Fabrication of Large, Free-standing Nanofilms of Platinum and Platinum–Palladium Alloy

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A facile approach was developed to fabricate macroscopic, free-standing nanofilms (thickness, 50 nm) of platinum and platinum–palladium alloy, which are flexible and remain intact in air.

Large, free-standing films with thicknesses less than 100 nm have been a theoretical and experimental curiosity for several decades, because, with macroscopic size and molecular scale thickness, they combine the properties of macroscopic materials and microscopic colloids. Compared with conventional nanostructures, such ultrathin films provide unique features: they undergo extensive changes of macroscopic morphology, have short diffusion paths to realize efficient air/fluid permeability, and are highly responsive to various external stimuli.[1] Their practical applications would be versatile, though largely unexplored. We have reported that sub-100-nm thick films of metal oxides were prepared by retaining centimeter sizes and free-standing characteristics.[2,3] More recently, robust, free-standing films with thickness of 30 nm and area of centimeter square were obtained from interpenetrating polymer networks of zirconia–acrylate hybrid.[4] It is important to extend a similar attempt for metallic film.

Noble metals are of great interest in a wide variety of applications including catalysis, fuel cell, selective gas permeation, sensing, microfluidic flow control, and actuation. Combination of their intrinsic functional properties with benefits of nanofilm should lead to novel aspects of their functions. Apart from unique quantum effects observed for noble metal nanoparticles,[5] metallic membrane reactors are another outstanding example that possesses catalytic property of noble metal and separation capability of membrane.[6] Recently, coupling of small thermal capacity and catalytic property was shown to give unique oscillatory thermomechanical instability in the case of a free-standing Pt film.[7] Apparently, the fabrication of free-standing ultrathin films of noble metals is highly relevant and is a scientific and industrial challenge. In the past, attempts to fabricate such metallic films have been restricted to the micrometer size. Xu and Goedel reported a simple method to fabricate free-standing porous metal films (e.g., Au/Pd) that remain intact only on electron microscopy grids.[8] Up to now, the minimum thickness of 100 nm was reported for free-standing metal films with centimeter lateral size, and the used metal was restricted to gold and gold alloy (e.g., Au/Ag),[9] probably owing to the best extensibility of metallic gold. Platinum and palladium are highly catalytic noble metals, and it is especially meaningful that ultrathin films of these metals become available in macroscopic (centimeter or greater) sizes.[1] Electroless plating and sputtering on suitable solid substrates will be useful for this purpose. In order to make them free-standing, film robustness is essential, in addition to facile isolation from the substrate. We selected the sputtering approach in this study, in which metal nanoclusters are deposited on the substrate. It is crucial that the nanoclusters are fused together to form a continuous layer, in order to obtain a free-standing film. Previously, we studied formation of silver nanoparticles on cellulose fiber matrix and found that calcination of the cellulose matrix induced extensive fusion of the nanoparticle to give a metallic replica of the matrix fiber.[10,11] This finding was illuminating.

A schematic illustration of the fabrication process is shown in Figure 1. The detailed experimental procedure of fabrication is given in Supporting Information. Firstly, a uniform layer of sacrificial polymer is formed on Si wafer by spin coating. Then, noble metals are sputtered on the polymer film. A free-standing metallic film is obtained after removing the sacrificial layer.

Reflectance infrared spectra of the PVA/Pt double-layer film show that characteristic peaks of PVA, C–H stretching at 2900–3000 cm^{-1} and broad OH peak at 3000–3500 cm^{-1}, totally disappeared after calcination at temperature as low as 300 °C. PVA film alone could not be burned away at such low temperatures, suggesting the catalytic effect of Pt for the decomposition. Figure 2 presents a camera image and SEM and TEM images of a free-standing Pt film. The film is silver-colored and has a size of 2.0 cm in diameter (Figure 2a). It is flexible and remains intact in air. The top view SEM image of Figure 2b shows that the thin film is made of Pt nanodomains of ca. 10-nm diameter. Among the closely connected nanodomains, small cracks are observed. The corresponding cross-section SEM image of Figure 2c shows that the Pt film has a uniform thickness of 50 nm with standard deviation of 5%. No cracks are observed in the cross section. This film has an aspect ratio of lateral size to thickness as high as 4×10^5. The TEM image of Figure 2d shows that 10-nm nanodomains are fused together to form a continuous film, and cracks are apparently derived from insufficient fusion of the domains. An HRTEM image of Figure 2e indicates the presence of the ordered structure with interplanar spacing of 0.226 nm and

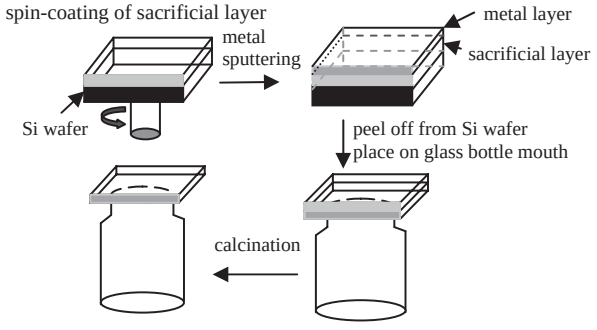

Figure 1. Schematic illustration of fabrication of free-standing noble metal ultrathin film.

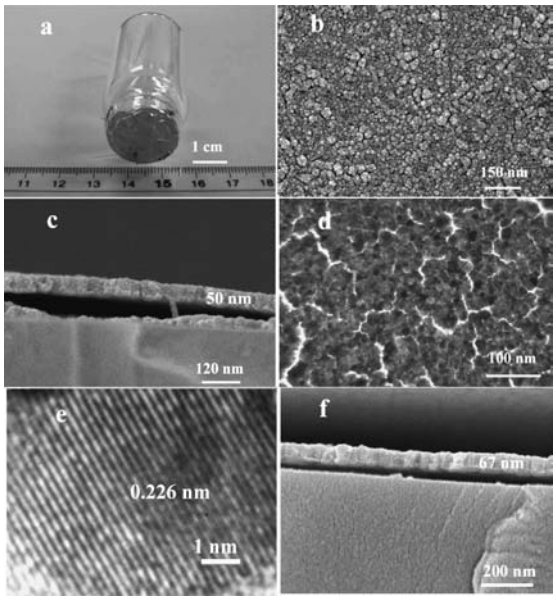

Figure 2. Morphology of the free-standing Pt film: a) camera picture, 50 nm film, b) top view SEM, 50 nm, c) cross-section SEM, 50 nm, d) TEM, 50 nm, e) HRTEM, 50 nm, f) cross-section SEM, 67 nm.

with random orientations. The film thickness is adjusted by changing the period of ion sputtering. When the sputtering time was increased from 180 to 240 s, the film thickness was enhanced from 50 to 67 nm (Figure 2f).

The XRD pattern of the free-standing Pt film (Figure S1)[14] possesses four diffraction peaks which are assigned to the (111), (200), (220), and (311) planes of the cubic structure of Pt (ICSD: Karlsruhe, Jan, 1997, Card No. 4-802), respectively. The intensity ratio of these peaks is 100:27:14:6, as against 100:53:31:33 of bulk Pt. Apparently, preferential ordering of the (111) plane exists. The corresponding spacing of the (111) plane is calculated to be 0.226 nm, in agreement with the value measured by HRTEM.

The free-standing film was placed on a glass slide, and its electrical resistance was measured between a spot at the film center and a spot in the edge of different directions. The average electrical resistance with three edge spots was 42 μΩ cm and was more than four times higher than that of bulk Pt (10.6 μΩ cm).[12] The deviation of the electrical resistance along the different directions was only 1.6%, showing that the Pt film is macroscopically continuous and uniform in terms of electrical property. The observed cracks and dislocation of nanodomains may be a cause of the increased resistance,[13] but their detrimental effect is limited.

The current film fabrication is applicable to other noble metals. By choosing Pt–Pd alloy as sputtering target, we successfully fabricated a 50-nm thick free-standing film of Pt–Pd alloy (Figure S2).[14] EDX analysis shows that it is made of 11 atom % Pd and 89 atom % Pt. The film is flexible, remains intact in air, and has a size of 2.0 cm in diameter (Figure S2a).[14] A cross-section SEM image (Figure S2b)[14] indicates that the Pt–Pd film has a uniform thickness of 50 nm, and a TEM image (Figure S2c)[14] shows that 10–15 nm domains are connected together to form a continuous texture. Seemingly, a smaller number of cracks are found in this film when compared with the Pt film (Figure S2c).[14] An HRTEM image of Figure S2d shows that the Pt–Pd alloy gives randomly oriented ordered domains with interplanar spacing of 0.226 nm. Its XRD pattern gives a slightly shifted peak to a higher angle by 0.04° (Figure S1 and inset).[14] This observation was consistent with measurement of electrical resistance. The electrical resistance of the Pt–Pd film was 33 μΩ cm. Bulk Pd has almost the same resistance (10.54 μΩ cm) of Pt (10.60 μΩ cm).[13] Compared to the free-standing Pt ultrathin film (42 μΩ cm), the free-standing Pt–Pd alloy ultrathin film has smaller electrical resistance due to fewer cracks in the film. Thus, Pt–Pd can form free-standing ultrathin film with better quality.

In summary, a facile approach was developed to fabricate macroscopic, free-standing nanofilms of Pt and Pt–Pd alloy. These films, though fragile, can maintain their macroscopic morphology in spite of their extreme thinness. The fundamental metallic property is clearly retained at this thickness. Unfortunately, we could not avoid the formation of cracks, and these films may be considered as porous membranes at this stage. Many efforts are being devoted to prepare crack-free nanofilms. In spite of this remaining problem, the current results prove that large-size nanofilms became available even for noble metals of Pt and Pt–Pd. In our previous papers, we demonstrated that large nanomembranes of inorganic and organic moieties were realized with aspect ratios (size/thickness) of over one million.[4] This is now extended to the metallic moiety. The crucial role of such free-standing nanomembranes in the construction of functional nanocomposites and nanodevices will be seen in the future study.

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