 36 nm, but for the majority of the particles, the pore size is around 18 nm. This pore size is moderate and therefore distinctive to the similar porous CdS materials which are usually either within 10 nm or well above 100 nm.

To further investigate porous textures of the CdS, this sample was characterized by nitrogen sorption. Fig. 4 plots isotherms of the sample. It shows that the material is predominantly mesoporous. Calculation from isotherm data gives these quantitative features of the mesoporous CdS: the specific surface area is $46 \text{ m}^2/\text{g}$; the total pore volume is $0.22 \text{ cm}^3/\text{g}$, and the average pore size is 19 nm. BJH pore size distribution of the CdS material is worked out from the desorption data, which is plotted as an inset in Fig. 4. It appears that the BJH pore size distribution is much narrower than the pore size distribution established

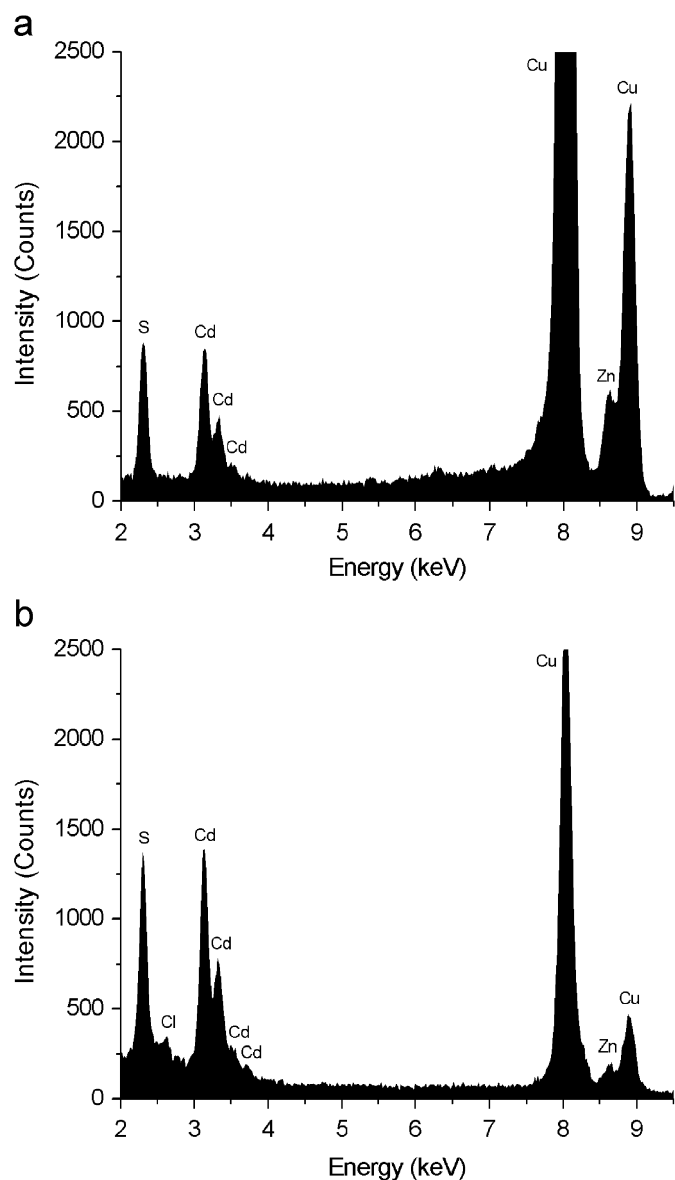


Fig. 2. EDXS of the samples obtained at room temperature without being autoclaved and acid washed (top), and obtained after being autoclaved and acid-washed (bottom).

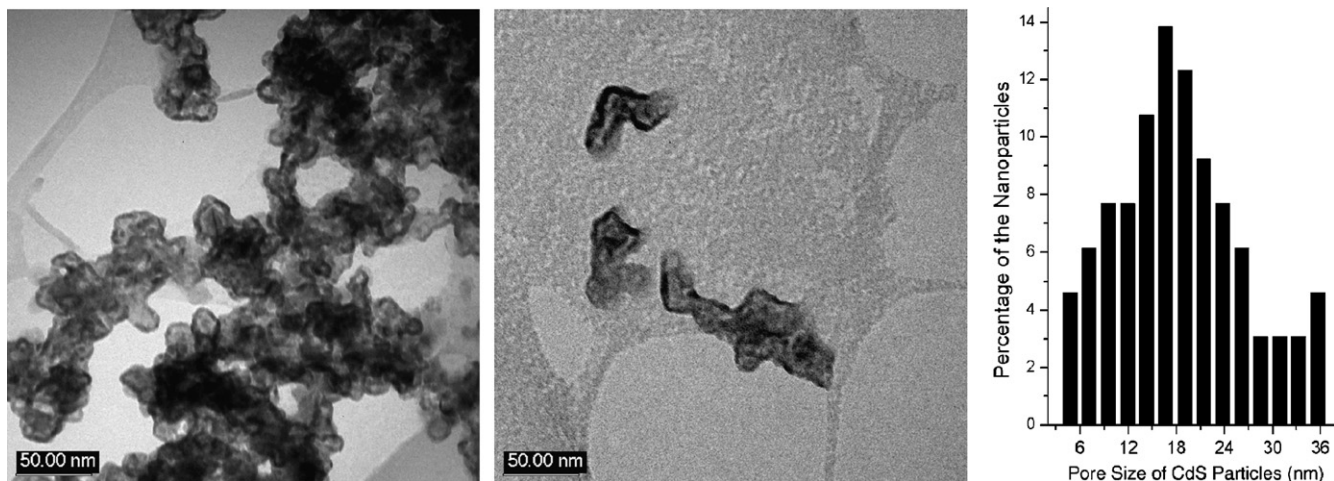


Fig. 3. TEM images of some typical CdS nanoparticles (left and middle) showing a mesoporous feature, and pore size distribution of the mesoporous nanoparticles based on the data measured from TEM images (right).

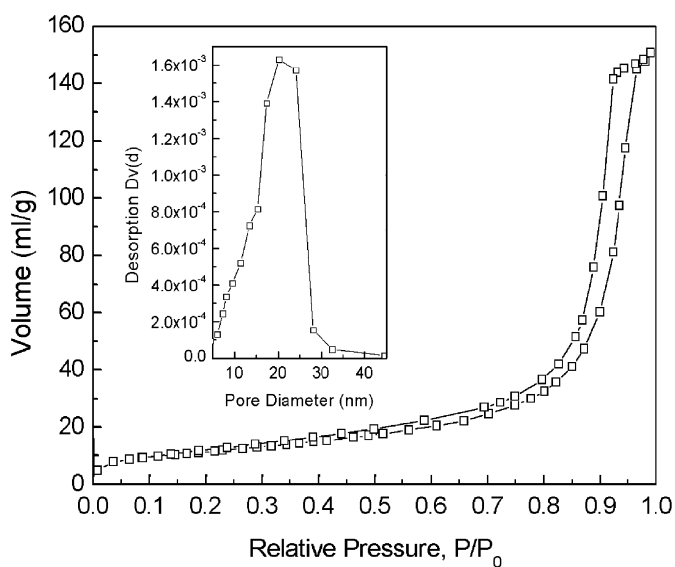


Fig. 4. Nitrogen sorption isotherm of the CdS. Inset: BJH pore size distribution of the mesoporous nanomaterial.

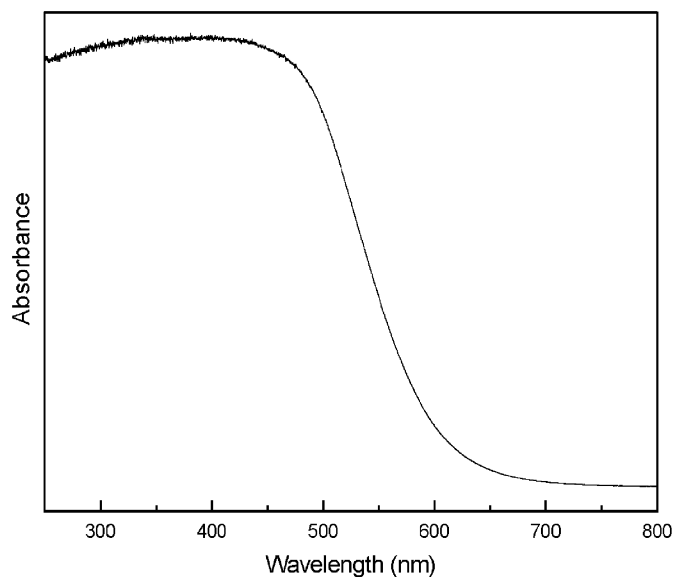


Fig. 5. UV-Visible absorption of the sample.

upon measured data from TEM images. This probably because many of the foam-like particles were aggregated and overlapped, which made the pore sizes look more variable than what they are, so a wider range of the pore size is observed from TEM images. However, the major peak of the two sets of pore size distributions match with each other very well, both of them refer to a pore size of about 18 nm for the majority of the mesoporous CdS nanoparticles. The mesoporous CdS with an average pore size close to 20 nm could be particularly interesting for some special applications that need such a range of moderate pore sizes.

UV-Visible absorption spectrum of the sample is presented in Fig. 5. It shows a broad absorption band of the porous CdS, the absorption threshold is at about 430 nm, the band gap of the sample is 2.89 eV, larger than

that of bulk material, which is 2.42 eV [19], so this sample shows blue shift compared with the bulk material.

4. Conclusion

In summary, mesoporous CdS nanomaterial with an average pore size of nearly 20 nm was obtained. No template was used at the beginning of the preparation, but a sacrificial template composing zinc component is produced during the reaction process and removed by acid washing so that to yield the porous CdS. Because the acid washing may not be able to remove the sacrificial template completely due to aggregation of the particles, the final CdS could contain traces of Zn. The pore size of the produced mesoporous CdS is moderate, fills in the gap between the previously prepared similar mesoporous

materials usually either as small as less than 10 nm or as large as over 100 nm. The mesoporous CdS with the moderate pore size could be particularly interesting to some applications requiring a moderate pore size around 20 nm that otherwise the pore size could be too small or too large for the applications. The reaction route is inspiring to other similar porous materials, for instance, it may be possible to prepare a large range of porous sulfide materials such as silver sulfide, lead sulfide, bismuth sulfide, copper sulfide, nickel sulfide and cobalt sulfide, which are indissolvable in dilute hydrochloric acid. These materials could have specific applications owing to their porous features.

Acknowledgments

This work has been supported partly by the Curtin Research Fellowship scheme at Curtin University of Technology, and partly by the discovery project (Project ID: DP0210065) from the Australian Research Council (ARC). Dr Zhu is indebted to the ARC for a QEII fellowship. The authors acknowledge Mr. James Hockridge at Curtin University of Technology for assistance in sample characterization.

References

- [1] A.P. Alivisatos, *Science* 271 (1996) 933.
- [2] V.L. Colvin, M.C. Schlamp, A.P. Alivisatos, *Nature* 370 (1994) 354.
- [3] D.L. Klein, R. Roth, A.K.L. Lim, A.P. Alivisatos, P.L. McEuen, *Nature* 389 (1997) 699.
- [4] B.A. Ridley, B. Nivi, J.M. Jacobson, *Science* 286 (1999) 746.
- [5] W. Shangquan, A. Yoshida, *J. Phys. Chem. B* 106 (2002) 12227.
- [6] M.K. Arora, N. Sahu, S.N. Upadhyay, A.S.K. Sinha, *Ind. Eng. Chem. Res.* 38 (1999) 2659.
- [7] M.K. Arora, A.S.K. Sinha, S.N. Upadhyay, *Ind. Eng. Chem. Res.* 37 (1998) 3950.
- [8] S. Yu, Y. Wu, J. Yang, Z. Han, Y. Xie, Y. Qian, X. Liu, *Chem. Mater.* 10 (1998) 2309.
- [9] C. Ye, G. Meng, Y. Wang, Z. Jiang, L. Zhang, *J. Phys. Chem. B* 106 (2002) 10338.
- [10] C.J. Barrelet, Y. Wu, D.C. Bell, C.M. Lieber, *J. Am. Chem. Soc.* 125 (2003) 11498.
- [11] Z. Han, H. Zhu, S.R. Bulcock, S.P. Ringer, *J. Phys. Chem. B* 109 (2005) 2673.
- [12] K. Iwasaki, T. Torimoto, T. Shibayama, H. Takahashi, B. Ohtani, *J. Phys. Chem. B* 108 (2004) 11946.
- [13] K. Jiang, Y. Wang, J. Dong, L. Gui, Y. Tang, *Langmuir* 17 (2001) 3635.
- [14] F. Gao, Q. Lu, D. Zhao, *Adv. Mater.* 15 (2003) 739.
- [15] P. Xue, R. Lu, Y. Huang, M. Jin, C. Tan, C. Bao, Z. Wang, Y. Zhao, *Langmuir* 20 (2004) 6470.
- [16] P.V. Braun, P. Osenar, V. Tohver, S.B. Kennedy, S.I. Stupp, *J. Am. Chem. Soc.* 121 (1999) 7302.
- [17] P.V. Braun, S.I. Stupp, *Mater. Res. Bull.* 34 (1999) 463.
- [18] Q. Zhang, Y. Li, F. Huang, Z. Gu, *J. Mater. Sci. Lett.* 20 (2001) 1233.
- [19] J.L. Mohanan, I.U. Arachchige, S.L. Brock, *Science* 307 (2005) 397.
- [20] B. Liu, S. Yu, F. Zhang, L. Li, Q. Zhang, L. Ren, K. Jiang, *J. Phys. Chem. B* 108 (2004) 4338.
- [21] E.S. Toberer, R. Seshadri, *Chem. Commun.* (2006) 3159.