COMMUNICATION www.rsc.org/chemcomm | ChemComm

Free-standing nanofibrous platinum sheets and their conductivity†

Xinsheng Peng,[a] Yan-Hong Luo,[a] Jian Jin,[a] Jianguo Huang,[a] Izumi Ichinose,*[a] Keiji Kurashima[a] and Fotios Papadimitrakopoulos[b]

Received (in Cambridge, UK) 16th August 2006, Accepted 20th September 2006
First published as an Advance Article on the web 6th October 2006
DOI: 10.1039/b611805d

Nanofibrous platinum sheets with a thickness of one to a few tens of nanometres were prepared over the submicron pores of polymer substrates by using long and rigid cadmium hydroxide nanostrands as templates, and these free-standing sheets gave metallic conductivity that varied greatly with the thickness.

Free-standing metallic films with a thickness of a few to several tens of nanometres are expected to play a key role in reactive separation technology. Metals, especially platinum family metals, are known to provide catalytic properties required for polymer electrolyte fuel cells and reduction of harmful emissions from vehicles. Advanced reactive membranes also require controlling the permeability of molecules, ions, and/or electrons, which should be achieved by the nanomorphology of metallic thin films. Various methods have been used to deposit metallic thin films on substrates for investigating their conductivity and catalytic properties.[1–4] However, precise design of ultrathin free-standing films of metals remains largely undeveloped.[5–7] In sharp contrast, free-standing metal oxide films have been actively studied. For instance, the mesoporous silica films obtained at an air–water interface were flexible and resilient enough to be transferred onto various substrates.[8] Porous silica and titania films were also fabricated by carefully peeling off from solid substrates.[9–11] Free-standing porous alumina membranes of submicron thicknesses were obtainable by the anodization of an aluminium layer on a silicon substrate and the selective etching of the substrate.[12,13] Structural diversity of metal oxides should be useful for designing the nanomorphology of free-standing metallic films.[14]

Tsukruk and his co-workers prepared free-standing nanocomposite films of gold nanoparticles and polyelectrolytes for membrane-based microsensor technology.[15] Very recently, ultrathin, free-standing films with centimetre dimensions were prepared by spin-coating assisted layer-by-layer deposition of polymers and metal oxides on a sacrificial layer.[16] Organic polymers and their network seems to provide superior mechanical stability, although these films are unlikely to exhibit electrical conductivity.

Recently, we found that cadmium hydroxide fibers with a width of 1.9 nm were spontaneously formed by raising the pH of an aqueous solution of cadmium ions. We named these fibers inorganic nanostrands, since their dimensions were very close to those of rigid double-stranded DNA of about 6–10 kbp.[17] Uniform free-standing films of such nanostrands could be readily fabricated by filtration using a polycarbonate membrane filter,[18,19] in which a dense and uniform network of the nanostrands covered the submicron pores of the membrane filter. This is because long, polymer-like nanostrands disperse in water without aggregating and the nanostrands deposit on the membrane filter in a random fashion. In this communication, we report that such nanostructured films can be converted into ultrathin nanofibrous platinum sheets. To the best of our knowledge, these sheets are the thinnest free-standing nanoporous films that have had their metallic conductivity confirmed.

Preparation of nanofibrous Pt sheets is schematically illustrated in Fig. 1. First, cadmium hydroxide nanostrands were synthesized by quickly mixing 10 ml of 0.8 mM aminoethanol into an equal volume of 4 mM cadmium chloride and aging the mixture for 15 min. Then, 1 ml of the mixed solution was filtered on a polycarbonate membrane filter with pores of 0.2 μm by suction filtration. Subsequently, the membrane filter was placed in a vacuum chamber of a magnetron-type ion sputter and an ultrathin platinum layer was deposited. The filter was carefully immersed in 1 ml of chloroform to dissolve polycarbonate, and then subjected to centrifugation (10 000 rpm, 10 min). After repeating the washing process three times, the free-standing sheets of Pt-coated nanostrands were obtained. These were converted into nanofibrous Pt sheets by dissolving the cadmium hydroxide nanostrands in 1 ml of 10 mM hydrogen chloride, followed by washing in pure water three times.

An SEM image of cadmium hydroxide nanostrands on a polycarbonate membrane filter is shown in Fig. 2A. The diameter of these nanostrands was close to the observation limit of our microscope for insulating materials. Their structure, however, can be clearly observed after coating them with a 2 nm thick platinum layer. A TEM image of pure cadmium hydroxide nanostrands is shown in Fig. 2B. To obtain this image, the nanostrands were peeled off by dissolving the membrane filter in chloroform. The

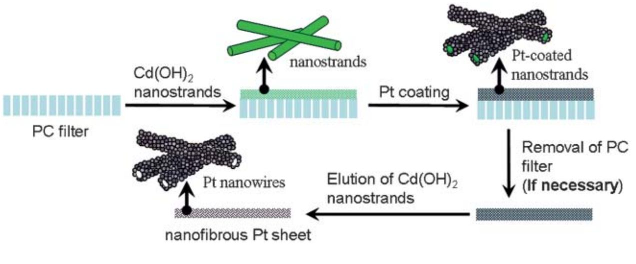

Fig. 1 Fabrication of free-stranding nanofibrous Pt sheets.

---

[a] *Organic Nanomaterials Center and Nanoscale Materials Center, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan. E-mail: ICHINOSE.Izumi@nims.go.jp; Fax: +81-29-852-7449; Tel: +81-29-851-3354*
[b] *Department of Chemistry, Institute of Materials Science, University of Connecticut, CT, 06269-3136, USA*

† Electronic supplementary information (ESI) available: Experimental details on platinum deposition and sheet resistance measurements. See DOI: 10.1039/b611805d

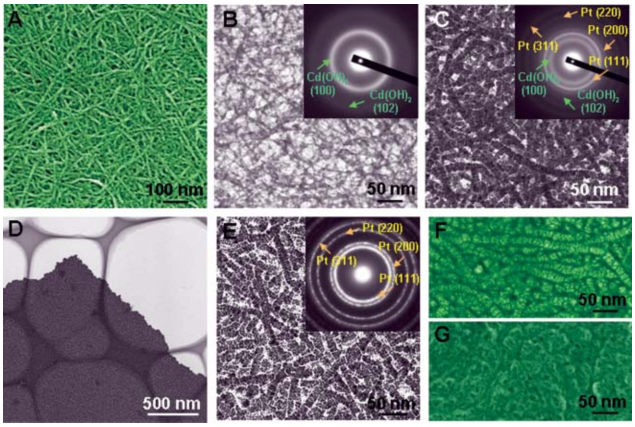

Fig. 2 SEM and TEM images of free-standing nanofibrous sheets. (A) SEM image of cadmium hydroxide nanostrands. (B) TEM image of the nanostrands and the SAED pattern. (C) TEM image of Pt-coated nanostrands and the SAED pattern. (D) Low magnification image of (C). (E) TEM image of nanofibrous Pt sheet and the SAED pattern. (F) SEM image of (E). (G) SEM image of the underside of (F). The thickness of Pt layer in (C)–(G) is 10 nm. The nanostrands in (A) are coated with a 2 nm thick Pt layer.

network structure of the narrow nanostrands was not destroyed after the removal of the polycarbonate membrane.

The selected area electron diffraction (SAED) pattern showed crystalline rings corresponding to (100) and (102) reflections of hexagonal $Cd(OH)_2$. When individual nanostrands were coated with a thin platinum layer and then removed from the membrane filter, free-standing sheets of Pt-coated nanostrands were obtained. The nanostrands in Fig. 2C were coated under conditions where a 10 nm thick platinum layer was deposited. The width of the Pt-coated nanostrands appeared to be 12 to 18 nm. The SAED pattern showed both diffractions from cadmium hydroxide and metallic platinum. A much lower resolution of this metallized nanostrand sheet is shown in Fig. 2D. The film size exceeded a few micrometres. Subsequently, inner cadmium hydroxide nanostrands were selectively removed by treating with aqueous hydrogen chloride. As shown in Fig. 2E and its corresponding inset, the obtained free-standing nanofibrous sheets have a network structure of polycrystalline platinum nanowires. Closer SEM observation of the top and bottom sides of the nanofibrous Pt sheet revealed that the upper side possesses the nanomorphology originated from the templated nanostrands, while the lower side exhibits considerably higher porosity, with a pore size of *ca.* 5 nm in diameter (Fig. 2F and 2G). The outermost nanostrands appear to be uniformly coated with a thin platinum layer. However, this is not the case at the bottom side.

Elemental compositions of these films were examined by energy-dispersive X-ray microanalysis (EDX) measurement. As shown in Fig. 3, the film made of Pt-coated nanostrands (blue spectrum) gave two cadmium peaks (3.15 and 3.33 keV) and three platinum peaks (2.1, 9.4, and 11.2 keV). On the other hand, the two cadmium peaks disappeared after the dissolution of the cadmium hydroxide nanostrands (yellow spectrum). The peak attributed to oxygen (0.5 keV) was also significantly decreased. This, along with the SAED pattern of the inset of Fig. 2E, provides convincing evidence that the free-standing nanofibrous sheets are made of platinum only.

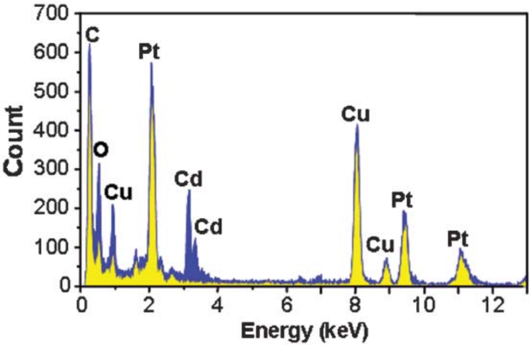

Fig. 3 EDX spectra of Pt-coated nanostrand sheet (blue) and nanofibrous Pt sheet (yellow). The peaks attributed to copper atoms are due to the copper microgrid.

The thickness of the nanofibrous Pt sheets can be controlled by adjusting the deposition time of platinum. In our experimental conditions, 2 nm, 5 nm, and 10 nm thick platinum layers were obtained by sputtering platinum for 30 s, 75 s, and 150 s, respectively. When the deposition time was 15 s, platinum thickness was estimated to be about 1 nm. We discovered that such an ultrathin Pt sheet was also free-standing. As shown in Fig. 4A, the sheet was made of platinum nanoparticles of about 1.5 nm. The edge was a bit soft for electron beam irradiation, and it shrunk during TEM observation. The enlarged image shows that this sheet has many pores of a few to several tens of nanometres. The 2 nm thick nanofibrous Pt sheet appeared to be more stable (Fig. 4B). At this thickness, the network of cadmium hydroxide nanostrands was clearly transferred into the nanofibrous Pt sheet. This sheet has pores in a range of 5–20 nm, giving an average pore diameter of 7.4 nm. The average diameter decreased to 3.4 nm when the thickness of the platinum layer became 5 nm, and then increased again to 5.6 nm when the platinum thickness was 10 nm. In the latter condition, the width of the platinum nanowires appreciably increased, as seen in Fig. 4D.

After platinum deposition, cadmium hydroxide nanostrands were able to be removed on a polycarbonate membrane filter.[20] We monitored the electric conductivity of free-standing sheets on

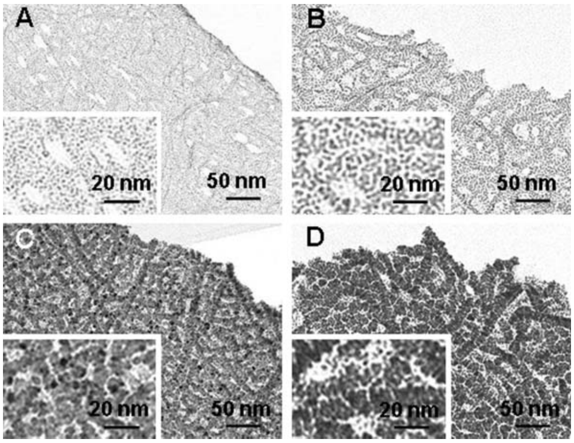

Fig. 4 TEM images of free-standing nanofibrous Pt sheets with thicknesses of (A) 1 nm, (B) 2 nm, (C) 5 nm, and (D) 10 nm. Insets show the high magnification images.

Table 1 Thickness-dependent resistance of Pt-coated nanostrand sheets and nanofibrous Pt sheets

	Sheet resistance/Ω per square[a]				
Thickness	100 nm	50 nm	20 nm	10 nm	5 nm
Pt-coated nanostrand sheet	29.6	46.2	414.7	1124	2748
Nanofibrous Pt sheet	31.2	48.9	489.8	5797	—[b]

[a] Sheet resistance was measured at 23 °C by using a four-point probe detector manufactured by Napson. [b] Above the measurement limit of our instrument.

the filters before and after removal of the nanostrands. As shown in Table 1, the sheet resistance of Pt-coated nanostrand sheets exponentially increased with the decrease of the thickness. This tendency was significant for the nanofibrous Pt sheets. The sheet resistance at 10 nm reached 5797 Ω per square, and the conductivity decreased with the thickness by more than two orders of magnitude.

The difference in sheet resistance of Pt-coated nanostrand and nanofibrous Pt sheets was not so clear when the thickness was no less than 20 nm. However, when the thickness was equal to or less than 10 nm, the conductivities dramatically decreased, especially for the nanofibrous Pt sheets. This difference is not due to the conductivity of the cadmium hydroxide nanostrand, because that is a complete insulator in our experimental conditions. We assume that when the thickness is lower than a critical value between 20 and 10 nm, the continuity of the free-standing nanofibrous Pt sheet declines. It is known that the conductivity of thin films composed of metal nanoparticles depends largely on the distribution of nanoparticles, their contacts and interfacial effects, and the overall texture of the thin films.[21] In particular, when the thickness of the nano-particulate thin films is less than 10 nm, the surface scattering and grain boundary scattering determine the electrical resistivity.[3] The same explanation should be applicable to the lower conductivity of our nanofibrous Pt sheets. In addition, of note is that the conductivity of these free-standing Pt sheets was much lower than that of the thin Pt films deposited on solid substrates at the same thickness.[2,3] The difference is more than one order of magnitude. This might be due to the nanofibrous structure derived from the templates, since such morphology limits the electron pathway through nanoparticles.

We have demonstrated that nanofibrous platinum sheets are stable against acids and organic solvents. They are free-standing, as the thickness is no less than 1 nm. The sheets have nanoporous structures and are obtainable over the submicron pores of a polymer substrate. These make it possible to design reactive membranes, in which the catalytic properties of platinum are combined with the permeation of ions and molecules,[22] and the activity should be readily controlled by applying electric potential. Furthermore, structural stability of these free-standing sheets is advantageous for nano-separation membranes. The separation of reactive gases is now being explored in our group.

Notes and references

1 J. C. Hensel, R. T. Tung, J. M. Poate and F. C. Unterwald, *Phys. Rev. Lett.*, 1985, **54**, 1840.
2 X. Fang, T. Ma, G. Guan, M. Akiyama and E. Abe, *J. Photochem. Photobiol., A*, 2004, **164**, 179.
3 M. Avrekh, O. R. Monteiro and I. G. Brown, *Appl. Surf. Sci.*, 2000, **158**, 217.
4 T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen and M. Leskelä, *Chem. Mater.*, 2003, **15**, 1924.
5 D. H. Pearson and R. J. Tonucci, *Science*, 1995, **270**, 68.
6 H. Xu and W. A. Goedel, *Small*, 2005, **1**, 808.
7 G. S. Attard, P. N. Bartllet, N. R. B. Coleman, J. M. Elliott, J. R. Owen and J. H. Wang, *Science*, 1997, **278**, 838.
8 H. Yang, N. Coombs, I. Sokolov and G. A. Ozin, *Nature*, 1996, **38**, 589.
9 M. Ogawa and T. Kikuchi, *Adv. Mater.*, 1998, **10**, 1077.
10 M. Hashizume and T. Kunitake, *Langmuir*, 2003, **19**, 10172.
11 H. Yun, H. Zhou and I. Honma, *Chem. Commun.*, 2004, 2836.
12 R. C. Furneaux, W. R. Rigby and A. P. Davidson, *Nature*, 1989, **337**, 147.
13 C.-S. Toh, B. M. Kayes, E. J. Nemanick and N. S. Lewis, *Nano Lett.*, 2004, **4**, 767.
14 S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, *Nature*, 2001, **412**, 169.
15 C. Jiang, S. Markutsya, Y. Pikus and V. Tsukruk, *Nat. Mater.*, 2004, **3**, 721.
16 R. Vendamme, S. Onoue, A. Nakao and T. Kunitake, *Nat. Mater.*, 2006, **5**, 494.
17 I. Ichinose, K. Kurashima and T. Kunitake, *J. Am. Chem. Soc.*, 2004, **126**, 7162.
18 I. Ichinose, J. Huang and Y. H. Luo, *Nano Lett.*, 2005, **5**, 97.
19 Y. H. Luo, J. Huang and I. Ichinose, *J. Am. Chem. Soc.*, 2005, **127**, 8296–8297.
20 The nanostrands were selectively removed by floating the membrane filter on a 0.5 mM aqueous EDTA solution for two days.
21 G. Palasantzas, *Phys. Rev. B: Condens. Matter*, 2005, **71**, 205320.
22 M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson and R. H. Baughman, *Science*, 2005, **309**, 1215.