Overgrowth Versus Galvanic Replacement: Mechanistic Roles of Pd Seeds during the Deposition of Pd–Pt

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Supporting Information

ABSTRACT: Here, a systematic study of the roles played by Pd seeds during seed-mediated coreduction of Pd–Pt is presented. Either nanoparticles with porous, hollow architectures or concave nanocubes were achieved, depending on whether the synthesis conditions favored galvanic replacement or overgrowth. Prior works have shown that the galvanic replacement reaction between seeds and a precursor can be suppressed by introducing a faster, parallel reaction that removes one of the reagents (e.g., adatom generation in solution rather than surface-catalyzed precursor reduction). Here, we show that the galvanic replacement reaction depends on the size and concentration of the Pd seeds; the former of which can be manipulated during the course of the reaction through the use of a secondary reducing agent. This insight will guide future syntheses of multimetallic nanostructures by seeded methods, allowing for a range of nanocrystals to be precisely engineered for a variety of applications.

INTRODUCTION

Many efforts have been directed toward the shape-controlled synthesis of metal nanoparticles using preformed metal seeds and/or chemical structure directing agents and surfactants.1−4 However, seed-mediated methods have attracted a great deal of attention because of their ability to precisely engineer the nanocrystal shape and achieve nanocrystals with defined shapes, complex compositions, and even hierarchical structures.5−14 Metal nanostructures prepared by seeded methods have potential applications in catalysis, plasmonics, nanomedicine, and more.15−19 Owing to the dependency of properties on composition and structural parameters, gaining insights into nanomaterial formation and developing new synthetic strategies to well-defined nanomaterials are paramount.15,20,21 Recently, seed-mediated coreduction has emerged as a premier route to multimetallic nanostructures, where multiple metal precursors are simultaneously reduced to deposit alloyed shells on shape-controlled metal seeds where the symmetry of the seeds is transferred to the multimetallic structure.4,22,23 In most demonstrations, the seeds used in this method do not have a sufficiently low reduction potential relative to the selected precursors for galvanic replacement (i.e., where the seeds themselves serve as the reducing agent, facilitating metal precursor reduction and deposition) to occur.24 Thus, a molecular reducing agent (e.g., l-ascorbic acid, l-aa) is employed to facilitate seed-mediated coreduction. Recently, Qin and co-workers reported codeposition of Pd–Ag and Ag–Au shells on Ag nanocube seeds, where the standard reduction potentials of the Pd and Au precursors relative to Ag were sufficient to facilitate galvanic replacement along with codeposition.25−27 This method produced Ag-enriched bimetallic surfaces through the titration of l-aa to reduce the Ag salt released by galvanic replacement of the nanocube templates. Interestingly, the hollowing of the Ag templates that characterizes galvanic replacement processes can be suppressed completely by tuning the pH of the l-aa solution. These nanostructures provide unique platforms for surface-enhanced Raman spectroscopy, where the Ag provides high sensitivity and the other metals can serve as catalysts.

Here, a systematic study of the roles played by Pd seeds during seed-mediated coreduction of Pd and Pt precursors is presented. Pd–Pt nanostructures have shown high catalytic activity specially for fuel cell reactions such as oxygen reduction reaction, methanol oxidation reaction, and formic acid oxidation reaction.28,29 Insights into the synthesis of such materials with structural precision is paramount to the design of new catalysts. This synthetic system is similar to those studied by Qin and co-workers in that the standard reduction potentials ([PtBr4]2−/([PtBr4]3−: 0.613 V vs standard hydrogen electrode (SHE), [PtBr4]2−/Pt: 0.698 V vs SHE, and [PdBr4]2−/Pd: 0.49 V vs SHE) should facilitate galvanic replacement of the Pd seeds by the Pt precursor.27 Likewise, l-aa was added to the system to facilitate reduction of the Pd precursor and any salt released from the template seeds. In this way, a bimetallic surface should be deposited on the seeds. Xia and co-workers have examined the galvanic replacement between H2PtCl6 and Pd nanocrystals, and the addition of citric acid as a secondary reducing agent was found to facilitate the coreduction of PdCl2 derived from the galvanic replacement in addition to the original PtCl4 present in the system. Pd–Pt alloy

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nanocages were produced in this example. They also demonstrated how bromide can direct a galvanic replacement reaction and could be used for the synthesis of concave Pd–Pt nanocrystals using Pd nanocubes as seeds. Specifically, galvanic replacement was initiated and facilitated by the preferential adsorption of Br\(^-\) ions on \{100\} crystallographic facets of Pd seeds. Simultaneous dissolution of Pd atoms from \{100\} facets and deposition of Pt atoms on \{111\} facets led to the formation of concave Pd@Pt nanocrystals. Here, we show that whether or not the galvanic replacement reaction proceeds depends on the size and concentration of the Pd seeds; the former of which can be manipulated during the course of the reaction through the use of the secondary reducing agent, L-\(\alpha\)-aa.

**RESULTS AND DISCUSSION**

Pd nanocubes with an average edge length of 18 ± 2 nm (unless otherwise noted) were prepared by standard methods. These nanocrystals then served as seeds during the coreduction of H\(_2\)PtCl\(_6\) and H\(_2\)PdCl\(_4\) (1-to-1 mole ratio unless noted) with L-\(\alpha\)-aa in an aqueous solution of cetyltrimethylammonium bromide (CTAB) as a capping agent. The synthesis was conducted at 55 °C. When only H\(_2\)PdCl\(_4\) is available for reduction, conformal Pd deposition occurs on the Pd nanocubes, as evident by the increase in Pd particle size from 18 ± 2 to 32 ± 2.1 nm (Figure S1a). When only H\(_2\)PtCl\(_6\) is available for reduction, porous Pd–Pt structures are produced, where the porosity indicates that precursor reduction is facilitated by galvanic replacement (Figure S1b). In contrast, Figure 1a shows a transmission electron microscopy (TEM) image of partially hollow nanoparticles with cubic profiles that are obtained from when H\(_2\)PtCl\(_6\) and H\(_2\)PdCl\(_4\) are coreduced in the presence of Pd nanocubes. The contrast between the lighter centers and darker peripheries is consistent with hollow structures. As shown by elemental mapping from scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDS), Pd is concentrated at the interior walls of the hollow cubes and Pt is concentrated at the outer edges of the cubes (Figure 1b). Porous, hollow core@shell Pd@Pt nanostructures are produced.

The hollow architecture indicates that galvanic replacement is occurring even with L-\(\alpha\)-aa present. We note that nearly collapsed structures are obtained without L-\(\alpha\)-aa, highlighting its role in depositing Pd to preserve the cubic shape of the seed template (Figure S2). This dependency of the final structure on the reducing capacity of the reductant was also observed in galvanic replacement between Au salts and Ag templates. Figure S3 shows TEM images of the progression from solid Pd nanocubes to the hollow, porous Pd@Pt nanostructures synthesized through codeposition. As shown in Figure S3c, the dissolution of Pd seeds is initiated at the sides of the nanocubes as Pt ions are reduced and deposited on nanocubes. Further Pd dissolution and Pt deposition leads to the formation of hollow, porous Pd@Pt structures after 18 h.

Interestingly, when the concentration of Pd seeds was decreased by 100 times (10 \(\mu\)L of seed solution compared to 1 mL), neither etching of the Pd nanocubes by Pt ions nor Pt deposition on the Pd nanocubes were observed. Figure 2 shows the TEM image of the product. Nanocubes with an average edge length of 33 ± 1.9 nm were produced. The STEM image (Figure 2c) suggests slightly concave surfaces on account of the darker contrast in the center of the particles compared to the edges. The larger size of the resulting nanocubes compared to the initial Pd seeds (18 ± 2 nm) as well as no Pt being detected by EDS indicates that Pd deposition on the Pd seeds is dominant. A complete seed concentration study can be found in Figure S4, which shows that as the concentration of seeds in solution increases, the size of the obtained product decreases and the degree of hollowing increases.

Figure S5 shows TEM images of the sample from Figure 2 as Pd deposition on the Pd nanocubes progresses, with the final size and morphology obtained within half an hour of reaction. No structural or compositional changes were observed with...
longer reaction times. The deposition of Pd before Pt during coreduction of Pd and Pt precursors has been reported previously, supporting the greater ease of Pd precursor reduction observed in our synthesis.\textsuperscript{34–36} Still, the observation of Pd seeds hollowing when their concentration in solution is higher suggests a seed size dependence to whether or not galvanic replacement or deposition will occur.

To understand the role of the seed-to-metal precursor ratio, a scheme outlining the shape and compositional transformations at different stages of the reaction for both high and low seed concentrations is shown in Figure 3. At a high seed-to-metal precursor ratio, the amount of Pd deposition per seed will be lower than that at low seed-to-metal precursor ratios. Thus, the change in Pd nanocube size at high seed-to-metal precursor ratios will be minimal, maintaining the electrochemical potential difference required for galvanic replacement and a suitable amount of Pt precursor available for galvanic replacement. At a lower seed-to-metal precursor ratio (Figure 3b), the rapid growth in particle size can both diminish the driving force for exchange and decrease the amount of Pt precursor available for notable exchange as the effective size of the Pd seeds is much larger.

To demonstrate how seed size affects galvanic replacement or deposition, seeds with two different edge lengths, 24 ± 2.5 and 46 ± 2.6 nm, were directly compared to one another and the original Pd nanocubes with an average edge length of 18 ± 2 nm. The products produced under standard conditions were characterized by TEM (Figure S6). The product obtained from Pd seeds with an average edge length of 24 nm shows some slight pitting, but the structures are not nearly as hollowed out as when smaller Pd nanocubes (18 nm) are used as seeds (Figure 1a). No cavities are observed when the larger Pd nanocrystals with desired composition and morphology by seed-mediated coreduction. As the external reducing agent, L-aa could incorporate facilely. As the external reducing agent, L-aa could not reduce the Pt precursor; the absence of Pt in the product not reduce the Pt precursor; the absence of Pt in the product shown in Figure 4c indicating overlap between Pd and Pt signals and not a core@shell architecture as in Figure 1.

Notably, the extent of galvanic replacement and Pt incorporation can be suppressed by increasing either the amount of L-aa (Figures S7) or the reaction pH (on account of the pH-dependent reducing capabilities of L-aa; Figure S8). These dependences are in addition to the seed size dependence reported here for the first time.

![Figure 3](Image 81x531 to 280x617)
Figure 3. Schematic illustrating the major morphological and compositional changes at (a) high seed-to-metal precursor ratio and (b) low seed-to-metal precursor ratio (red color represents Pd, and green represents Pt).

![Figure 4](Image 345x508 to 544x585)
Figure 4. TEM images of the Pd@Pt nanoparticles prepared using Pt precursor solutions of different concentrations: (a) 120, (b) 240, and (c) 480 μM. Pd concentration in all samples is 120 μM.

![Figure 5](Image 345x671 to 544x749)
Figure 5. (a) STEM image. (b) Pd and (c) Pt elemental mapping from Pd@Pt nanoparticles shown in Figure 4c.

**CONCLUSIONS**

In conclusion, core@shell Pd@Pt nanoparticles with porous hollow architectures are obtained by seed-mediated coreduction of Pd and Pt precursors in the presence of Pd nanocubes. Galvanic replacement between the Pd nanocubes and Pt precursor accounts for the hollow nature of the nanoparticles. Interestingly, simply changing the concentration of seeds in solution results in concave Pd nanocubes. Pt could not be incorporated facilely. As the external reducing agent, L-aa could not reduce the Pt precursor; the absence of Pt in the product particles illustrates the size dependence to the galvanic replacement process in this system. The elucidation of this dependence will allow experimentalists to select between overgrowth and galvanic replacement and ultimately synthesize nanocrystals with desired composition and morphology by seed-mediated coreduction.

**EXPERIMENTAL SECTION**

**Chemicals and Materials.** Hexadecyltrimethylammonium bromide or CTAB (C<sub>16</sub>H<sub>33</sub>NBr, 98%), L-aa (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, 99%), PdCl<sub>2</sub> (99.98%), and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (99.98%) were used as purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 12.1 M) was purchased from Mallinckrodt. Nanopure water with resistivity of 18.2 MΩ·cm was used in all experiments. H<sub>2</sub>PdCl<sub>4</sub> solution (10 mM) was prepared by stirring 17.7 mg of PdCl<sub>2</sub> in 10 mL of HCl (20 mM) for 2 h while heating and stirring at 40 °C.

**Synthesis. Pd Nanocubes (18 nm).** To synthesize small nanocubes, 0.5 mL H<sub>2</sub>PdCl<sub>4</sub> (10 mM) was added to 10 mL CTAB (12.5 mM) and preheated in a 95 °C oil bath for 5 min.
Then, 0.08 mL L-aa (100 mM) was added. The mixture was stirred for 30 min in the 95 °C oil bath and kept at 40 °C before using as the seed for large nanocubes or PdPt synthesis. Prior to use for PdPt synthesis, the solution was centrifuged and diluted to 1 mL.

**Large Pd Nanocubes.** To synthesize large nanocubes, 0.125 mL H2PdCl4 (10 mM) was added to 5 mL CTAB (50 mM) and stirred in a 40 °C oil bath. Then, a certain amount of unwashed Pd nanocubes was injected (0.07 mL for 24 nm and 0.01 mL for 46 nm Pd nanocubes), and 0.025 mL L-aa (100 mM) was added to the mixture. After mixing by shaking the vial, it was left for 14 h in a 40 °C oil bath. Prior to use for PdPt synthesis, the solution was centrifuged and diluted to 1 mL.

In a typical synthesis of hollow Pd–Pt nanoparticles, 60 μL H2PdCl4 (10 mM) and 60 μL H2PtCl6 (10 mM) were added to 5 mL CTAB (50 mM) solution and stirred in a 55 °C oil bath. Then, 1 mL of the above-mentioned small Pd seeds and 0.025 mL L-aa (100 mM) were injected to the mixture. After mixing by shaking the vial, it was left for 24 h in a 55 °C oil bath.

**Characterization.** TEM images were taken by a JEOL JEM 1010 microscope operating at 80 kV. High-resolution TEM images and EDS spectra were obtained via a JEOL JEM 3200FS microscope (operating at 300 kV) interfaced with a liquid nitrogen cooled Oxford INCA dispersive X-ray system. High-resolution transmission electron microscopy samples were prepared by drop-casting a dispersed particle solution onto a 300-mesh carbon-coated copper TEM grid (Formvar removed by dipping in chloroform).

### ASSOCIATED CONTENT

- **Supporting Information**
  - The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00394.
  - TEM images of samples obtained from control experiments (PDF)

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**Notes**
The authors declare no competing financial interest.

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