Chemical Vapor Deposition of Macroporous Platinum and Palladium−Platinum Alloy Films by Using Polystyrene Spheres as Templates

Maoqi Feng and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Received March 18, 2003
Revised Manuscript Received June 10, 2003

There has been intense interest in the preparation of ordered mesoporous and macroporous materials composed of polymers,[1] metal oxides,[2] metals,[3,4] or metal alloys.[5] Such metallic materials have potential applications as electrochemical sensors,[6] as active components in catalytic converters,[7] or as recyclable heterogeneous catalysts for coupling reactions.[8] A versatile method for forming these porous materials is to deposit the material on monodisperse spheres (typically polystyrene or silica) as templates, followed by removal of the template material.[1−5] Ordered macroporous metals have now been deposited in this method by hydrogen reduction of preformed macroporous oxides[2] and by electroless or electrochemical deposition.[3−5] Chemical vapor deposition (CVD) has a potential advantage for deposition of metals on polystyrene spheres since no solvent, which can disrupt the ordered spheres, is needed. However, low-temperature CVD is needed since polystyrene is thermally sensitive. This article reports the low-temperature CVD of Pt and Pt−Pd alloy on polystyrene and its application for making porous ordered films of these catalytically active metals.

Low-pressure CVD of platinum on polystyrene films (thickness 1.5 μm supported on Al disks) was investigated using the precursor[9] [PtMe$_2$(COD)], COD = 1,5-cyclooctadiene, with air as the carrier gas (flow rate of 60 mL min^{-1}) and the precursor warmed to 65 °C to increase volatility, but no deposition was possible at temperatures below the softening temperature of 85 °C. However, in the presence of catalytic amounts of the palladium precursor[10] [Pd(C$_4$H$_7$)(hfac)], C$_4$H$_7$ = η^3-2-methylallyl, hfac = hexafluoroacetylacetonate, introduced, in a separate carrier gas stream of air, near to the substrate, deposition of platinum on polystyrene films was possible over the temperature range 70−85 °C. This is an example of catalyst-enhanced CVD (CECVD) which, with palladium precursors as catalysts, is known to reduce the temperatures of several other deposition processes.[11] Alternatively, the surface of the polymer film could be primed by introducing the palladium precursor as a solution in acetone, after which the CVD could be carried out using pure platinum precursor at 70−85 °C. In either case, the palladium precursor presumably decomposes to create palladium seeds that initiate the platinum CVD. Once deposition begins, the CVD is catalyzed by the growing platinum film in an autocatalytic fashion, and the oxygen in the carrier gas keeps the surface clean by oxidation of surface hydrocarbon fragments.[9−12] Platinum films grown in this way had a shiny silver appearance, with good adhesion on the polymer substrate, and the presence of metallic platinum was confirmed by XPS (BE Pt 4f$_{7/2}$ = 71.34 eV).[13] No palladium was detected in thick films by XPS. Carbon impurity was 13 at. % in a typical film prepared using air as a carrier gas, and this could be reduced to about 5% by annealing the films under hydrogen at 70 °C, but very pure platinum on the organic substrate was not achieved. Platinum−palladium alloy films were most simply prepared by using a mixture of the precursors [PtMe$_2$(COD)] and [Pd(hfac)$_2$].[14] These precursors have similar volatilities and the mixture was warmed to 65 °C to enhance the vapor pressure, with air as a carrier gas. No extra catalyst was required in this case. With use of equimolar amounts of the two precursors, a typical film analyzed as Pt = 75, Pd = 7, C = 14, and O = 4 at. %. Thus, although the palladium is required to initiate CVD, the film growth appears more efficient for platinum under the experimental conditions used. The XPS binding energies were Pt 4f$_{7/2}$ = 71.4 eV and Pd 3d$_{5/2}$ = 335.6

---

(1) (a) Park, S. H.; Xia, Y. *Chem. Mater.* **1998**, *10*, 1745. (b) Park, S. H.; Xia, Y. *Adv. Mater.* **1998**, *10*, 1045. (c) Johnson, S. A.; Ollivier, P. J.; Mallouk, T. E. *Science* **1999**, *283*, 963. (d) Jiang, P.; Hawang, K. S.; Mittleman, D. M.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 11630.

(2) (a) Holland, B. T.; Blanford, C. F.; Do, T.; Stein, A. *Science* **1998**, *281*, 538. (b) Yan, H.; Blanford, C. F.; Holland, B. T.; Smyrl, W. H.; Stein, A. *Chem. Mater.* **2000**, *12*, 1134. (c) Yang, P.; Deng, T.; Zhao, D.; Feng, P.; Pine, D.; Chmelka, B. F.; Whitesides, G. M.; Stucky, G. D. *Science* **1998**, *282*, 2244.

(3) Yan, H.; Blanford, C. F.; Holland, B. T.; Parent, M.; Smyrl, W. H.; Stein, A. *Adv. Mater.* **1999**, *11*, 1003. (b) Jiang, P.; Cizeron, J.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 7957. (c) Velev, O. D.; Tessier, P. M.; Lenhoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548. (d) Xu, L.; Zhou, W. L.; Frommen, C.; Baughman, R. H.; Zakhidov, A. A.; Malkinski, L.; Wang, J. Q.; Wiley, J. B. *Chem. Commun.* **2000**, 997.

(4) (a) Bartlett, P. N.; Baumberg, J. J.; Birkin, P. R.; Ghanem, M. A.; Netti, M. C. *Chem. Mater.* **2002**, *14*, 2199. (b) Bartlett, P. N.; Birkin, P. R.; Ghanem, M. A. *Chem. Commun.* **2000**, 1671.

(5) (a) Yan, H.; Blanford, C. F.; Smyrl, W. H.; Stein, A. *Chem. Commun.* **2000**, 1477. (b) Attard, G. S.; Leclerc, S. A. A.; Maniguet, S.; Russell, A. E.; Nandhakumar, I.; Bartlett, P. N. *Chem. Mater.* **2001**, *13*, 1444.

(6) Tierney, M. J.; Kim, H. L. *Anal. Chem.* **1993**, *65*, 3435.

(7) Heck, R. M.; Farrauto, R. J. *Catalytic Air Pollution Control, Commercial Technology*; Van Nostrand Reinhold: New York, 1995; pp 71−112.

(8) Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642.

(9) (a) Kumar, R.; Roy, S.; Rashidi, M.; Puddephatt, R. J. *Polyhedron* **1989**, *8*, 551. (b) Dryden, N. H.; Kumar, R.; Ou, E.; Rashidi, M.; Roy, S.; Norton, P. R.; Puddephatt, R. J.; Scott, J. D. *Chem. Mater.* **1991**, *3*, 677. (c) Puddephatt, R. J. *Polyhedron* **1994**, *13*, 1233. (d) Hierso, J.-C.; Serp, P.; Feurer, R.; Kalck, P. *Appl. Organomet. Chem.* **1998**, *12*, 161. (e) Serp, P.; Feurer, R.; Kihn, Y.; Kalck, P.; Faria, J. L.; Figueiredo, J. L. *J. Phys. IV* **2002**, *12*, 29. (f) Hierso, J.-C.; Feurer, R.; Kalck, P. *Chem. Mater.* **2000**, *12*, 390.

(10) Zhang, Y.; Yuan, Z.; Puddephatt, R. J. *Chem. Mater.* **1998**, *10*, 2293.

(11) Zhang, Y.; Choi, S. W.-K.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 9295.

(12) (a) Xue, Z.; Strouse, M. J.; Shuh, D. K.; Knobler, C. B.; Kaesz, H. D.; Hicks, R. F.; Williams, R. S. *J. Am. Chem. Soc.* **1989**, *111*, 8779. (b) Xue, Z.; Thridandam, H.; Kaesz, H. D.; Hicks, R. F. *Chem. Mater.* **1992**, *4*, 162. (c) Nixon, B.; Norton, P. R.; Ou, E.; Puddephatt, R. J.; Roy, S.; Young, P. A. *Chem. Mater.* **1991**, *3*, 222.

(13) Clark, D. T. *Handbook of X-ray and ultraviolet photoelectron spectroscopy*; Briggs, D., Ed.; Heyden: London, 1977.

(14) Lin, W.; Wiegand, B. C.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1996**, *118*, 5977.

10.1021/cm034170x CCC: $25.00

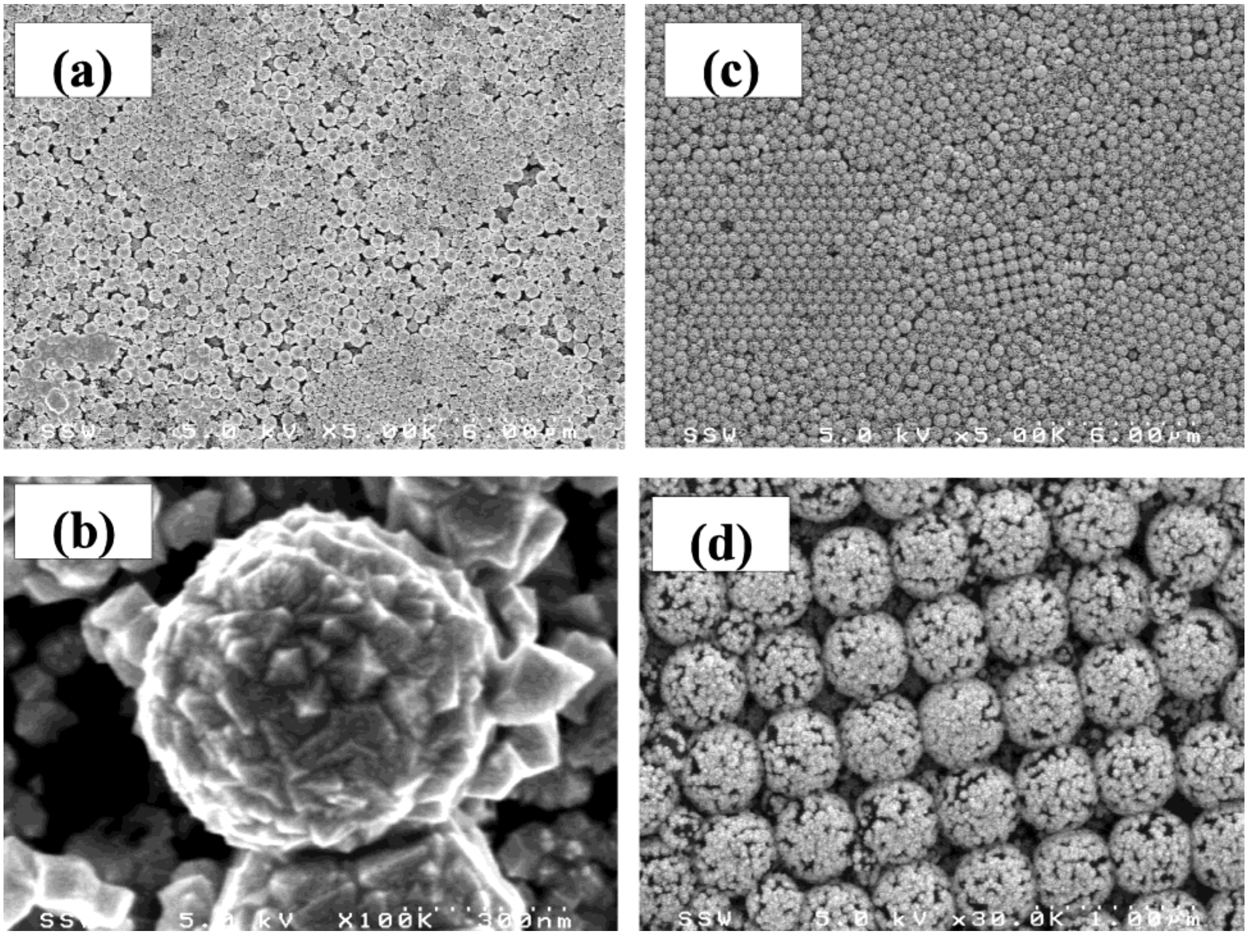

Figure 1. Scanning electron micrographs (Hitachi S-4500 SEM at 5.0 kV) of macroporous Pt−Pd alloy films: (a) the packing of the spheres before polystyrene was removed; (b) a close-up view of a coated polystyrene sphere; (c) the packing of spheres after pyrolysis of the polystyrene; and (d) a more detailed view of the macroporous film showing how some surface crystallites are lost to give holes in the surface of each hollow sphere.

eV, consistent with metallic alloy formation.[13] Thus, conditions for low-temperature CVD of Pt or Pt−Pd alloy films on polystyrene were established and then applied to CVD on polystyrene spheres.

The polystyrene spheres (diameter 500 nm, from a 2.5% dispersion in water, from Alfa Aesar) were assembled at a thickness of about 1.5 μm (three layers deep) according to the reported method,[4] but on aluminum or copper foil (0.5-mm thickness, 1-cm diameter) substrates. Since the polystyrene spheres soften at 85 °C and melt at 90 °C, the CVD was carried out at the lowest possible temperature of 70 °C. Pretreatment of the assembled spheres with an acetone solution containing [$Pd(hfac)_2$] was found to disrupt the ordering of the spheres, so this method of activating the surface for CVD of platinum was not useful, but the CECVD procedure using [$PtMe_2(COD)$], with [$Pd(C_4H_7)(hfac)$] “catalyst,” was successful for platinum deposition. The Pt−Pd alloy film was deposited in the same way as on the polystyrene films using a [$PtMe_2(COD)$]/[$Pd(hfac)_2$] precursor mixture. After CVD was complete (typically 24 h at 70 °C), the polystyrene latex sphere template was removed by pyrolysis at 400−450 °C for 4 h to give the macroporous metal film supported on an aluminum or copper substrate. Attempts to remove the polymer sphere template by dissolution in toluene were unsuccessful, as also found in related systems,[15] since swelling of the polymer damaged the macroporous metal films.

The films obtained showed diffractive colors from green to red, depending on the viewing angle, when illuminated from above with white light, and they were further characterized by XPS and SEM. The analytical data of the metal-coated polystyrene spheres were similar to those above. However, after pyrolysis of the polystyrene the impurities were much higher. Thus, a macroporous platinum film analyzed as follows: Pt, 60 at. %; C, 32 at. %; O 8 at. %. The Pt−Pd alloy analyzed as follows: Pd, 8 at. %; Pt, 49 at. %; C, 22 at. %; O, 21 at. %. The XPS binding energies were not changed by the pyrolysis step and indicated the presence of the metallic state [Pt $4f_{7/2} = 71.6$ eV for platinum film; Pt $4f_{7/2} = 71.4$ eV and Pd $3d_{5/2} = 335.6$ eV for Pt−Pd alloy film].[13] The high carbon content evidently arises as a result of pyrolysis of the polystyrene. It was not greatly reduced by annealing of the films in an atmosphere of oxygen or hydrogen. The film morphology was determined at each stage of the preparation by SEM, as illustrated for the Pt−Pd alloy film grown on 500-nm diameter polystyrene spheres supported on aluminum in Figure 1. Parts (a) and (b) in Figure 1 show the metallic film before and after pyrolysis, respectively, and show that the 500-nm polystyrene sphere size is re-

---

(15) Wijnhoven, J. E. G.; Vos, W. L. *Science* **1998**, *281*, 802.

tained in the metallic films and that the spheres were reasonably well ordered. Figure 1b shows a close-up view of a single metal-coated sphere and shows that the polystyrene is completely coated with crystallites of Pt−Pd alloy with sizes averaging ∼100 nm. Figure 1d shows a view of a section of the film after pyrolysis of the polystyrene and shows that each sphere of Pt−Pd alloy is hollow and that some surface crystallites were displaced as the organic material was evaporated during pyrolysis.

In summary, it is shown that self-assembled polystyrene latex spheres (500-nm diameter on aluminum or copper) can act as templates for the low-temperature CVD of platinum and platinum−palladium alloy films. The polystyrene latex sphere templates can then be removed by pyrolysis at 400−450 °C to leave the structured metal films. CVD is a particularly useful deposition method since it does not require a solvent that can lead to desorption or loss of the structure of the self-assembled polystyrene spheres. The method should be applicable to the formation of macroporous films of other materials, provided that deposition can be carried out below the softening temperature of the polystyrene.

Acknowledgment. We thank the NSERC (Canada) and MMO (Ontario) for financial support.

CM034170X