

## Synthesis and characterization of highly ordered functional mesoporous silica thin films with positively chargeable $-\text{NH}_2$ groups

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Highly ordered mesoporous organic–inorganic hybrid silica thin films with covalently bonded, positively chargeable  $-\text{NH}_2$  terminal groups were synthesized by evaporation induced self-assembly of tetraethoxysilane, 3-aminopropyltriethoxysilane, and a nonionic surfactant under acid conditions and characterized using TEM, GISAXS, FTIR, SAW-based  $\text{N}_2$  sorption, and TGA.

In the burgeoning field of functional nanostructured materials synthesized by surfactant and block copolymer directed self-assembly, thin films represent perhaps the most promising functional form due to their potential applications in membrane separations, sensing, and smart coatings and their ability to be readily integrated into devices.<sup>1,2</sup> However, previous reports on functional mesoporous materials mainly focused on powder materials which, comparatively, have limited applications.<sup>3–6</sup> Recently, we reported a general route to prepare highly ordered mesoporous thin films with  $-\text{COOH}$  terminated pore surfaces.<sup>7</sup>  $-\text{COOH}$  groups, which are negatively chargeable in neutral to basic media, are very important in the development of purely synthetic inorganic ion channels.<sup>8</sup> Both structural studies and Poisson–Nerst–Planck theory applied to biological ion channels emphasized the importance of chargeable groups positioned on the channel surfaces for influencing transport.<sup>9,10</sup>  $-\text{NH}_2$  ligands, which are similar to  $-\text{COOH}$  ligands but positively chargeable in neutral to acid media, are able to both serve as binding sites for biomolecules such as enzymes, antibodies, and other proteins and create an electropositive environment which may be selective to anion transport.

Macquarrie<sup>11</sup> and Fowler *et al.*<sup>4</sup> reported the direct synthesis of  $-\text{NH}_2$  terminated MCM-41 type of mesoporous powder through co-condensation of tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (ATES) under basic conditions. Here we report the synthesis of  $-\text{NH}_2$  functionalized mesoporous thin films. To our knowledge, these functional mesoporous thin films have not been reported yet. Evaporation induced self-assembly (EISA) is a common method used to prepare thin films.<sup>12,13</sup> Acidic conditions in EISA are important to make films of good quality. However,  $-\text{NH}_2$  is a base which will catalyze the hydrolysis reaction of TEOS and ATES in the presence of  $\text{H}_2\text{O}$ . Here we developed a procedure to prevent the fast hydrolysis reaction by first neutralizing  $-\text{NH}_2$  with a strong acid.

Hybrid mesoporous silica thin films with  $-\text{NH}_2$  functional groups were fabricated by an EISA procedure using the nonionic surfactant, Brij56 ( $\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ,  $n \sim 10$ ), as a structure-directing agent. ATES was mixed with TEOS and Brij56 in an EtOH solution. 6 M HCl was added to neutralize  $-\text{NH}_2$ . The starting sol with a molar ratio of 1 TEOS : 0.25 ATES : 0.082 B56 : 24 EtOH : 5.2  $\text{H}_2\text{O}$  : 0.28 HCl was deposited on a silicon substrate *via* coating or casting procedures to form mesostructured thin film samples (**a**). The surfactant molecules were removed from the condensed film sample (**a**) by an acidic solvent extraction procedure, leaving the corresponding amino-functionalized mesoporous films (**b**).†

The TEM image (Fig. 1A) and electron diffraction pattern (Fig. 1B) of sample **b** exhibit highly ordered structures which are consistent with [100] cubic symmetry. Grazing incidence small angle X-ray scattering (GISAXS) data of sample **b** is shown in Fig. 2‡. Combining TEM and GISAXS results, we determined that the pores are arranged in a face-centered cubic (FCC,  $Fm\bar{3}m$  space group) structure with the unit cell parameter  $a = 9.08$  nm ( $d_{400} = 2.27$  nm, calculated from the electron diffraction pattern and GISAXS data). It also indicates that the (100) plane is parallel to the substrate.

Fourier-transformed infrared (FTIR) spectra of sample **b** showed four characteristic vibrational bands of  $\text{R}-\text{NH}_3^+\text{Cl}^-$ : the N–H stretching band ( $3300\text{--}2600$   $\text{cm}^{-1}$ , broad peak, overlapped with the stretching bands of silanol and  $-\text{CH}_2-$  groups); overtone band ( $1975$   $\text{cm}^{-1}$ , broad); asymmetrical  $-\text{NH}_3^+$  bending band ( $1606$   $\text{cm}^{-1}$ ) and the symmetrical  $-\text{NH}_3^+$  bending band ( $1505$   $\text{cm}^{-1}$ ).  $-\text{CH}_2-$  stretching bands ( $2925$ ,  $2976$   $\text{cm}^{-1}$ ) and silica framework vibrational bands ( $1200$  (shoulder),  $1054$  (very strong),  $940$ ,  $794$ ,  $571$ ,  $444$   $\text{cm}^{-1}$ ) were consistent with a previous report.<sup>5</sup> The Si–C stretching bands ( $1147$   $\text{cm}^{-1}$ ) overlapped with the strong  $1200$  and  $1054$   $\text{cm}^{-1}$  vibrational bands of the Si–O–Si framework.§ After sample **b** was dipped in 0.001 M NaOH for 30 minutes, washed with copious amounts of water and ethanol, and dried in a vacuum,

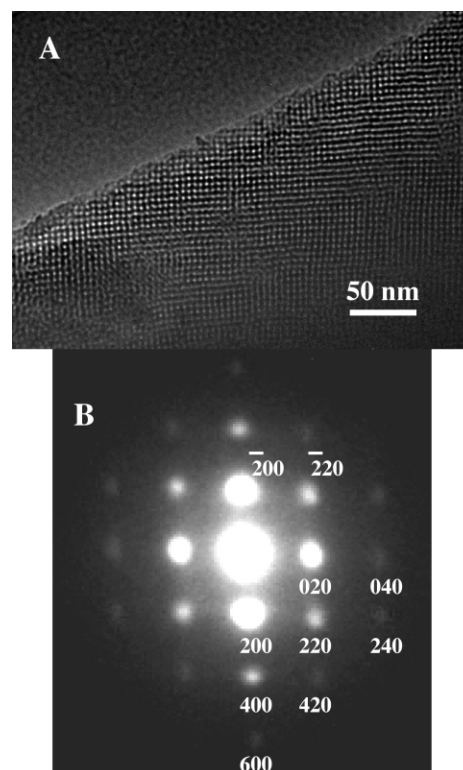


Fig. 1 TEM images of sample **b** with cubic structure: A) viewed in [100] direction; B) electron diffraction pattern for A.

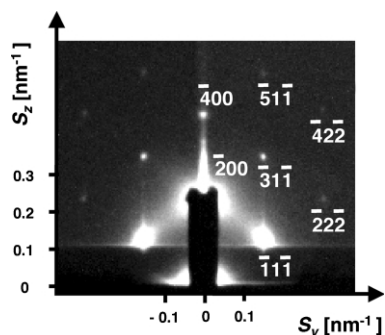


Fig. 2 GISAXS data of sample *b* in [011] direction.

FTIR spectra showed the vibrational bands of R-NH<sub>2</sub>: N-H stretch (~3350 cm<sup>-1</sup>, overlapped with silanol groups), N-H bending (1617 cm<sup>-1</sup>). This result demonstrates that the functional amino groups are water-accessible, and hence located on the pore surfaces.

<sup>29</sup>Si MAS NMR data of samples *a* and *b* are shown in Table 1. The total amount of T species (T<sup>2</sup> + T<sup>3</sup>) in samples *a* and *b* was 19.4% and 18.9%, respectively, somewhat less than the ATEs amount in the starting sol (20%) but within the experimental error limits. <sup>13</sup>C MAS NMR spectra of sample (*b*) consisted primarily of three peaks at 9.3, 20.8, and 42.3 ppm, corresponding to the C atoms of the Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N group in sequence from left to right. These results demonstrated that the Si-C bonds are stable during the film preparation process and that the amino-functional mesoporous materials were successfully prepared.

Nitrogen adsorption/desorption isotherms of sample *b* (Fig. 3) 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 3.2 nm with a narrow distribution using the Barrett-Joyner-Halenda (BJH) model with a corrected Kelvin equation (Fig. 3 inset).<sup>14</sup> The Brunauer-Emmett-Teller (BET) surface area is 681 m<sup>2</sup> g<sup>-1</sup> and porosity is 51%.

Thermogravimetric analysis (TGA) of sample *b* in argon to a temperature of 800 °C showed *ca.* 8% weight loss of adsorbed solvent (*T* < 120 °C), *ca.* 15% weight loss at 120–340 °C, and

Table 1 <sup>29</sup>Si MAS NMR data of samples (*a* and *b*)

	Sample ( <i>a</i> )	Sample ( <i>b</i> )
T <sup>3</sup> /ppm	-57.1	-56.8
T <sup>2</sup> /ppm	-65.6	-65.2
Q <sup>2</sup> /ppm	-91.2	-91.4
Q <sup>3</sup> /ppm	-100.2	-99.8
Q <sup>4</sup> /ppm	-109.9	-108.4
Q%, total	80.6	81.1
T%, total	19.4	18.9

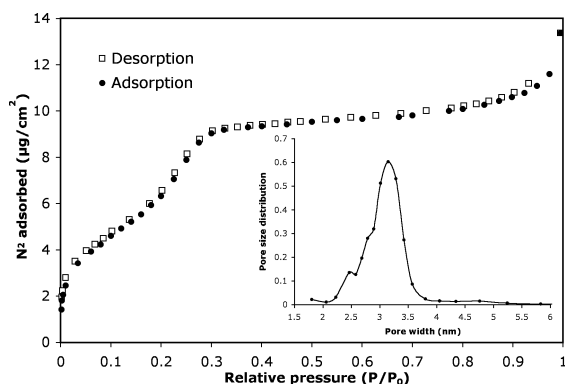


Fig. 3 Nitrogen adsorption/desorption isotherms of sample (*b*). Inset is pore size distribution calculated from adsorption isotherm.

*ca.* 10% weight loss at 340–640 °C; the latter two events corresponded to the decomposition of -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> groups, which were consistent with the previous report on amino-functionalized MCM-41 type powder materials.<sup>11</sup> Based on surface area and weight loss, the surface coverage of -NH<sub>2</sub> groups for sample *b* is calculated to be *ca.* 2 -NH<sub>2</sub> nm<sup>-2</sup>.

The approach described provides a general route to the functionalization of mesoporous materials with -NH<sub>2</sub> groups, which could serve as receptors for biomolecules. The positively chargeable -NH<sub>2</sub> groups may have implications for new type of purely synthetic inorganic ion channels.

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## Notes and references

† In a typical preparation, 0.604 g Brij56 was dissolved in a solution containing 2.4 ml TEOS (98%, Aldrich), 0.63 ml ATEs (98%, GELEST), and 15 ml ethanol (200 proof). The solution was stirred vigorously and 0.50 ml 6.0 M HCl was added quickly to neutralize the -NH<sub>2</sub>. Then 0.50 ml DI H<sub>2</sub>O was added and the sol was sonicated for 5 minutes and aged at room temperature for 30 minutes to 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 hours, they were dipped in an acidic solution (10 ml 9 M HCl mixed with 80 ml ethanol) and refluxed for 12 hours to remove Brij56. Mesoporous film samples were washed with copious amounts of ethanol and dried in air.

‡ The GISAXS experiments were performed at the Advanced Photon Source at Argonne National Laboratory (Illinois) on the 1-BM-C beamline. A 2D CCD detector (Bruker) was used to acquire GISAXS data, the pixel size was 0.16 × 0.16 mm. The wavelength was λ = 0.112714 nm (Si(111) monochromator by Physical Sciences Lab) and the sample-detector distance was 39.1 cm. The samples were mounted on a stage which could be finely adjusted in the x-, y- and z-directions. 1/d = S = 2sin(θ)/λ. The shadow is an effect of the silicon substrate.

§ FTIR, NMR, TGA samples were scratched from thick films prepared by casting technique.

¶ To prepare SAW samples, thin films were coated on crystalline quartz substrates prepared with interdigitated Au electrodes, and other steps were the same as those of film samples deposited on silicon substrates.

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