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COMMUNICATION

Vertically oriented hexagonal mesoporous zirconia thin films by block copolymer templating†

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We report the synthesis of vertically oriented, long-range ordered hexagonal mesoporous zirconia thin films. The orientation of hexagonally ordered cylindrical mesopores in thin films was effectively controlled by taking advantage of the temperature dependent hydrophobicity of the templating block copolymer PEO–PPO–PEO. Vertical orientation was obtained when temperature was 30 °C or above throughout the process. Dehydration and enhanced chemical incompatibility between the PEO and PPO blocks at slightly elevated temperatures are proposed to play a key role in the vertical orientation of the mesopores. The temperature changes act on the entire film rather than just at the interfaces and the process can be applied to any mesoporous inorganic film.

Mesoporous materials with long-range ordered structures have long been synthesized by various methods.^{1,2} However, controlling the orientation of the mesopores is still at the early progress stages. Orientation control of cylindrical mesopores in such materials is important in applications where directed transport of molecules in a single direction is required.¹ Regulation of permeability is also possible in thin films having pores vertically oriented with respect to the air/film interface (and substrate) by chemical modification of inner pore surfaces.³ In thin films, the ordered cylindrical pores tend to orient in the plane of the substrate mainly due to interfacial interactions.^{4,5} The difficulty of obtaining vertically oriented pores has previously been overcome either by surface modification of the solid substrates (such as nanometre-scale epitaxy on a patterned surface,⁵ solid surfaces modified with the cross-linked block copolymer^{6,7}) or by external fields (application of magnetic field,⁸ cathodic electrodeposition⁹). In addition to substrate surface modification, adjustment of the air/film interfacial energy by mixed organic solvent annealing may also be required.¹⁰ These methods were not effective in producing vertically oriented structures in large areas or required multi-step complicated processes.²

In this communication, we report successful synthesis of vertically oriented, hexagonally ordered mesoporous zirconia thin films and show that the orientation of hexagonally ordered cylindrical

mesopores can effectively be controlled by adjusting the process temperature. The synthesis procedure can be applied to any mesoporous inorganic film provided that the templating block copolymer has temperature dependent hydrophobicity. The change in the hydrophobicity of the templating block copolymer with temperature is effective because it acts on the entire film rather than just at the interfaces. The kinetics of solvent evaporation also contributes to the vertical orientation of the mesopores.

The evaporation induced self-assembly block copolymer templating method¹¹ was used. Mesoporous zirconia thin films were synthesized by Pluronic F127 (poly(ethylene oxide)₁₀₆–poly(propylene oxide)₇₀–poly(ethylene oxide)₁₀₆, PEO₁₀₆PPO₇₀–PEO₁₀₆) as the block copolymer template. The films were prepared in the hybrid phase (inorganic salt and block copolymer) by spin coating on solid substrates from solutions containing 0.25 M ZrOCl₂·8H₂O, 20 mg ml^{−1} Pluronic F127 in 80 vol% ethanol–20 vol % water. The hybrid phase films were water vapour treated and aged at constant humidity and temperature before calcination (see ESI† for details).

The temperature throughout the process—coating, water vapour treatment and aging—was critical for the orientation control in mesoporous zirconia thin films and had to be kept at or above 30 °C to obtain the ordered pore structure perpendicular to the substrate plane. For vertically oriented pores, the films were coated (spin coating or solvent casting) at ambient temperatures of 30 °C or higher. After coating, the films were immediately transferred to a humidity chamber which was kept at 30 °C and purged by N₂ gas passing through boiling water. The water vapour carried by the gas was directed onto the surface of the film for ~3 minutes. The films were then moved into another chamber kept at 30 °C and 50% relative humidity (RH) for 5–10 days for aging during which partial dehydration of the sample happened slowly. Finally, the samples were calcined at 450 °C for 4 hours during which the organic phase was removed and the zirconium oxide was formed.¹²

Both UV-visible spectra and atomic force microscopy (AFM) investigations clearly show that the diffusion of water vapour into the films allows equilibration of the film morphology (see ESI† for details). The low transmittance of the as-prepared films is expected to be both due to the presence of randomly oriented ordered domains having sizes comparable to the optical wavelengths and due to the large surface roughness. The observed increase in optical transparency with water vapour treatment can thus be attributed to the growth of the ordered domains to sizes much larger than the optical

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wavelengths and the simultaneous decrease of the surface roughness, both of which reduce the intensity of the scattered light.

The inorganic compound after aging in the bulk hybrid mesophase was identified by X-ray powder diffraction (XRD) measurements (Fig. 1a) as tetragonal $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ which is the precursor inorganic salt. The PEO block of the Pluronic F127 copolymer template was also found to be crystalline ($2\theta = 19.104^\circ$) in the hybrid mesophase. The second PEO reflection at $2\theta = 23.224^\circ$ overlapped with the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ reflections. The fact that the precursor inorganic salt can re-crystallize with the same crystal structure in the crystalline matrix of the hydrophilic PEO block indicates the existence of a mixture consisting of the two substances. The ability of both the inorganic and the organic phase to hydrate during water vapour treatment increases the mobility of the molecules and the constituents rearrange to their final equilibrium structure and orientation.

The hybrid mesophase was calcined at 450°C for 4 hours based on the thermal analysis results (see ESI† for details). The removal of the block copolymer and the reaction of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with oxygen by mild heat treatment resulted in tetragonal mesoporous zirconia (ZrO_2). Fig. 1b shows the X-ray powder diffraction data of the resulting mesoporous substance. Small-angle X-ray scattering of the bulk samples showed a broad peak at $2\theta = 0.84^\circ$ ($d = 10.5\text{ nm}$) corresponding to the pore sizes which was also confirmed by SEM measurements (see ESI† for details).

Calcination of the hybrid mesophase without water vapour treatment resulted in disordered morphology in mesoporous zirconia thin films. Both water vapour treatment and aging were required to obtain ordered morphologies. The orientation of the ordered morphology on the substrate depended significantly both on the ambient temperature during spin coating (T_a) and on the temperature of the chamber during water vapour treatment (T_{wvt}) and aging (T_{aging}) steps. When all three temperatures were below 30°C , the cylindrical pores oriented predominantly in the plane of the film parallel to the underlying substrate. Fig. 2a shows the AFM height image of a film for which the temperature was $\sim 25^\circ\text{C}$ at each step. The cylinders have an average diameter of $\sim 20\text{ nm}$ and are oriented from the lower right to the upper left corner in the substrate plane.

Vertical orientation of hexagonally ordered cylinders (Fig. 2b) was obtained when all three temperatures were $\sim 30^\circ\text{C}$ or above. When

Fig. 1 (a) X-Ray powder diffraction data of the hybrid mesophase consisting of a mixture of crystalline $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and Pluronic F127. (b) X-Ray powder diffraction data after calcination at 450°C . The resulting substance is crystalline tetragonal ZrO_2 .

Fig. 2 Atomic force microscopy height images of calcined ZrO_2 thin films. The samples were water vapour treated for 3 minutes, aged at $\sim 50\%$ RH for 1 week and calcined at 450°C for 4 hours. (a) The sample was prepared at $T_a \approx T_{\text{wvt}} \approx T_{\text{aging}} \approx 25^\circ\text{C}$. (b) The sample was prepared at $T_a \approx T_{\text{wvt}} \approx T_{\text{aging}} \approx 32^\circ\text{C}$. The insets show the Fourier Transform (FT) of the images.

T_a and T_{wvt} were 21°C , but T_{aging} was kept at 30°C , a mixture of horizontal and vertical orientations was observed in the films (see ESI† for details). This indicates a transition from initially induced parallel orientation at 21°C to the equilibrium vertical orientation at 30°C . Fig. 2b shows the AFM height image of vertically oriented hexagonal mesoporous zirconia prepared (spin coating, water vapour treatment and aging) at 32°C and calcined at 450°C . The hexagonal morphology of the hybrid mesophase has been stable and the structure did not collapse upon thermal treatment.

The FT of the height image (Fig. 2b) showed slightly distorted hexagonal morphology with an average period (center-to-center distance of the cylinders) of ~ 18 to 22 nm which is the same as the diameter of the cylinders lying in the plane of the film (Fig. 2a). The distorted hexagonal morphology has commonly been observed in thin films with horizontal cylindrical mesopores due to the dominance of contraction in the direction perpendicular to the substrate during calcination.¹¹ In the case of vertical orientation, the distorted morphology indicates the presence of in-plane contraction during calcination.

The orientation of the mesopores in thin films has been confirmed by grazing-incidence small-angle X-ray scattering (GISAXS) measurements. Fig. 3a and b show the 2D GISAXS patterns of the films shown in Fig. 2a and b, respectively. Fig. 3c shows the integrated intensity along the in-plane momentum transfer vector q_y at low q_z values. Both films showed the first order scattering peak at $2\theta \approx 0.57^\circ$ ($q_y^* = 0.405\text{ nm}^{-1}$) corresponding to $d = 15.5\text{ nm}$ and the

Fig. 3 GISAXS data of the films seen in Fig. 2. (a) The sample was prepared at $T_a \approx T_{\text{wvt}} \approx T_{\text{aging}} \approx 25^\circ\text{C}$. (b) The sample was prepared at $T_a \approx T_{\text{wvt}} \approx T_{\text{aging}} \approx 32^\circ\text{C}$. (c) The integrated intensity of the data in (a) and in (b) along q_y at low q_z . The curve showing a more pronounced secondary peak corresponds to the film in Fig. 2b and GISAXS data of (b).

second order scattering peak at $2q_y^*$. The film that showed hexagonal morphology at the top surface by AFM (Fig. 2b) also showed pronounced order along q_z . Well-defined streaks along q_z are seen in the GISAXS pattern together with the Bragg spots. These observations indicate the presence of the vertical cylindrical mesopores going down to the substrate with high orientational order which was further confirmed by SEM characterization of the bottom part (film/substrate interface) of the mesoporous zirconia film after lifting it off the substrate (see ESI, Fig. S7 and S8†). The film that showed cylinders lying in-plane at the top surface (Fig. 2a) also showed streaks along q_z , but they were much broader and overlapping. We attribute these broad streaks to the presence of domains having vertically oriented cylinders resulting in poorer orientational order throughout the film. An average center-to-center distance between cylindrical mesopores of 15.5 nm is consistent with ~ 18 to 20 nm as measured by AFM.

The water vapour and the temperature influence the order and the orientation of hexagonal morphology through different mechanisms. Water vapour treatment and aging under humidity are commonly applied in the synthesis of mesoporous metal oxides to enhance the order.¹¹ During the initial water vapour treatment (100% RH, ~ 3 min in this work), the mesophase evolves towards an ordered equilibrium structure of PPO cylinders in the matrix of PEO and ZrOCl_2 . During the aging step (50% RH, 5–10 days), the removal of water from hydrated PEO chains results in slow crystallization of PEO together with the nucleation of the ZrOCl_2 phase. The cylindrical PPO domains orient in the plane of the film below 30°C . This is expected as inorganic precursor (ZrOCl_2) containing PEO blocks interacts favourably both with the underlying substrate and with water vapour that is in touch with the top surface.

The temperature was crucial in controlling the orientation of the hexagonal morphology and had to be above 30°C for perpendicular orientation of PPO cylinders to the underlying substrate, independent of the substrate type. Both thermodynamic (dehydration and enhanced incompatibility between PPO and PEO with increasing temperature¹³) and kinetic factors (solvent evaporation¹⁴) are

expected to contribute to the observed change in the orientation. The observed perpendicular orientation being independent of the substrate suggests that the nucleation of the perpendicular orientation starts at the top surface, probably due to the stronger tendency of dehydration at higher temperatures. This ordering then propagates down to the substrate. Increased temperature also contributes to order through both faster annihilation of defects and faster diffusion of water molecules in the Pluronic F127 film.^{15,16}

Conclusions

Vertically oriented, long-range ordered mesoporous zirconia films were successfully synthesized. The order and the orientation of the pores were effectively controlled by humidity and temperature, respectively, resulting in horizontal orientations below 30°C and vertical orientations at or above 30°C . The synthesis procedure used can be applied to any mesoporous inorganic film provided that the templating block copolymer has temperature dependent hydrophobicity. The change in the hydrophobicity of the templating block copolymer with temperature is more effective in obtaining vertical orientations because it acts on the entire film rather than just at the interfaces. This relatively simple preparation route and orientation control in thin films may open up new perspectives in sensing and catalysis applications of mesoporous metal oxide films.

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