

# Fabrication of macroporous cadmium sulfide with three-dimensional structure by solvothermal synthesis

Zhibin Lei,<sup>a</sup> Jianmin Li,<sup>\*a</sup> Yanxiong Ke,<sup>a</sup> Yugen Zhang,<sup>b</sup> Hua Wang<sup>a</sup> and Gaofei He<sup>a</sup>

<sup>a</sup>Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, 230026, P.R.China. E-mail: jnli@ustc.edu.cn

<sup>b</sup>Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, P.R.China

Received 11th April 2001, Accepted 10th May 2001

First published as an Advance Article on the web 22nd May 2001

**A three-dimensional well-ordered network of macroporous CdS has been fabricated by a novel solvothermal synthesis route using SiO<sub>2</sub> beads as a template; the CdS particles, which were introduced in the voids of the template and used as crystal seeds for the further growth of CdS from the liquid phase, were found to play a very important role in the formation of the final pore structure.**

Currently there exists an increasing interest in new methods for the fabrication of diverse macroporous periodic structures. The main thrust of these intensive investigations stems from their wide range of applications such as separation,<sup>1</sup> chemical sensors<sup>2</sup> and membranes. However, the most important application of these three-dimensionally (3D) periodic materials relates to the field of photonic bandgap technology.<sup>3</sup> Compared with lithographic techniques,<sup>3</sup> chemical methods based on recently developed colloidal crystal templates have apparent advantages in fabricating really 3D macroporous materials due to their versatile and cost-effective procedures. So far, various macroporous materials, including oxides,<sup>4–8</sup> graphite and diamond,<sup>9</sup> BaTiO<sub>3</sub>,<sup>10</sup> polymers,<sup>11–15</sup> semiconductor Si,<sup>16</sup> Ge,<sup>17</sup> CdSe,<sup>18</sup> metals<sup>19–22</sup> and alloys,<sup>23</sup> have been fabricated by this universally applied template-directed synthesis.

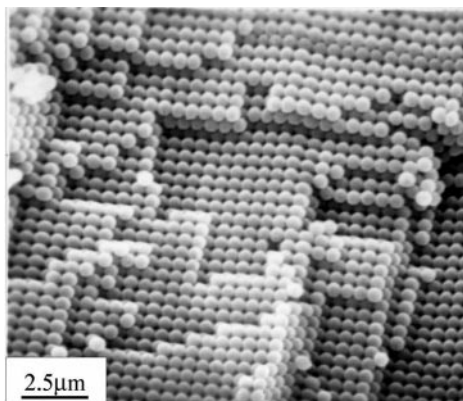
The optimum choices for the matrix in photonic bandgap materials, however, are wide bandgap semiconductors such as diamond,<sup>9</sup> II–VI semiconductors,<sup>18</sup> titania<sup>6</sup> and tin dioxide. Among these, CdS is one of the most promising candidates because of its high refractive index ( $n=2.5$  at 600 nm), its optical transparency in the visible and near IR regions,<sup>24</sup> as well as its semiconductor and photoelectric properties. It has been, however, difficult to fabricate 3D interconnected macroporous CdS by template-directed methods because during fabrication there are many factors to be taken into account. Owing to the sublimation and easy oxidation of CdS in air at elevated temperatures, calcining a composite of CdS and a polymer template in a protective atmosphere will result in the loss of CdS and incomplete degradation of the organic compound. For instance, in macroporous Ni/PS samples, 39% carbon remained after heating in N<sub>2</sub> at 450 °C for 10 h.<sup>25</sup> In addition, unlike SiO<sub>2</sub><sup>4</sup> and TiO<sub>2</sub>,<sup>5,6</sup> the interaction between CdS molecules is mainly dominated by weak van der Waals forces, which readily results in pore collapse when the template is eliminated. Although Norris and coworkers<sup>26</sup> have successfully introduced semiconductor nanoparticles CdSe into the voids of an SiO<sub>2</sub> template, due to the weak molecule interactions, the skeleton of macroporous CdSe manifests itself as locally unconnected fragments. This property is detrimental to photonic bandgap materials, which need a

completely interconnected structure. 3D macroporous CdS and CdSe have been fabricated by electrochemical deposition.<sup>18</sup> However, difficulties often arise from the preparation of working electrodes, control over the wall thickness and purification of the final products.<sup>19</sup> In this communication we report a novel solvothermal synthesis route for the preparation of macroporous CdS using SiO<sub>2</sub> beads as a template. Compared with other methods, the present synthesis route has the advantages that it is easy-to-handle, cost-effective and may provide a new route for the fabrication of other macroporous sulfides.

Nearly monodisperse SiO<sub>2</sub> spheres with relative standard deviations smaller than 5% are obtained by hydrolyzing tetraethyl orthosilicate under basic conditions,<sup>27</sup> followed by a seed growth polymerization reaction.<sup>28</sup> The SiO<sub>2</sub> templates are assembled by a vertical deposition technique as previously reported.<sup>29</sup> Firstly, we introduce CdS particles in the voids of the SiO<sub>2</sub> template. This procedure can be readily accomplished by successively soaking the dried SiO<sub>2</sub> template in 10% aqueous CdCl<sub>2</sub> and the dried CdCl<sub>2</sub>–SiO<sub>2</sub> template in 5% (NH<sub>4</sub>)<sub>2</sub>S aqueous solution. About 0.35 g analytically pure CdCl<sub>2</sub>·0.5H<sub>2</sub>O, 0.18 g thiourea (NH<sub>2</sub>CSNH<sub>2</sub>), 1 g CdS–SiO<sub>2</sub> template and 5 ml CS<sub>2</sub> were mixed and put into a Teflon-coated steel autoclave (designated as no. 1) of 8 ml capacity and then heated at 160 °C for 24 h. After washing the resulting composite with deionized water, the SiO<sub>2</sub> template was removed by immersing the composite in 10% aqueous HF overnight.

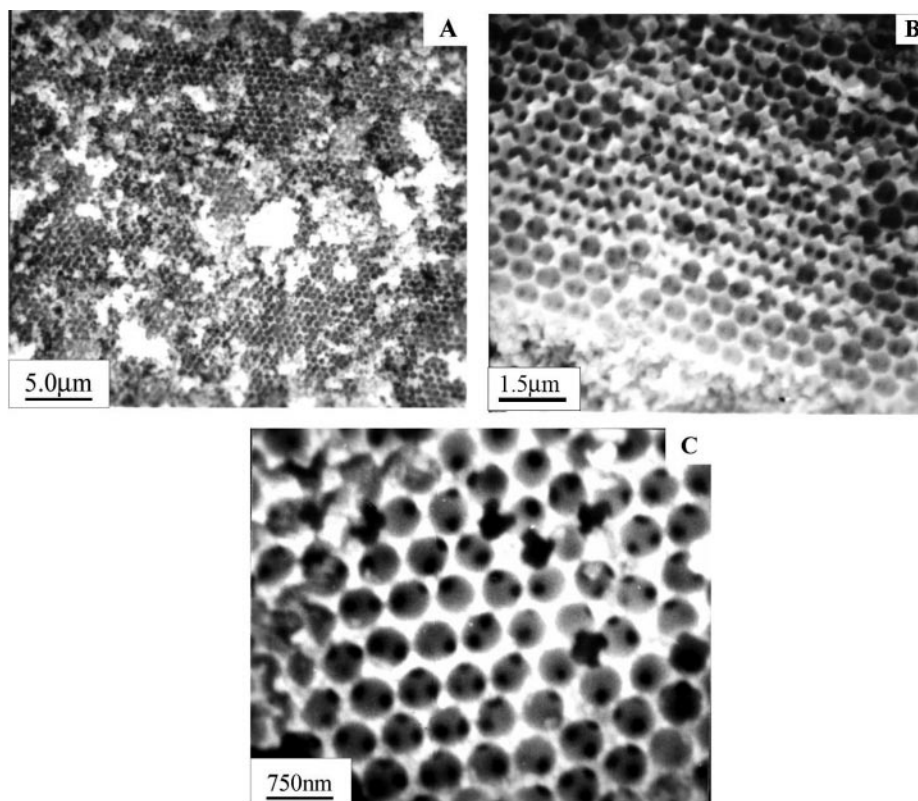
The quality of any materials formed *via* template-directed method depends mainly on the order and properties of the starting template. According to a convective self-assembly technique,<sup>30–32</sup> SiO<sub>2</sub> nanospheres can self-assemble into opalescent colloidal crystals. Before fabrication these colloidal crystals were sintered at 820 °C for 3 h.<sup>33</sup> This thermal treatment leads to the formation of small necks between the SiO<sub>2</sub> spheres and thereby provides the template with mechanical robustness and makes it easy to transport. The necks (see the small pores in Fig. 2c) also allow the HF solution to flow through the whole structure to dissolve away the SiO<sub>2</sub> template. Fig. 1 is the SEM image of SiO<sub>2</sub> spheres of 546 nm diameter on the (100) plane of the face-centered cubic (f.c.c.) template after heat treatment. The SiO<sub>2</sub> beads are in physical contact with each other and assemble into a close-packed structure. Different crystalline terraces prove that the template is long-range ordered in three dimensions.

Fig. 2 shows typical SEM images of macroporous CdS fabricated by using SiO<sub>2</sub> beads of various sizes as templates. The honeycomb structure confirms that CdS has retained the morphology of the starting template, see Fig. 2a. Fig. 2b shows

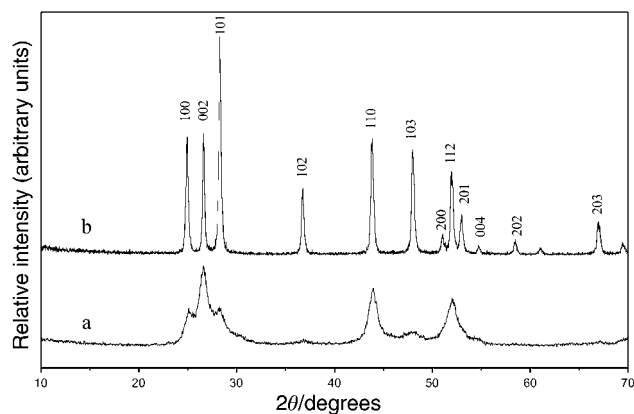


**Fig. 1** Scanning electron micrograph of 546 nm SiO<sub>2</sub> beads on the (100) plane of f.c.c. template after sintering at 820 °C for 3 h. Many steps confirm the long-range order and three-dimensional structure.

that the open voids and interconnected walls extend this honeycomb structure over a range of tens of microns in three dimensions. Average pore diameters of about 504 nm were obtained by using 596 nm SiO<sub>2</sub> spheres as the template, indicating that the pore shrinkage during the removal of the template by chemical etching is less than that by calcining at higher temperature.<sup>10</sup> The next lower layer of pores is clearly seen in the high-magnification image of Fig. 2c. These windows, formed around the points where the starting SiO<sub>2</sub> beads had touched, are clearly seen as three dark areas within each pore. The dimensions of these windows largely depended on the degree of physical contact between adjacent colloidal spheres, and can be adjusted over a certain range by sintering the template at different temperatures and times.<sup>33</sup> Elemental analysis (found Cd, 78.54%; S, 20.59%; Si, 0.02%. calc. Cd, 77.80%; S, 22.20%) found only trace amounts of silica, suggesting that the template has been completely removed.



**Fig. 2** SEM images of the resulting macroporous CdS fabricated by using SiO<sub>2</sub> beads of various sizes as template. (a) Pore sizes about 467 nm were obtained with 546 nm SiO<sub>2</sub> spheres. (b) Details of the honeycomb structure confirm that the walls are interconnected in three dimensions. (c) High-magnification micrograph of CdS. Windows which formed around the points where the starting SiO<sub>2</sub> spheres had touched are clearly seen as three dark areas in each pore.



**Fig. 3** Powder X-ray diffraction patterns of (a) as-prepared CdS in the voids of the SiO<sub>2</sub> template and (b) the resulting macroporous CdS.

The strongest (101), and the second strongest (100) and (002) diffraction peaks (Fig. 3) are in good agreement with bulk hexagonal CdS. Both of these results indicate that the final product is pure CdS rather than any other cadmium compound.

During the whole fabrication process, the CdS particles initially introduced in the voids of the template play important roles in the formation of the pore structure. Firstly, they mineralize a portion of the space within the template. Besides this, they provide crystal seeds for the further growth of CdS from the liquid phase. This mechanism is confirmed by the following parallel experiments. In a second autoclave (no. 2), 0.35 g CdCl<sub>2</sub>·0.5H<sub>2</sub>O, 0.18 g thiourea, 1 g bare SiO<sub>2</sub> template (without CdS in the voids) and 5 ml CS<sub>2</sub> were mixed, while 5 ml CS<sub>2</sub> and 1 g CdS-SiO<sub>2</sub> template were placed in a third autoclave (no. 3). Along with autoclave no. 1, these autoclaves were simultaneously heated at 160 °C for 24 h. SEM results

show that the sample in autoclave no. 2 has a small number of unconnected pores, which indicates that the CdS tends to be deposited in the voids. In autoclave no. 3, however, we did not observe any apparent pores, which suggests that most of the pores have collapsed because of the incomplete filling. In addition, the XRD patterns also support this mechanism. Fig. 3 shows the XRD patterns<sup>34</sup> of as-prepared CdS in the CdS-SiO<sub>2</sub> template and of the final macroporous CdS. Despite the different peak intensities, the reflections can be indexed to the same hexagonal phase. In other words, the CdS phase within the CdS-SiO<sub>2</sub> template is hexagonal even under ambient conditions and can act as crystal seeds, around which CdS can grow within the voids of the template. Based on these points, our method is very analogous to the electrochemical deposition technique because both methods have the common feature that they allow for the mineralization of voids as completely as possible.

The solvent CS<sub>2</sub> may serve as an inert medium rather than guiding the crystal growth direction. For comparison, CS<sub>2</sub> was replaced by ethylenediamine while keeping the other experimental conditions the same. Almost the same results were obtained as those for autoclave no. 3. A possible reason for this is that Cd<sup>2+</sup> was chelated by ethylenediamine, which disperses CdS in the liquid rather than in the voids of the template.

In summary, we have fabricated 3D ordered macroporous CdS by a convenient and cost-effective solvothermal synthesis route. This framework will confer upon CdS many interesting applications such as in photoelectron devices and as photonic crystals. Further investigations involving the physical and chemical properties of macroporous CdS and the extension of the present method to the fabrication of other chalcogenides are under way.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China and the National Education Committee of China. Grant Nos. 20071030, 50072026 and 29871027.

## Notes and references

- 1 R. R. Bhave, *Inorganic Membranes: Synthesis, Characteristics and Applications*, Van Nostrand Reinhold, New York, 1991.
- 2 M. J. Tierney and H. O. L. Kim, *Anal. Chem.*, 1993, **65**, 3435.
- 3 J. D. Joannopoulos, P. R. Villeneuve and S. Fan, *Nature*, 1997, **386**, 143.
- 4 O. D. Velev, T. A. Jede, R. F. Lobo and A. M. Lenhoff, *Nature*, 1997, **389**, 447.
- 5 B. T. Holland, C. F. Blanford and A. Stein, *Science*, 1998, **281**, 538.
- 6 J. E. G. J. Wijnhoven and W. L. Vos, *Science*, 1998, **281**, 802.

- 7 B. T. Holland, L. Abrams and A. Stein, *J. Am. Chem. Soc.*, 1999, **121**, 4308.
- 8 H. W. Yan, C. F. Blanford, B. T. Holland, W. H. Smyrl and A. Stein, *Chem. Mater.*, 2000, **12**, 1134.
- 9 A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. X. Cui, I. Khayrullin, S. O. Dantas, J. Marti and V. G. Ralchenko, *Science*, 1998, **282**, 897.
- 10 Z. B. Lei, J. M. Li, Y. G. Zhang and S. M. Lu, *J. Mater. Chem.*, 2000, **10**, 2629.
- 11 S. A. Johnson, P. J. Ollivier and T. E. Mallouk, *Science*, 1999, **283**, 963.
- 12 S. H. Park and Y. N. Xia, *Adv. Mater.*, 1998, **10**, 1045.
- 13 P. Jiang, K. S. Hwang, D. M. Mittleman, J. F. Bertone and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 11630.
- 14 B. Gates, Y. D. Yin and Y. N. Xia, *Chem. Mater.*, 1999, **11**, 2827.
- 15 T. Sumida, Y. Wada, T. Kitamura and S. Yanagida, *Chem. Commun.*, 2000, 1613.
- 16 A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader and H. M. Driel, *Nature*, 2000, **405**, 437.
- 17 H. Miguez, F. Meseguer, C. Lopez, M. Holgado, G. Andreasen, A. Mifsud and V. Fornes, *Langmuir*, 2000, **16**, 4405.
- 18 P. V. Braun and P. Wiltzius, *Nature*, 1999, **402**, 603.
- 19 P. Jiang, J. Cizeron, J. F. Bertone and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 7957.
- 20 O. D. Velev, P. M. Tessier, A. M. Lenhoff and E. W. Kaler, *Nature*, 1999, **401**, 548.
- 21 P. N. Bartlett, P. R. Birkin and M. A. Ghanem, *Chem. Commun.*, 2000, 1671.
- 22 L. B. Xu, W. L. Zhou, C. Frommen, R. H. Baughman, A. A. Zakhidov, L. Malkinski, J. Q. Wang and J. B. Wiley, *Chem. Commun.*, 2000, 997.
- 23 H. W. Yan, C. F. Blanford, W. H. Smyrl and A. Stein, *Chem. Commun.*, 2000, 1477.
- 24 L. I. Berger, *Semiconductor Materials*, CRC Press, Boca Raton, FL, 1997.
- 25 H. W. Yan, C. F. Blanford, B. T. Holland, M. Parent, W. H. Smyrl and A. Stein, *Adv. Mater.*, 1999, **11**, 1003.
- 26 Y. A. Vlasov, N. Yao and D. J. Norris, *Adv. Mater.*, 1999, **11**, 165.
- 27 W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.
- 28 G. H. Bogush, M. A. Tracy IV and C. F. Zukoski, *J. Non-Cryst. Solids*, 1988, **104**, 95.
- 29 P. Jiang, J. F. Bertone, K. S. Hwang and V. L. Colvin, *Chem. Mater.*, 1999, **11**, 2132.
- 30 N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura and K. Nagayama, *Nature*, 1993, **361**, 26.
- 31 A. S. Dimitrov and K. Nagayama, *Chem. Phys. Lett.*, 1995, **243**, 462.
- 32 M. Yamaki, J. Higo and K. Nagayama, *Langmuir*, 1995, **11**, 2975.
- 33 H. Miguez, F. Meseguer, C. Lopez, A. Blanco, J. S. Moya, J. Requena, A. Mifsud and V. Fornes, *Adv. Mater.*, 1998, **10**, 480.
- 34 The powder X-ray diffraction (XRD) patterns were recorded in the  $2\theta$  range from 10 to 70° on a Japan Rigaku D/max- $\gamma$ A rotating anode X-ray diffractometer using CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). A Hitachi X-650 Scanning Electron Microanalyzer with an accelerating voltage of 25 KV was used to observe the morphology of samples. Elemental analysis was performed using an Atomscan Advantage ICP-Atomic Emission Spectrometer.