Synthesis and characterization of highly ordered mesoporous thin films with –COOH terminated pore surfaces

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Highly ordered mesoporous inorganic–organic hybrid thin films with covalently bonded carboxylic acid (–COOH) terminal groups on the pore surfaces were synthesized by evaporation induced self-assembly of tetraethoxysilane, organosilanes, and a nonionic surfactant followed by acid hydrolysis and characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, surface acoustic wave (SAW) based N_2 sorption, and thermogravimetric analysis (TGA) techniques.

Surfactant templated mesoporous silicates have potential applications in catalysis, separation, adsorption, and sensing because of their high surface area, controllable pore size, and narrow pore size distribution.[1] In order to expand the range of applications as well as create new properties, various organic functional groups, including phenyl, octyl, aminoalkyl, cyanoalkyl, thioloalkyl, epoxyl, and vinyl groups have been incorporated onto the pore surfaces of mesoporous silica materials using a direct synthesis method.[2–4] Such inorganic–organic hybrid materials have been prepared mainly in basic media resulting in powders. However, thin films of such organo-functionalized materials are of great interest for applications in membrane separations, sensing, and smart coatings.

Mesoporous materials with carboxylic acid (–COOH) terminated pore surfaces represent robust host matrices for binding biomolecules such as enzymes, antibodies, and other proteins and for solid phase protein/peptide syntheses involving reactions between –COOH and –NH$_2$ groups on the biomolecules.[5] –COOH groups can also carry negative charges in neutral to basic environments that may have further applications for synthetic ion channels.[6] In 1996, Macquarrie reported the direct synthesis of a cyanoethyl derivatized MCM-type powder material under basic conditions.[4] Here we report the formation of highly ordered mesoporous silica thin films with –COOH terminated pore surfaces through the acid-catalyzed hydrolysis of –CN groups to –COOH groups. To our knowledge, ordered, –COOH derivatized mesoporous films have not yet been reported.

Hybrid silica thin films with –CN terminated pore surfaces were fabricated by an evaporation induced self-assembly (EISA) procedure using the nonionic surfactant, Brij56 ($C_{16}H_{33}(OCH_2CH_2)_nOH$, $n \sim 10$), as a structure-directing agent.[7] 2-Cyanoethyltriethoxysilane (CTES) was mixed with tetraethyl orthosilicate (TEOS) and Brij56 in a homogeneous acidic solution with a molar ratio of 1 TEOS : 0.28 CTES : 25 EtOH : 6.4 H$_2$O : 0.0081 HCl : 0.076 Brij56. The sol was deposited on a silicon substrate by spin- or dip-coating to form thin film samples (**a**). In EISA, ethanol evaporation accompanying the coating process enriches the depositing film in water, surfactant, and the silica constituents resulting in the self-assembly of silica–surfactant micelles and their further organization into liquid crystalline mesophases.[7] An acidic solvent extraction procedure was adopted to remove the surfactant molecules and prepare the corresponding cyano-functionalized mesoporous films (**b**).[2] The –CN group is reactive to water under acidic conditions. We exploited this property to hydro-

lyze the cyano-functionalized mesoporous thin films using sulfuric acid resulting in the corresponding –COOH derivatized mesoporous thin films (**c**).†

Fig. 1 shows the FTIR spectra of Brij56 templated thin films.‡ For sample **c** we observe the almost complete disappearance of the –CN stretching vibration (2256 cm^{-1}, samples **a** and **b**) along with the appearance of the –COOH stretching vibration (1718 cm^{-1}, strong), indicating a very high degree of conversion of –CN to –COOH and, importantly, establishing the accessibility of these organic groups. Comparing samples **a** and **b** we also observe the –CH$_2$– stretching bands (2850 and 2920 cm^{-1}) were drastically reduced in relative intensity after the solvent extraction process, indicating effective removal of the surfactant molecules.

The 1D XRD pattern of sample **c** shows a strong reflection at 4.6 nm and a weaker reflection at 2.3 nm. The TEM images (Fig. 2) and electron diffraction pattern (Fig. 2 inset) exhibit highly ordered structures which are consistent with [111] cubic symmetry (Fig. 2A) and [100] cubic symmetry (Fig. 2B). The average distances between neighboring pores in Fig. 2A and B are 5.4 nm and 4.6 nm, respectively. Based on these results, it is most plausible that the pores are arranged in a body-centered cubic structure (BCC, $Im\bar{3}m$ space group, was reported previously.[8]) with lattice parameter $a = 6.4$ nm, allowing the two reflections in the XRD pattern to be indexed as d_{110} and d_{220}, respectively.

The density of –COOH groups on the pore surfaces was controlled by the TEOS/CTES ratio, a lower ratio creating a higher density of –CN on the pore surfaces, and, accordingly, a higher density of –COOH groups after hydrolysis. Fig. 3 shows XRD data for thin film samples prepared using different amounts of CTES in the starting sol. d-Spacings of these films are 4.6, 4.5, 4.6, 4.7, and 5.4 nm, respectively, initially remaining constant with increasing CTES and finally increasing after the TEOS/CTES ratio fell below 4. When the TEOS/CTES ratio reached 1, the sample lost long range order. We postulate that –CN terminated groups are located on the pore surfaces. So, beyond a certain limit where the –CN surface coverage is
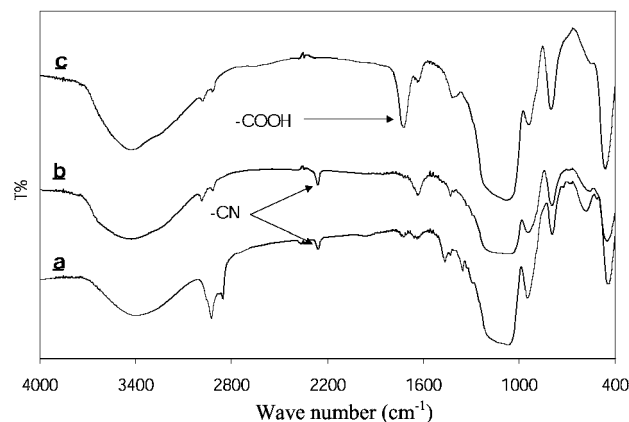

Fig. 1 FTIR data of Brij56 templated thin film samples (**a**–**c**) prepared by the direct synthesis method.

maximized, an ordered mesostructure can no longer accommodate additional –CN, and mesostructural order is lost. It could be argued that the film mesostructures are different and accordingly exhibit different *d*-spacings. However, the latter explanation was not supported by XRD and TEM, which showed qualitatively the same diffraction patterns and TEM images for samples prepared with TEOS/CTES ranging from 19 to 3.3.

^{29}Si MAS NMR studies of sample **c** showed T^2, T^3, Q^2, Q^3, and Q^4 resonances at -62.53, -68.87, -90.54, -100.34, and -109.82 ppm, respectively. The extent of condensation of T and Q species is 91% and 90%, respectively. This result demonstrates the stability of Si–C bonds and the covalent attachment of organic groups to the silica wall. Nitrogen adsorption/desorption isotherms of sample **b** (Fig. 4) were measured by a surface acoustic wave (SAW) technique§ and yielded a type IV isotherm with a very narrow hysteresis loop that is typical for mesoporous materials. The pore size is determined to be 2.6 nm with a narrow distribution using the BJH model (Fig. 4 inset). The BET surface area is 668 $m^2\ g^{-1}$. The film sample **c** is crack-free with thickness and refractive index of 201 nm and 1.25, respectively. TGA analysis of sample **c** in argon to a temperature of 800 °C showed *ca.* 14% weight loss (200–450 °C) which corresponded to the decomposition of –CH_2CH_2COOH groups. Based on surface area and weight loss, the surface coverage of –COOH groups for sample **c** is calculated to be *ca.* 2 –COOH nm^{-2}.

The approach described provides a general route to the functionalization of mesoporous materials with –COOH groups, which could serve as receptors for biomolecules. Furthermore, the synthesis of thin films with uniform and precisely controlled pore size and negatively charged –COO^-
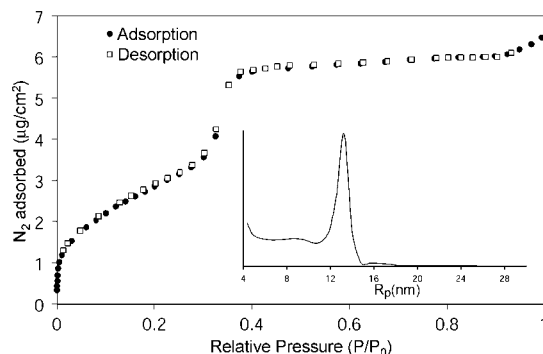
Fig. 4 Nitrogen adsorption/desorption isotherms of sample **b**. Inset is pore size distribution calculated from adsorption isotherm.

groups on the pore surfaces could create inorganic membranes with structures and properties mimicking those of biological ion channels.[6] This could represent a breakthrough toward the formation of robust, synthetic ion channel devices.

Notes and references

† In a typical preparation, 0.56 g Brij56 was dissolved in a solution containing 2.4 ml TEOS, 0.649 g CTES, and 15.5 ml ethanol. 1.25 ml 0.07 M HCl was added, and the sol mixture was sonicated for 5 minutes and aged at room temperature for 1 hour. Thin film samples were prepared by spin- or dip-coating the sol on silicon substrates. After the films were dried in air for 24 h, they were dipped in an acidic solution (10 ml 9 M HCl mixed with 80 ml ethanol) and refluxed for 12 h to remove Brij56. Porous film samples were washed with copious amounts of ethanol, dried in air, and transferred to a bottle containing 30 ml 60% wt H_2SO_4 which was kept at 100 °C for 6 h. Finally, they were washed with copious amounts of water and ethanol and dried in air.

‡ FTIR samples were scratched from thicker films prepared by multiple coating steps and diluted in KBr.

§ To prepare SAW samples, thin films were coated on crystalline quartz substrates prepared with interdigitated Au electrodes. Because the Au electrodes were not stable during the hydrolysis process, we only measured N_2 adsorption/desorption isotherms of the mesoporous thin film sample **b**, which should be a good estimation of the corresponding –COOH derivatized sample **c**.

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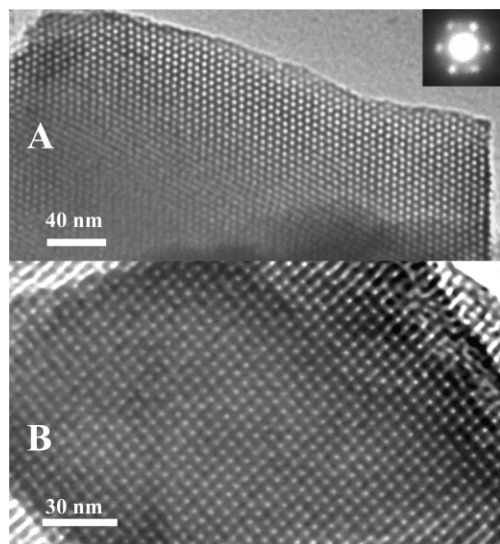
Fig. 2 TEM images of sample **c** with cubic mesostructure: (A) [111] direction; (B) [100] direction. Inset is electron diffraction pattern for A.
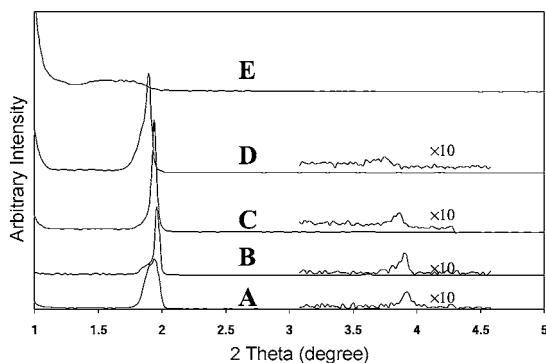
Fig. 3 XRD data of thin films prepared with different molar ratios of TEOS/CTES. (A) 19; (B) 9; (C) 4; (D) 3.3; (E) 1.