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Ethanol vapor-mediated maturing for the enhancement of structural regularity of hexagonal mesoporous silica films†

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Structural regularity of hexagonal mesoporous silica films is dramatically enhanced when allowed to stand for a few hours in an ethanol vapor-containing closed bottle before dryness.

Mesoporous silica films have been recognized as attractive materials for use in optical and optoelectronic applications, because of their micrometer-scale thickness, high transparency and ability to accommodate and align functional guest molecules in nanoscopic channels.[1] In general, mesoporous silica films are fabricated by spin-coating, dip-coating or casting on a glass plate template-containing silica sols aged by partial hydrolytic condensation of alkoxysilanes. However, if the precursor sols are insufficiently aged or overage, low-quality or even nonstructured silica films result.[2] Here we report a very simple and versatile method using an EtOH vapor for enhancing the mesostructural regularity of hexagonal silica films.

A standard procedure[3] for the synthesis of mesoporous silica films involves partial hydrolytic condensation of tetraethyl orthosilicate (TEOS) for 1 h at 25 °C in an ethanolic HCl solution, followed by aging of the precursor sol for 20 h at 25 °C in the presence of cetyltrimethylammonium chloride (CTACl) for further promotion of the condensation ([CTACl]/[TEOS]/[H_2O]/[HCl]/[EtOH] = 1.0/10/98/0.088/160). Spin-coating of the resulting sol on a glass plate, followed by air-drying for 12 h, resulted in the formation of a mesoporous silica film, whose X-ray diffraction (XRD) pattern was characteristic of a hexagonal geometry (Fig. 1(A)(b)).‡ As shown in Fig. 2 (open circles), the structural regularity of the mesoporous silica film is significantly affected by the aging time of the precursor sol. When the sol was aged for 34 h, the (100) diffraction peak of the resulting silica film became very intense. However, further elongation of the aging time to, *e.g.*, 125 h resulted in a non-structured silica film (Fig. 1(B)(b)).

To our surprise, such overaged sols are still able to give mesoporous silica films when the corresponding spin-coated films, before air-drying, are immersed in an EtOH vapor (Fig. 2, filled circles).§ For example, when the silica film, prepared from a sol aged for 125 h, was placed in a 1000-mL closed bottle containing one drop of EtOH and then immersed for 3 h at 25 °C,¶ the resulting silica film showed intense diffraction peaks (Fig. 1(B)(a)) comparable to those of the silica film obtained by using a 20 h-aged sol under standard conditions (Fig. 1(A)(b)). The diffraction peaks remained after calcination for 3 h at 450 °C (ESI†). Transmission electron microscopy (TEM) confirmed a honeycomb array of hexagonal silicate channels with an interpore distance of 4.3 nm (Fig. 1(C)). We also found that this simple method is even effective for enhancing the hexagonal structural regularity of silica films prepared under the standard conditions.§ Thus, a spin-coated silica film was prepared using a 20 h-aged sol containing CTACl and air-dried for 12 h after immersion in an EtOH vapor for 3 h at 25 °C. As shown in Fig. 1(A)(a), the X-ray diffraction peaks of the resulting silica film were more than twice as intense as those untreated with the EtOH vapor.‡||

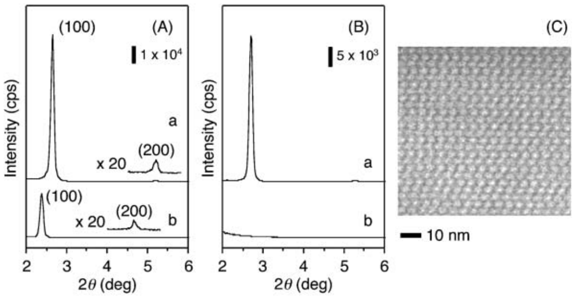
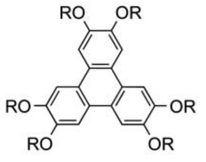
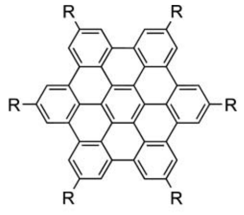


Fig. 1 X-Ray diffraction patterns of silica films prepared by spin-coating of a precursor sol composed of [CTACl]/[TEOS]/[H_2O]/[HCl]/[EtOH] = 1.0/10/98/0.088/160, (a) with and (b) without immersion in an EtOH vapor before dryness. The sol was used after being aged for (A) 20 and (B) 125 h. (C) A TEM micrograph of the silica film shown in (B)(a). Insets in (A): magnified diffraction patterns (×20).



TP

R = $(CH_2)_{10}(OCH_2CH_2)_3OCH_3$



HBC

R = $(CH_2)_8CO_2(CH_2CH_2O)_3CH_3$

The above interesting observations prompted us to investigate further by using as templates other cationic surfactants such as cetylpyridinium chloride (CPyCl) and 1-cetyl-3-methylimidazolium chloride (CMICl), and nonionic discotic amphiphiles such as TP[6] and HBC† with extended π-electronic conjugation. When

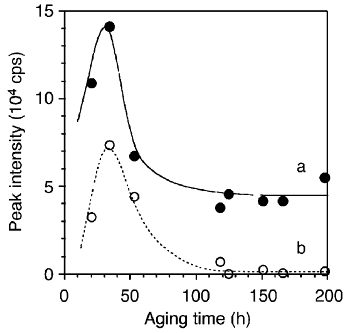


Fig. 2 Intensities of (100) X-ray diffractions of spin-coated silica films (a) with and (b) without immersion in an EtOH vapor before dryness. A precursor sol ([CTACl]/[TEOS]/[H_2O]/[HCl]/[EtOH] = 1.0/10/98/0.088/160) was aged at 25 °C for 20, 34, 53, 118, 125, 151, 166 and 198 h and then spin-coated.

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† Electronic supplementary information (ESI) available: Experimental section. See http://www.rsc.org/suppdata/cc/b4/b410095f/

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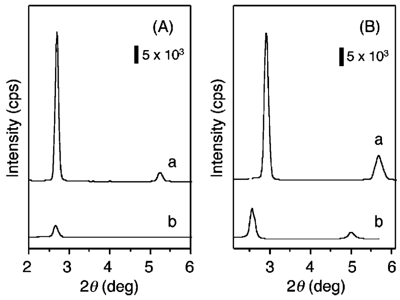

Fig. 3 X-Ray diffraction patterns of silica films prepared by casting of precursor sols containing (A) TP/TCNB and (B) HBC as templates, followed by being aged for 15 days and 24 h, respectively. Films (a) were prepared by being allowed to stand for 3 h in a closed bottle without addition of EtOH and dried. Films (b) were prepared by drying immediately after casting.

immersed in an EtOH vapor, spin-coated films templated by CPyCl, CMICl and a mixture of TP and 1,2,4,5-tetracyanobenzene (TCNB), a charge-transfer donor/acceptor pair, all showed intense X-ray diffraction peaks due to the hexagonal geometry. In sharp contrast, unimmersed silica films showed only very weak or even no diffraction peaks (ESI†). This method is also applicable to cast silica films that are much thicker than spin-coated films. Successful examples include those with amphiphilic TP/TCNB and HBC as templates (Fig. 3), where maturing of the hexagonal structure was self-promoted in a closed bottle by a trace of EtOH remaining unevaporated in the cast films.

Although the mechanism of the mesostructural regularity enhancement is not yet clear, we assume the effect of EtOH as follows. A precursor sol contains coassemblies of an organic template with partially condensed silanols. On spin-coating or casting, they are concentrated and further condensed to give immature silica fragments. On subsequent air-drying, condensation and reorganization of the intermediate silicate fragments both take place, so that the structural regularity of the resulting silica should depend on the relative rate of these two processes. Namely, when the condensation is much faster, the system loses enough fluidity for the reorganization. On the other hand, in the presence of EtOH, such an ill-behaved condensation may be retarded, and the system likely has a chance to reorganize into a hexagonal structure.

In conclusion, we have reported an interesting phenomenon, referred to as "ethanol vapor-mediated mesostructure maturing", which is very simple and effective for enhancing the hexagonal structural regularity of mesoporous silica films. This method is widely applicable to sol–gel reactions with a variety of functional organic templates and even allows overage sols to be revived for use.[7]

Notes and references

‡ As typically observed for mesoporous silica with a hexagonal geometry, the silica film preserved X-ray diffraction peaks after calcination at 450 °C for 3 h (ESI†). In general, mesoporous silica films with a hexagonal geometry hardly show a (110) diffraction in a standard XRD analysis.[4]

§ When spin-coated films were allowed to stand in a closed bottle without addition of EtOH before drying, no enhancement of the structural regularity resulted.

¶ A typical procedure for EtOH vapor-mediated mesostructure maturing: Tetraethyl orthosilicate (TEOS, 13 mmol) was subjected to hydrolytic condensation in an ethanolic HCl solution (1.3×10^{-2} M, 8.6 mL) at 25 °C for 1 h at a molar ratio [TEOS]/[H_2O]/[HCl]/[EtOH] = 1.0/9.8/0.0088/8.3. To the resultant solution was added an EtOH solution (5.7 mL) of CTACl (1.3 mmol), and the mixture ([CTACl]/[TEOS]/[H_2O]/[HCl]/[EtOH] = 1.0/10/98/0.088/160) was aged at 25 °C. After 125 h, the precursor sol, thus obtained, was spin-coated on a glass plate, and the film was immediately placed and allowed to stand at 25 °C in a 1000 mL closed plastic bottle ((89 mm − ϕ) × 187 mm) containing one drop of EtOH (10 μL). After 3 h, the film was taken out from the bottle, air-dried at 25 °C for 12 h, and then dried at 100 °C for 12 h.

|| When immersed in an EtOH vapor before dryness, the resulting mesoporous silica film showed a smaller *d*-spacing of the (100) diffraction (3.3 nm, Fig. 1A(a)) than that untreated (3.7 nm, Fig. 1A(b)). This is most likely due to shrinkage of the template micelle upon absorption of EtOH.[5]

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