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Electrochemical deposition of macroporous platinum, palladium and cobalt films using polystyrene latex sphere templates

Philip N. Bartlett,* Peter R. Birkin and Mohamed A. Ghanem

Chemistry Department, University of Southampton, Highfield, Southampton, UK SO17 1BJ.
E-mail: P.N.Bartlett@soton.ac.uk

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Highly ordered macroporous films of platinum, palladium and cobalt with regular arrays of spherical pores with diameters of 0.40, 0.70 or 1 μm are prepared by electrochemical deposition into the interstitial spaces of a template formed by polystyrene latex spheres self-assembled on gold electrodes; after deposition of platinum, palladium or cobalt, the polystyrene spheres are fully removed by washing in toluene to leave a highly periodic, hexagonal close packed, interconnected network of monodisperse spherical pores within the metal film, the size of which is determined by the diameter of the polystyrene latex particles used to prepare the template.

The production of materials with micron and submicron scale structure in two and three dimensions is of importance in a range of applications, such as photonic materials,[1,2] high density magnetic data storage devices,[3] microchip reactors[4] and biosensors.[5] Several new templating techniques are being developed to achieve such macroporous solids with highly ordered structure and high surface area.[6–11] Highly ordered three-dimensional macroporous oxides with pore diameters of a few hundred nanometers have recently been prepared by the chemical hydrolysis of the corresponding metal alkoxide in the interstitial spaces of close packed arrays of polystyrene latex spheres as the template.[12–14] Macroporous titanium dioxide photonic crystals synthesised by a similar procedure have been shown to exhibit photonic band gaps.[15,16] In related studies other authors have described the synthesis of three-dimensional microporous films of semiconducting cadmium selenium (CdSe) by electrochemical deposition in the interstitial spaces in a close packed array of polystyrene latex spheres assembled on an indium tin oxide substrate surface.[17] Van Duyne *et al.*[18,19] have reported using monolayers or bilayers of polystyrene latex particles as masks for the deposition by evaporation of two-dimensional arrays of isolated silver nanoparticles on an insulating substrate.

Here we report the preparation of highly ordered macroporous metal films with pores of predetermined sizes. The preparation of the structured macroporous films was carried out by the electrochemical reduction of $[PtCl_6]^{2-}$, $[PdCl_4]^{2-}$, or $[Co(Ac)_2]$ complex ions in aqueous solution within the interstitial spaces of a close packed polystyrene latex sphere template, self-assembled on a gold surface. The thickness of the resulting films can be many multiples of the diameter of the polystyrene latex spheres used to prepare the template and is readily controlled by the amount of charge passed during deposition of the metal film.†

Most recently Xu *et al.* have described the electrochemical deposition of nanoscale Ni and Au meshes through templates made from close-packed silica sphere arrays (opal).[20] Although the two approaches give similar metal meshes there are several important differences between the method described in our work over that of Xu *et al.* First, the polystyrene latex particles we use are commercially available in a range of sizes; second, our close-packed templates can be prepared by evaporation in 2 d rather than by sedimentation over a period of several months; third, there is no need to sinter the template; fourth, the metal deposition is achieved in a few minutes rather than over 36 h; fifth, the template can be removed by dissolving the polystyrene in toluene rather than requiring the use of HF.

Scanning electron micrographs of cobalt films prepared by electrochemical deposition of cobalt at −0.90 V *vs.* SCE through a template formed from 0.40 and 1.0 μm diameter polystyrene latex spheres are shown in Figs. 1(*a*) and 1(*b*) respectively. The quantities of charge passed were −0.80 and −1.15 C cm^{-2} respectively. These values were chosen in order to grow films whose thickness corresponded to the radius of the template particles used in each case. Fig. 1(*a*) shows that the cobalt film made using the 0.40 μm polystyrene latex sphere template has a highly ordered two dimensional hexagonal network of monodisperse submicron voids each with a hemispherical shape. In the most ordered regions, the pores have a diameter of 380 ± 10 nm (n = 10) and pore to pore centre separation of 450 ± 10 nm (n = 30) The cobalt films made by using the larger, 1.00 μm, polystyrene latex spheres [Fig. 1(*b*)] have a pore diameter of 980 ± 10 nm (n = 10), however, this film shows less two-dimensional order. We attribute this to the fact that the larger latex spheres take a longer time to assemble into a highly ordered structure.[21]

Fig. 1(*c*) shows a scanning electron micrograph of a platinum film deposited into a template formed from 0.70 μm polystyrene latex spheres at a deposition potential of 0.10 V *vs.* SCE (total charge passed −1.20 C cm^{-2}). The image shows that the electrochemically deposited platinum film consists of a highly

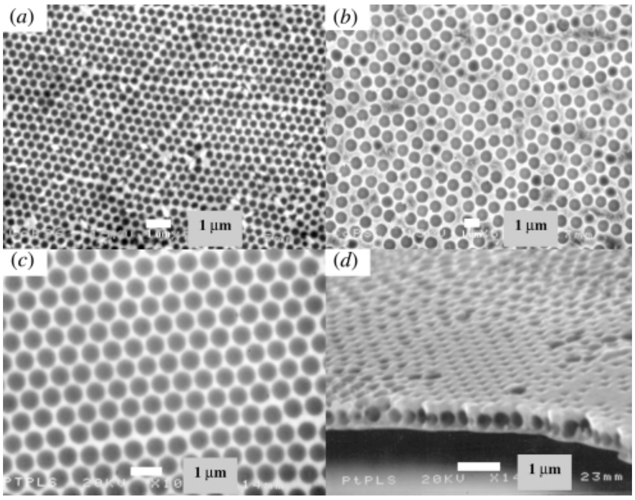

Fig. 1 Scanning electron micrographs of macroporous platinum and cobalt films electrochemically deposited, at 0.10 and −0.90 V *vs.* SCE respectively, through templates formed using polystyrene latex spheres pre-assembled on gold electrode surfaces. (*a*) Cobalt film, deposition charge −0.85 C cm^{-2}, polystyrene latex sphere diameter 0.40 μm; (*b*) cobalt film, deposition charge −1.15 C cm^{-2}, polystyrene latex sphere diameter 1.0 μm; (*c*) platinum film, deposition charge −1.20 C cm^{-2}, polystyrene latex sphere diameter 0.70 μm; (*d*) cross-sectional image of a platinum film, deposition charge −1.00 C cm^{-2}, polystyrene latex sphere diameter 0.40 μm.

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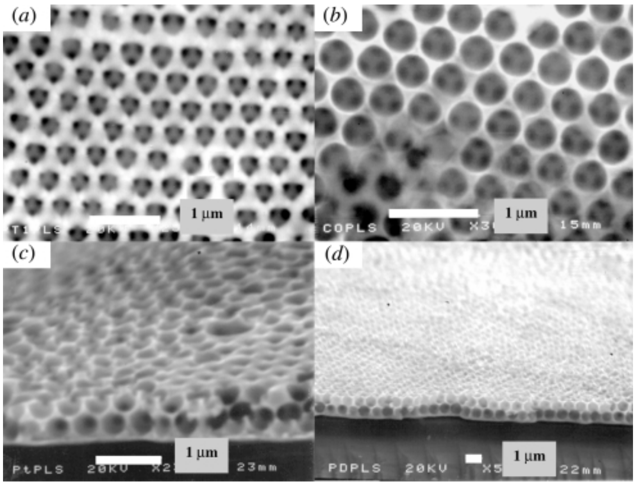

Fig. 2 Scanning electron micrographs of macroporous films of platinum, palladium and cobalt electrochemically deposited, at potentials of 0.10, 0.25 and −0.90 V *vs.* SCE respectively, through templates formed using polystyrene latex spheres pre-assembled on gold electrode surfaces. (*a*) Platinum film, deposition charge −2.00 C cm^{-2}, polystyrene latex sphere diameter 0.40 μm; (*b*) cobalt film, deposition charge −1.40 C cm^{-2}, polystyrene latex sphere diameter 0.40 μm; (*c*) cross-sectional image of a platinum film, deposition charge −1.50 C cm^{-2}, polystyrene latex sphere diameter 0.40 μm; (*d*) palladium film, deposition charge −1.15 C cm^{-2}, polystyrene latex sphere diameter 0.70 μm.

periodic hexagonal array of monodisperse pores. The pore to pore centre separation in this case was 770 ± 10 nm (n = 30). Fig. 1(*d*) shows a cross sectional image of a platinum film prepared by deposition of −1.00 C cm^{-2} through a template of 0.40 μm polystyrene latex spheres. The formation of a monolayer of spherical pores embedded in the platinum film (which in this case was grown to a thickness of approximately 0.4 μm) can be clearly seen.

Figs. 2(*a*) and 2(*b*) show scanning electron micrographs of thicker films of platinum and cobalt where sufficient charge has been passed to deposit films several multiples of the polystyrene latex sphere diameter in thickness. The micrographs show that the spherical pores left in the platinum or cobalt films after removal of the polystyrene latex spheres are arranged in a well ordered three dimensional hexagonal close packed structure. In addition, the connections between the spherical voids within the film, formed where the polystyrene latex spheres in one layer were in contact with those in the underlayer, can be seen as the three dark areas within each pore. In Fig. 2(*a*) the mouths of the pores have a rounded triangular shape. This appears to be a regular feature of films which are grown to a thickness corresponding to about $(n + \frac{3}{4})$ layers of spheres, where n = 0, 1, 2, …. Figs. 2(*c*) and 2(*d*) show cross-sectional images of platinum and palladium films prepared using templates formed from 0.40 and 0.70 μm polystyrene latex spheres. These micrographs also demonstrate the formation of three dimensional macroporous films with thickness of 1.5 or 2.0 times the pore diameters for the platinum and palladium films respectively. The spherical voids have a diameter determined by the diameter of the polystyrene latex spheres used for the template and are arranged as part of an hexagonal lattice, again indicating that the polystyrene latex particles were arranged in three-dimensional hexagonal close packed structure. This was also confirmed by scanning electron micrographs of the templates themselves before the deposition of the metal (not shown).

Our studies have shown that self-assembled layers of polystyrene latex particles formed on gold surfaces by slow evaporation of water from the latex suspension can be used as templates through which to electrochemically deposit metal films. In the resulting metal/polystyrene composite the polystyrene spheres are in contact and can be dissolved out of the metal to leave a regular array of interconnected spherical voids. The size of these voids is determined by the size of the polystyrene latex particles used. Since polystyrene latex particles of tightly controlled size distribution are readily commercially available in sizes from 0.05 to 90 μm the size of the voids can be readily controlled. Control over the quantity of charge passed in the electrochemical deposition of the film allows control over the final film thickness. Thus this method represents a simple route to the production of ordered macroporous films of metals, metal alloys, and polymers with potentially interesting and useful photonic, catalytic, magnetic, or other properties.

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Notes and references

† *Experimental:* Cobalt acetate [Co(Ac)$_2$·4H$_2$O, 99.5%] and potassium acetate (KAc, 99.4%) were obtained from Fluka. Hexachloroplatinic acid and diammonium tetrachloropalladate were obtained from Aldrich (purity 99.99%). 0.5 wt% suspensions of 0.40 and 1.00 μm diameter polystyrene latex spheres in water were obtained from Agar Scientific, 2.5 wt% suspensions of 0.70 μm diameter polystyrene latex spheres in water were obtained from Alfa Asear. The working electrodes were prepared by evaporating 10 nm of a chromium adhesion layer followed by 200 nm of gold onto thin glass microscope slides. A large area platinum gauze was used as the counter electrode and home made saturated calomel (SCE) as the reference electrode. Before use, the gold working electrodes were sonicated in propanol for 1 h and then rinsed with deionised water. A volume of *ca.* 0.3 cm^3 of the suspension of polystyrene latex spheres diluted with water to 0.5 wt% was spread over *ca.* 1 cm^2 area of the gold electrode and allowed to dry slowly over 2 d in a controlled humidity chamber. The working electrode, together with the adherent, dry, polystyrene latex bead template, was dipped in to the appropriate electrolyte solution to deposit the metal film. The deposition solutions were either 50 mmol dm^{-3} H$_2$PtCl$_6$, 40 mol dm^{-3} (NH$_4$)$_2$PdCl$_4$, or 0.1 mol dm^{-3} Co(Ac)$_2$ with 0.1 mol dm^{-3} KAc. The deposition was carried out potentiostatically at potentials of 0.10, 0.25 or −0.90 V *vs.* SCE for the electrochemical deposition of platinum, palladium, or cobalt. After deposition the polystyrene latex spheres were dissolved out of the metal films by soaking in toluene for 24 h.

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