

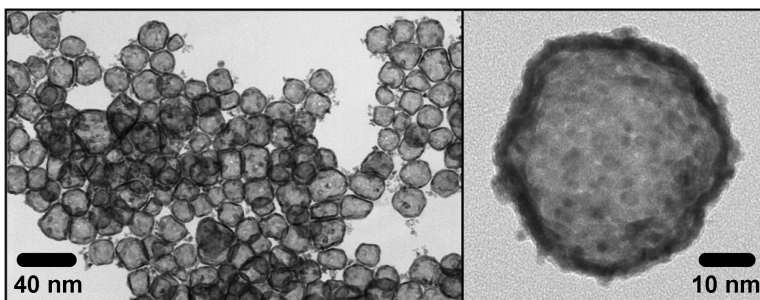
Communication

One-Pot Synthesis of Hollow Superparamagnetic CoPt Nanospheres

Yolanda Vasquez, Amandeep K. Sra, and Raymond E. Schaak

J. Am. Chem. Soc., **2005**, 127 (36), 12504-12505 • DOI: 10.1021/ja054442s • Publication Date (Web): 17 August 2005

Downloaded from <http://pubs.acs.org> on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 28 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

One-Pot Synthesis of Hollow Superparamagnetic CoPt Nanospheres

Yolanda Vasquez, Amandeep K. Sra, and Raymond E. Schaak*

Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012

Received July 5, 2005; E-mail: schaak@mail.chem.tamu.edu

Hollow nanospheres have emerged as intriguing materials for diverse applications that include drug delivery,¹ bioencapsulation,² medical diagnostics,³ catalysis,⁴ plasmonics,⁵ and composite electronic and structural materials.⁶ Hollow metal nanostructures are particularly interesting, as they can often impart multiple functionalities on a single particle. For example, hollow Au nanospheres have tunable plasmon resonances and well-established surface chemistry, making them appropriate for use in photothermal drug delivery⁷ and as contrast agents.³ Hollow metal nanospheres are often synthesized using sacrificial templates, such as polymer or SiO₂ spheres, which define the shape and size of nanoshells that are generally deposited using layer-by-layer⁸ or electroless deposition methods.⁹ Galvanic displacement reactions that exploit differences in the reduction potentials of two or more metals can also be used to prepare hollow metal nanostructures.^{10–13}

Despite recent advances in synthesizing metal nanostructures with controlled morphologies, there are very few reports of bimetallic hollow nanospheres.^{12,13b} Bimetallic systems often offer advantages over single-metal systems. For example, metal alloy nanoparticles can show enhanced catalytic activity and selectivity relative to their single-metal components,¹⁴ and both optical¹⁵ and magnetic¹⁶ properties can be fine-tuned by adjusting the metal ratios in alloy nanoparticles. The technologically relevant Co–Pt and Fe–Pt systems are important targets since hollow nanospheres of these alloy systems could find widespread use in magnetic, catalytic, and biomedical applications. Here, we report the first example of hollow magnetic CoPt nanospheres synthesized through a novel and potentially general one-pot reaction that exploits an in situ sacrificial template.

In a typical synthesis, CoCl₂·6H₂O (8.5 mg) and poly(vinyl pyrrolidone) (PVP, MW = 40 000, 100 mg) are dissolved in 50 mL of NANOpure H₂O (18.2 MΩ), sonicated for 15 min, and purged with Ar for 15 min. A freshly prepared solution of NaBH₄ (10 mg in 20 mL of H₂O) is then added dropwise with stirring. Immediately after all of the NaBH₄ has been added, K₂PtCl₆ (16.4 mg in 20 mL H₂O) is added dropwise with stirring. After 30 min, the product is collected by centrifugation, washed several times with H₂O and ethanol, and dried under ambient conditions.

Transmission electron microscope (TEM) images of the products are shown in Figure 1a. The reaction appears to form hollow spheres with average diameters of 10–50 nm in yields of 70–90% (see Figure S1). The individual nanosphere shown in Figure 1b is consistent with a hollow structure and shows that the shell is comprised of smaller nanoparticles. High-resolution TEM micrographs show randomly oriented nanocrystals in the shell, indicating that oriented attachment does not occur in this system. Elemental mapping data for a single sphere (Figure 1c) indicate that the hollow spheres contain both Co and Pt. Energy-dispersive X-ray spectroscopy (EDS) data for many spheres confirm an average stoichiometry of Co₅₈Pt₄₂ (Figure 2a), and selected area electron diffraction (SAED) patterns show a single-phase fcc structure (Figure 2a, inset). Powder X-ray diffraction (XRD) data are also consistent with a

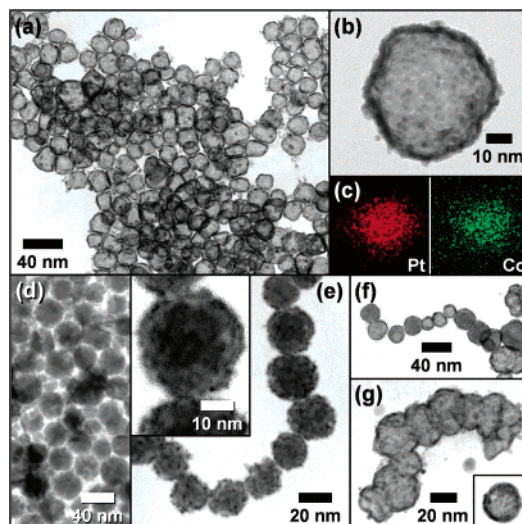


Figure 1. TEM micrographs of (a) CoPt hollow spheres and (b) a single hollow sphere showing that it is comprised of smaller particles; (c) elemental mapping data (Co and Pt) for the sphere in (b); TEM micrographs of (d) the Co nanoparticle template generated in situ and CoPt samples taken after reaction times of (e) 1 min and (f) 5 min. The hollow structures remain stable after heating to 300 °C on a TEM grid (g).

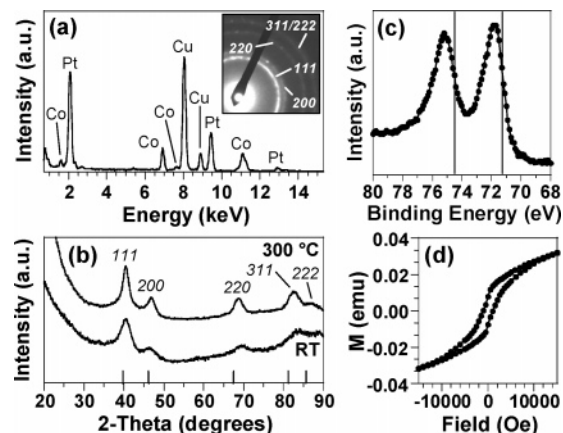


Figure 2. (a) EDS data and SAED pattern (inset) for CoPt hollow spheres (Cu is from the TEM grid); (b) XRD data for hollow CoPt nanospheres as synthesized at room temperature (RT) and after heating to 300 °C, showing shifting relative to the peak positions for Pt (tick marks); (c) XPS data for the Pt 4f peaks of CoPt hollow nanospheres (vertical lines show the 4f_{5/2} and 4f_{7/2} peak positions for Pt); (d) hysteresis loop at 5 K for hollow CoPt nanospheres.

single-phase fcc structure (Figure 2b). Importantly, the lattice constant for the fcc-type CoPt phase is $a = 3.88 \text{ \AA}$, which is measurably smaller than that of pure Pt ($a_{\text{Pt}} = 3.92 \text{ \AA}$). Taken together, the TEM, EDS, SAED, and XRD data are all consistent with the formation of hollow nanospheres with a CoPt alloy structure. This is further confirmed by XPS measurements (Figure 2c), which show that the Pt 4f_{7/2} peak is at 71.8 eV, compared to

71.2 eV that is expected for pure Pt. (The Pt 4f peaks are known to shift to higher energies upon alloy formation with Co.¹⁷) The broad peaks in the XRD pattern in Figure 2b are also consistent with the nanocrystalline nature of the shell, yielding an average particle size of 5 nm based on analysis using the Scherrer equation.

The TEM images in Figure 1d–f provide insight into the formation mechanism of the hollow CoPt nanospheres. Figure 1d shows a TEM micrograph of Co nanospheres that were isolated after NaBH₄ was added to the solution of Co²⁺ and PVP (before Pt⁴⁺ was added), suggesting that these dense spheres provide an in situ template for the formation of the hollow CoPt spheres. The TEM micrographs in Figure 1e,f correspond to samples reacted for 1 and 5 min, respectively. The spheres in Figure 1e are mostly dense, but a hollow region between the shell and the core is evident (Figure 1e, inset). This is consistent with a replacement reaction, where the Co core is sacrificially dissolved as the Pt shell is deposited. The standard reduction potentials for the Co²⁺/Co [$E^\circ = -0.277$ eV vs standard hydrogen electrode (SHE)] and PtCl₆²⁻/Pt [$E^\circ = 0.735$ eV vs SHE] redox pairs support this hypothesis. Very few nanospheres that simultaneously show well-defined core, hollow, and shell regions (Figure 1e) were observed. In most cases, the nanospheres were either dense or hollow (Figure 1f), suggesting that once an individual Co sphere begins to react with Pt⁴⁺, the reaction goes to completion very quickly. Once the hollow spheres form, they are thermally stable up to 300 °C when immobilized on a TEM grid (Figure 1g) and maintain the CoPt alloy structure (Figure 2b).

While there are several reports of hollow sphere formation via galvanic displacement reactions,^{10–13} there are no examples where Co-based alloys form as the final products when Co nanoparticles are used as templates.¹³ We believe that the formation of hollow CoPt alloy nanospheres, which is a significant result, is directly related to the synthetic details involved in the one-pot reaction. There is excess BH₄⁻ in the reaction flask, so any Co that is oxidized to Co²⁺ during Pt deposition will be reduced back to Co. At the same time, PVP is present as the surface stabilizer, and its long polymeric chain structure will completely surround one or more nanospheres. Since PVP is known to bind metal cations,¹⁸ it can trap the Co²⁺ that is liberated during the galvanic displacement reaction and allow it to combine with Pt⁴⁺ and co-reduce near the surface of the template nanosphere. The result is a shell that contains both Co and Pt in the form of an alloy. Previous reports of Pt, Au, and Au–Pt hollow nanospheres formed via Co nanoparticle templates use *molecular* stabilizers, such as citric acid, and always yield hollow spheres containing no Co.¹³

Measurements of magnetization versus applied field, obtained using a SQUID magnetometer, showed hysteresis at 5 K (Figure 2d) with a coercivity of 980 Oe, indicating ferromagnetism. The significant paramagnetic background and lack of saturation is likely a result of impurity phases, such as cobalt oxides, or the dispersity in size and particle–particle separation of the constituent nanoparticles. Higher-temperature magnetic measurements indicate superparamagnetism, which is consistent with the small size of the individual nanoparticles that comprise the hollow nanostructures. Detailed magnetic measurements and mechanistic studies are in progress and will be addressed in future work.

The successful synthesis of hollow nanospheres of a CoPt alloy phase has several important implications. First, alloy systems have received much less synthetic development than single-metal systems. This work describes a straightforward way to control the synthetic details to yield hollow alloy nanostructures and, as such,

adds to an important and growing toolbox of reactions that yield morphologically controlled CoPt and FePt nanomaterials.^{16,19} Further synthetic development may even provide access to intermetallic hollow spheres, which should have superior magnetic properties.¹⁶ Second, hollow magnetic nanospheres of CoPt have important potential applications in drug delivery, catalysis, and composites. In particular, there is interest in synthesizing high surface area alloy catalysts, and these nanomaterials may be targets for such studies. Finally, since the synthetic strategy exploits polymer stabilizers and redox couples, we expect it to be applicable to other bimetallic systems, and preliminary evidence with the Ni–Pt system suggests that it is.

Acknowledgment. This work was supported by startup funds from Texas A&M University and funding from the Robert A. Welch Foundation (Grant No. A-1583). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The SQUID magnetometer was obtained with funds provided by an equipment grant from the NSF. Electron microscopy was performed at the Microscopy and Imaging Center at Texas A&M University, and XPS data were acquired at the TAMU/CIMS Materials Characterization Facility.

Supporting Information Available: Experimental details and large-area TEM image of hollow spheres. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Mathiowitz, E.; Jacob, J. S.; Jon, Y. S.; Carino, G. P.; Chickering, D. E.; Chaturvedi, P.; Santos, C. A.; Vijayaraghavan, K.; Montgomery, S.; Bassett, M.; Morrell, C. *Nature* **1997**, *386*, 410–414. (b) Bergbreiter, D. E. *Angew. Chem., Int. Ed.* **1999**, *38*, 2870.
- (2) (a) Marinakos, S. M.; Novak, J. P.; Brousseau, L. C., III; House, A. B.; Edeki, E. M.; Feldhaus, J. C.; Feldheim, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 8518–8522. (b) Marinakos, S. M.; Anderson, M. F.; Ryan, J. A.; Martin, L. D.; Feldheim, D. L. *J. Phys. Chem. B* **2001**, *105*, 8872–8876.
- (3) Tartaj, P.; Morales, M. P.; Veintemillas-Verdaguer, S.; González-Carreño, T.; Serna, C. J. *J. Phys. D* **2003**, *36*, R182–R197.
- (4) Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642–7643.
- (5) Oldenburg, S. J.; Averitt, R. D.; Westcott, S. L.; Halas, N. J. *Chem. Phys. Lett.* **1998**, *288*, 243–247.
- (6) Cochran, J. K. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 474–479.
- (7) (a) Sershen, S. R.; Westcott, S. L.; Halas, N. J.; West, J. L. *J. Biomed. Mater. Res.* **2000**, *51*, 293–298. (b) Hirsch, L. R.; Stafford, R. J.; Bankson, J. A.; Sershen, S. R.; Rivera, B.; Price, R. E.; Hazle, J. D.; Halas, N. J.; West, J. L. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 13549–13554.
- (8) Caruso, F. *Top. Curr. Chem.* **2003**, *227*, 145–168.
- (9) Liu, J. B.; Dong, W.; Zhan, P.; Wang, S. Z.; Zhang, J. H.; Wang, Z. L. *Langmuir* **2005**, *21*, 1683–1686.
- (10) (a) Sun, Y. G.; Xia, Y. N. *Science* **2002**, *298*, 2176–2179. (b) Sun, Y.; Mayers, B. T.; Xia, Y. *Nano Lett.* **2002**, *2*, 481–485. (c) Sun, Y.; Mayers, B.; Xia, Y. *Adv. Mater.* **2003**, *15*, 641–646.
- (11) Selvakannan, P. R.; Sastry, M. *Chem. Commun.* **2005**, 1684–1686.
- (12) (a) Metraux, G. S.; Cao, Y. C.; Jin, R.; Mirkin, C. A. *Nano Lett.* **2003**, *3*, 519–522. (b) Sun, Y.; Wiley, B.; Li, Z.-Y.; Xia, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9399–9406.
- (13) (a) Liang, H.-P.; Zhang, H.-M.; Hu, J.-S.; Guo, Y.-G.; Wan, L.-J.; Bai, C.-L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1540–1543. (b) Liang, H.-P.; Guo, Y.-G.; Zhang, H.-M.; Hu, J.-S.; Wan, L.-J.; Bai, C.-L. *Chem. Commun.* **2004**, 1496–1497. (c) Liang, H.-P.; Wan, L.-J.; Bai, C.-L.; Jiang, L. *J. Phys. Chem. B* **2005**, *109*, 7795–7800.
- (14) (a) Scott, R. W. J.; Wilson, O. M.; Oh, S.-K.; Kenik, E. A.; Crooks, R. M. *J. Am. Chem. Soc.* **2004**, *126*, 15583–15591. (b) Lang, H.; Maldonado, S.; Stevenson, K. J.; Chandler, B. D. *J. Am. Chem. Soc.* **2004**, *126*, 12949–12956.
- (15) Mulvaney, P. *Langmuir* **1996**, *12*, 788–800.
- (16) Sun, S. H.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989–1992.
- (17) Lee, Y.-S.; Lim, K.-Y.; Chung, Y.-D.; Whang, C.-N.; Jeon, Y. *Surf. Interface Anal.* **1999**, *30*, 475–478.
- (18) (a) Pastoriza-Santos, I.; Liz-Marzan, L. M. *Langmuir* **2002**, *18*, 2888–2894. (b) Shin, H. S.; Yang, H. J.; Kim, S. B.; Lee, M. S. *J. Colloid Interface Sci.* **2004**, *274*, 89–94.
- (19) Wang, Y.; Yang, H. *J. Am. Chem. Soc.* **2005**, *127*, 5316–5317.

JA054442S