Autoprogrammed Synthesis of Triple-Layered Au@Pd@Pt Core−Shell Nanoparticles Consisting of a Au@Pd Bimetallic Core and Nanoporous Pt Shell

Liang Wang[†] and Yusuke Yamauchi*,[†],[‡]

World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan, and PRESTO, Japan Science and Technology Agency (JST), 5 Sanban-cho, Chiyoda, Tokyo, 102-0075, Japan

Received June 28, 2010; E-mail: Yamauchi.Yusuke@nims.go.jp

Abstract: Here we report an autoprogrammed synthesis of unique Au@Pd@Pt triple-layered core−shell structured nanoparticles consisting of a Au core, Pd inner layer, and nanoporous Pt outer shell. The proposed synthesis rationally utilizes the temporal separations of the depositions of Au, Pd, and Pt which affords spontaneously step-by-step formation of triple-layered core−shell colloids. The proposed one-step method is unique in its simplicity and is a significant finding for the facile creation of multilayered nanoarchitectures with designed compositions and desired functions.

Recently, core−shell colloidal nanoparticles have attracted considerable interest because of the fact that their nanoarchitectures, compositions, and particle sizes can be easily adjusted in a controllable way to tune their magnetic, optical, electrical, and catalytic properties.[1,2] Currently, all-metal core−shell colloids with controlled shapes have become increasingly important, providing attractive perspectives for effectively tuning the functionalities of metallic nanocrystals. The cases of Au-, Pd-, and Pt-based core−shell colloids are particularly interesting due to their excellent optical and catalytic activities. For instance, Au@Pd,[3] Au@Pt,[4] Pt@Pd,[5] and Pd@Pt[6] core−shell structured nanoparticles have attracted considerable attention and show superior catalytic properties which are not attainable by their monometallic counterparts. Compared with Pt alone, Au@Pt and Pd@Pt core−shell structured nanoparticles show enhanced CO tolerance for hydrogen activation[7] and higher activity for oxygen reduction reaction,[6] respectively. It is noted that in previous studies on core−shell structured metallic nanoparticles the focus has been on bimetallic nanoparticles. Furthermore, the demonstrated core−shell bimetallic nanoparticles are usually prepared by a two-step seed-mediated growth method.[3−8] Therefore, one-step synthesis of multilayered core−shell structured nanoparticles with designed multiple compositions is a grand challenge for the development of multifunctional smart materials. For instance, multilayered core−shell structured nanoarchitectures consisting of Au, Pd, and Pt are expected to be promising materials in catalysis, hydrogen storage, and surface enhanced Raman scattering (SERS) studies.

Another problem in almost all core−shell colloids reported previously is that the shell regions have no nanoporosity. Therefore, it is difficult for guest species to access the inner cores in various applications, which seriously devalues the advantages of the core−shell structures. In order to overcome this barrier, it should
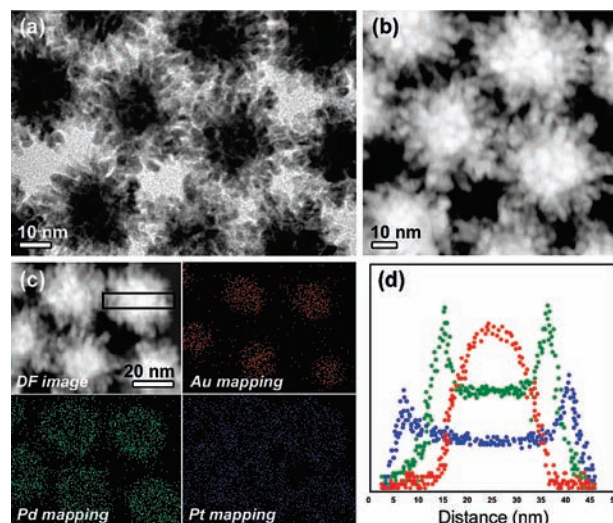

Figure 1. (a) TEM image. (b) HAADF-STEM image. (c) HAADF-STEM-EDS mapping images of the Au@Pd@Pt nanoparticles. (d) Cross-sectional compositional line profiles of the square area in Figure c.

be a more challenging target to create desired nanoarchitectures in the shell regions for creation of core−shell colloids with integrated functionalities derived from both the core and the shell. Although uniform coating of nanoporous shells onto the metal-based cores has been sparsely reported, the shell compositions are very limited to silica and carbon.[9−11]

In this communication, we demonstrate a one-step and effective route to synthesis of "all-metal" Au@Pd@Pt triple-layered core−shell colloids, which consist of a Au core, Pd inner layer, and nanoporous Pt outer shell, in aqueous solution at room temperature within 1 h. As-prepared triple-layered nanoarchitectures with designed compositions are expected with desired functions, e.g., a superior catalytic property. The proposed autoprogrammed synthesis is performed by spontaneous step-by-step depositions of metal precursors without the need for any additional and complex treatments, which is quite different from the previous studies using a two-step seed-mediated growth method to synthesize core−shell structured metallic nanoparticles in which the particle size and shape are uncontrollable without ready-made uniform seeds.[3−8] The proposed concept, i.e., "autoprogrammed synthesis", is scientifically and technologically important for the creation of novel multilayered nanoarchitectures with designed compositions and desired functions.

Figure 1a showed a transmission electron microscopy (TEM) image of the typically synthesized product prepared from a 0.08 mmol Pt precursor amount. As displayed in Figure 1a, as-prepared product was well-defined dendritic nanoparticles and strikingly
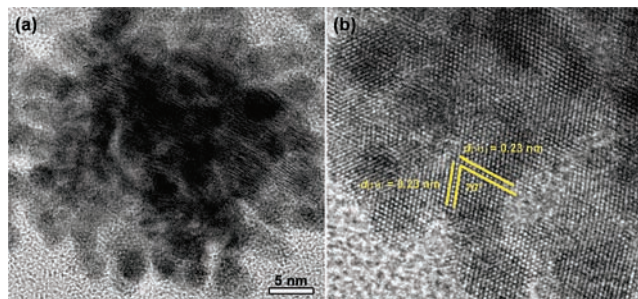
Figure 2. (a) Highly magnified TEM image of one nanoparticle. (b) HRTEM image revealing the lattice fringes in the nanoarms.

uniform in shape. The particle sizes were roughly distributed from 20 to 55 nm with an average diameter of 35 nm (Figure S1). The image obtained by high-angle annular dark-field scanning TEM (HAADF-STEM) (Figure 1b) further clearly revealed the dendritic nature of the nanostructures. The X-ray diffraction (XRD) pattern (Figure S2) recorded on the nanostructures showed the face-centered cubic (*fcc*) structure nature of the nanoparticles. An elemental mapping investigation (Figure 1c) revealed the nanoparticles were triple-layered nanostructures consisting of a Au core, Pd inner layer, and nanodendritic Pt outer shell. The compositional line profiles (Figure 1d) further confirmed the presence of three layers with Au, Pd, and Pt, respectively, in a nanoparticle, and revealed the Au/Pd/Pt atomic ratio to be 1/1/1.6, which well agreed with the atomic ratios (5/5/8) in the initial solution. It implied that all of the metal precursors were reduced by ascorbic acid (AA). A high-resolution transmission electron microscopy (HRTEM) image of the Pt outer shell in one nanoparticle indicated the lattice fringes were coherently extended across several dendritic arms (Figure 2a). The observed *d*-spacing (0.23 nm) for the adjacent fringes in the Pt outer shell region corresponded to the (111) planes of the Pt *fcc* structure (Figure 2b).

The nanodendritic Pt arms with an average diameter of 3 nm well covered the surface of the Au@Pd binary cores. The Pt nanoarms were highly branched in various directions, resulting in the formation of nanoporous shell regions of an individual entity (Figure 2). The rich edges and corner atoms derived from the dendritic Pt nanoporous architectures were highly valuable for enhancement of the Pt catalytic performance.[12] Analysis of the N_2 adsorption−desorption isotherm gave a surface area of 31 m^2 g^{-1} (Figure S3). It was believed that such a high surface area was originated from the interspaces among the Pt nanodendritic arms of each individual entity. The nanodendritic Pt shell not only could provide high surface area, rich absorption sites, and favorable surface permeability but also should be important for guest species to access the inner binary core.

Interestingly, by changing the amount of the Pt precursor in the initial solution, the configuration of the Pt outer shells could be effectively tuned. With the decrease of the Pt precursor amount to 0.02 mmol, the nanodendritic Pt configuration was dramatically changed to a near smooth morphology (Figure S4a−b) and the triple-layered structure was still well reserved (Figure S5). When the amount of the Pt precursor was >0.05 mmol, an obvious nanodendritic Pt shell was observed (Figure S4c). A further increase of the Pt precursor amount from 0.08 mmol (Figure 1) to 0.10 mmol (Figure S4d) resulted in exuberant Pt nanoarms spreading in various directions from the surface of the Au@Pd binary core. Thus, the thickness of the Pt shell was controllable by simply changing the Pt precursor amount, which was very important for tuning the catalytic property.

The shapes of the monometallic Pd, Au, and Pt nanoparticles prepared under the identical synthetic procedure were near spherical, roughly spherical, and dendritic, respectively (Figure S6), indicating that Pluronic F127 was only favorable for Pt dendritic growth. The reduction of binary Au−Pd and Au−Pt precursors led to formation of Au@Pd core−shell particles with a smooth Pd shell (Figures S6 and S7) and Au@Pt core−shell particles with a nanodendritic Pt shell (Figures S6 and S8), respectively. The presence of a Pd shell remarkably decreased the Au core size by suppressing the growth of Au nanoparticles (Figure S6), which played a critical role in the overgrowth process to form the Au@Pd@Pt triple-layered core−shell structured nanoparticles with a uniform and smaller particle size (described in Figure S6).

To elucidate the formation process of the Au@Pd@Pt triple layered core−shell structured nanoparticles, three intermediate products sampled at different formation stages have been followed by TEM (Figure S9). Au@Pd core−shell structured nanoparticles were initially formed, and the Pd shell grew in thickness followed by Pt becoming deposited onto the surface of the Au@Pd binary core. With continuous Pt reduction by AA, Pt atomic addition continuously occurred, resulting in the continuous growth of the intermediate Pt outer shell, and then more and more Pt nanoarms began to grow from the Au@Pd binary core surface, until the complete consumption of Pt precursor in the reaction solution (Figure 1). Based on the formation process investigations, it was revealed that the formation of the Au@Pd@Pt triple-layered core−shell structured nanoparticles was initiated by the initial formation of near spherical Au nanoparticles, serving as the *in situ* seeds for the subsequent depositions of the Pd inner layer and Pt outer shell, in tandem. During the later Pt deposition, Pluronic F127 served as a structure-directing agent to direct the nanodendritic Pt outer shell growth.[13] The Pluronic F127 chains adsorbed on the Pt surface during the Pt deposition with its hydrophobic poly(propylene oxide) (PPO) group and formed cavities which facilitated the formation of the dendritic Pt outer shell.[13] The temporal separation of the formations of the Au core and Pd inner layer from the formation of the Pt outer shell owing to the different reduction kinetics was critical to the formation of the demonstrated triple-layered core−shell structured colloids. The developed one-step autoprogrammed strategy has a remarkably advantage over the traditional two-step seed-mediated approach in its simplicity for synthesis of core−shell structured metallic nanoparticles. As-prepared Au@Pd@Pt triple-layered nanoparticles (as displayed in Figure 1) showed higher catalytic performance than that of Au@Pt core−shell structured nanoparticles (as shown in Figure S8) for the methanol oxidation reaction (Figure S10).

In summary, by rational design, reported herein, the newly discovered Au@Pd@Pt triple-layered core−shell structured nanoparticles were created by a simple, rapid, one-step synthesis. The proposed autoprogrammed synthesis rationally utilizes the temporal separations of the depositions of Au, Pd, and Pt which affords spontaneously step-by-step formation of triple-layered core−shell colloids. The proposed one-step method is unique in its simplicity and is a significant finding for the facile creation of multilayered nanoarchitectures with designed compositions and desired functions.

Supporting Information Available: Experimental details and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Zhang, F.; Braun, G. B.; Shi, Y. F.; Zhang, Y. C.; Sun, X. H.; Reich, N. O.; Zhao, D. Y.; Stucky, G. *J. Am. Chem. Soc.* **2010**, *132*, 2850.

(2) (a) Ow, H.; Larson, D. R.; Srivastava, M.; Baird, B. A.; Webb, W. W.; Wiesner, U. *Nano Lett.* **2005**, *5*, 113. (b) Burns, A.; Ow, H.; Wiesner, U. *Chem. Soc. Rev.* **2006**, *35*, 1028.

(3) Lee, Y. W.; Kim, M.; Kim, Z. H.; Han, S. W. *J. Am. Chem. Soc.* **2009**, *131*, 17036.

(4) Fan, F. R.; Liu, D. Y.; Wu, Y. F.; Duan, S.; Xie, Z. X.; Jiang, Z. Y.; Tian, Z. Q. *J. Am. Chem. Soc.* **2008**, *130*, 6949.

(5) Habas, S. E.; Lee, H.; Radmilovic, V.; Somorjai, G. A.; Yang, P. D. *Nat. Mater.* **2007**, *6*, 692.

(6) Lim, B.; Jiang, M. J.; Camargo, P. H. C.; Cho, E. C.; Tao, J.; Lu, X. M.; Zhu, Y. M.; Xia, Y. N. *Science* **2009**, *324*, 1302.

(7) Zhou, S. H.; McIlwrath, K.; Jackson, G.; Eichhorn, B. *J. Am. Chem. Soc.* **2006**, *128*, 1780.

(8) Lim, B.; Wang, J. G.; Camargo, P. H. C.; Jiang, M. J.; Kim, M. J.; Xia, Y. N. *Nano Lett.* **2008**, *8*, 2535.

(9) Joo, S. H.; Park, J. Y.; Tsung, C. K.; Yamada, Y.; Yang, P. D.; Somorjai, G. A. *Nat. Mater.* **2009**, *8*, 126.

(10) (a) Deng, Y. H.; Cai, Y. E.; Sun, Z. K.; Liu, J.; Liu, C.; Wei, J.; Li, W.; Liu, C.; Wang, Y.; Zhao, D. Y. *J. Am. Chem. Soc.* **2010**, *132*, 8466. (b) Deng, Y. H.; Qi, D. W.; Deng, C. H.; Zhang, X. M.; Zhao, D. Y. *J. Am. Chem. Soc.* **2008**, *130*, 28.

(11) (a) Feyen, M.; Weidenthaler, C.; Schüth, F.; Lu, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 6791. (b) Ikeda, S.; Ishino, S.; Harada, T.; Okamoto, N.; Sakata, T.; Mori, H.; Kuwabata, S.; Torimoto, T.; Matsumura, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7063.

(12) (a) Mahmoud, M. A.; Tabor, C. E.; El-Sayed, M. A.; Ding, Y.; Wang, Z. L. *J. Am. Chem. Soc.* **2008**, *130*, 4590. (b) Lim, B.; Lu, X. M.; Jiang, M. J.; Camargo, P. H. C.; Cho, E. C.; Lee, E. P.; Xia, Y. N. *Nano Lett.* **2008**, *8*, 4043.

(13) Wang, L.; Yamauchi, Y. *J. Am. Chem. Soc.* **2009**, *131*, 9152.

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