Synthesis and Characterization of Hierarchical Porous Gold Materials

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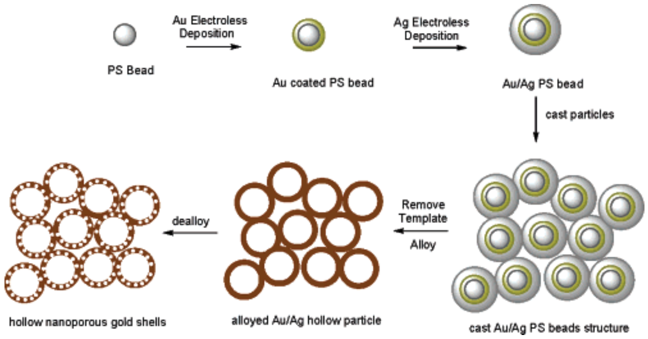
Received October 27, 2006
Revised Manuscript Received December 5, 2006

Metallic porous materials are of great interest for electronic, catalytic, and sensor applications.[1] In addition, materials with multimodal porosity or hierarchical porous materials are of interest because larger pores in the structure facilitate mass transport while smaller pores increase the surface area. Although porous noble metal materials have been used extensively in catalytic, electrochemical, and purification processes,[2] synthesis of hierarchical porous noble metal materials is challenging despite significant progress in preparing multimodal porous ceramics and metal oxides.[3]

Templating and dealloying are two approaches to incorporate and control porosity within metals. Templating uses sacrificial inorganic or organic materials to generate pore sizes ranging from the nanometer to the micron scale.[4] The dealloying process is a method that uses corrosion to selectively remove the least noble element(s) within an alloy, resulting in a nanoporous material of the more noble element.[5] For example, immersion of a $Ag_{70}Au_{30}$ bulk alloy in nitric acid selectively removes the silver atoms leaving behind a nanoporous gold network. We reasoned that combining templating and dealloying techniques would allow the synthesis of multimodal porous noble metal materials. In this communication, we report the first synthesis of ultra-low-density gold monoliths with multimodal pore structure.

Scheme 1. Synthesis of Hollow Nanoporous Gold Shells



To prepare hierarchical porous gold materials, our strategy was to prepare templated hollow silver/gold (Ag/Au) shells that could subsequently be dealloyed (Scheme 1). We adopted a core−shell approach to prepare the hollow Ag/Au shells since synthetic routes to prepare gold-coated silica[6] and polystyrene[7] (PS) core−shell particles are well developed. PS beads (10 and 1 μm) were chosen as templates since they are readily available and can be easily removed at elevated temperatures. In order to study the physical properties of individual particles, current synthetic procedures for gold-coated core−shell particles have been optimized for preparing limited quantities of material at high dilution and therefore are inadequate for the preparation of macroscopic porous materials. Synthesis of gold-coated particles at higher concentrations leads to particle aggregation which in turn interferes with the particle casting process. To minimize particle aggregation at higher particle concentrations, we experimented with polymer stabilizers during gold deposition.[8] Electroless gold deposition on PS beads, in the presence of the stabilizer poly(vinyl pyrrolidinone) (PVP), proceeded smoothly with little apparent particle aggregation.[9] Once the electroless gold deposition is complete, the PS beads are isolated, re-dispersed in distilled water, and then cast to create a PS-gold monolith. The casting procedure is analogous to slip-casting of ceramic[10] and metal[11] particles in which a suspension of PS/Au particles is placed in a plaster of paris

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(1) (a) Stein, A. *Adv. Mater.* **2003**, *15*, 763. (b) Schüth, F. *Chem. Mater.* **2001**, *13*, 3184. (c) Sanchez, C.; Lebeau, B.; Chaput, F.; Boilot, J. P. *Adv. Mater.* **2003**, *15*, 1969. (d) Bond, G. C.; Thompson, D. T. *Catal. Rev. Sci. Eng.* **1999**, *41*, 319. (e) van Noort, D.; Mandenius, C. F. *Biosens. Bioelectron.* **1999**, *15*, 203.

(2) (a) Bond, G. C.; Thompson, D. T. *Gold Bull.* **2000**, *33*, 41. (b) Bond, G. C.; Thompson, D. T. *Catal. Rev. Sci. Eng.* **1999**, *41*, 319. (c) Burke, L. D.; Nuget, P. F. *Electrochim. Acta* **1997**, *42*, 399. (d) Padilla, A. P; Rodriguez, J. A.; Saitua, H. A. *Desalination* **1997**, *114*, 203.

(3) (a) Kuang, D.; Brezesinski, T.; Smarsly, B. *J. Am. Chem. Soc.* **2004**, *126*, 1053. (b) Vasiliev, P. O.; Shen, Z.; Hodgkins, R. P.; Bergstrom, L. *Chem. Mater*. **2006**, *18*, 4933. (c)Wang, H.; Huang, L.; Wang, Z.; Mitra, A.; Yan, Y. *Chem. Commun*. **2001**, 1364. (d) Smatt, J. H.; Weidenthaler, C.; Rosenholm, J. B.; Linden, M. *Chem. Mater.* **2006**, *18*, 1443.

(4) (a) Velev, O. D.; Tessier, P. M.; Lenhoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548. (b) Soler-Illia, G. J. D. A.; Sanchez, C.; Lebeau, B.; Patarin, J. *Chem. Rev.* **2002**, *102*, 4093 and references therein. (c) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548. (d) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, 12, 693. (e) Kulinowski, K. M.; Jiang, P.; Vaswani, H.; Colvin, V. L. *Adv. Mater.* **2000**, *12*, 833. (f) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132. (g) Yan, H.; Blanford, C. F.; Holland, B. T.; Parent, M.; Smyrl, W. H.; Stein, A. *Adv. Mater*. **1999**, *11*, 1003. (h) Yang, H.; Shi, Q.; Tian, B.; Lu, Q.; Gao, F.; Xie, S.; Fan, J.; Yu, C.; Tu, B.; Zhao, B. *J. Am. Chem. Soc.* **2003**, *125*, 4724. (i) Walsh, D.; Arcelli, L.; Ikoma, T.; Tanaka, J.; Mann, S. *Nat. Mater.* **2003**, *2*, 386. (j) Tappan, B. C.; Huynh, M. H.; Hiskey, M. A.; Chaves, D. E.; Luther, E. P.; Mang, J. T.; Son, S. F. *J. Am. Chem. Soc*. **2006**, *128*, 6589. (k) Shin, H. C.; Liu, M. *Chem. Mater.* **2004**, *16*, 5460.

(5) (a) Erlebacher, J.; Aziz, M. J.; Karma, A.; Dimitrov, N.; Sieradzki, K. *Nature* **2001**, *410*, 450. (b) Ding, Y,; Erlebacher, J. *J. Am. Chem. Soc*. **2003**, *125*, 7772. (c) Newman, R. C.; Sieradzki, K. *Science* **1994**, *263*, 1708.

(6) (a) Pham, T.; Jackson, J. B.; Halas, N. J.; Lee, T. R. *Langmuir* **2002**, *18* 4915. (b) Westcott, S. L.; Oldenburg, S. J.; Lee, T. R.; Halas, N. J. *Langmuir* **1998**, *14*, 5396. (c) Graf, C.; van Blaaderen, A. *Langmuir* **2002**, *18*, 524. (d) Caruso, F.; Spasova, M.; Salgaueirino-Maceira, V.; Liz-Marzan, L. M. *Adv. Mater.* **2001**, *13*, 1090. (e) Caruso F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, *282*, 1111. (e) Liang, Z.; Susha, A.; Caruso, F. *Chem. Mater.* **2003**, *15*, 3176. (f) Grabar, K. C.; Smith, P. C.; Musick, M. D.; Davis, J. A.; Walter, D. G.; Jackson, M. A.; Guthrie, A. P. Natan, M. J. *J. Am. Chem. Soc*. **1996**, *118*, 1148. (g) Grabar, K. C.; Allison, K. J.; Baker, B. E.; Bright, R. M.; Brown, K. R.; Freeman, R. G.; Fox, A. P.; Keating, C. D.; Musick, M. D.; Natan, M. J. *Langmuir* **1996**, *12*, 2353. (h) Park, S. W.; Park, M. Y.; Han, P. K.; Lee, S. W. *Bull. Korean Chem. Soc.* **2006**, *27*, 1341.

(7) (a) Shchukin, D. G.; Caruso, R. A. *Chem. Commun.* **2003**, 1478. (b) Shi, W.; Sahoo, Y.; Swihart, M. T.; Prasad, P. N.; *Langmuir* **2005**, *21*, 1610. (c) Ji, T.; Lirtsman, V.; Avny, Y.; Davidov, D. *Adv. Mater.* **2001**, *13*, 1253. (d) Khan, M. A.; Perruchot, C.; Armes, S. P.; Randall, D. P. *J. Mater. Chem.* **2001**, *11*, 2363.

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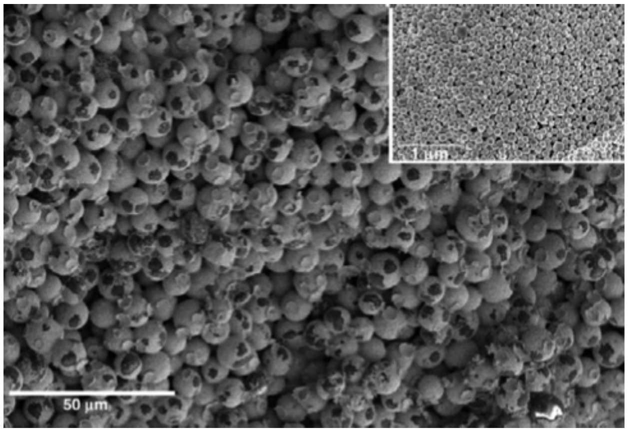

Figure 1. SEM micrograph of filter-cast gold-coated PS spheres (9.6 mm diameter) fracture surface. The darker interior is the PS core, which is exposed due to surface fracture, while the lighter exterior surface is the gold surface coating. Inset shows higher magnification of the gold surface.

mold and allowed to settle. The plaster of paris is a deposition surface for the particles and slowly removes water from the suspension to create a dry monolith. SEM images of cast PS/Au beads are shown in Figure 1. The relative polydispersity of the particles, high suspension concentration (≈ 10 wt %), and high rate of sedimentation result in randomly packed PS/Au spheres[12] with void spaces between individual particles. Unlike previous examples of gold deposition on silica and PS particles, the gold coating is not a conformal film but is comprised of discrete gold particles, 100−150 nm in size (see inset). The PVP stabilizer likely favors growth of individual gold particles while inhibiting gold film formation.[13]

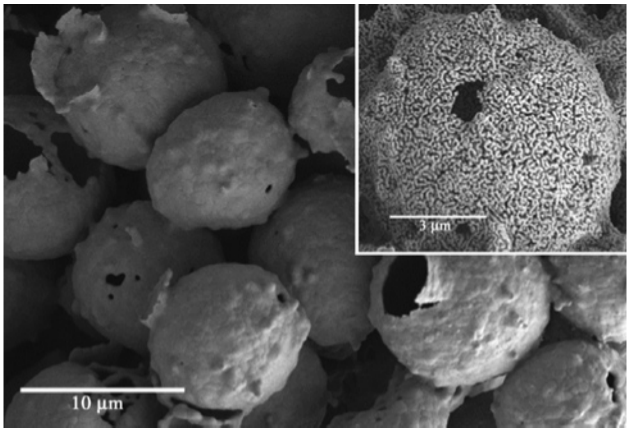

Figure 2. Fracture surface of a monolith containing hollow $Ag_{0.85}Au_{0.15}$ shells before dealloying. Inset showing surface of gold shell after dealloying.

Ag/Au PS core−shell particles were prepared by electroless deposition of silver on PS/Au spheres (Scheme 1). The sequence of metal deposition is important since depositing gold on silver may result in competing Ag^0/Au^{3+}galvanic and electroless deposition reduction reactions.[14] The Au:Ag ratio can be adjusted by varying the gold and silver mole ratios during plating conditions; however, in the present work, we have focused on preparing $Ag_{0.85}Au_{0.15}$ and $Ag_{0.7}Au_{0.3}$ alloys.[15] Casting the Ag/Au PS beads and heating the monolith in an inert atmosphere at 400 °C removes the PS template and alloys the Ag/Au layers. Ag/Au alloy times were estimated using Fick's second law of diffusion.[16] Preparation of Ag/Au alloys is facile due to matching crystalline structures, nearly identical lattice constants,[17a] and high diffusion rates of silver and gold atoms at elevated temperature.[17b]

Large cylindrical $Ag_{0.85}Au_{0.15}$ monoliths were readily synthesized with measured densities of 0.8 g/cm^3.[18] Little dimensional change in the monolith was observed after heat treatment, but 23% mass loss was observed. The monolith microstructure (shown in Figure 2) is composed of hollow homogeneous $Ag_{0.85}Au_{0.15}$ shells, roughly 10 mm in diameter, confirmed by energy-dispersive X-ray analysis (EDAX).[19] The diameter of the shells roughly corresponds to the size of the PS bead template, indicating negligable shrinkage upon template removal. Holes in the shell walls are presumably due to the release of organic volatiles during bakeout.

To begin the dealloying process, a monolith, comprised of the hollow $Ag_{0.85}Au_{0.15}$ shells, was placed in concentrated nitric acid, which resulted in a violent reaction and cracked the monolith. Introducing a dilute nitric acid solution that

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(8) To prepare the PS beads (10 or 1 μm) for gold deposition, PS beads were soaked in a gold sol to deposit gold nanoparticles (AuNP) on the PS surface to provide a surface for further gold deposition. The amount of deposited AuNP was modest and was estimated by measuring the gold sol Surface Plasmon Resonance (SPR) absorbance before and after PS bead treatment. Concentrations were measured by comparing the supernatant absorbance to a standard curve of AuNP of known concentrations For the 10 mm and 1 mm PS beads used in this study, we estimate that 1.2 mg of gold/g of styrene and 1.5 mg of gold/g of styrene were seeded on the PS beads, respectively.

(9) (a) Brown, K. R.; Walter, D. G.; Natan, M. J. *Chem. Mater.* **2000**, *12*, 306. (b) Brown, K. R.; Natan, M. J. *Langmuir* **1998**, *14*, 726.

(10) Callister, W. D. *Materials Science and Engineering: An Introduction*, 6th ed.; John Wiley & Sons, Inc.: New York, 2003.

(11) Hayes, J. R.; Nyce, G. W.; Kuntz, J. D.; Satcher, J. H.; Hamza, A. V. Manuscript in preparation.

(12) Sedimentation of monodispersed colloidal spheres has been used to make ordered 3D crystalline thin films, see: (a) Everett, D. H. *Basic Principles of Colloid Science*; Royal Society of Chemistry: London, 1988. (b) Sanders, J. V. *Nature* **1964**, *204*, 1151.

(13) Robust cylindrical gold monoliths (diameter = 4.5 mm, height = 2.6 mm) with a relative density of 9%, 1.7 g/cm^3, were prepared by h eating the PS-gold monolith to 400 °C under an inert atmosphere. Under these conditions, the PS template is removed, and AuNPs are sintered together to form a smooth hollow gold shell. The monolith structure was composed of hollow gold shells with void space between packed shells, as determined by SEM analysis. Although the PS templates were 9.6 mm in diameter, the resultant hollow gold shells were 5 μm in diameter and 200 nm thick, indicating significant shrinkage during bakeout. See Supporting Information.

(14) (a) Sun, Y.; Xia, Y. *J. Am. Chem. Soc.* **2004**, *126*, 389. (b) Sun, Y.; Mayers, B.; Xia, Y. *Nano Lett.* **2002**, *2*, 481.

(15) For literature on colloidal Au/Ag alloys, see: (a) Morris, R. H.; Collins, L. F. *J. Chem. Phys.* **1964**, *41*, 3357. (b) Link, S.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 3529. (c) Papavassiliou, G. C. *Prog. Solid State Chem.* **1980**, *12*, 185. (d) Henglein, F.; Henglein, A.; Mulvaney, P. Ber. *Bunsen-Ges. Phys. Chem.* **1994**, *98*, 180. (e) Shibata, T.; Bunker, B. A.; Zhang, Z.; Meisel, D.; Vardeman, C. F., II; Gezelter, J. D. *J. Am. Chem. Soc.* **2002**, *124*, 11989.

(16) Fick's second law can be used to estimate times required for complete alloying. Fick's second law for an interdiffusing interface with mutually soluble components is: $C(x,t) = 0.5 + 0.5erf(x/(2(Dt)^{1/2}))$. See Porter, D. A.; Easterling, K. E. *Phase Transformations in Metals and Alloys*, 2nd ed.; Chapman & Hall: London, 1992. The interdiffusion coefficient D used was 10^{-19} m^2/s.

(17) (a) Gold and silver are both face centered cubic with lattice contants of 4.0786 and 4.0862 Å, respectively. (b) Dick, K.; Dhanasekaran, T.; Zhang, Z.; Meisel, D. *J. Am. Chem. Soc.* **2002**, *124*, 2312.

(18) Typical cylinder dimensions are 0.45 cm in diameter by 0.8−1 cm in height. Calculated full density of 85:15 (atom %) silver:gold alloy is 11.8 g/cm^3.

(19) Monoliths comprised of hollow 1 μm Ag/Au (70:30 atom %) shells were also synthesized. Typical monolith dimensions are 0.35 cm in diameter by 1.07 cm in height. Density of these monoliths were estimated at 1 g/cm^3. See Supporting Information.

was slowly increased in concentration until concentrated nitric acid was the final etching solution was found to be more successful. After etching, monoliths were washed several times in distilled water to remove residual nitric acid and then placed in acetone. Once the water was completely exchanged with acetone, the monoliths were dried by supercritical CO_2 extraction ($T_c = 31.1$ °C, $P_c = 7.4$ MPa).[20] Cylindrical gold monoliths (diameter = 0.45 cm, height = 0.8−1 cm) were isolated with measured densities as low as 0.28 g/cm^3 or 1.5% relative density. SEM images of a dealloyed shell is shown in Figure 2 (see inset).

Dealloyed shell dimensions are roughly 9.6 mm in diameter and 200 nm thick, similar to non-dealloyed silver/gold shell dimensions, suggesting little volume change during the dealloying/drying steps. The dealloyed gold nanostructure on the shell surface is similar to previous reports with ligament spacings of 10−100 nm[5a] with no evidence of silver found in the EDAX spectrum. The gold foam surface area of 1.48 m^2/g, as determined by BET surface analysis, is comparable to previously reported values for dealloyed Au porous materials.[5a] Interestingly, the mole fraction of gold in the $Ag_{0.85}Au_{0.15}$ hollow shells is below the 3D site percolation threshold for bulk alloys and dealloying is not predicted to form a stable bicontinuous gold structure.[21] Many factors may account for the stable dealloyed $Ag_{0.85}$-$Au_{0.15}$ shells (e.g., alloy preparation, length scale, geometry, and etching conditions). Further investigations to understand this result are underway.

We have synthesized hierarchical porous gold monoliths by dealloying cast hollow Ag/Au shells. Large ultra-low-density gold monoliths were synthesized by slipcasting, templating, and dealloying techinques. We are currently investigating the generality of this approach to prepare other hierarchical metallic porous materials. Monolithic catalysts are of interest as alternatives to traditional powder/slurry systems due to catalyst reusability and minimization of environmental waste.[22] The catalytic oxidation activity as well as the mechanical strength properties of these materials are currently under investigation.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Lab under Contract W-7405-Eng-48. The authors thank Jim Ferreira for SEM analysis.

Supporting Information Available: Synthesis of metal-coated PS beads and casting process; additional SEM images of prepared foams with EDAX spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Monoliths dried from water or organic solvents at ambient temperature were more susceptible to cracking and densification.

(21) Vukmirovic, M. B.; Dimitrov, N.; Sieradski, K. *J. Electron. Chem. Soc.* **2002**, *149*, B428.

(22) (a) Boger, T.; Zieverink, M. M. P.; Kreutzer, M. T.; Kaptejn, F.; Moulijn, J. A.; Addiego, W. P. *Ind. Eng. Chem. Res.* **2004**, *43*, 2337. (b) Irandoust, S.; Andersson, B. *Catal. Rev.-Sci. Eng.* **1988**, *30*, 314. (c) Kapteijn, F.; Nijhuis, T. A.; Heiszwolf, J. J.; Moulijn, J. A. *Catal. Today* **2001**, *66*, 133. (d) Cybulski, A.; Moulijn, J. A. *Catal. Rev.-Sci. Eng.* **1994**, *36*, 179.