

Liquid-Crystal Templating in Ammonia: A Facile Route to Micro- and Mesoporous Metal Nitride/Carbon Composites**

Hao Qi, Xavier Roy, Kevin E. Shopsowitz, Joseph K.-H. Hui, and Mark J. MacLachlan*

Microporous (pore size < 2 nm), mesoporous (pore size 2–50 nm) and macroporous materials (pore size > 50 nm) have long captured the imaginations of scientists and are important to numerous technological processes, such as hydrocracking, ion exchange, adsorbents, and catalysis.^[1] The porosity of solid-state materials can be defined through the use of a template, which can be molecular, polymeric, or supramolecular. With molecular templates, diverse zeolitic structures have been prepared.^[2] In 1992, Kresge et al. reported the use of lyotropic liquid-crystalline (LC) templates in water to obtain mesoporous silica materials.^[3] This approach has since been exploited, and a multitude of organosilicates,^[4] chalcogenides,^[5] and other structures have been reported.^[6] Moreover, block copolymers (e.g., pluronics) may be employed to form mesoporous materials with larger pores.^[7] Through the use of even larger templates (e.g., latex spheres), macroporous structures have been obtained.^[8]

In nearly all of these reports, the materials were prepared in water or sometimes in alcohol. Extension to formamide enabled access to materials that could not easily be prepared in water, such as mesostructured metal/germanium sulfides,^[9] metal/tin selenides,^[10] Prussian blue analogues,^[11] and germanium.^[12,13] Still, there are compositions that cannot be prepared by templating in water or in formamide (e.g., metal nitrides and carbides) due to instability of the target solid in these solvents or reactions of the necessary reagents with the solvent. Alternative strategies are required to develop these new materials.

Metal nitrides possess outstanding properties, such as high thermal, mechanical and chemical stability, high conductivity, and even superconductivity in some cases.^[14] They are of great technological interest in different areas, including catalysis (e.g., Fischer–Tropsch reaction), optics, as supercapacitor electrodes, and in coatings.^[14] Nanoporous metal nitrides with large surface areas and pore volumes are expected to have outstanding properties for some of these applications, but routes to these materials are very limited. The typical liquid-crystalline templating approach in aqueous solution cannot be

used for porous metal nitrides since precursors are hydrolytically sensitive and oxides would instead form. Metal nitrides with low surface areas (e.g., 0.27 m² g^{−1}) are commonly prepared by ball-milling, but lack porosity.^[15] Several groups reported porous nanocrystalline metal nitrides by ammonolysis of nanostructured metal oxides at high temperature.^[16] For example, Zhao and co-workers reported using mesoporous SBA-15 silica as a hard template for mesoporous metal nitrides (CoN, CrN) through a three-step reaction involving nitridation of metal oxides.^[17] More recently, Thomas et al. used a reactive templating approach to obtain mesoporous metal nitride–carbon composites through a four-step process.^[18]

In this study, we report a new and simple liquid-crystalline templating approach in liquid NH₃ to synthesize nanoporous metal nitride/carbon composites. Although nonaqueous solvents have been long recognized for preparing certain types of mesoporous materials to prevent the precipitation of non-structured phases, this is the first report of template synthesis of porous materials using liquid NH₃ as solvent. We show that the known LC phase of cellulose in NH₃/NH₄SCN can be used to obtain microporous or mesoporous titanium nitride or vanadium nitride/carbon composites. Both microporous and mesoporous products show high specific surface areas varying from 77 to 581 m² g^{−1}, and exhibit interesting porous structures with hierarchical organization.

Metal nitrides can be prepared by condensation of dialkylamidometal complexes in liquid NH₃, forming polymeric networks which, after calcination, transform into metal nitrides.^[19] This method has been applied to several metals including Ti, Cr, Ni, V, Cu, and Co.^[20] The polymerization in ammonia is chemically similar to the sol–gel condensation of silicates and other molecules in water. Given the similarity of water to ammonia in terms of many properties (hydrogen bonding, immiscibility with *n*-alkanes),^[21] we thought it may be possible to use liquid ammonia as a solvent to form mesoporous metal nitrides using surfactants as template. Unfortunately, most surfactants are insoluble in liquid ammonia, and there are few reports of lyotropic liquid crystals formed in liquid ammonia.^[22]

We chose instead to use the cellulose/NH₃/NH₄SCN system to prepare porous metal nitrides. It is known that at concentrations above 7.5 % w/v, cellulose exhibits a LC phase in ca. 25:75 w/w NH₃/NH₄SCN.^[23] Also, it has been shown that when microgranular pure cellulose powder (cellulose CC41) is used as the cellulose source, it forms a chiral nematic phase in NH₃/NH₄SCN,^[23a] which is an unusual LC phase for preparing nanoporous materials. We employed tetrakis(diethylamido)titanium(IV) (TDEAT) and tetrachlorovanadium(IV) as the precursors to titanium nitride and vanadium

[*] Dr. H. Qi, X. Roy, K. E. Shopsowitz, J. K.-H. Hui, Prof. Dr. M. J. MacLachlan
Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, BC, V6T 1Z1 (Canada)
Fax: (+1) 604-822-2847
E-mail: mmaclach@chem.ubc.ca
Homepage: <http://www.chem.ubc.ca/personnel/faculty/macLachlan/index.shtml>

[**] We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for funding.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201004974>.

nitride, respectively. Table 1 summarizes the experimental parameters and porous properties of prepared nanoporous metal nitrides.

In a typical preparation, liquid NH_3 was added to a preweighed quantity of NH_4SCN and stirred at room temperature to form a clear solution. Cellulose was added to give a milky, homogeneous mixture. In each preparation, we kept the ratio of NH_3 and NH_4SCN constant (ca. 9 g NH_3 + 26 g NH_4SCN) and varied the proportion of cellulose CC41 and metal-organic precursor.^[24] Three sets of cellulose concentration were chosen ranging from 1 g of CC41 (7.7% w/v), which is reported to form the LC phase,^[23a] to 4 g of CC41 (30% w/v), which gives a gel phase with junction zones consisting of highly viscous LC regions.^[25] Once the liquid crystal/gel phase formed, the metal-containing precursor was added by syringe (neat in the case of TDEAT, diluted with hexanes for VCl_4). After adding the Ti (or V) precursor and stirring the mixture at room temperature, excess NH_3 was removed by heating the samples under vacuum at 150 °C. Finally, the samples were calcined at 600 °C for 3 h under a flow of $\text{NH}_3(\text{g})$ to give nanoporous titanium nitride or vanadium nitride composite materials as flaky black powders. The new materials were analyzed by powder X-ray diffraction, elemental analysis, gas absorption, IR spectroscopy, energy-dispersive X-ray (EDX) analysis, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Table 1 lists the starting compositions, surface areas, and pore volumes measured for a series of titanium and vanadium nitride materials. All samples were calcined under a flow of NH_3 . We also tried calcinations under air or N_2 , but the samples prepared under those conditions showed no porosity. Indeed, calcination under a flow of NH_3 has been shown to be necessary to obtain nanocrystalline TiN.^[26]

Samples were analyzed by metal analysis, CNH analysis, and energy-dispersive X-ray analysis (see the Supporting Information, Tables S1 and S2). From the analyses, the samples contain up to ca. 25 wt % metal, 10–20 wt % N, a small amount of H, and a substantial amount of C (5–50 %). There is a strong correlation between the amount of cellulose employed in the preparation and the relative amount of carbon in the product. Samples prepared with higher amounts

of cellulose (such as **TiN-1**, **VN-1**) showed the highest carbon content while those prepared with less cellulose showed lower carbon deposition. Thus, similar to mesoporous TiN prepared using carbon nitride as a hard template,^[18b] it is more appropriate to label the materials as porous metal nitride/carbon composites. Depending on the type of application, the existence of carbon may not be a drawback, considering the good conductivity and stability of carbon.^[27] Furthermore, it may be possible to reduce the carbon component by optimizing the calcination conditions.

From the EDX results, the materials contain oxygen, which is not surprising since oxides from the cellulose will passivate the nitride particles and may also be present in the remaining organic material. Traces of sulfur (from the thiocyanate) were also observed in some samples.

X-ray diffraction (Figure 1 and Figure S1) verified that metal nitrides were obtained. Some samples (e.g., **TiN-2**) showed only amorphous halos. A broad peak observed near 27° 2 θ corresponds to d_{002} of graphitic carbon. Other samples showed improved crystallinity. For example, **TiN-5** showed broad peaks that correspond to crystalline osbornite (TiN, JCPDS File No. 38-1420).^[28] From the Scherrer equation,^[29] the crystallites are ca. 5.9 nm on average. When the calcination was performed at higher temperature, nanocrystalline metal nitride with improved order was obtained (e.g., **TiN-6**).

Nitrogen gas adsorption measurements showed that all of the materials prepared by the cellulose templating in ammonia are porous (Table 1). The materials have high surface area (most > 300 m² g⁻¹), with the highest one being 581 m² g⁻¹. Figure 2 shows N_2 absorption-desorption isotherms for three of the materials (the others are shown in the Supporting Information). According to Brunauer-Deming-Deming-Teller (BDDT) classification,^[30] the isotherm of **TiN-2** is type I, which is a typical isotherm for microporous materials, whereas the isotherms of **TiN-5** and **TiN-6** are type IV with an H4 hysteresis loop, meaning that **TiN-5** and **TiN-6** are typical mesoporous materials. The products that were prepared with a large amount of cellulose (**TiN-1**, **TiN-2** and **VN-1**), where the gel phase is expected, show typical type I isotherms (microporous). All of the other products were synthesized using a lower proportion of cellulose and show type IV isotherms (mesoporous). Thus, with this templating method, we can rationally change the porous structure by simply varying the reactant ratios.

Table 1: Preparation conditions and absorption data for TiN and VN materials.^[a]

Sample code	TDEAT (or VCl_4)/cellulose/ NH_3 / NH_4SCN ^[b]	Surface area [m ² g ⁻¹] ^[c]	Pore volume [cm ³ g ⁻¹]
TiN-1	0.93:4:9:26	398	0.15
TiN-2	2.79:4:9:26	581	0.20
TiN-3	1.86:2:9:26	337	0.17
TiN-4	0.93:1:9:26	404	0.29
TiN-5	1.86:1:9:26	305	0.30
TiN-6^[d]	1.86:1:9:26	117	0.19
TiN-7	2.79:1:9:26	324	0.32
VN-1	5.4:4:9:26	448	0.14
VN-2	3.6:2:9:26	77	0.13

[a] See the Experimental Section for details. Samples were calcined at 600 °C, except **TiN-6**. [b] Presented as weight ratio. [c] BET or Langmuir surface area, the one with higher correlation coefficient is presented. [d] Calcined at 800 °C.

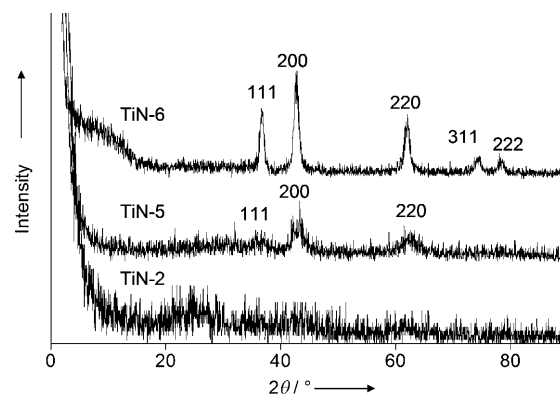


Figure 1. Powder XRD patterns of **TiN-2**, **TiN-5**, and **TiN-6**.

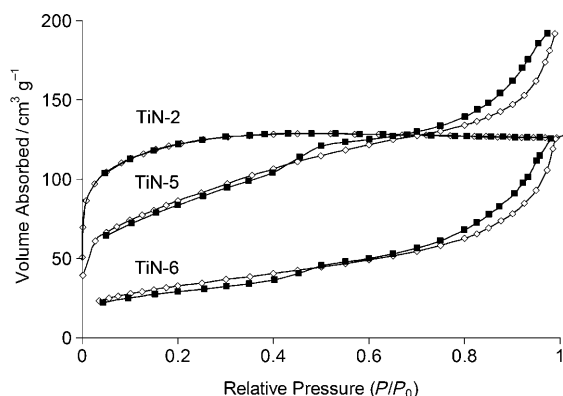


Figure 2. N_2 adsorption–desorption isotherms of **TiN-2**, **TiN-5**, and **TiN-6**. $\diamond$: adsorption, $\blacksquare$: desorption.

Pore size distributions of all the materials are shown in Figures S4 and S5. The mesoporous materials show similar pore size distributions using BJH method from the adsorption branch (with one exception, **VN-2**). For the microporous materials, pore size distributions were obtained with the Horvath–Kawazoe equation.^[31]

It is noteworthy that calcination at higher temperature (800 °C vs. 600 °C) led to materials with reduced porosity. Compared with **TiN-5**, the shape of the isotherm of **TiN-6** has not changed, but only the pore volume is reduced. This suggests that the increased calcination temperature has less effect on the pore structure and size, only inducing the collapse of a large fraction of the pores. Indeed, the pore size distributions of **TiN-5** and **TiN-6** are quite similar.

It is known that cellulose contains a hierarchical structure composed of elementary fibrils (2–3 nm dimensions), microfibrils (20–35 nm), and cellulose fibrils with micrometer size dimensions. Further, the elementary fibrils are made of β -linked D-glucose polymers, and the dimensions of these units fall into the subnanometer regime. The hierarchical structure of the cellulose is mediated by inter- and intramolecular hydrogen bonding.^[32] We believe that this structure is disrupted with NH_3 that can compete for hydrogen bonds, and the extent of structural change depends on the relative ratio of NH_3 and cellulose. Thus, the morphology differences observed and the changes in porosity that depend on the proportion of cellulose employed may arise from these interactions. Unlike the traditional synthesis of mesoporous materials using surfactant or block copolymers, where the template is relatively inflexible and gives distinct pore structures (lamellar, hexagonal or cubic),^[33] here the cellulose acts as a dynamic template that is capable of introducing porosity and features on different length scales. This intriguing feature of cellulose may be useful for making diverse porous materials. Thomas and Antonietti reported microporous silica using cellulose as template.^[34]

We investigated the morphology of the new materials by SEM and TEM. Representative SEM images are displayed in Figure 3. In SEM images of **TiN-2** (Figure 3a,b), a typical microporous product, the particles appear relatively smooth, with large micrometer-sized cavities on the surface. The micropores themselves could not be imaged by SEM or TEM.

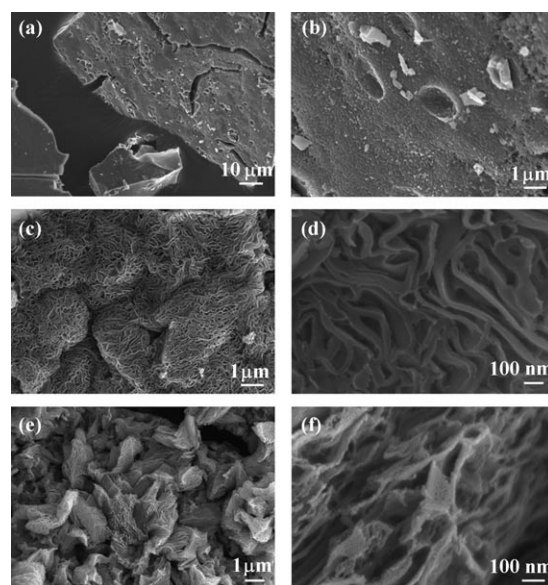


Figure 3. SEM images of a,b) **TiN-2**, c,d) **TiN-5**, and e,f) **TiN-6**.

Considering the size regime, the large macropores likely emerge from templating the intact cellulose fibrils. When lower quantities of cellulose were used, the resulting mesoporous materials show lamellar-like morphology (Figure 2c–f). Although layered structures have been reported before,^[35] to the best of our knowledge, this kind of morphology has never been observed in inorganic porous materials. The materials exhibiting the most similar morphology to these are the polyolefin blends reported by Wang et al.^[36] In their case, the morphology was attributed to liquid–liquid phase separation, and that may also be the explanation here, where phase separation occurs during the polymerization process. Figure 3e,f shows the SEM images of **TiN-6**, prepared by calcination at 800 °C. It is clear that the morphology of the materials is significantly affected by the calcination temperature.

From TEM and SEM images (Figures S6–S9), we do not observe long-range order in the liquid-crystal-templated materials. This is not surprising, since the nematic phase applied in the system is the least-ordered LC phase. Nevertheless, the remarkable morphologies observed in these solid-state materials support the LC templating of the solids in liquid ammonia using cellulose as template.

In summary, we have presented the first porous materials formed by templating in liquid ammonia, utilizing the liquid-crystalline phase formed by cellulose/ NH_3 / NH_4SCN . By changing the proportions of reactants, the porosity, surface area, and morphology of the materials can be modified. The materials exhibit high surface areas and porosity spanning the entire range from micro- to meso- to macropores. The combination of mesoporosity and lamellar morphology will provide unique characteristics for potential applications, such as in heterogeneous catalysts or supercapacitors. We have demonstrated that the process can be applied to make both porous titanium and vanadium nitride composites, and we expect that it can be generalized to other inorganic materials. We hope that using cellulose in liquid ammonia to template

nanoporous inorganic materials will lead to a wealth of new inorganic porous structures with potential applications in catalysis, as electrode materials, and as adsorbents.

Experimental Section

The entire procedure was conducted under a nitrogen atmosphere. In a typical synthesis, 13 mL (9 g) of liquid NH_3 ($d = 0.68 \text{ g mL}^{-1}$) was condensed into a graduated cylinder and quickly transferred into a cooled (in a dry ice/acetone bath at -78°C) three-necked flask containing 26 g of ammonium thiocyanate (NH_4SCN). The flask was equipped with a condenser that was cooled with a dry ice/acetone bath to prevent the evaporation of NH_3 . After the mixture warmed to room temperature under N_2 , it was stirred until the NH_4SCN completely dissolved in the liquid NH_3 and a clear solution was formed. The flask was then cooled in a dry ice/acetone bath before the weighed quantity of cellulose (e.g., 4 g) was added. The mixture was then warmed slowly to room temperature and was stirred for about 2 h to give a uniform milky suspension. At this time, an appropriate amount of tetrakis(diethylamido)titanium(IV) (TDEAT) (e.g., 3 mL, $d = 0.931 \text{ g mL}^{-1}$) was added dropwise through syringe while the reaction mixture was vigorously stirred. The mixture was stirred at room temperature for an additional 2 h, then the condenser was removed and the temperature was raised to 50°C overnight to allow the evaporation of free NH_3 . Finally, the material was put under vacuum ($\approx 10^{-2}$ Torr) and the temperature was raised to 150°C to remove any remaining NH_3 and to further condense the network prior to calcination. In the final step, the black solid mixture was heated to 600°C (heating rate of $1.7^\circ\text{C min}^{-1}$) under a flow of NH_3 gas, then calcined at that temperature for 3 h to give flaky black powders. In the preparations of vanadium nitride composites, the VCl_4 precursor was first diluted using 5 mL of hexanes before addition to the cellulose/ $\text{NH}_3/\text{NH}_4\text{SCN}$ system as the neat VCl_4 underwent too vigorous of a reaction.

Received: August 10, 2010

Published online: November 15, 2010

Keywords: liquid ammonia · liquid-crystal templating · mesoporous materials · metal nitrides · microporous materials

- [1] *Nanoporous Materials—Science and Engineering*, (Eds.: G. Q. Lu, X. S. Zhao), World Scientific, Singapore, **2004**.
- [2] See, for example: a) S. T. Wilson, B. M. Lok, E. M. Flanigen, U.S. Patent 4310440, **1982**; b) B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan, E. M. Flanigen, *J. Am. Chem. Soc.* **1984**, *106*, 6092–6093; c) J. B. Parise, *J. Chem. Soc., Chem. Commun.* **1985**, 606–607; d) A. Merrouche, J. Patarin, H. Kessler, M. Souldard, L. Delmotte, J. L. Guth, J. F. Joly, *Zeolites* **1992**, *12*, 226–232.
- [3] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712.
- [4] a) B. J. Melde, B. T. Holland, C. F. Blanford, A. Stein, *Chem. Mater.* **1999**, *11*, 3302–3308; b) S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **1999**, *121*, 9611–9614; c) T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867–871.
- [5] a) P. V. Braun, P. Osenar, S. I. Stupp, *Nature* **1996**, *380*, 325–328; b) J. Li, H. Kessler, M. Souldard, L. Khouchaf, M.-H. Tuillier, *Adv. Mater.* **1998**, *10*, 946–949; c) M. Fröba, N. Oberender, *Chem. Commun.* **1997**, 1729–1730.
- [6] M. G. Kanatzidis, *Adv. Mater.* **2007**, *19*, 1165–1181.
- [7] P. D. Yang, T. Deng, D. Y. Zhao, P. Y. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, *282*, 2244–2246.
- [8] B. T. Holland, C. F. Blanford, A. Stein, *Science* **1998**, *281*, 538–540.
- [9] M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *397*, 681–684.
- [10] P. N. Trikalitis, K. K. Rangan, T. Bakas, M. G. Kanatzidis, *Nature* **2001**, *410*, 671–675.
- [11] X. Roy, L. K. Thompson, N. Coombs, M. J. MacLachlan, *Angew. Chem.* **2008**, *120*, 521–524; *Angew. Chem. Int. Ed.* **2008**, *47*, 511–514.
- [12] G. S. Armatas, M. G. Kanatzidis, *Science* **2006**, *313*, 817–820.
- [13] For an example of mesoporous germanium formed in ethylenediamine, see: D. Sun, A. E. Riley, A. J. Cadby, E. K. Richman, S. D. Korlann, S. H. Tolbert, *Nature* **2006**, *441*, 1126–1130.
- [14] *The Chemistry of Metal Carbides and Nitrides*, (Ed.: S. T. Oyama), Blackie, New York, **1996**.
- [15] V. I. Itin, O. G. Terekhova, N. G. Kasatskii, N. N. Golobokov, O. A. Shkoda, A. A. Knyazeva, N. N. Volkovnyak, V. K. Smolyakov, Y. M. Maksimov, *Inorg. Mater.* **2005**, *41*, 1157–1161.
- [16] a) X. Zhou, H. Chen, D. Shu, C. He, J. Nan, *J. Phys. Chem. Solids* **2009**, *70*, 495–500; b) A. M. Glushenkov, D. Hulicova-Jurcakova, D. Llewellyn, G. Q. Lu, Y. Chen, *Chem. Mater.* **2010**, *22*, 914–921.
- [17] Y. F. Shi, Y. Wan, R. Y. Zhang, D. Y. Zhao, *Adv. Funct. Mater.* **2008**, *18*, 2436–2443.
- [18] a) A. Fischer, Y.-S. Jun, A. Thomas, M. Antonietti, *Chem. Mater.* **2008**, *20*, 7383–7389; b) Y.-S. Jun, W. H. Hong, M. Antonietti, A. Thomas, *Adv. Mater.* **2009**, *21*, 4270–4274.
- [19] G. M. Brown, L. Maya, *J. Am. Ceram. Soc.* **1988**, *71*, 78–82.
- [20] D. V. Baxter, M. H. Chisholm, G. J. Gama, V. F. DiStasi, A. L. Hector, I. P. Parkin, *Chem. Mater.* **1996**, *8*, 1222–1228.
- [21] E. Brunner, *J. Chem. Thermodyn.* **1988**, *20*, 273–297.
- [22] S. Bzik, M. Jansen, *Chem. Eur. J.* **2003**, *9*, 613–620.
- [23] a) Y.-S. Chen, J. A. Cuculo, *J. Polym. Sci. Part A: Polym. Chem.* **1986**, *24*, 2075–2084; b) A. W. DeGroot, D. E. Guinnup, M. H. Theil, J. A. Cuculo, *J. Polym. Sci. Part B: Polym. Phys.* **1991**, *29*, 547–556; c) A. W. DeGroot, D. E. Guinnup, M. H. Theil, J. A. Cuculo, *J. Polym. Sci. Part B: Polym. Phys.* **1991**, *29*, 557–563.
- [24] A slight excess of NH_3 was employed, anticipating that evaporation of NH_3 would bring the ratio to the optimal concentration for LC formation.
- [25] a) S. Z. D. Cheng, S. K. Lee, J. S. Barley, S. L. C. Hsu, F. W. Harris, *Macromolecules* **1991**, *24*, 1883–1889; b) K. Tohyama, W. G. Miller, *Nature* **1981**, *289*, 813–814.
- [26] D. Choi, P. N. Kumta, *J. Electrochem. Soc.* **2006**, *153*, A2298–A2303.
- [27] For example: K. Miyasaka, K. Watanabe, E. Jojima, H. Aida, M. Sumita, K. Ishikawa, *J. Mater. Sci.* **1982**, *17*, 1610–1616.
- [28] M. Hasegawa, T. Yagi, *J. Alloys Compd.* **2005**, *403*, 131–142.
- [29] R. C. Rau, *Advances in X-ray Analysis*, Vol. 5, Plenum, New York, **1962**, p. 104.
- [30] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, T. Siemieniowska, *Pure Appl. Chem.* **1985**, *57*, 603–619.
- [31] P. Kowalczyk, A. P. Terzyk, P. A. Gauden, G. Rychlicki, *Adsorpt. Sci. Technol.* **2002**, *20*, 295–305.
- [32] a) Y. Z. Zhang, X. L. Chen, J. Liu, P. J. Gao, D. X. Shi, S. J. Pang, *J. Vac. Sci. Technol. B* **1997**, *15*, 1502–1507; b) C. J. Kennedy, G. J. Cameron, A. Štuncová, D. C. Apperley, C. Altaner, T. J. Wess, M. C. Jarvis, *Cellulose* **2007**, *14*, 235–246, and reference therein.
- [33] a) G. J. de A. A. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin, *Chem. Rev.* **2002**, *102*, 4093–4138; b) Y. Wan, D. Zhao, *Chem. Rev.* **2007**, *107*, 2821–2860.
- [34] A. Thomas, M. Antonietti, *Adv. Funct. Mater.* **2003**, *13*, 763–766.
- [35] T.-Y. Ma, Z.-Y. Yuan, J.-L. Cao, *Eur. J. Inorg. Chem.* **2010**, 716–724.
- [36] L. Yang, Y. Niu, H. Wang, Z. Wang, *Polymer* **2009**, *50*, 627–635.