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Highly Ordered Macroporous Au and Pd by Colloidal Crystal Templating

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Abstract: The highly ordered macroporous Au and Pd with regular arrays of spherical pores have been synthesized by poly (styrene-co-acrylic) (PSA) colloidal crystal template. The pore size is tuneable in the range of 100-400 nm according to the size of PSA latex. The mechanism is based on the *in-situ* impregnating and reducing of metal ions in the interspaces of the PSA spheres then removing the template.

Keywords: Macroporous materials, chemical synthesis, scanning electron microanalyzer.

The generation of ordered macroporous materials is a topic of current scientific research owing to their wide range of applications as solid catalysis, absorbents, chromatographic supports, optoelectronic sensors, and photonic crystals[1-4]. Various products have been fabricated, including silica, metal oxides, metals, metal chalcogenides, carbon, and polymers[5-9] by the methods such as sol-gel technique[2,10], nanoparticles infusion[2,11], electrodeposition[7,13], melt-imbibing[12], electroless deposition[14,15] and so on.

Platinum and gold mesoporous replicas have been prepared from a template of monodisperse colloidal silica[14]. Yan and coworkers have synthesized 3D ordered macroporous alloys of Ni_xCo_{1-x} and Mn_3Co_7 by PMMA colloidal crystal templating[16]. Gold has also grown in the form of flakes that clearly carry the imprints of the original colloidal spheres *via* electrochemical deposition[17]. However, some methods lead to obvious damage of periodic structure while the others need two or more steps to gain the ordered porous products.

In this letter, high ordered macroporous Au and Pd with pores of predetermined sizes have been fabricated by PSA (polystyrene-co-acrylic) colloidal crystal template. The monodispersed PSA spheres were synthesized in our group and could self-assemble to colloidal crystal structure[18,19].

Figure 1 (cross-section) presents the typical SEM(scanning electronic microscopy) image of the PSA colloidal crystal template that is taken on an X-650 scanning electron

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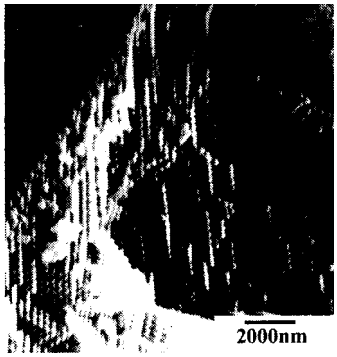
microanalyzer. It suggests that the ordering extends over all three-dimensions. The latex used in this investigation is about 300 nm in diameter that could be adjusted in the range of 100 nm to 400 nm by selecting the proper polymerization condition[18].

Figure 1 SEM of the PSA colloidal template



(cross-section)

Figure 2 The Au formed around the PSA spheres in the template

(cross-section)

To form 3D ordered Au periodic macroporous structure, a PSA colloidal crystal pellet was impregnated with an aqueous solution of 50wt% $HAuCl_4$ and held in an oven at 60℃in the flow of N_2. It has been known that noble metal ions could be reduced under slight heating in the matrix of poly(methyl methacrylate)[20]. So the $HAuCl_4$ was *in-situ* reduced, making the Au formed around the PSA latex (**Figure 2**). Then the template was removed by washing in THF several times, leaving porous Au behind. The same process was performed on H_2PdCl_6 to the Pd macroporous product.

Figure 3 SEM image of macroporous Au

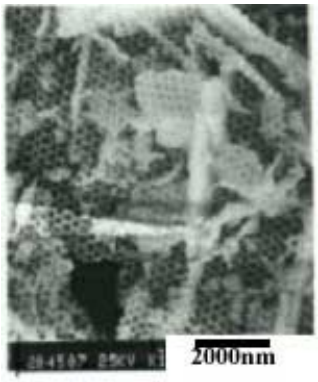


Figure 4 The corresponding electronic diffraction pattern(ED)

A typical SEM image of the Au inverse opal (**Figure 3**) shows that the material is built up of three-dimensional ordered arrays of uniform pores. The electronic diffraction

pattern of the sample (ED) is shown in **Figure 4**, indicating that the walls of the porous sample are composed by Au single-crystal. Some gold crystals formed on the surface of the sample, which was due to the gold extended growth from those in the template grain boundaries[17]. The pore size in the product is about 280 nm. Only slight shrinkage occurs during the removal of the template.

Figure 5 TEM image of Pd nanoparticles formed around the PSA spheres

Figure 6 TEM image of Pd macroporous product.

The **Figure 5** is the composite of Pd nanoparticles surrounding the PSA latex. The TEM(transmission electronic microscopy) image of macroporous Pd (**Figure 6**) exposes some ordered layers of closely packed air spheres. Spherical voids represent the original positions of the PSA spheres. Its corresponding ED pattern (not given here) indicates that the walls of the porous Pd are composed by Pd polycrystallines. The difference between the porous Au and porous Pd may be due to their different dynamic process during the growth of the crystals. The more information is under work. Comparing with the silica template, the PSA colloidal crystal makes the metal replica retaining more ordered regions. This type of products may hold the merits of both nanomaterials and ordered macroporous materials.

The method is based on the *in-situ* impregnating and reducing of metal ions in the interstitial cavern of the PSA colloidal crystal template. PSA latex spheres are beneficial to the penetration of the precursor solution owing to their better wettability. They are also favorable for the infusion of the inorganic salts owing to the existence of carboxyl group on the surface[19]. The milder conditions of reduction result in the lower density of nuclei forming in the process and therefore lead to more remaining of the ordered structure in the porous products[14]. It may suggest a convenient path to fabricate other porous metal materials.

Acknowledgments

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