

Interfacial Synthesis of Dendritic Platinum Nanoshells Templated on Benzene Nanodroplets Stabilized in Water by a Photocatalytic Lipoporphyrin

Haorong Wang,^{†,‡} Yujiang Song,[†] Craig J. Medforth,[†] and John A. Shelnutt^{*,†,‡}

Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico 87106, and Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received March 22, 2006; E-mail: jasheln@unm.edu

Platinum has extraordinary chemical and physical properties, and Pt nanostructures have been used as sensors, molecular switches, magnetic materials, and nanoreactors.¹ Studies of platinum nanoparticles, nanorods, nanowires, nanotubes, nanodendrites, and shape-controlled nanoparticles have been reported.² Pt nanostructures with hollow interiors (nanoshells) are rare,³ even though they have advantages over nanoparticles for some applications. For example, metallic shell structures have reduced material costs, lower densities, and, in some cases, special optical properties. Metal nanoshells can also be used as highly active catalysts and as capsules for other functional nanomaterials.^{3b,4} Emulsion droplets have long been used as templates for synthesizing hollow nanostructures composed of glass, ceramics, or semiconductors,⁵ but we are not aware of the droplet-templated synthesis of hollow metal spheres. Herein, we describe the first synthesis of platinum nanoshells using stabilized nanodroplets as templates.

The synthesis of platinum nanoshells uses a tin–lipoporphyrin photocatalyst to initiate the reduction of platinum onto the surface of benzene nanodroplets in water. Tin–porphyrin photocatalysts have previously been used by our group to synthesize nanostructured platinum metal using micelles or liposomes as templates.^{2d} The structure of the lipoporphyrin, Sn(IV) tetrakis(*N*-octadecyl-4-pyridyl)porphyrin hexachloride (SnP18), used in the synthesis is given in Figure 1. The porphyrin ring acts as the hydrophilic headgroup due to the charged pyridinium groups surrounding the macrocycle, and it is expected to localize at the benzene–water interface while the alkyl tails reside within the benzene droplet (Figure 1a). These surfactant-like properties are found to be essential for the formation of the stable nanodroplets that serve as the nanoshell templates. Remarkably, the tin–lipoporphyrin stabilizes the benzene droplets even as the benzene concentration is lowered below the solubility limit in water. The net result is nanoscale benzene droplets with reproducible droplet number, size distribution, and thus total surface area.

In the presence of a sacrificial electron donor (ascorbic acid), SnP18 acts as a photocatalyst that is capable of reducing a Pt(II) complex to platinum metal (Figure 1a). When irradiated with visible light, Pt nanoparticles deposit evenly over the surface of the nanodroplets, as illustrated in a proposed mechanism shown in Figure 1, which is based on earlier studies of Pt growth on micelles and liposomes.^{2d} The Pt seeds subsequently grow autocatalytically (Figure 1b) and ultimately complete the coverage of the benzene nanodroplets to form the Pt nanoshells (Figure 1c). Because the total surface area is constant below the solubility limit, the thickness of the Pt deposited onto the droplets can be controlled by varying the amount of Pt complex.

The preparation of benzene nanodroplets containing the SnP18 photocatalyst is described below.⁶ For the Pt nanoshell forming

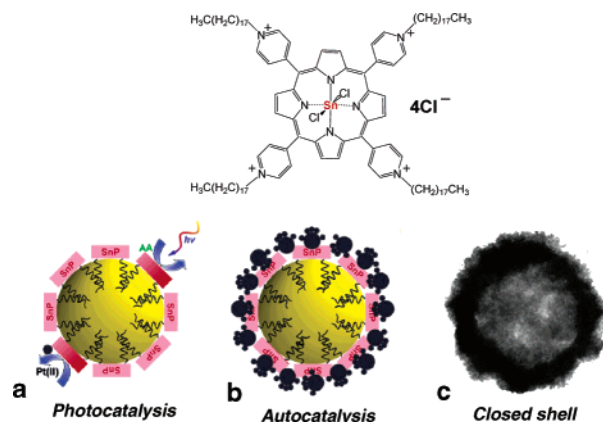


Figure 1. Structure of Sn(IV) tetrakis(*N*-octadecyl-4-pyridyl)porphyrin hexachloride (SnP18) and the proposed mechanism for formation of the Pt nanoshells: porphyrins localized at the benzene–water interface (a) photocatalytically grow platinum seeds and continue to grow autocatalytically (b) to form Pt dendrites that join to form a nanoshell (c).

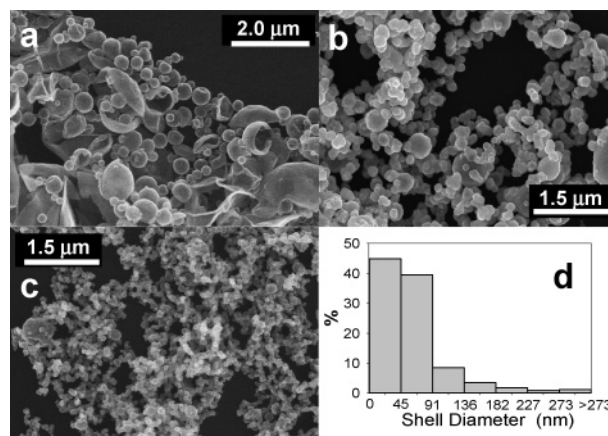


Figure 2. SEM images of Pt nanoshells synthesized under different conditions: (a) 0.5% benzene/SnP18 in water and 1 mM Pt complex, (b) 0.25% and 1 mM Pt complex, (c) 0.125% and 0.5 mM Pt complex. Size distribution of the Pt nanoshells (d) obtained from four independent preparations of (c) by measuring 300 shells in each TEM image.

reaction, 2 mL of the diluted emulsion is transferred to a 4 mL reaction vial, and aged K_2PtCl_4 solution^{2d} (20 mM) is added to give final Pt concentrations of 0.025–1.00 mM (depending upon the desired coverage). Freshly prepared ascorbic acid (AA) solution (150 mM) is then added to produce an AA:Pt ratio of 7.5:1, and the vial is sealed and irradiated with incandescent light ($800 \text{ nmol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) for 30 min during which time a black suspension gradually forms as the Pt(II) complex is reduced.

Figure 2a–c shows SEM images of Pt shells made using the SnP18-containing nanodroplets prepared with 0.5, 0.25, and 0.125% v/v benzene in water.⁷ With 0.5% v/v benzene in water as the

[†] Sandia National Laboratories.

[‡] University of Georgia.

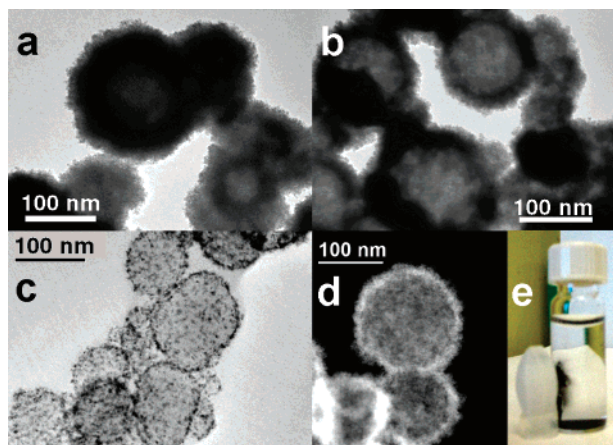


Figure 3. TEM images of Pt nanoshells prepared using SnP18 in 0.125% benzene in water and various concentrations of Pt complex: (a) 1 mM, (b) 0.5 mM (same as Figure 2c), (c) 0.25 mM. Panel (d) is an STEM dark field image of Pt nanoshells prepared using 0.25% benzene/SnP18 containing ~ 5 nm Fe_3O_4 nanoparticles. Panel (e) is a photograph showing a magnetic stirring bar attracting the nanoshells to the side of the reaction vessel.

template, the product consists of hollow Pt structures with a wide range of sizes with a significant quantity of micron-sized structures present (Figure 2a). At 0.25%, relatively few micron-scale structures are seen, mostly consisting of spherical Pt shells in the range of 100–400 nm (Figure 2b). Finally, at 0.125% (Figure 2c), the size of the Pt spheres is further reduced and most are less than 100 nm in diameter (Figure 2d). The reduction to a restricted size range upon dilution below the solubility of benzene in water (0.22%) indicates a limited loss of benzene from the droplets with SnP18 behaving as an unexpectedly good surfactant for stabilizing the nanodroplets. The size distribution of the nanodroplets is reproducible at concentrations below 0.22% (see Figure S2), giving a repeatable surface area. Consequently, the Pt concentration can be varied to produce the desired thickness of the Pt nanoshells.

TEM images (Figure 3b) show that the surfaces of the shells have a “furry” appearance consistent with dendritic Pt growth.^{2d} In addition, XRD spectra (Figure S3) show peaks characteristic of nanocrystalline platinum in agreement with the nanoscale structural features of Pt dendrites. Since the total surface area of the nanodroplets is nearly the same for similarly prepared 0.125% v/v benzene in water templates, the thickness of the shells can be modified by simply altering the concentration of the Pt complex. Figure 3 shows the effect of decreasing the Pt concentration; the average wall thickness decreases from approximately 40 nm at 1 mM Pt complex (Figure 3a) to 20 nm at 0.5 mM (Figure 3b); the shells are thin and porous at 0.25 mM Pt (Figure 3c) and consist of particles and small dendrites with sufficient connectivity to preserve the shell structure (see Figure S4).

In the absence of light exposure, the Pt structures obtained are irregular and the platinum coverage is uneven (Figure S5) since only a few seeds are spontaneously produced, as observed previously for templating surfactant assemblies.^{2d} The importance of photocatalytic seeding in producing the more evenly coated shell structures shown in Figures 2 and 3 is that a large population of seed particles is distributed uniformly over the surface of the droplets, and most of these seeds are formed at the beginning of the reaction giving them equal autocatalytic growth times. The equal growth times lead to more consistent dendrite size and more uniform wall thickness.^{2d}

The benzene droplets can also carry other nanomaterials that will be subsequently enclosed inside the Pt shells. For example, magnetic Pt nanoshells were synthesized using templating nanodroplets

containing suspended 5 nm diameter Fe_3O_4 particles (see details in the Supporting Information). Figure 3d shows an STEM image of the Fe_3O_4 -containing Pt nanoshells. The edge of the spheres appears brighter than their center region in these dark field images, consistent with an encasing electron-dense Pt shell. EDS analysis of the shell edge area (Figure S6) confirms that it is mainly Pt (Pt:Fe, 93:7), and EDS of the center area indicates that it is mainly Fe (Pt:Fe, 33:67). The magnetite-filled shells are clearly magnetic, as shown by their attraction to a magnetic stirring bar placed on the sidewall of the vial (Figure 3e).

In conclusion, we have developed a method for using lipophilic porphyrin-stabilized nanodroplets of an organic solvent in water as templates to synthesize dendritic Pt nanoshells. A key feature of the method is the use of a tin–porphyrin complex both as a surfactant that stabilizes the nanoscale benzene droplets and as a photocatalyst to initiate Pt reduction onto the surfaces of the nanodroplets. At benzene concentrations below its solubility limit in water, the thicknesses of the Pt nanoshells can be controlled continuously from ~ 5 to over 50 nm by varying the amount of the Pt complex. The organic phase can also be used as a medium for placing functional nanomaterials inside the nanoshells. The photocatalytic interfacial synthesis of nanoshells composed of other metals is currently being studied in our laboratory.

Acknowledgment. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DEAC04-94AL85000. Research partially supported by the DOE Division of Chemical Sciences, Geosciences and Biosciences (DE-FG02-02ER15369).

Supporting Information Available: Synthesis details, UV–visible spectra, XRD spectra, EDS and TEM data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Matkoc, I.; Gaidia, M.; Hazemann, J. L.; Cheneviera, B.; Labeau, M. *Sens. Actuators, B* **1999**, *59*, 210. (b) De, S.; Pal, A.; Pal, T. *Langmuir* **2000**, *16*, 6855. (c) Carpenter, E. E.; Sims, J. A.; Wienmann, J. A.; Zhou, W. L.; O’Connor, C. J. *J. Appl. Phys.* **2000**, *87*, 5615. (d) Joo, S. H.; Choi, S. J.; Oh, I.; Kwak, J.; Liu, Z.; Terasaki, O.; Ryoo, R. *Nature* **2001**, *412*, 169.
- (2) (a) Han, Y. J.; Kim, J. M.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2068. (b) Shin, H. J.; Ko, C. H.; Ryoo, R. *J. Mater. Chem.* **2001**, *11*, 260. (c) Luo, Y.; Lee, S. K.; Hofmeister, H.; Steinhart, M.; Gosele, U. *Nano Lett.* **2004**, *4*, 143. (d) Song, Y. J.; Yang, Y.; Medforth, C. J.; Pereira, E.; Singh, A. K.; Xu, H. F.; Jiang, Y. B.; Brinker, C. J.; van Swol, F.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 635. (e) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924. (f) Herricks, T.; Chen, J. Y.; Xia, Y. N. *Nano Lett.* **2004**, *4*, 2367.
- (3) (a) Sun, Y. G.; Mayers, B. T.; Xia, Y. N. *Nano Lett.* **2002**, *2*, 481. (b) Liang, H. P.; Zhang, H. M.; Hu, J. S.; Guo, Y. G.; Wan, L. J.; Bai, C. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1540.
- (4) (a) Kumar, R.; Maitra, A. N.; Patanjali, P. K.; Sharma, P. *Biomaterials* **2005**, *26*, 6743–6753. (b) Kim, S. W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642.
- (5) (a) Nakashima, T.; Kimizuka, N. *J. Am. Chem. Soc.* **2003**, *125*, 6386. (b) Fowler, C. E.; Khushalani, D.; Mann, S. *J. Mater. Chem.* **2001**, *11*, 1968. (c) Huang, J. X.; Xie, Y.; Li, B.; Liu, Y.; Qian, Y. T.; Zhang, S. Y. *Adv. Mater.* **2000**, *12*, 808.
- (6) A milky stock emulsion was prepared by sonicating a 1:99 mixture of benzene (containing 1 mM SnP18) and water. This was diluted with water for the nanoshell syntheses. UV–visible spectra (Figure S1) show that SnP18 is negligibly soluble in water or benzene, but the porphyrin Soret band of the diluted emulsion (0.25%) indicates that SnP18 is partially dissolved and probably resides at the benzene–water interface (Figure 1a).
- (7) Under imaging conditions, benzene probably evaporates from within the shells, while in aqueous suspension some benzene likely remains.

JA0619859