Nanotechnology

Preparation of Higher-Order Zeolite Materials by Using Dextran Templating**

*Dominic Walsh, Alexander Kulak, Kensuke Aoki, Toshiyuki Ikoma, Junzo Tanaka, and Stephen Mann**

The chemical construction of organized inorganic matter by using nanoparticle or microcrystal building blocks—nanotectonics[1,2]—offers a novel approach to hierarchical, multi-

---

[*] Dr. D. Walsh, Dr. A. Kulak, K. Aoki, Prof. S. Mann
School of Chemistry
University of Bristol
Bristol BS8 1TS (UK)
Fax: (+44) 117 929 0509
E-mail: s.mann@bristol.ac.uk

Dr. D. Walsh, Dr. T. Ikoma, Dr. J. Tanaka
ICYS Centre/Advanced Material Group
National Institute for Material Science
1-1 Namiki, Tsukuba, Ibaraki 305-0051 (Japan)

K. Aoki
Central Technology Laboratory
Asahi Kasei Corporation
2-1 Samejima, Fuji, Shizuoka 416-8501 (Japan)

[**] We thank EPSRC (UK), JST(CREST) and Asahi Kasei Corp. for financial support.

DOI: 10.1002/ange.200460146

functional materials with complex architectures. The multiscale ordering, interlinking, and interfacing of preformed nanoparticles and small crystals can be directed internally by programmed assembly or externally by using a variety of structured organic templates. The former is achieved by self-coding of the inorganic building blocks with information-rich connectors, such as DNA duplexes,[3] antibody–antigen complexes[4] and streptavidin–biotin conjugates,[5] complementary force fields based on electrostatic matching,[6] or shape-directed hydrophobicity.[7] In contrast, preformed nanoparticles can be organized within porous templates such as silica/polymer opals,[8] polymer sponges[9] or perfluorohexane foams[10] to produce ordered macroporous inorganic replicas, or assembled onto polymer beads to form core–shell or hollow microspheres.[11] Inorganic nanoparticles have also been assembled by using miniemulsion droplets,[12] and recent studies involving sonicated water-in-oil emulsions have shown that highly complex spheroids can be assembled from silica/Au nanoparticles.[13]

Exploitation of the above strategies in catalysis and separation science is timely as the chemical synthesis and fabrication of self-supported multifunctional materials with hierarchical porosity, complex formation, and multiscale ordering remains a significant challenge. Recently, nanoslabs of the aluminium-free zeolite, silicalite, were assembled into periodically ordered mesostructures by surfactant templating.[14] Silicalite nanoparticles, about 50 nm in size, have also been organized on extended length scales to produce macroporous architectures by using multicellular bacterial threads,[15] starch sponges,[16] or polyurethane foams,[17] or assembled around latex beads to produce hollow microspheres with hierarchical porosity.[18] Other studies have demonstrated that zeolite crystals several micrometers in size can be organized into 2D arrays by using patterned solid substrates,[19] or arranged into self-supporting complex hollow microspheres by sonication of aqueous dispersions in toluene.[20]

Herein we demonstrate two new routes to the formation of higher-order zeolite materials based on template-directed processes that use the water-soluble polysaccharide, dextran and involve preformed zeolite crystals/nanoparticles as inorganic building blocks. In the first approach, which is based on a recent discovery in the preparation of metal and metal-oxide sponges,[21] centimeter-sized macroporous framework monoliths of interconnected filaments composed of NaY crystals and amorphous silica nanoparticles are prepared by slow thermal processing of dextran/inorganic pastes. The zeolite crystals are embedded in the silica matrix to promote homogeneity in the distribution of active sites within the filamentous framework, and increase the strength of the macroporous monoliths. In the second approach, macroscopic threads of dextran are prepared and used to align linear chains of 100 nm-sized silicalite crystals to produce inorganic fibers with an ordered superstructure of crystallographically oriented prismatic crystals. The silicalite chains, which consist of up to 20 coaligned crystals, are prepared by a novel process involving hydrothermal synthesis in the presence of the cationic polymer, poly(diallydimethylammonium hydroxide). Our results demonstrate that superstructural ordering of zeolite crystals within complex macroscopic morphologies can be achieved, and suggest that further development of these proof-of-concept studies should provide a range of novel hierarchical multifunctional materials for potential use in catalysis and separation science.

Open-framework zeolite monoliths were prepared as follows. Dextran ($M_r = 70\,000$) was dissolved in an aqueous suspension, consisting of 20:1 wt ratio, respectively, of submicron-sized NaY zeolite crystallites (size range, 0.7–1 µm) and silica nanoparticles (diameter, 14 nm) to produce a viscous paste that was air dried for two days. Controlled heating of the paste resulted in thermal decomposition of the dextran matrix at around 270 °C with associated outgassing of steam and carbon dioxide to produce an expanded carbon-based foam that served as a template for patterning the thermally induced aggregation of the silica/zeolite particles. Increasing the temperature slowly to 470 °C at a heating rate of $2\,^{\circ}\mathrm{C\,min^{-1}}$ resulted in the gradually destruction and removal of the carbon foam, and the formation of an intact inorganic spongelike replica, 1–2 cm in size, that was further heated to 600 °C to remove residual organic constituents.

In general, the above procedure resulted in the preparation of self-supporting replicas that were fragile but sufficiently robust to be handled with care. SEM investigations indicated that the replicas consisted of a continuous open framework of interconnected filaments, about 15 µm in width and 100–150 µm in length (Figure 1). The filaments intersected at distinct three-point junctions to produce open cells that were usually five- or six-sided and 100–300 µm across. Interestingly, the inorganic frameworks exhibited a gradient in pore sizes, with cells produced close to the outer surface of the dextran paste generally larger than those formed deep

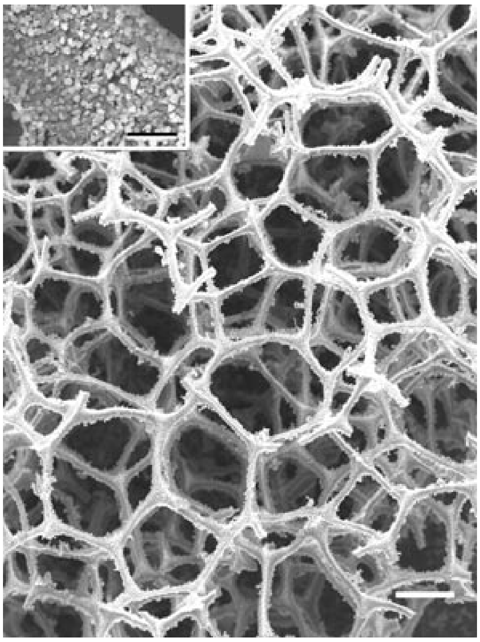

Figure 1. SEM micrograph showing open macroporous zeolite/silica framework prepared by dextran templating; scale bar = 100 µm. Inset; high magnification of a single-wall filament showing NaY crystals embedded in a continuous silica matrix; scale bar = 5 µm.

within the matrix. High-magnification images indicated that the filaments were composed of discrete micrometer-sized zeolite crystals embedded within a continuous matrix of condensed silica nanoparticles (Figure 1, inset). Significantly, X-ray diffraction studies showed almost identical reflections for the NaY crystals before and after heating the dextran composites to 600 °C, and BET analysis revealed no corresponding change in the type I isotherm, micropore size distribution, or surface area (650 $m^2 g^{-1}$), thus indicating that no degradation in the zeolite structure occurred during formation of the spongelike material.

Interestingly, closed-framework structures were obtained when NaY particles with size distribution of 0.3–0.4 μm were used in combination with colloidal silica solution at a respective weight ratio of 20:1. Under these conditions, the zeolite particles were small enough to stabilize the formation of thin self-supporting NaY/silica films across the 100–300 μm-sized apertures of the cellular framework (Figure 2). The supporting filamentous frame was typically 50 μm in width, whereas the membranes enclosing each cell were only about 150 nm in thickness. Although the thin inorganic membranes were present throughout the framework monolith, they were very fragile and often split or destroyed when examined by SEM.

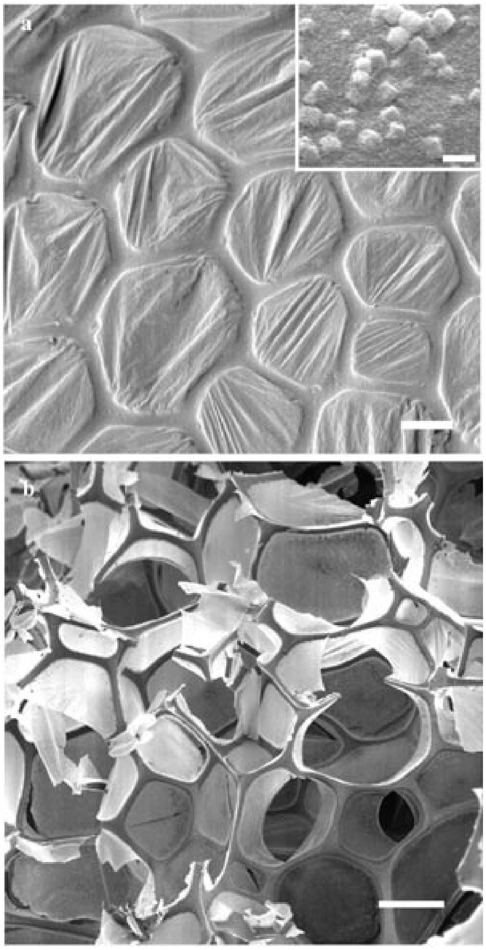

Figure 2. SEM images of closed cell NaY/silica frameworks. a) Top view showing underlying framework and intact aperture membrane; scale bar = 100 μm. Inset; high magnification image of the ultrathin membrane showing NaY crystals and silica matrix; scale bar = 0.5 μm. b) interior view showing details of closed cell architecture; scale bar = 100 μm.

The above results indicate that spongelike silica/NaY composites with porosity at both the nano- and macroscale can be prepared by sacrificial dextran templating that involves the in situ formation of thermally induced dextran-derived foams. Other investigations showed that formation of the intact macroporous frameworks depended on the composition of the paste, as well as the heating rates used during thermal processing. For example, by using the above paste composition but with a higher heating rate of 10 °C min^{-1}, samples that contained residual carbon even at 500 °C were produced. Consequently, it was necessary to heat the materials to 650 °C for several hours to prepare carbon-free replicas. However, these conditions resulted in the collapse of the NaY structure, as evidenced by the XRD data, to give frameworks with a low wall porosity of 20 $m^2 g^{-1}$ (BET analysis). Whereas intact macroporous sponges could be prepared by using silica nanoparticles and dextran alone, significantly, samples synthesized by using NaY and dextran at a low heating rate 2 °C min^{-1} in the absence of silica gave frameworks that were too fragile to be routinely handled. Similar results were also observed when mixtures of dextran and silicalite nanocrystals were used.

Dextran templating was also used to prepare intact macroscopic fibers of aligned silicalite crystals. Significantly, the crystals were preorganized in the form of discrete self-assembled chains (Figure 3 a), which were prepared by hydrothermal synthesis in the presence of the water-soluble cationic polymer, poly(diallydimethylammonium hydroxide. The chains were formed in situ within the reaction medium and consisted of prismatic particles that were coaligned with their crystallographic *b* axes parallel to the chain axis, as shown by TEM/electron diffraction analysis (data not shown) and XRD (Figure 4 a,b). An aqueous suspension of the chains was mixed with dextran and long fibers up to 20 cm in length were pulled from the mixture, and air-dried. This process resulted in an intact composite fiber that consisted of a densely packed network of silicalite chains oriented preferentially along the morphological long axis, which was subsequently slowly heated to 550 °C to remove the dextran matrix. In general, this procedure resulted in intact inorganic replicas when the precursor threads were a few centimetres in length, whereas longer threads tended to disintegrate into smaller inorganic fibers. In each case, the calcined materials were highly textured and consisted of a superstructure of silicalite crystals. Significantly, materials prepared from dextran/silicalite threads, 20–30 μm in width, were highly ordered with chains of silicalite crystals preferentially aligned along the fiber axis (Figure 3 b,c). Corresponding XRD measurements indicated that the silicalite micropore structure was retained after thermal treatment, and that the peak intensity of the (0100) reflection was reduced compared to a nonoriented control sample (Figure 4 c). The data confirmed that under these conditions, the silicalite crystals within the oriented superstructure were preferentially aligned such that the crystallographic *b* axis was parallel to the fiber direction.

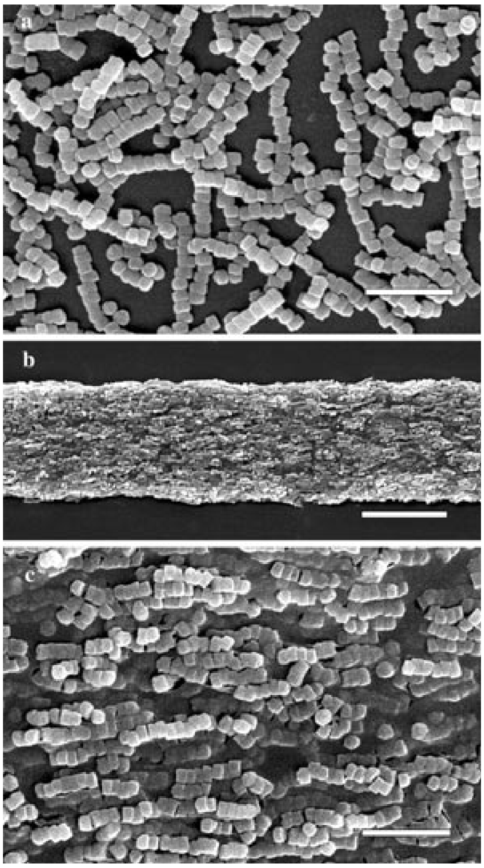

Figure 3. a) As-synthesized ordered chains of silicalite crystals viewed by SEM; scale bar = 1 μm. b) Inorganic fiber with ordered superstructure of silicalite crystals prepared from calcined dextran/silicalite thread; scale bar = 5 μm. c) High-magnification image showing *iso*-oriented texture of prismatic silicalite crystals aligned parallel to the fiber axis; scale bar = 1 μm.

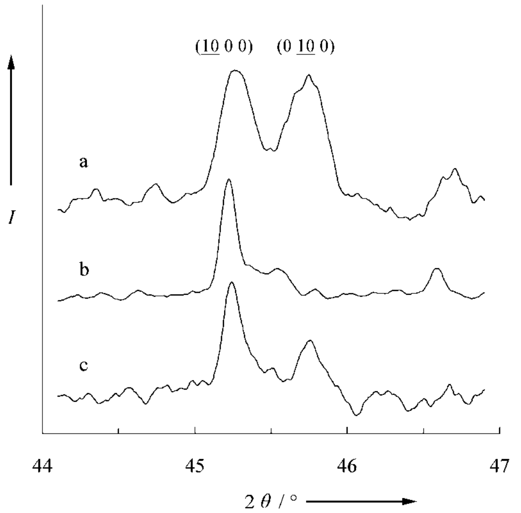

Figure 4. XRD data showing relative peak intensities for silicalite (1000) and (0100) reflections for a) control crystals (non-oriented), b) as-synthesized silicalite chains, and c) inorganic fiber with ordered silicalite superstructure. *I* is intensity, arbitrary units.

In contrast, the use of thicker dextran/silicalite precursor threads introduced increased levels of particle disorder and macroporous voids in the inorganic replicas, presumably due to enhanced entrapment of gas bubbles and associated disruption of the silicalite chains during thermal processing.

In conclusion, the above results indicate that dextran/inorganic composites can be used for the facile preparation of zeolite materials with higher-order structure, morphology, and porosity. The methods use the ability of dextran to be readily drawn into macrothreads from viscous solutions, or prepared as thick pastes as precursors to thermally induced foams. In both cases, the polysaccharide matrix is used as a sacrificial template to coalign or spatially pattern the zeolite crystals. Removal of dextran by heating the soft macrothreads results in minimal disruption to the constituent silicalite crystals, and the high level of crystal packing induced by the fiber-drawing process, as well as preorganization of the silicalite particles into chainlike assemblies, are sufficient to produce intact fibrous superstructures during sintering. In contrast, thermal decomposition of the pastes gives rise to an open framework of interconnected NaY-containing filaments due to temporary stabilization of CO_2 microbubbles in the lower-density matrix, which induces phase separation and spatial patterning of the zeolite crystals. However, in this case, the level of sintering between zeolite crystals is insufficient to form a self-supporting framework, and a silica "mortar" is required to stabilize the inorganic microfilaments. Interestingly, the presence of silica in association with NaY crystals of relatively small size (300–400 nm) produces intact frameworks in which the individual cell apertures are veiled in a thin micrometer-thick inorganic membrane. Although these structures are very fragile, the ability to prepare both open and closed frameworks of organized zeolite crystals could have interesting applications, for example in high-resolution separation processes. Further work is in progress to extend the above templating procedures to higher-order zeolite architectures with appropriate stability for applications testing and development.

Experimental Section

Preparation of NaY zeolite/silica framework monoliths: NaY zeolite crystals 0.7–1 μm in size were separated from a commercial sample (Aldrich Cat. No. 33, 444-8, SiO_2/Al_2O_3 mole ratio = 5.1; Na_2O wt% = 13) by fractional sedimentation in ethanol by using successive centrifugation at 3000 rpm for 3 min. The BET surface area was 450 m^2g^{-1} (as supplied) and 610 m^2g^{-1} (after heating at 2 °Cmin^{-1} to 600 °C). Alternatively, NaY particles with size a distribution of 0.3–0.4 μm were synthesized according to previous methods.[22] An aqueous suspension consisting of NaY and silica particles at a respective weight ratio of 20:1 was prepared by the addition of 0.1 g of submicrometer-sized NaY crystals to 1 mL distilled water, followed by 0.025 g of a 20wt% colloidal silica suspension (Snowtex C, Nissan Chem. Co., particle size, 14 nm). Dextran (2 g, M_r 70000) was then dissolved in the suspension to form a viscous solution which was transferred to an open dish and left to air-dry for 2 days. The dried paste was heated to 600 °C at a heating rate of 2 °Cmin^{-1}, held at 600 °C for 30 min, and then cooled to room temperature in the furnace. Samples were removed and investigated by SEM, XRD, TGA, FTIR spectroscopy and BET analysis (TGA is thermogravimetric analysis).

Preparation of silicalite chains and oriented multichain fibers: Linear chains of prismatic crystals of silicalite-1 were prepared as follows: Tetraethylorthosilicate (TEOS; 16 g, 76.8 mmol) was slowly added to a stirred aqueous solution that contained 1M tetrapropylammonium hydroxide (TPAOH; 27.32 g, 27.0 mmol) and 20wt% poly(diallydimethylammonium hydroxide) (PDAC;10 g, 0.015 mmol). After the reaction had been stirred for 24 h at room temperature, large agglomerates were removed and 10 ml of the resulting cloudy suspension poured into a 20 mL hydrothermal bomb, and placed in a preheated oven at 150 °C and left at this temperature for 24 h. After cooling to room temperature, the white suspension was centrifuged and the supernatant fluid removed, and deionized water added and the precipitate resuspended by shaking. This washing procedure was repeated four times to give suspension 6–7wt% in solids that slowly sedimented over a period of a few days.

Inorganic macrofibers comprising coaligned chains of silicalite crystals were prepared as follows: 2.0 g of dextran (M_r 70000) was dissolved in 1 mL of an aqueous suspension containing about 3 wt% silicalite crystals in the form of linear chains to form a viscous solution. Dextran/silicalite threads, often 20–30 µm in width and up to 20 cm in length, were then drawn from the vicsous solution by insertion and slow removal of a spatula tip. The composite threads were air-dried and then heated to 550 °C at 2 °C min^{-1} for 12 h before cooling to room temperature in the furnace. The resulting intact inorganic fibers were removed and investigated by a range of physical methods.

Received: March 29, 2004
Revised: June 16, 2004

Keywords: higher-order assembly · inorganic building blocks · nanoparticles · template synthesis · zeolites

---

[1] S. Mann, S. A. Davis, S. R. Hall, M. Li, K. H. Rhodes, W. Shenton, S. Vaucher, B. Zhang, *Dalton Trans.* **2000**, 3753.
[2] S. A. Davis, M. Breulmann, K. H. Rhodes, B. Zhang, S. Mann, *Chem. Mater.* **2001**, *13*, 3218.
[3] a) C. A. Mirkin, R. L. Lesinger, R. C. Mucic, J. J. Storhoff, *Nature* **1996**, *382*, 607; b) P. Alivasatos, K. P. Johnsson, X. Peng, T. E. Wilson, C. J. Loweth, M. Bruchez, P. G. Schultz, *Nature* **1996**, *382*, 609; c) A. N. Shipway, I. Willner, *Chem. Commun.* **2001** 2035; d) L. Josephson, J. M. Perex, R. Weissleder, *Angew. Chem.* **2001**, *40*, 3304; *Angew. Chem. Int. Ed.* **2001**, *40*, 3204; e) E. Dujardin, L. B. Hsin, C. R. C. Wang, S. Mann, *Chem. Commun.* **2001**, 1264.
[4] W. Shenton, S. A. Davis, S. Mann, *Adv. Mater.* **1999**, *11*, 449.
[5] a) S. Connolly, D. Fitzmaurice, *Adv. Mater.* **1999**, *11*, 1202; b) M. Li, K. K. W. Wong, S. Mann, *Chem. Mater.* **1999**, *11*, 23.
[6] a) T. H. Galow, A. K. Boal, V. M. Rotello, *Adv. Mater.* **2000**, *12*, 576; b) A. K. Boal, T. H. Galow, F. Ilhan, V. M. Rotello, *Adv. Funct. Mater.* **2001**, *11*, 461.
[7] M. Li, H. Schnablegger, S. Mann, *Nature* **1999**, *402*, 393.
[8] a) B. T. Holland, C.F Blanford, T. Do, A. Stein, *Chem. Mater.* **1999**, *11*, 795; b) Y. A. Vlasov, N. Yao, D. J. Norris, *Adv. Mater.* **1999**, *11*, 165; c) G. Subramania, V. N. Manoharan, J. D. Thorne, D. J. Pine, *Adv. Mater.* **1999**, *11*, 1261; d) O. D. Velev, P. M. Tessier, A. M. Lenhoff, E. W. Kaler, *Nature* **1999**, *401*, 548; f) O. D. Velev, E. W. Kaler, *Adv. Mater.* **2000**, *12*, 531.
[9] M. Breulmann, S. A. Davis, S. Mann, H. P. Hentze, M. Antonietti, *Adv. Mater.* **2000**, *12*, 502.
[10] F. Carn, F. A. Colin, M. F. Achard, H. Deleuze, Z Saadi, R. Backov, *Adv. Mater.* **2004**, *16*, 140.
[11] a) F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, *282*, 1111; b) A. Rogach, A. Susha, F. Caruso, G. Sukhorukov, A. Kornowski, S. Kershaw, H. Möhwald, A. Eychmüller, H. Weller, *Adv. Mater.* **2000**, *12*, 333; c) D. I. Gittens, A. S. Susha, B. Schoeler, F. Caruso, *Adv. Mater.* **2002**, *14*, 508.
[12] B. zu Putlitz, K. Landfester, H. Fischer, M. Antonietti, *Adv. Mater.* **2001**, *13*, 500.
[13] A. Kulak, S. A. Davis, E. Dujardin, S. Mann, *Chem. Mater.* **2003**, *15*, 528.
[14] S. P. B. Kremer, C. E. A. Kirschhock, A. Aerts, K. Villani, J. A. Martens, O. I. Lebedev, G. V. Tendeloo, *Adv. Mater.* **2003**, *15*, 1705.
[15] B. Zhang, S. A. Davis, N. H. Mendelson, S. Mann, *Chem. Commun.* **2000**, 781.
[16] B. Zhang, S. A. Davis, S. Mann, *Chem. Mater.* **2002**, *14*, 1369.
[17] L. Huerta, C. Guillem, J. Latorre, A. Beltran, D. Beltran, P. Amoros, *Chem. Commun.* **2003**, 1448.
[18] a) K. H. Rhodes, S. A. Davis, F. Caruso, B. Zhang, S. Mann, *Chem. Mater.* **2000**, *12*, 2832; b) X. D. Wang, W. L. Yang, Y. Tang, Y. J. Wang, S. K. Fu, Z. Gao, *Chem. Commun.* **2000**, 2161; c) A. G. Dong, Y. J. Wang, Y. Tang, N. Ren, Y. H. Zhang, Z. Gao, *Chem. Mater.* **2002**, *14*, 3217; d) A. G. Dong, N. Ren, W. L. Yang, Y. J. Wang, Y. H. Zhang, D. J. Wang, H. H. Hu, Z. Gao, Y. Tang, *Adv. Funct. Mater.* **2003**, *13*, 943.
[19] a) K. Ha, Y.-J. Lee, Y. S. Chun, Y. S. Park, G. S. Lee, K. B. Yoon, *Adv. Mater.* **2001**, *13*, 594; b) K. Ha, Y.-J. Lee, D.-Y. Jung, J. H. Lee, K. B. Yoon, *Adv. Mater.* **2000**, *12*, 1614.
[20] A. Kulak, Y. J. Lee, Y. S. Park, H. S. Kim, G. S. Lee, K. B. Yoon, *Adv. Mater.* **2002**, *14*, 526.
[21] D. Walsh, L. Arcelli, T. Ikoma, J. Tanaka, S. Mann, *Nat. Mater.* **2003**, *2*, 386.
[22] G. S. Lee, Y.-J. Lee, K. Ha, K. B. Yoon, *Adv. Mater.* **2001**, *13*, 1491.