Synthesis of mesoporous titania networks consisting of anatase nanowires by templating of bacterial cellulose membranes

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Mesoporous titania networks consisting of interconnected anatase nanowires have been synthesized by using unique bacterial cellulose membranes as natural biotemplates; the titania networks exhibit enhanced photocatalytic activity compared with titania microfiber networks.

Recently, the controlled synthesis of porous, crystalline titania with tailored pore structure and size has attracted much attention because of its potential applications in various areas including photovoltaics, photocatalysis, separation, chemical sensing, and optical devices. In particular, bio-inspired fabrication by templating or nanocasting procedures[1] has been demonstrated to be a versatile route to either macroporous (pore size >50 nm) or mesoporous (pore size 2–50 nm) titania. A variety of templates, such as colloidal crystals,[2] emulsions,[3] reverse micelles,[4] foams,[5] and polymer gels,[6] membranes[7] and beads,[8] have been employed for the synthesis of macroporous crystalline TiO_2 while ordered mesoporous TiO_2 films with anatase nanocrystallites have been fabricated by using nonionic amphiphilic block copolymer templates.[9] On the other hand, considerable attention has been paid to the shape-controlled synthesis of anisotropic titania nanorods or nanowires due to the unique properties of one-dimensional (1D) nanostructures;[10] moreover, interlinked structures of titania nanofibers have been prepared and considered as potential functional biocompounds for bone-tissue engineering.[11] It is expected that the combination of a mesoporous structure and an interlinking nanowire network would endow the titania material with unique properties and multiple functions. Therefore, it is worthwhile to explore the synthesis of mesoporous titania networks constructed by interconnected crystalline titania nanowires.

For the preparation of porous inorganic materials with tailored structures, a rich variety of biological structures with complex morphologies have been used as sophisticated templates. Typical examples of natural biological templates include bacterial threads,[12] echinoid skeletal plates,[13] eggshell membranes,[14] insect wings,[15] pollen grains,[16] plant leaves,[17] and wood.[18] Notably, hierarchical, nanotubular titania structures with nano-precision replication from natural cellulose matrices such as filter paper, cloth, and cotton were prepared by a novel surface sol-gel process.[19] Furthermore, hierarchical, crystalline TiC networks were fabricated by carbothermal reduction of titania-coated cellulose paper.[20] It is noted that although the chain-like biopolymer cellulose is predominantly isolated from plants, bacterial cellulose (BC) is produced by bacteria, especially the acetic acid bacteria Acetobacter. Bacterial cellulose, which has recently been studied for use as artificial skin and blood vessels and as a substrate for tissue engineering of cartilage, is identical to plant cellulose with respect to molecular structure but it has an ultrafine nanofiber network structure and unique properties including high crystallinity, high water holding capacity, high tensile strength, and mouldability during formation.[21] In this work, BC membranes were used as biological templates, for the first time, for synthesizing mesoporous TiO_2 networks consisting of interconnected anatase nanowires. The obtained mesoporous TiO_2 networks exhibited enhanced photocatalytic activity compared with the TiO_2 networks templated by eggshell membranes.[14]

BC pellicles were first prepared by static culture of Suzhou sweet wine koji containing multiple species of acetic acid bacteria in 10 wt% glucose solution at room temperature for 30 days. The BC pellicles ($\sim$5 mm in thickness) formed at the air/liquid interface were washed with water, cut into pieces (about 2 cm $\times$ 2 cm), and purified in 0.2 M NaOH solution at 100 °C for 3 h. After washing with water thoroughly, the BC pellicles were dehydrated and transferred into isopropanol *via* a gradual solvent exchange process[14] and the resultant BC membranes ($\sim$1 mm in thickness) were stored in isopropanol prior to use. For the sol-gel titania coating, the BC membranes were dipped into a closed vessel containing a solution of tetra-*n*-butyl titanium, acetyl acetone and isopropanol with a volume ratio of 1 : 0.4 : 19 for 24 h. Then, the membranes were filtered under reduced pressure to remove solution held in the membranes and held in air at room temperature for 48 h to complete the hydrolysis reaction. Finally, the obtained BC–titania hybrid membranes were heated at 500 °C in air for 6 h, resulting in the formation of crystalline titania thin films ($\sim$0.2 mm in thickness).

The samples were characterized by scanning electron microscopy (SEM, FEI STRATA DB235, 10 kV), transmission electron microscopy (TEM, JEOL JEM 200CX, 160 kV), high-resolution TEM (HRTEM, FEI TECNAI F30, 300 kV), X-ray powder diffraction (XRD, Rigaku Dmax-2000, Cu Kα) and nitrogen adsorption–desorption measurements (Micromeritics ASAP 2010). The photocatalytic activity of the obtained porous titania films was characterized by measuring the titania-assisted photodegradation of the xanthene dye Rhodamine B,[22] with the eggshell membrane-templated titania films employed as a control sample for comparison. The titania films were broken into smaller pieces ($\sim$100 μm) and suspensions containing the titania photocatalysts (100 mg L^{-1}) and Rhodamine B ($\sim 10^{-5}$ M) were placed in the dark for 30 min before illumination to allow sufficient adsorption of Rhodamine B. The stirred suspensions were illuminated with a 250 W high-pressure mercury lamp 25 cm high over the solution

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and the change of the Rhodamine B concentration with irradiation time was monitored by measuring the UV-vis absorption of the suspensions centrifuged to remove titania at different periods.

The SEM image shown in Fig. 1a gives an overview of the BC membrane template, which suggests that the BC membrane has an ultrafine network structure comprising interwoven nanofibers with diameters less than 100 nm, which is much smaller than the diameters of typical plant cellulose bundles ($\sim$10 μm). An enlarged image presented in Fig. 1b shows that the nanofibers generally adopt a ribbon-like morphology with widths 40–100 nm and thickness $\sim$10 nm. It is noted that the high-magnification image is not very clear due to the poor conductivity of the organic substance; however, the image quality can be largely improved after the BC membranes are coated with titania. As shown in Fig. 1c, a typical SEM image of the BC–titania hybrid membranes clearly exhibits interconnected ribbon-like nanofibers that faithfully replicate the morphology of the original BC template. Thermogravimetric analysis (TGA) of the BC–titania hybrid membranes suggested that the BC template started pyrolyzing at $\sim$280 °C and was completely pyrolyzed by 500 °C, leaving 9 wt% inorganic solid. After calcination at 500 °C to remove the template, porous titania networks comprising interwoven nanowires typically 20–30 nm in diameter were obtained (Fig. 1d). It was indicated that considerable shrinkage occurred during template removal and the original ribbon-like morphology was not preserved probably due to the very thin thickness of the ribbons.

Fig. 2a shows a typical TEM image of the interconnected titania nanowires and the related electron diffraction pattern (ED) exhibits sharp rings corresponding to the anatase crystals, indicating the polycrystalline structure of the titania nanowires. A representative HRTEM image of the titania nanowires is shown in Fig. 2b, which revealed the presence of many crystallites showing clear anatase lattice fringes, confirming that the nanowires consisted of anatase nanocrystals. The XRD pattern of the obtained titania networks demonstrated that anatase was actually the only crystal phase present in the product (Fig. 3a). An average crystallite size of about 14 nm was estimated according to line width analysis of the (101) reflection based on the Scherrer formula. Nitrogen sorption isotherms of the titania networks along with the Barret–Joyner–Halenda (BJH) pore size distribution plot are presented in Fig. 3b, which suggest that the networks are basically mesoporous with pore sizes predominantly less than 40 nm and a pore size distribution centered around 9 nm. The BET specific surface area and pore volume were measured to be 61 $m^2 g^{-1}$ and 0.20 $cm^3 g^{-1}$, respectively. This result suggested that the mesopores mainly originated from the interstices between the interconnected titania nanowires, in good agreement with the SEM observations.

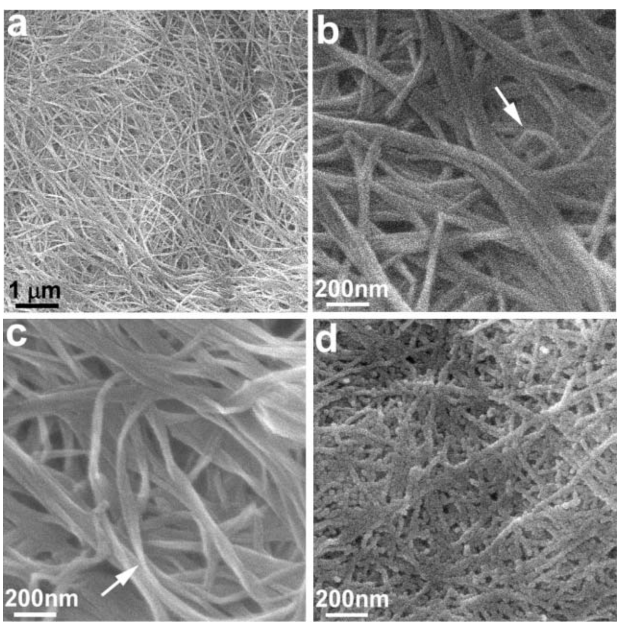

Fig. 1 SEM images of BC membranes (a, b), BC–titania hybrid membranes (c), and titania networks templated by BC membranes (d). Arrows indicate the twisted structure of ribbon-like nanofibers.

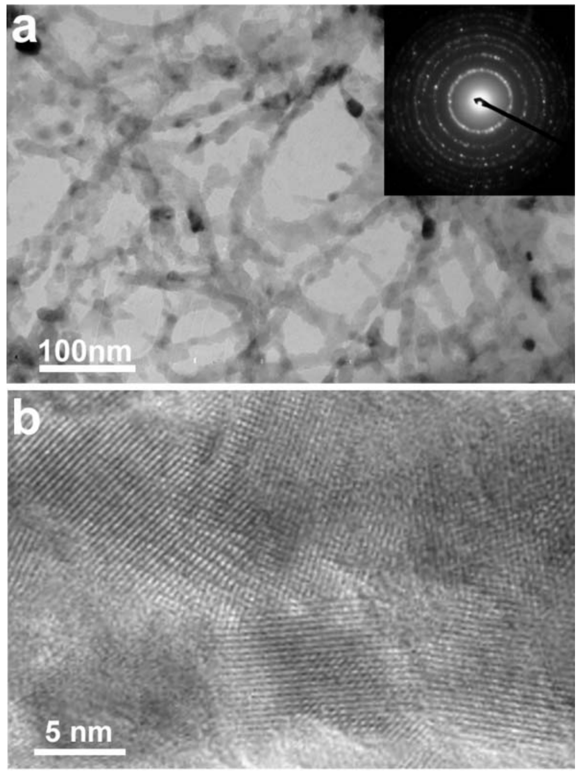

Fig. 2 TEM (a) and HRTEM (b) images of titania nanowires constituting networks templated by BC membranes. Inset shows the corresponding ED pattern.

Fig. 4 illustrates the photodegradation of Rhodamine B in the presence of the BC membrane-templated titania networks as well as its photodegradation in the presence of the macroporous titania networks obtained by sol-gel coating of eggshell membranes followed by calcination at 500 °C, as reported previously.[14] It suggests that the current mesoporous titania networks exhibit a considerably enhanced photocatalytic activity compared with the macroporous titania networks obtained through a similar sol-gel nanocasting procedure. It is noted that the macroporous titania networks showed both crystallinity and surface areas comparable to the present mesoporous titania networks but much larger diameters of the interwoven fibers (typically $\sim$1 μm). Therefore, the higher photocatalytic activity of the mesoporous titania networks consisting of anatase nanowires may be attributed to the larger accessible surface areas.

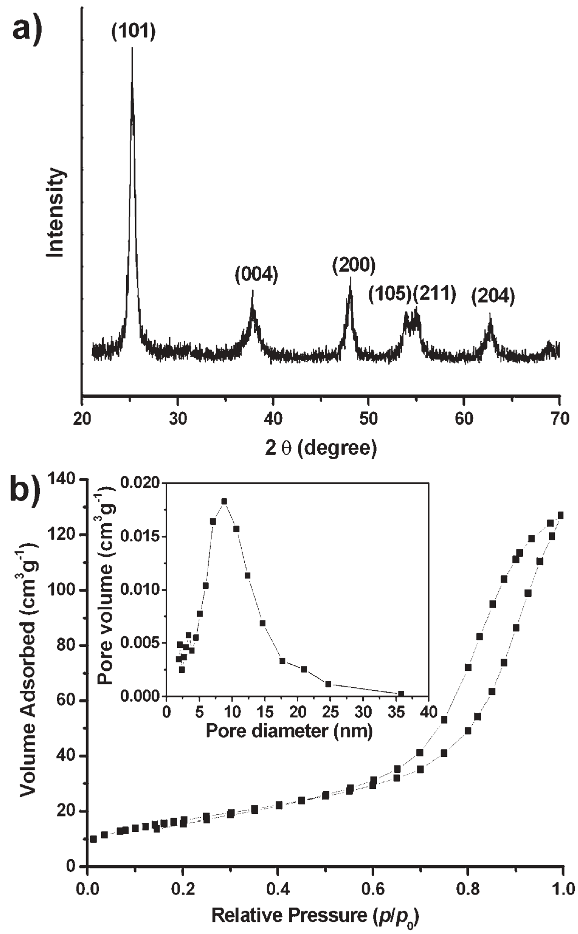

Fig. 3 XRD pattern (a) and nitrogen adsorption–desorption isotherms (b) of titania networks templated by BC membranes. Inset shows the pore-size distribution determined from the desorption branch.

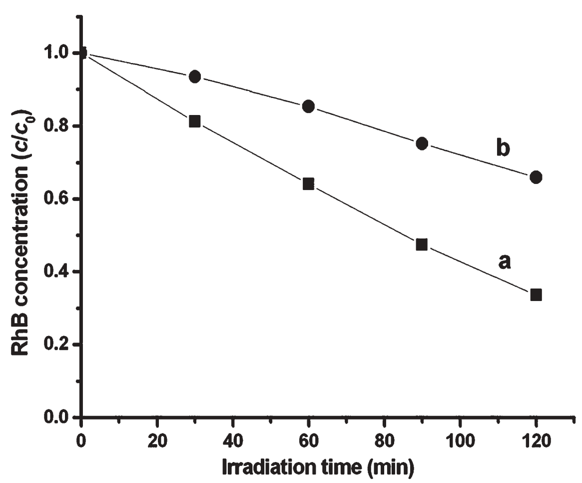

Fig. 4 Photodegradation of Rhodamine B monitored as the normalized concentration change *versus* irradiation time in the presence of titania networks templated by BC membranes (a) and eggshell membranes (b).

In summary, mesoporous titania networks consisting of interconnected anatase nanowires have been synthesized by using unique bacterial cellulose membranes as natural biotemplates. The novel titania nanowire networks may find potential applications in areas including photocatalysis, photovoltaics, and bone-tissue engineering. The templating strategy is generally extendable to the synthesis of mesoporous nanowire networks of other metal oxide systems.

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Notes and references

1 S. Polarz and M. Antonietti, *Chem. Commun.*, 2002, 2593.
2 (*a*) J. E. G. J. Wijnhoven and W. L. Vos, *Science*, 1998, **281**, 802; (*b*) D. Wang, R. A. Caruso and F. Caruso, *Chem. Mater.*, 2001, **13**, 364; (*c*) S. Kuai, S. Badilescu, G. Bader, R. Brüning, X. Hu and V.-V. Truong, *Adv. Mater.*, 2003, **15**, 73.
3 A. Imhof and D. J. Pine, *Nature*, 1997, **389**, 948.
4 Z.-Y. Yuan, T.-Z. Ren and B.-L. Su, *Adv. Mater.*, 2003, **15**, 1462.
5 (*a*) I. M. Arabatzis and P. Falaras, *Nano Lett.*, 2003, **3**, 249; (*b*) F. Carn, A. Colin, M.-F. Achard, H. Deleuze, C. Sanchez and R. Backov, *Adv. Mater.*, 2005, **17**, 62.
6 (*a*) R. A. Caruso, M. Antonietti, M. Giersig, H.-P. Hentze and J. Jia, *Chem. Mater.*, 2001, **13**, 1114; (*b*) J. H. Schattka, D. C. Shchukin, J. Jia, M. Antonietti and R. A. Caruso, *Chem. Mater.*, 2002, **14**, 5103; (*c*) D. G. Schukin, J. H. Schattka, M. Antonietti and R. A. Caruso, *J. Phys. Chem. B*, 2003, **107**, 952.
7 (*a*) R. A. Caruso and J. H. Schattka, *Adv. Mater.*, 2000, **12**, 1921; (*b*) D. G. Shchukin and R. A. Caruso, *Adv. Funct. Mater.*, 2003, **13**, 789.
8 (*a*) U. Meyer, A. Larsson, H.-P. Hentze and R. A. Caruso, *Adv. Mater.*, 2002, **14**, 1768; (*b*) D. C. Shchukin and R. A. Caruso, *Chem. Mater.*, 2004, **16**, 2287; (*c*) H. Zhang, G. C. Hardy, Y. Z. Khimyak, M. J. Rosseinsky and A. I. Cooper, *Chem. Mater.*, 2004, **16**, 4245.
9 (*a*) E. L. Crepaldi, G. Soler-Illia, D. Grosso, F. Cagnol, F. Ribot and C. Sanchez, *J. Am. Chem. Soc.*, 2003, **125**, 9770; (*b*) J. C. Yu, X. Wang and X. Fu, *Chem. Mater.*, 2004, **16**, 1523; (*c*) S. Haseloh, S. Y. Choi, M. Mamak, N. Coombs, S. Petrov, N. Chopra and G. A. Ozin, *Chem. Commun.*, 2004, 1460; (*d*) S. Y. Choi, M. M. Mamak, N. Coombs, N. Chopra and G. A. Ozin, *Adv. Funct. Mater.*, 2004, **14**, 335; (*e*) T. A. Ostomel and G. D. Stucky, *Chem. Commun.*, 2004, 1016; (*f*) J. Tang, Y. Wu, E. W. McFarland and G. D. Stucky, *Chem. Commun.*, 2004, 1670.
10 (*a*) Y. Jun, M. F. Casula, J.-H. Sim, S. Y. Kim, J. Cheon and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2003, **125**, 15981; (*b*) J. Polleux, N. Pinna, M. Antonietti and M. Niederberger, *Adv. Mater.*, 2004, **16**, 436.
11 Z.-Y. Yuan, W. Zhou and B.-L. Su, *Chem. Commun.*, 2002, 1202.
12 S. A. Davis, S. L. Burkett, N. H. Mendelson and S. Mann, *Nature*, 1997, **385**, 420.
13 F. C. Meldrum and R. Seshadri, *Chem. Commun.*, 2000, 29.
14 D. Yang, L. Qi and J. Ma, *Adv. Mater.*, 2002, **14**, 1543.
15 G. Cook, P. L. Timms and C. Goeltner-Spickermann, *Angew. Chem., Int. Ed.*, 2003, **42**, 557.
16 S. R. Hall, H. Bolger and S. Mann, *Chem. Commun.*, 2003, 2784.
17 V. Valtchev, M. Smaihi, A.-C. Faust and L. Vidal, *Angew. Chem., Int. Ed.*, 2003, **42**, 2782.
18 Y. Shin, C. Wang and G. J. Exarhos, *Adv. Mater.*, 2005, **17**, 73.
19 J. Huang and T. Kunitake, *J. Am. Chem. Soc.*, 2003, **125**, 11834.
20 Y. Shin, X. S. Li, C. Wang, J. R. Coleman and G. J. Exarhos, *Adv. Mater.*, 2004, **16**, 1212.
21 (*a*) D. Klemm, D. Schumann, U. Udhardt and S. Marsch, *Prog. Polym. Sci.*, 2001, **26**, 1561; (*b*) A. Svensson, E. Nicklasson, T. Harrah, B. Panilaitis, D. L. Kaplan, M. Brittberg and P. Gatenholm, *Biomaterials*, 2005, **26**, 419.
22 (*a*) T. Wu, G. Liu, J. Zhao, H. Hidaka and N. Serpone, *J. Phys. Chem. B*, 1998, **102**, 5845; (*b*) C. Chen, W. Zhao, P. Lei, J. Zhao and N. Serpone, *Chem. Eur. J.*, 2004, **10**, 1956.