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Mesoporous silicon oxynitride thin films†

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Highly-ordered, pore-modified with amine groups, and glass-like mesoporous silicon oxynitride thin films were prepared by heat treatment of as-synthesized mesoporous silica thin films in a flowing ammonia environment at high temperatures.

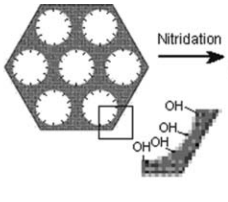
Mesostructured silicate thin films have been a worldwide focus of research work because they have potential applications in many fields including chemical sensors, catalysis, optical coating, molecule separation, *etc*. Silicate thin films have been produced by dip-coating, spin-coating and spontaneous formation at air–water or oil–water interfaces.[1–11]

Pure silica thin films possess neutral Si frameworks which limit their applicability. Now, a large amount of work is focused on adequately characterizing and synthesizing new mesoporous silica thin films by different methods. Post-synthesis grafting and direct synthesis are two popular methods. Post-synthesis modification of mesoporous silicate thin films is mainly focused on incorporation of metal and oxide nanoparticles within the channels by incipient-wetness, ion-exchange, *etc.* followed by treatment.[12–14] At the same time, some researchers used silane coupling agents to react with Si–OH groups on the internal pore surfaces; various kinds of organic groups could be grafted onto the mesoporous silica thin films.[15a,b] By adding silane coupling agents into the mother sol, new organic–inorganic composite films were obtained.[15c] More chemical functionalisations of mesoporous silica thin films can be seen in the feature article by Lionel Nicole and his co-workers.[16] However, research concerning modification of the framework in mesoporous silica thin films is scarce. By addition of other metal ions into the prehydrolyzed silica solutions, impurity atom doped mesoporous silica thin films could be made.[17] In the reported papers, the partial substitution of bridging oxygen atoms by N or NH species occurring in porous materials such as ZSM-5,[18] AlPO,[19] SBA-15,[20] MCM-48/41,[21] *etc.* could result in kinds of nitrogen-containing materials which have increased basicity. But reports about nitrogen incorporation into mesoporous silica thin films and their structural changes have not been found.

Herein, we use as-synthesized ordered mesoporous silica thin films (MSTFs) as precursors to prepare brand new highly-ordered, glasslike, basic and crack-free mesoporous silicon oxynitride thin films (MSONTFs) by heat-treatment in ammonia at high temperatures for the first time. The structural change of the MSTFs is also reported. After nitridation in ammonia for a long time, the films still remain intact and also have well ordered hexagonal mesostructures. Nitrogen incorporation is achieved by a one-step high-temperature treatment of the as-synthesized MSTFs under a flowing NH_3 atmosphere, without need to remove the template. Concretely, through a gas–solid reaction between silica and NH_3, the silanol groups on the mesopore surface can react with NH_3 to produce amine groups and water steam at high temperatures as shown in Scheme 1. At higher temperatures (>1000 °C), the ammonia can attack the siloxane Si–O–Si to form Si–NH_2 and then Si–NH_2 can condense to form Si–NH–Si bridges.[20c] So, large amounts of amine groups exist on the surface of the mesoporous silicon oxynitride thin films. This kind of new MSONTF might be an alternative to film-shaped solid basic catalysts, controlled delivery channels, adsorbents for acid molecules, microsensors, *etc*.

Mesoporous silicon oxynitride thin films (MSONTFs) are prepared by the following two steps. Firstly, mesoporous silica thin films (MSTFs) were synthesized by dip-coating, synthetic information on which can be found elsewhere.[15] The obtained thin films have a thickness of about 200 nm. Secondly, MSONTFs were prepared by heating the as-synthesized MSTFs in flowing ammonia at the expected temperatures for 12 hours. According to the treatment temperatures, we defined the ordered MSONTFs as MSONTFs-*T*. For example, MSONTFs-1000 means the MSTF was treated at 1000 °C. The synthetic details of the MSTFs and MSONTFs can be found in the ESI.

Incorporation of nitrogen into the framework of MSTFs was investigated by Fourier-transform infrared spectroscopy (FTIR‡). Fig. 1A shows the FTIR spectra of MSTFs, MSONTFs-900 and MSONTFs-1050. In the spectrum of pure MSTFs (a), the peaks at ~804, ~966, ~1086 cm^{-1} are ascribed to symmetric stretching of Si–O–Si, the Si–OH stretching mode, and asymmetric stretching of Si–O–Si, respectively.[22] After nitridation, the disappearance of the absorption peak of the surface silanols in the spectrum of the obtained MSONTFs-900 (b) and MSONTFs-1050 (c) demonstrates that the pore surface of MSTFs has been modified with basic amine groups such as –NH_2 and –NH– groups.[20,21] Moreover, the asymmetric Si–O–Si stretching vibration at ~1086 cm^{-1} broadens and shifts towards smaller wave numbers



Scheme 1 Schematic drawings of nitrogen incorporating into the framework of mesoporous silica thin films.

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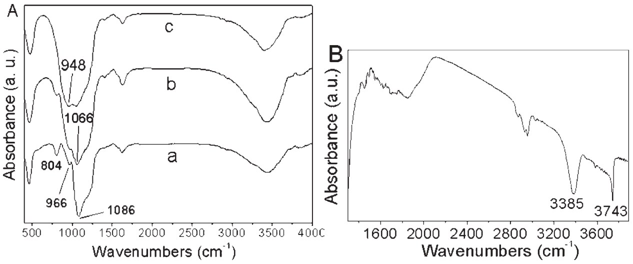

Fig. 1 (A) FTIR spectra of (a) MSTFs, (b) MSONTFs-900 and (c) MSONTFs-1050. (B) IR spectrum of MSONTFs-1050 which was evacuated for 4 h at 300 °C in a vacuum.

($\sim$1066 cm^{-1}) for the MSONTFs. At the same time, with increasing treatment temperature, the Si–O–Si (ν_S) band at $\sim$804 cm^{-1} gradually vanishes for the MSONTFs samples, which suggests that more Si–O–Si groups react with NH_3 molecules and the MSONTFs at higher temperatures have a higher nitrogen content. For nitrided MSTFs, a new band at $\sim$948 cm^{-1}develops gradually. The appearance of the band at $\sim$948 cm^{-1} and the broadening and shift of the band at $\sim$1086 cm^{-1} in MSONTFs can be attributed to greater disorder and bond strain caused by the incorporation of nitrogen into the framework.[20c,22] In order to prove the formation of a large number of amine groups, an IR spectrum of the MSONTFs-1050 (Fig. 1B) was obtained after the sample was heated in the cell for 4 h at 300 °C in a vacuum to remove the adsorbed water. In Fig. 1B, an intense peak at $\sim$3385 cm^{-1} due to N–H stretching modes is clearly visible.[21] At the same time, the Si–OH peak at $\sim$3743 cm^{-1} which does not exist in Fig. 1A(a–c) can be evidently observed due to removal of the adsorbed water in Fig. 1B. From the results of FTIR, it can be concluded that nitrogen has incorporated into the framework of MSTFs after nitridation.

The mesostructural ordering of the as-synthesized MSTFs and MSONTFs was characterized by small-angle X-ray diffraction (SXRD§) measurements. Fig. 2 shows the SXRD patterns of the MSTFs and MSONTFs. One intense diffraction peak and one weak peak of the as-synthesized MSTFs at 2θ = 1.04 and 2.0°, indexed as the 100 and 200 reflections, are characteristic of a two-dimensional hexagonal (*P6mm*) structure with d_{100}-spacing of about 8.5 nm. The absence of the 110 reflection peak is typical in the XRD patterns for the hexagonal unit cells with the *c* and *a* axes parallel to the film substrate.[1,2] Similar oriented growth of mesostructural silica films has also been reported. Heat treatment of the as-synthesized MSTFs in ammonia at high temperatures results in an obvious decrease in intensity of the two peaks, indicating a lower level of long-range ordering in the MSONTFs. It can be evidently seen that the higher the temperature of heat treatment is, the smaller the d_{100}-spacing of MSONTFs is. For example, the d_{100}-spacing of MSONTFs is shifted from 8.5 nm to 5.4, 5.0, 4.8 and 4.7 nm (shown in Table 1) for MSONTFs-900, MSONTFs-950, MSONTFs-1000 and MSONTFs-1050, respectively, although the reflections were retained, indicating preservation of the hexagonal mesostructured ordering. So, the lattice parameters (a_0) of MSONTFs also decrease with the increase of heat-treatment temperature. This may be mainly attributed to the extent of silica lattice condensation of the MSTFs framework on exposure to the high temperatures. At the same time, when the as-synthesized MSTFs were thermally treated at 900 °C in an air atmosphere for 12 h, its mesostructure completely collapsed. This implies that the ammonia atmosphere is an important factor in maintaining structural ordering during nitridation.

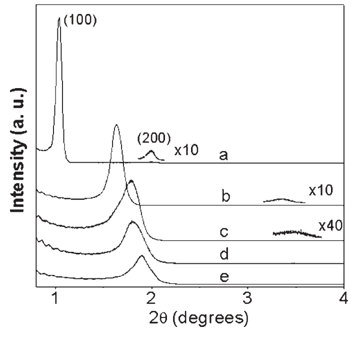

Fig. 2 Small angle XRD patterns of the (a) as-synthesized MSTFs, (b) MSONTFs-900, (c) MSONTFs-950, (d) MSONTFs-1000 and (e) MSONTFs-1050 on quartz.

The structural ordering of MSONTFs can be directly observed by high-resolution transmission electron microscopy (HRTEM¶). Fig. 3 shows representative HRTEM images of the as-synthesized MSTFs (a) and MSONTFs-1050 (b) which was obtained through treating MSTFs in flowing ammonia at 1050 °C for 12 h. The as-synthesized MSTFs on quartz have a good hexagonal mesostructure. The pore size and wall thickness are estimated to be 6.3 and 3.6 nm, respectively. After nitridation, it can be found that the mesostructure of MSONTFs-1050 keeps very well and there are lots of regular arrays of uniform channels which are highly ordered. This is greatly consistent with the SXRD result of the sample MSONTFs-1050. The pore size and wall thickness can be estimated to be 3.2 and 2.1 nm, respectively. The wall thicknesses of the as-synthesized MSTFs and MSONTFs-1050 are very consistent with the values calculated using the formula wall thickness = $a_0 - D_{\text{Pore}}$ as shown in Table 1. The MSONTFs obtained through treating MSTFS with ammonia at temperatures <1050 °C also possess good hexagonal mesostructures (not shown here).

Table 1 shows the structural and physical properties of the MSTFs and MSONTFs. Quasi-quantitative elemental analysis by X-ray photoelectron spectroscopy (XPS‖) shows that MSONTFs-900, MSONTFs-950, MSONTFs-1000 and MSONTFs-1050 contain 8.7, 11.5, 13.1 and 15.8 wt% of N, respectively. It is very clear that the nitrogen incorporated into the framework increases accordingly with the increase in nitridation temperatures. The calculated wall thicknesses here are very consistent with the results of the HRTEM images. At the same time, it can be seen that the

Table 1 Structural and physical properties of MSTFs and MSONTFs

Sample	N (wt%)	d_{100}/Å	a_0[a]/Å	D_{Pore}[b]/Å	D_{Wall}[c]/Å
MSTFs	—	85	98	63	35
MSONTFs-900	8.7	54	62	36	26
MSONTFs-950	11.5	50	58	33	25
MSONTFs-1000	13.1	48	55	32	23
MSONTFs-1050	15.8	47	54	32	22

[a] The lattice parameter, from the XRD data using the formula $a_0 = 2d_{100}/\sqrt{3}$. [b] The pore diameter coming from HRTEM images. [c] Wall thickness = $a_0 - D_{\text{Pore}}$.

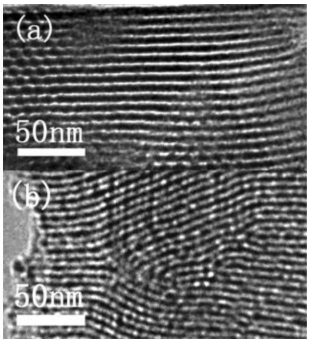

Fig. 3 Representative HRTEM micrograph of the (a) as-synthesized MSTFs and (b) MSONTFs-1050 on quartz.

higher the temperature of heat treatment is, the smaller the pore size and wall thickness of MSONTFs is. Concretely, the pore sizes of MSONTFs-900, MSONTFs-950, MSONTFs-1000, MSONTFs-1050 are 3.6, 3.3, 3.2, and 3.2 nm, which decreased 43%, 48%, 49%, and 49% compared with that of the as-synthesized MSTFs, respectively. The wall thicknesses of MSONTFs are 2.6, 2.5, 2.3, and 2.2 nm which decreased 26%, 29%, 34%, and 37% compared with that of the as-synthesized MSTFs, respectively. Here, it can be clearly seen that the pore size decreased much while the wall thickness reduced a little. This phenomenon is just opposite to that reported in our previous paper on the nitridation process of mesoporous SBA-15 powder.[20c] The main reason is that the starting material of nitridation is SBA-15 powder (not film) which was calcined in an air atmosphere at 500 °C for 5 h to remove the organic template. Thus, the silica framework of SBA-15 has condensed much to make the pore size steady before nitridation and the pore sizes were basically kept unchanged after nitridation. The obvious reduction in wall thickness is due to the collapse of the micropores in the walls for the powder samples. However, we used the as-synthesized MSTFs that were uncalcined as the starting materials to prepare MSONTFs in this paper. So, the heavy condensation of the silica framework necessarily resulted in a clear reduction of the pore size when nitriding the as-synthesized MSTFs at high temperatures in flowing ammonia.

SEM images (not shown) show that the MSONTFs-1050 on the quartz substrate is homogeneous, does not crack and has a smooth glasslike surface, though they experienced high-temperature treatment in flowing ammonia. At the same time, we found that the connection of the interface between the thin films and quartz substrate was more close due to silica lattice condensation of MSTFs framework.

In conclusion, we have synthesized ordered MSONTFs with different N contents through the gas–solid reaction of the as-synthesized MSTFs with ammonia. This kind of MSONTF has not only a highly-ordered hexagonal mesoporous structure, but also a modified pore structure due to the large amount of $-NH_2$ and –NH– groups on the surface of pore channels. At the same time, the MSONTFs had glasslike surfaces and did not crack though they experienced high-temperature treatments. This kind of new and highly ordered mesoporous silicon oxynitride film might be a better candidate for applications as film-shaped solid basic catalysts, controlled delivery channels, adsorbents for acid molecules, *etc.*

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Notes and references

‡ Infrared spectroscopic investigations were carried out on a Bruker Vector 22 spectrometer using the KBr pellet method.

§ X-Ray powder diffraction patterns were collected on a Rigaku D/MAX-c β instrument using CuKα (λ = 0.15406 nm) radiation at 40 kV and 60 mA.

¶ High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL 2010CX TEM.

‖ X-Ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

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