ADVANCED MATERIALS

[1] P. S. Drzaic, *Liquid Crystal Dispersions*, World Scientific, Singapore **1995**.
[2] *Liquid Crystals in Complex Geometries* (Eds: G. P. Crawford, S. Zumer), Taylor and Francis, London **1996**.
[3] I. Dierking, *Adv. Mater.* **2000**, *12*, 167.
[4] D.-K. Yang, L.-C. Chien, J. W. Doane, *Appl. Phys. Lett.* **1992**, *60*, 3102.
[5] D.-K. Yang, J. L. West, L.-C. Chien, J. W. Doane, *J. Appl. Phys.* **1994**, *76*, 1331.
[6] Y. K. Fung, A. Borstnik, S. Zumer, D.-K. Yang, J. W. Doane, *Phys. Rev. E* **1997**, *55*, 1637.
[7] I. Dierking, M. A. Osipov, S. T. Lagerwall, *Eur. Phys. J. E* **2000**, *2*, 303.
[8] R. A. M. Hikmet, *Liq. Cryst.* **1991**, *9*, 405.
[9] Y. K. Fung, D.-K. Yang, S. Ying, L.-C. Chien, S. Zumer, J. W. Doane, *Liq. Cryst.* **1995**, *19*, 797.
[10] A. Y.-G. Fuh, M.-S. Tsai, C.-Y. Huang, *Jpn. J. Appl. Phys.* **1996**, *35*, 3960.
[11] I. Dierking, L. L. Kosbar, A. Afzali-Ardakani, A. C. Lowe, G. A. Held, *J. Appl. Phys.* **1997**, *81*, 3007.
[12] G. A. Held, L. L. Kosbar, I. Dierking, A. C. Lowe, G. Grinstein, V. Lee, R. D. Miller, *Phys. Rev. Lett.* **1997**, *79*, 3443.
[13] I. Dierking, L. Komitov, S. T. Lagerwall, T. Wittig, R. Zentel, *Liq. Cryst.* **1999**, *26*, 1511.
[14] I. Dierking, L. L. Kosbar, A. Afzali-Ardakani, A. C. Lowe, G. A. Held, *Appl. Phys. Lett.* **1997**, *71*, 2454.
[15] C. V. Rajaram, S. D. Hudson, L.-C. Chien, *Chem. Mater.* **1995**, *7*, 2300.
[16] D. S. Muzic, C. V. Rajaram, L.-C. Chien, S. D. Hudson, *Polym. Adv. Technol.* **1996**, *7*, 737.
[17] C. V. Rajaram, S. D. Hudson, L.-C. Chien, *Chem. Mater.* **1996**, *8*, 2451.
[18] C. V. Rajaram, S. D. Hudson, L.-C. Chien, *Polymer* **1998**, *39*, 5315.
[19] I. Dierking, L. L. Kosbar, A. C. Lowe, G. A. Held, *Liq. Cryst.* **1998**, *24*, 387.
[20] I. Dierking, L. L. Kosbar, A. C. Lowe, G. A. Held, *Liq. Cryst.* **1998**, *24*, 397.
[21] B. Mandelbrot, *The Fractal Geometry of Nature*, Freeman, San Francisco **1982**.
[22] *Fractals in Science* (Eds: A. Bunde, S. Havlin), 1st ed., Springer, Berlin **1994**.
[23] *Fractals and Disordered Systems* (Eds: A. Bunde, S. Havlin), 2nd ed., Springer, Berlin **1996**.
[24] M. Daoud, H. Van Damme, in *Soft Matter Physics* (Eds: M. Daoud, C. E. Williams), Springer, Berlin **1999**, Ch. 2.
[25] I. Dierking, *J. Phys. D: Appl. Phys.* **2002**, *35*, 2520.

Sonochemical Synthesis of CdSe Hollow Spherical Assemblies Via an In-Situ Template Route**

By *Jun-Jie Zhu*,* *Shu Xu*, *Hui Wang*, *Jian-Min Zhu*, and *Hong-Yuan Chen*

Inorganic materials with hollow spherical structures have wide application in various fields of chemistry, biotechnology, and materials science.[1–3] Up to now, there have been a number of methods for the preparation of inorganic materials with hollow spherical structures, such as nozzle-reaction system, sacrificial cores, and emulsion/water extraction techniques.[4–7] For the fabrication of hollow spherical materials with nanoscale shell dimensions, a core consisting of polymer, or some other material, should be prepared. Then assembly on the core is carried out to obtain core–shell spheres. In recent years, many new templates have been employed, including a variety of colloids and composite particles, and at the same time some new techniques for the production of the core–shell structure have been widely adopted. For example, the layer-by-layer (LBL) self-assembly technique, based on electrostatic interaction or hydrogen bonding between alternately deposited layers, has been applied to coat colloids.[8,9] However, only a small variety of silica, zeolite, and magnetic hollow spheres have been fabricated using this strategy because of the difficulty of removing the template cores. Currently, we are still trying to find new methods that meet the goal of avoiding the disassembly of the shell in the process of removing the cores to produce the final hollow spherical materials.

In recent years, a sonochemical method has been widely used to fabricate nanoparticles with special structures. The chemical effects of ultrasound arise from acoustic cavitation. That is, the formation, growth, and implosive collapse of bubbles in a liquid can drive many chemical reactions.[10–14] Hence it offers a very attractive method for the preparation of nanoparticles with different morphologies, including metals, metal carbides, oxides, and chalcogenides.[11–21] Sonochemical synthesis of a variety of mesoporous materials, such as tin oxide, silica, and titania, has also been recently reported.[22]

Nanosized cadmium selenide is a very useful photoconducting semiconductor material due to its high photosensitivity.[23,24] To the best of our knowledge, the preparation of CdSe hollow spherical structures has never before been reported. Herein, hollow spherical structural CdSe was synthesized sonochemically via an in-situ template route. We found that ultrasonic irradiation and cadmium hydroxide play an important role in the fabrication of the CdSe hollow spherical assemblies. The product was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS).

The powder XRD pattern of the product is shown in Figure 1. The diffraction peaks in this pattern can be indexed to

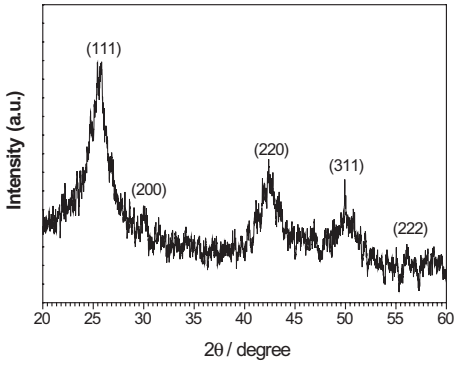

Fig. 1. Powder XRD pattern of CdSe hollow sphere.

[*] Prof. J. J. Zhu, S. Xu, H. Wang, Prof. H. Y. Chen
Laboratory of Mesoscopic Materials Science and
State Key Laboratory of Coordination Chemistry
Department of Chemistry, Nanjing University
Nanjing 210093 (P.R. China)
E-mail: jjzhu@nju.edu.cn
J. M. Zhu
National Laboratory of Solid State of Microstructures
Nanjing University
Nanjing 210093 (P.R. China)

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the pure cubic phase of CdSe (JCPDS No.19-191). No peaks corresponding to impurities are detected, indicating the high purity of the product. The average size of the CdSe nanoparticles is calculated to be 5 nm according to the Debye–Scherrer formula.[25]

The XPS spectra shown in Figure 2 give further evidence for the purity of the product. All the peaks were calibrated by using C(1s) (284.6 eV) as the reference. The two peaks located at 405.5 eV and 412.3 eV are assigned to Cd(3d) and that at 54.5 eV corresponds to Se(3d). The ratio of Cd to Se is approximately 6:4, which shows that the sample is rich in cadmium.

In the TEM images (Fig. 3a,b), uniform and regular hollow spheres with an average diameter of 120 nm are observed. These hollow spheres consist of spherical nanoparticles about 5 nm in diameter. The HRTEM image (Fig. 3c) of a single hollow sphere exhibits the clear crystalline lattice of CdSe particles on the spherical surface and the hollow center can be clearly observed. In Figure 3d, the selected area electron diffraction (SAED) pattern recorded on a CdSe hollow sphere has clear diffraction rings that correspond to the cubic phase of CdSe, and the hollow spheres are polycrystalline in nature.

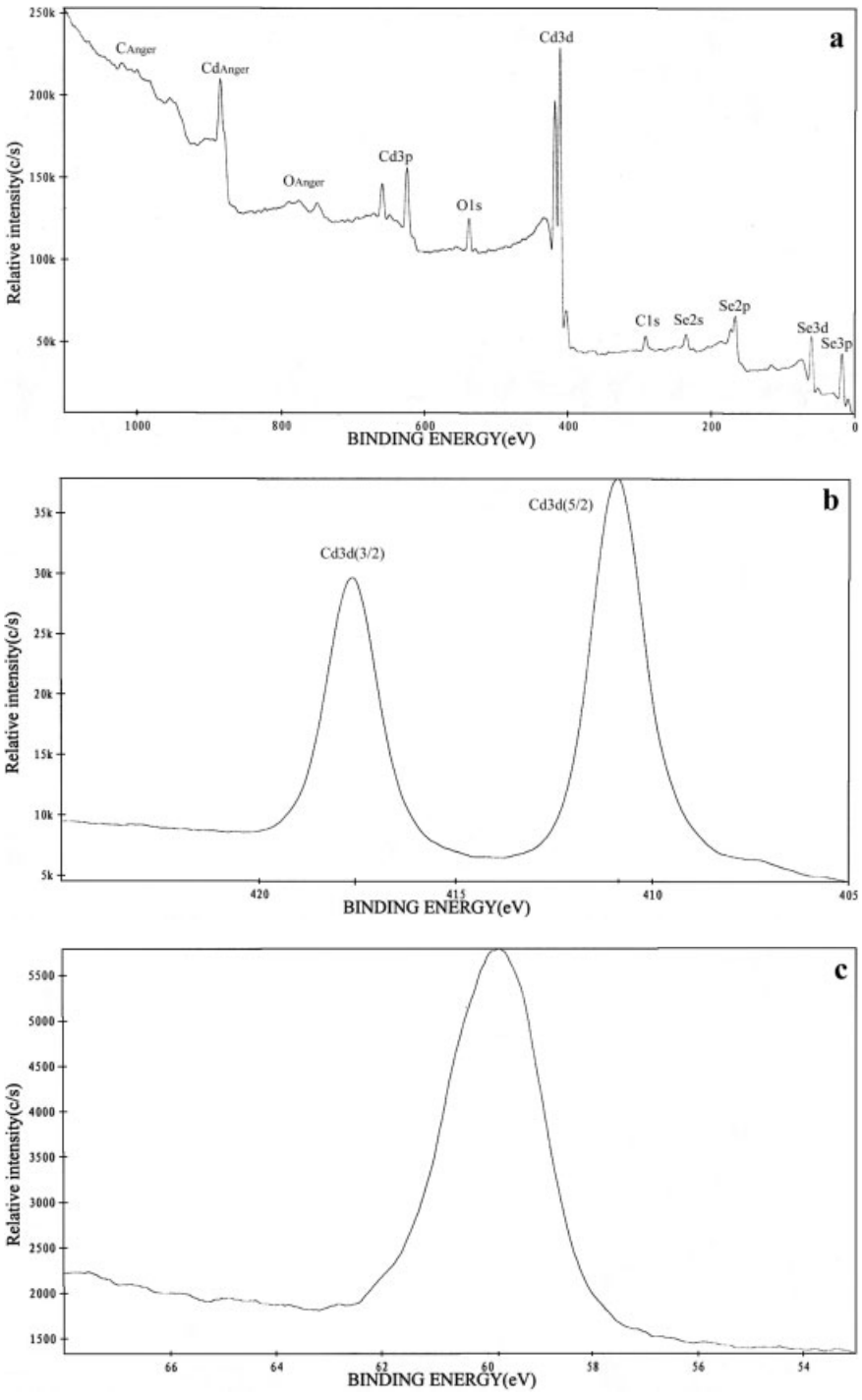

Fig. 2. XPS spectra of CdSe hollow spheres. a) Wide XPS spectrum. b) Cd(3d). c) Se(3d).

Figure 4 shows the UV-vis absorption spectra of the CdSe hollow sphere material. The bandgap is calculated to be 2.7 eV by the direct conversion method.[26] This is much larger than the reported value for bulk CdSe ($E_g = 1.7$ eV),[27] indicating the quantum size effect of this sample.

Gedanken's group has established a sonochemical route to produce a variety of mesoporous oxide materials that have wide application in catalysis.[22] The advantage in the application of ultrasound irradiation to the synthesis of mesoporous materials is a drastic reduction in the fabrication time and the ability to induce aggregation of the nanoparticles into porous structures without destroying the micellar structure. Herein, we extended the sonochemical method to the synthesis of hollow spherical structures composed of chalcogenide nanoparticles. Scheme 1 outlines the procedure for the formation of CdSe hollow spherical assemblies. Initially, amorphous $Cd(OH)_2$ is obtained via the reaction between $CdCl_2$ solution and ammonia. Then $Cd(OH)_2$ particles as the precursor are reacted with sodium selenosulfate giving rise to CdSe nanoparticles. The mechanism of the sonochemical formation of CdSe nanoparticles is probably related to the radical species generated from water molecules by the absorption of ultrasound energy. It has been known that during an aqueous sonochemical process, the elevated

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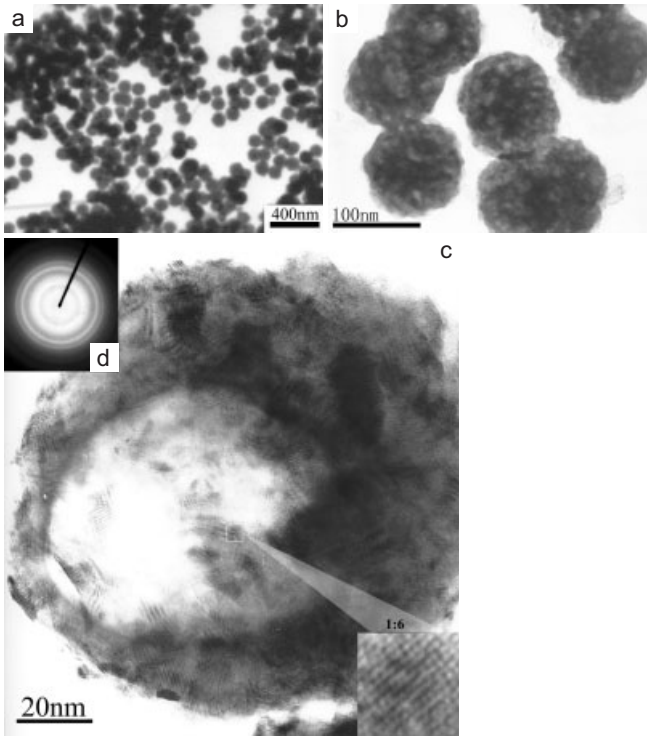


Fig. 3. TEM and HRTEM images of the product after sonication for 30 min in the presence of ammonia (the concentration of NH_3 is 0.8 mol/L). a,b) TEM images of the product. c) HRTEM image of an individual CdSe hollow spherical assembly. d) SAED pattern recorded on the hollow sphere shown in (c).

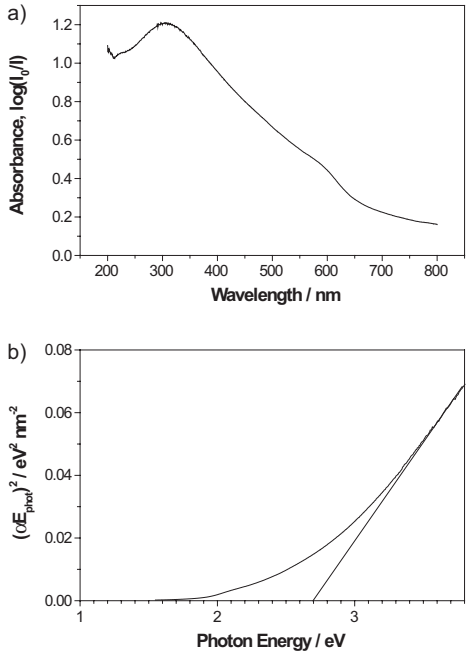
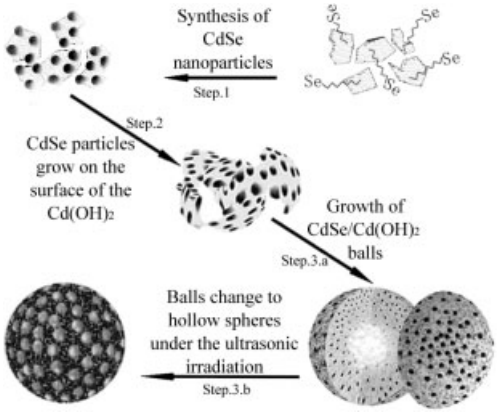


Fig. 4. a) The UV-vis absorption spectrum of the product (in EtOH suspension) prepared using 20 W cm^{-2} sonic intensity. b) Plots of $(\alpha E_{phot})^2$ vs. E_{phot} for a direct transition.

temperatures and pressures inside the collapsing bubbles cause water to vaporize and further pyrolyze into H$^{\bullet}$ and OH$^{\bullet}$ radicals. The probable reaction process for the sonochemical formation of CdSe nanoparticles in aqueous solution can be summarized as follows:



Scheme 1. Proposed mechanism for the synthesis of hollow CdSe spheres.

$$H_2O \longrightarrow H^{\bullet} + OH^{\bullet} \quad (1)$$

$$2H^{\bullet} + SeSO_3^{2-} \longrightarrow Se^{2-} + 2H^{+} + SO_3^{2-} \quad (2)$$

$$Cd(OH)_2 + Se^{2-} \longrightarrow CdSe + 2OH^{-} \quad (3)$$

$$n\mathrm{CdSe} \longrightarrow (\mathrm{CdSe})n \quad (4)$$

During sonication, a large number of dangling bonds, defects, or traps will appear gradually on the surface of $Cd(OH)_2$, which provides some active spots for the formation of CdSe nuclei. These freshly born nuclei will grow into large particles until they finally become stable.[28] Since the CdSe only grows on the surface of $Cd(OH)_2$, CdSe hollow spherical assemblies are formed when all the $Cd(OH)_2$ is converted into CdSe. In such a process, amorphous $Cd(OH)_2$, which acts as the in-situ template, directs the growth of the primary CdSe nanoparticles and the formation of their assembly into hollow spherical structures. The advantage of utilizing such a template is that is automatically removed at the end of the reaction. This method avoids the step of removing the template to obtain the pure product. We have also carried out other experiments replacing ammonia with triethylamine (TEA). It was found that when enough TEA was added in order to make it sufficiently basic to form $Cd(OH)_2$ colloids, CdSe hollow spherical structures could also be obtained (Fig. 5b). The intermediate structure formed during the sonochemical formation of the final product is shown in Figure 5a, which obviously indicates the tendency to form a hollow spherical structure.

In conclusion, a hollow spherical assembly composed of CdSe nanoparticles has been successfully synthesized via a sonochemical route. $Cd(OH)_2$ acts as the in-situ template that directs the final formation of the unusual structure. Further investigation may lead to the extension of this technique to the preparation of other materials with hollow spherical structure.

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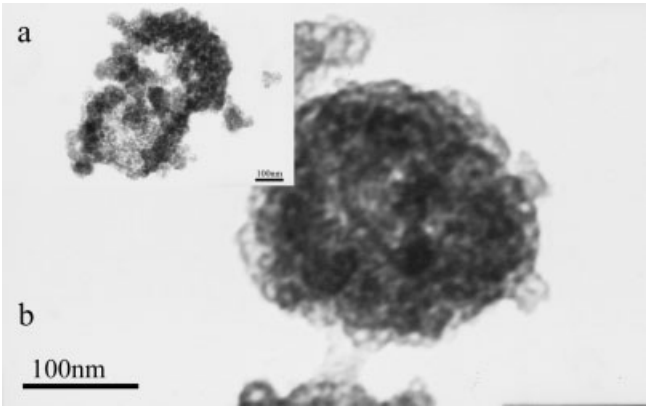

Fig. 5. CdSe spheres prepared in the presence of TEA (the concentration of TEA is 0.8 mol/L). a) The intermediate structure, after sonication for 25 min. b) The final spheres, after sonication for 35 min.

Experimental

All the reagents used were of analytical purity. A 0.2 M Na_2SeSO_3 solution was prepared by stirring 0.2 M Se and 0.5 M Na_2SO_3 at approximately 70 °C for 24 h.

0.5 g $CdCl_2$ was dissolved in 50 mL distilled water and then added to 5 mL ammonia (30 % NH_3) or 11 mL TEA. A white colloid was produced immediately in the solution. This solution, 10 mL 0.2 M Na_2SeSO_3, and an appropriate amount of distilled water were added to a 150 mL round-bottom flask until the total volume was 100 mL. After several seconds, when the solution turned yellow and turbid, it was irradiated with a high-intensity ultrasonic horn (Xinzhi Co., China, Ti-horn, 20 kHz, 60 W cm^{-2}) under ambient air for 30 min and dark red precipitates were obtained. After cooling to room temperature, the precipitates were centrifuged, washed sequentially with distilled water and acetone, and then dried in air.

The XRD patterns were recorded on a Shimadzu XD-3 A X-ray diffractometer (Cu Kα radiation, $\lambda = 0.15418$ nm). The TEM and SAED examinations were carried out on a JEOL JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV. The surface of the products was detected by the X-ray photoelectron spectra recorded on an ESCALAB MK II X-ray photoelectron spectrometer, using a non-monochromatized Mg K X-ray as the excitation source and choosing C(1s) (284.6 eV) as the reference line. A Ruili 1200 photospectrometer (Peking Analytical Instrument Co.) was used to record the UV-vis absorption spectra of the as-prepared materials.

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[1] D. L. Wilcox, M. Berg, T. Bernat, D. Kellerman, J. K. Cochran, *Hollow and Solid Spheres and Microspheres: Science and Technology Associated with Their Fabrication and Application*, Materials Research Society Symposium Proceedings, Vol. 372, MRS, Pittsburgh, PA **1995**.
[2] H. Huang, E. E. Remsen, *J. Am. Chem. Soc.* **1999**, *121*, 3805.
[3] T. K. Mandal, M. S. Fleming, D. R. Walt, *Chem. Mater.* **2000**, *12*, 3481.
[4] J. K. Cochran, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 474.
[5] G. Decher, *Science* **1997**, *277*, 1232.
[6] Z. Y. Zhong, Y. D. Yin, B. Gates, Y. N. Xia, *Adv. Mater.* **2000**, *12*, 206.
[7] H. Lin, Y. Cheng, C. Mou, *Chem. Mater.* **1998**, *10*, 3772.
[8] F. Caruso, *Chem. Eur. J.* **2000**, *6*, 413.
[9] X. D. Wang, W. L. Yang, Y. Tang, Y. J. Wang, S. K. Fu, Z. Gao, *Chem. Commun.* **2000**, 2161.
[10] K. S. Suslick, *Ultrasound: Its Chemical, Physical and Biological Effects*, VCH, Weinheim **1988**.
[11] K. S. Suslick, D. A. Hammerton, R. E. Cline, *J. Am. Chem. Soc.* **1986**, *108*, 5641.
[12] K. S. Suslick, S. B. Choe, A. A. Cichowlas, M. W. Grinstaff, *Nature* **1991**, *353*, 414.
[13] T. Hyeon, M. Fang, K. S. Suslick, *J. Am. Chem. Soc.* **1996**, *118*, 5492.
[14] K. S. Suslick, G. J. Price, *Annu. Rev. Mater. Sci.* **1999**, *29*, 295.
[15] N. Arul Dhas, A. Gedanken, *J. Phys. Chem. B* **1997**, *101*, 9495.
[16] R. V. Kumar, Y. Diamant, A. Gedanken, *Chem. Mater.* **2000**, *12*, 2301.
[17] J. J. Zhu, Yu. Koltypin, A. Gedanken, *Chem. Mater.* **2000**, *12*, 73.
[18] R. Kerner, O. Palchik, A. Gedanken, *Chem. Mater.* **2001**, *13*, 1413.
[19] H. Wang, J. J. Zhu, J. M. Zhu, H. Y. Chen, *J. Phys. Chem. B* **2002**, *106*, 3848.
[20] H. Wang, J. J. Zhu, J. M. Zhu, X. H. Liao, S. Xu, T. Ding, H. Y. Chen, *Phys. Chem. Chem. Phys.* **2002**, *4*, 3794.
[21] J. J. Zhu, H. Wang, S. Xu, H. Y. Chen, *Langmuir* **2002**, *18*, 3306.
[22] A. Gedanken, X. Tang, Y. Wang, N. Perkas, Y. Koltypin, M. V. Landau, L. Vradman, M. Herskowitz, *Chem. Eur. J.* **2001**, *7*, 4547.
[23] L. E. Brus, *J. Chem. Phys.* **1984**, *80*, 4403.
[24] A. P. Alivisatos, T. D. Harris, P. J. Carroll, M. L. Stiegerwald, L. E. Brus, *J. Chem. Phys.* **1989**, *90*, 3463.
[25] *X-ray Diffraction Procedures* (Eds: H. Klug, L. Alexander), Wiley, New York **1962**.
[26] S. Tsunekawa, T. Fukuda, A. Kasuya, *J. Appl. Phys.* **2000**, *87*, 1319.
[27] K. R. Patil, D. V. Paranjape, S. D. Sathaye, A. Mitra, S. R. Padalkar, A. B. Mandale, *Mater. Lett.* **2000**, *46*, 81.
[28] W. Chen, Z. Wang, Z. Lin, L. Lin, *J. Appl. Phys.* **1997**, *82*, 3111.

Ordered Arrays of Nanopillars Formed by Photoelectrochemical Etching on Directly Imprinted TiO_2 Single Crystals

By *Hideki Masuda*,* *Kenji Kanezawa*, *Masashi Nakao*, *Atsushi Yokoo*, *Toshiaki Tamamura*, *Takashi Sugiura*, *Hideki Minoura*, and *Kazuyuki Nishio*

TiO_2 has been widely applied to several types of functional devices, such as photoanodes,[1] chemical sensors,[2,3] and photocatalysts,[4] due to its unique chemical and physical properties. In addition, TiO_2 is a candidate material for the fabrication of optical devices,[5,6] represented by photonic crystals, due to its large bandgap and high refractive indices. Much effort has been made to produce ordered, fine structures of TiO_2 in order to optimize the performance of the devices obtained. Textured, polycrystalline TiO_2 membranes have been prepared by sol–gel[5–8] and electrochemical[9,10] processes. For single-crystal TiO_2, ordered structures have reportedly been obtained by anisotropic photoetching in H_2SO_4 electrolyte.[11–13] In this photoetching process, rectangular holes were produced in the ⟨001⟩ direction by illuminating rutile-type TiO_2. However, the degree of ordering and uniformity in the rectangular holes obtained in this process is not satisfactory, due to the random development of holes during the photoelectrochemical etching. In previous reports, we stated that the imprinting process using silicon carbide (SiC) molds was applicable to the texturing of semiconductor (InP)

[*] Prof. H. Masuda,[+] K. Kanezawa
Department of Applied Chemistry, Tokyo Metropolitan University
1-1 Minamiosawa, Hachioji, Tokyo 192-0397 (Japan)
E-mail: masuda-hideki@c.metro-u.ac.jp
Dr. M. Nakao, Dr. A. Yokoo, Dr. T. Tamamura
Nippon Telegraph and Telephone Corporation
3-1 Morinosato-Wakamiya, Atsugi, Kanagawa 243-0198 (Japan)
Prof. T. Sugiura, Prof. H. Minoura
Graduate School of Engineering, Gifu University
Yanagido 1-1, Gifu 501-1193 (Japan)
Prof. K. Nishio
Department of Applied Chemistry, Tokyo Metropolitan University
1-1 Minamiosawa, Hachioji, Tokyo 192-0397 (Japan)
[+] Present address: CREST, JST (Japan Science and Technology) 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan.

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