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Replication of dendrimer monolayer as nanopores in titania ultrathin film†

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An ultrathin titania film with molecular-sized cavities was synthesized by treating a *ca.* 8 nm thick $(TiO_2)_3$(dendrimer)$(TiO_2)_2$ sandwich film with activated oxygen gas.

The preparation of porous materials as films of nanometer-scale thickness is attracting much attention because of their rapidly growing applications. For example, cutting-edge integrated circuits require a coating technique of low dielectric constant materials for reducing heat generation in the LSI devices.[1] Nanoporous metal oxides are advocated to be candidates for such materials. Ultrathin films with size-controlled pores are also considered instrumental in separation of carbon dioxide, as environmental sensors, and as the catalytic layer of fuel cells.

Fabrication of uniform nanoporous films has been extensively studied in recent years.[2–5] However, thin metal oxide films obtained by conventional spin-coating and dip-coating methods cannot be fabricated in thicknesses smaller than submicrometers. The morphology of such films may be altered significantly due to crystallization in the subsequent calcination. We have shown recently that the surface sol–gel process[6,7] provides uniform alternate multilayers of titania and poly(acrylic acid), which are then converted to nanoporous films by treatment with activated oxygen gas.[8] This approach would be useful for creating designed nanopores from organic templates. It is essential to see if molecular structures are replicated as the shape of nanopores. We report herein a successful demonstration of the formation of nanopores by using a single layer of chemisorbed dendrimer as molecular template. A hydroxy-terminated fourth-generation poly(amidoamine) (PAMAM) dendrimer (G4-OH) (Fig. 1a) was chosen for this purpose, because this rigid molecule is readily immobilized onto a titania surface to form a monolayer. Morphological robustness and high affinity with metal oxide matrices are requisites for template molecules. Other dendrimers such as carboxylate-terminated PAMAM G4.5 and sugar ball,[6] and protein molecules like cytochrome C and diaphorase appeared less satisfactory under the current conditions, due to their conformational flexibility.

The film formation process is schematically illustrated in Fig. 1b.‡ First, a titania-gel underlayer is formed *via* the surface sol–gel process, and then dendrimer molecules are adsorbed as monolayer onto the under layer. The single layer of the dendrimer is covered with an additional two cycles of the surface sol–gel process to yield a nanocomposite film. The monitoring of these processes was conducted by using a quartz crystal microbalance (QCM). Fig. 2 shows QCM frequency shifts for deposition of three bottom layers of titania, one layer of PAMAM-OH G4 dendrimer and two top layers of titania (denoted as $(TiO_2)_3$(PAMAM-OH)$(TiO_2)_2$ hereafter). The thickness of the lower and upper titania layers is estimated by using the bulk density of the titanium dioxide based gel (1.7 g cm^{-3})[7] as 1.7 nm and 1.2 nm, respectively. And the dendrimer monolayer is estimated to be 4.5 nm thick by assuming a spherical shape for the dendrimer itself.[9]

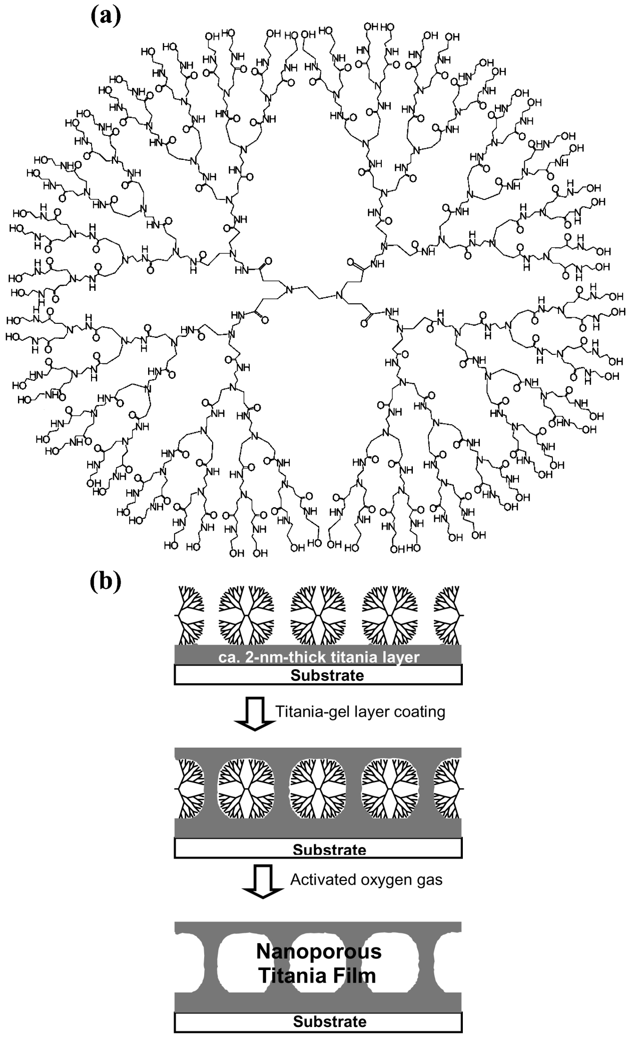

Fig. 1 (a) Structure of the PAMAM G4-OH dendrimer with 64 terminal hydroxy units. (b) Schematic representation of the formation process of a nanoporous titania film.

The organic moiety is then removed at room temperature by treating the film with activated oxygen gas produced in an oxygen plasma generator at an extremely low oxygen gas pressure (176 mTorr) and weak applied power (10 W) (Fig. 1b). After exposure to the activated oxygen gas, the QCM frequency increased by 137 Hz in Fig. 2, which is in a close agreement with the 148 Hz decrement in frequency upon chemisorption of the dendrimer monolayer. This suggests complete removal of the dendrimer template. In fact, the amide I and II bands arising from the dendrimer branches (1650 and 1560 cm^{-1}) in the as-prepared film completely disappeared. A UV-vis absorption spectrum of the activated oxygen-treated film gave a band near 250 nm and the absorption threshold was estimated to be 340 nm, indicating the existence of a nanometer-thick titania film.[10]

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† Electronic supplementary information (ESI) available: experimental details and TEM micrograph. See http://www.rsc.org/suppdata/cc/b2/b206208a/

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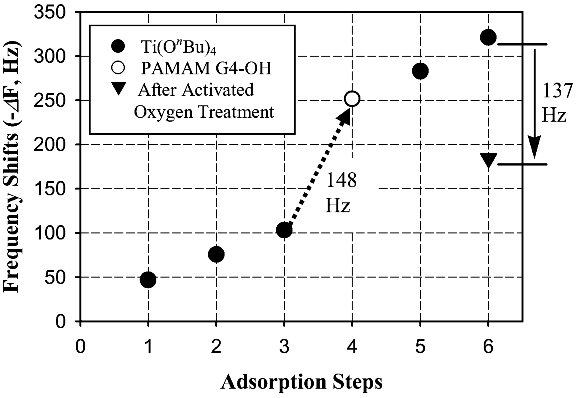

Fig. 2 QCM frequency shifts ($-\Delta F$) due to adsorption of Ti(O^{n}Bu)$_4$ (100 mM in 1 : 1 v/v toluene/ethanol, 25 °C) (●) and PAMAM G4-OH (1 wt.% in methanol, 25 °C) (○) during the deposition of a $(TiO_2)_3$(PAMAM-OH)$(TiO_2)_2$ film, and frequency shift (▼) after treatment with activated oxygen gas for template removal.

The titania film has constant thickness of 8–10 nm, as revealed by the cross-sectional film image obtained by field emission scanning electron microscopy (FE-SEM).

Transmission electron microscopy (TEM) and FE-SEM observations were made in order to confirm formation of nanosized pores in the film. The film surface of the as-prepared sample is smooth, uniform, and crack-free (Fig. 3a), indicating that the PAMAM G4-OH dendrimer layer is embedded into the titania matrix, otherwise the film would show a much rougher surface. The film retains a similar surface morphology even after it is treated with activated oxygen gas (Fig. 3b). The corresponding TEM images are shown in Fig. 3c and d. The individual dendrimer molecules embedded in titania film matrix can be distinguished in Fig. 3c (schematically shown in the inset). The separation of the individual domain is around 5 nm, in close agreement with the size of the dendrimer molecule. After the template removal, nanopore structures are clearly seen in the TEM image (Fig. 3d, and the inset scheme). Approximately 50% of the film is occupied by nanopores of 4–7 nm in size. The two-dimensional distribution of the nanopores in Fig. 3d is similar to that of the dendrimer templates in Fig. 3c, suggesting strongly that the nanopore is formed as a direct result of the template removal. Certain discrepancy in sizes may arise from distortion of the titania matrix during the course of template removal. In contrast, a 5-layer titania film prepared without dendrimer does not show such nanoporosity.

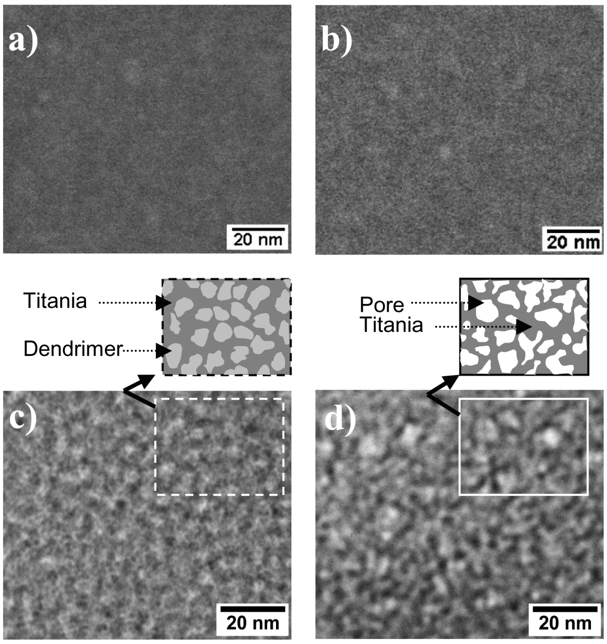

Fig. 3 FE-SEM images of the surface of a $(TiO_2)_3$(PAMAM)$(TiO_2)_2$ nanocomposite film deposited on Si(100) before (a) and after (b) template removal, and their corresponding TEM images (c and d). The inset of (c) and (d) schematically shows the contours of dendrimer domains in the as-prepared film and nanopores after the template removal, respectively. The nanocomposite film for the TEM observation was deposited on a silicon oxide-coated copper grid and subjected to activated oxygen gas treatment under the same experimental conditions. The SEM micrographs were obtained on a Hitachi S-5200 at an acceleration voltage of 5.0 kV. The TEM photos were acquired on a JEOL JEM-2000 operating at 100 kV.

It is clear from the above results that the size and shape of nanopores may be designed by selecting suitable organic molecules as templates. The current finding is the first, direct proof of such possibility. This conclusion should be highly beneficial for the molecular design of selective adsorbents and permselective membranes using metal oxide films.

Notes and references

‡ Various solid substrates including gold (QCM electrode, 1 Hz frequency decrease corresponds to 0.9 ng surface mass increase), mica, quartz, Si(100), and siliconoxide-coated TEM grid (before film deposition, formvar film was removed from the grid by solvent extraction and the grid was successively plasma cleaned) were used for film deposition. A titania layer was deposited by immersing a solid substrate in 100 mM Ti(O^{n}Bu)$_4$ in 1 : 1 (v/v) toluene/ethanol for 3 min, followed by rinsing in ethanol for 1 min to remove the physisorbed species, and hydrolysis in pure water for 1 min, then finally dried by flushing with nitrogen gas. Formation of PAMAM G4-OH monolayer was achieved by 20 min immersion of the titania gel layer-coated substrate in its 1 wt.% solution in methanol (Aldrich, supplied as 10 wt.% solution in methanol), followed by thorough rinsing with methanol and drying with nitrogen gas. Activated oxygen gas is generated by using a PE-2000 plasma etcher (South Bay Technology). FTIR-RA and UV-vis spectroscopic measurements were carried out on the films deposited on mica and quartz substrates, respectively.

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