Communications

Simplifying the Creation of Hollow Metallic Nanostructures: One-Pot Synthesis of Hollow Palladium/Platinum Single-Crystalline Nanocubes**

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Hollow nanoparticles[1–4] represent an emerging class of nanomaterials that exhibit unique catalytic, magnetic, electronic, and optical properties.[5–8] Currently, hollow nanostructures are mainly created by using sacrificial templates.[9–15] The templates necessary for the creation of void space are either preformed or produced in situ. After the growth of shell materials, the templates are removed by thermal/chemical treatments to generate the void space. Nevertheless, without any necessary post-treatment, it is also possible to fabricate hollow nanostructures by depleting the core templates during the shell growth. The outer diffusion of the inner core is normally driven by oxidation, sulfidation, phosphidation, galvanic replacement, or reduction between the core materials and reactants in the reaction environment,[3,4,16,17] which is analogous to the Kirkendall diffusion effect.[18]

When hollow metal nanostructures are taken as the example,[2,17,19,20] it should be noted that they are dominantly prepared by galvanic replacement reactions that strictly require perfect redox match between the oxidizable metal-core template and oxidizing metal cations in the solution. Furthermore, the preparation of the metal core and its redox reaction with oxidizing metal species have to be carried out sequentially by supplying the metal reagents at different stages to prevent their co-reduction. Very recently, hollow monometal nanocrystals were also prepared in situ by reducing the corresponding metal oxide nanoparticles, which was demonstrated only in the case of cobalt.[17]

Herein we report a synthetic strategy that allows the one-pot fabrication of uniform single-crystalline palladium nanocubes and hollow palladium/platinum alloyed nanocubes. To the best of our knowledge, it is the first time that hollow alloyed nanoparticles have been prepared where both metal precursors are present simultaneously. Together with the use of iodide ions as the morphology controller, the selection of acetylacetonates as the metal precursors is critical to the formation of hollow nanocubes. With respect to the solid palladium/platinum nanocubes of identical size, the hollow nanocubes have an increased accessible surface area, leading to improved electrocatalytic activity.

In a typical synthesis of palladium nanocubes, palladium acetylacetonate ($[Pd(acac)_2]$), polyvinylpyrrolidone (PVP), and an aqueous solution of sodium iodide (NaI) were mixed together with DMF (see the Experimental Section). The resulting homogeneous solution was transferred to a teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 150°C for 8 h. The black nanoparticles were collected by centrifugation, and washed several times with ethanol and acetone. The procedure for synthesis of palladium/platinum was similar to that of the palladium nanocubes, except that half of the $[Pd(acac)_2]$ was replaced by platinum acetylacetonate ($[Pt(acac)_2]$).

As illustrated in the transmission electron microscopy (TEM) images, the prepared particles are cubic in shape and substantially uniform in size, averaging (12.5 ± 0.8) nm in dimensions (Figure 1 a). The single-crystalline nature of the nanocubes is evident from the appearance of continuous lattice fringes oriented in the same direction across each cube. The spacing of the fringes is 0.194 nm (Supporting Information, Figure S1), corresponding to the {200} interplanar distance of face centered cubic (fcc) palladium.

The iodide ions play an important role in the formation of the monodispersed palladium nanocubes. Unlike many previous studies in which disodium tetrachloropalladate

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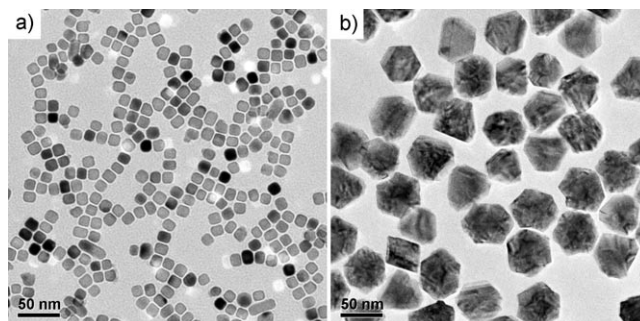Homepage: http://chem.xmu.edu.cn/person/nfzheng/index.html

Figure 1. TEM images of Pd nanoparticles: a) nanocubes prepared with the use of I⁻ ion; b) multiply twinned nanoparticles prepared without the use of any halide.

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(Na$_2$PdCl$_4$) was applied in the synthesis, the use of [Pd(acac)$_2$] as the palladium precursor in our synthesis provides the opportunity to examine the role of halides without the influence of chloride from the precursor. The reactions at the same conditions, but without any halide yield semiregular polyhedral nanoparticles with a size of about 50 nm (Figure 1b). These particles are characterized by their multiply twinned structure (Supporting Information, Figure S1). Such a structural feature is also presented in the particles prepared from the systems where NaI is replaced by an equal amount of NaF, NaCl, or NaBr (Supporting Information, Figure S2). The dimensions of the twinned particles prepared using halides are in the order of F$^-$ > Cl$^-$ > Br$^-$, however, they are all smaller than those synthesized without halide.

Different halides result in the formation of different palladium nanostructures, suggesting the importance of halide in controlling the shape and size of noble metal nanoparticles, which is consistent with many previous reports.[21–23] Xia and co-workers have demonstrated that bromide ions but not other halides facilitate the formation of palladium nanocubes in ethylene glycol. They have proposed that the chemisorption of chloride or iodide on the surface of the nanocrystals is either too weak or too strong for particles to develop the cubic shape.[23] However, the results from our system suggest that the halide effect in the formation of metal nanoparticles should be discussed in more depth by considering the different reaction media or precursors. For example, iodide is better than bromide in the preparation of uniform palladium nanocubes in the DMF system reported herein.

The more interesting result is that if half of the [Pd(acac)$_2$] is replaced by [Pt(acac)$_2$] in the synthesis of palladium nanocubes the reaction leads to the formation of uniform hollow nanocubes (Figure 2). As measured by EDX (energy dispersive X-ray spectroscopy), these hollow nanocubes are essentially alloy particles containing 52% palladium and 48%
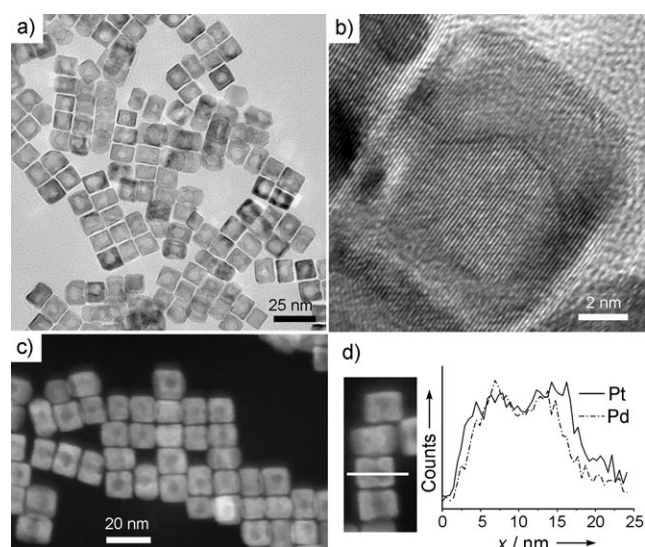
platinum. The high-quality single-crystalline nature of the as prepared hollow cubes is also confirmed by the high-resolution TEM analysis. The analysis presents lattice fringes with an interplanar distance of 0.195 nm perpendicular to the edge direction of each cube. The spacing of 0.195 nm is between 0.194 and 0.196 nm, corresponding to the {200} interplanar distance of fcc palladium and platinum, respectively. Similar to the palladium nanocubes, the hollow palladium/platinum alloy nanocubes are enclosed mainly by {100} facets. While the HAADF-STEM (high-angle annular dark-field scanning transmission electron microscopy) images confirm the hollow feature of the palladium/platinum nanocubes, the EDX line scanning profile across single palladium/platinum nanocubes shows a rather homogenous distribution of both palladium and platinum in each nanocube.

Being able to fabricate hollow metal alloy nanocrystals in one step is the most striking feature of the synthesis reported herein. Considering that the standard reduction potentials (E^0) for Pd^{II}/Pd are typically more negative than Pt^{II}/Pt pairs when they are in the same coordination environment, the formation of hollow palladium/platinum nanocrystals is not expected from the simple mixture of palladium(II) and platinum(II) with the same ligands coordinated. As expected from the reduction potentials, platinum(II) should be reduced before palladium(II). Therefore, the galvanic reaction between platinum(0) and palladium(II) would not occur in the system to create the hollow structure. To better understand the formation mechanism of hollow nanocubes in our system, we have monitored their formation process by running the reactions under the same conditions but for different lengths of time.

As shown by TEM and EDX analysis (Figure 3; Supporting Information Figure S3), only dense palladium nanocubes are formed at the end of one hour. When the reaction time is increased to two hours, edges of the cubes become partly etched. A small amount of platinum is found in these etched nanocubes. Together with the appearance of the hollow feature, an increasing platinum content in the particles is evidenced at the end of three hours of reaction time. By further increasing the reaction time to four hours, the void space in each cube becomes more distinct. The palladium/platinum ratio in the sample after six hours is close to the ratio supplied in the reaction. The time-domain composition
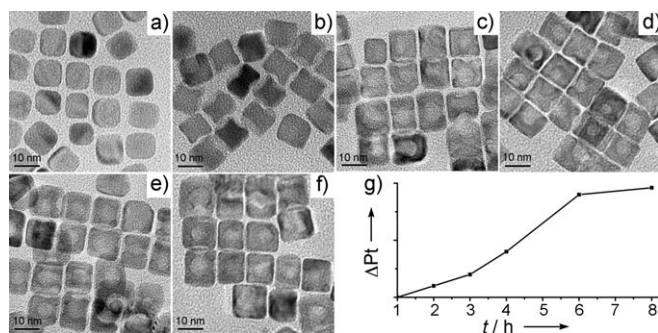

Figure 2. a,b) TEM images of Pd/Pt hollow nanocubes at low and high magnification; c) representative HAADF-STEM image of hollow nanocubes; d) line-scanning profile across a hollow Pd/Pt nanocube is indicated (left).

Figure 3. TEM images of nanoparticles collected at different reaction times: a) 1 h, b) 2 h, c) 3 h, d) 4 h, e) 6 h, f) 8 h, and g) change in mole % of Pt (ΔPt) during 8 h of reaction. All scale bars are 10 nm.

change revealed by EDX analysis is confirmed by our inductively coupled plasma mass spectroscopy measurements (ICP-MS). Beyond six hours, no significant change in either the structure or composition is observed up to eight hours. Therefore, it can be concluded that the formation of hollow palladium/platinum particles relies upon the initial formation of palladium nanocubes followed by its galvanic replacement by platinum(II) species in the solution. This mechanism is further confirmed by the result of our two-step synthesis in which palladium nanocubes are first produced and then used as templates to react with [Pt(acac)$_2$] separately in two steps. This procedure also yields monodispersed hollow palladium/platinum nanocubes (Supporting Information, Figure S4).

As discussed above, the one-pot temporal separation of palladium nanocubes from their galvanic replacement with platinum(II) species is the key to the formation of the hollow palladium/platinum nanocubes. To achieve such a separation, the selection of metal precursors, reducing agent, and also reaction temperature is crucial. The simultaneous use of both iodide ions and acetylacetonate precursors makes it possible for the palladium(II) to get reduced before the platinum(II) species. The reactions in the absence of either iodide or acetylacetonates did not yield hollow cubes (Supporting Information; Figure S5, S6). Solid palladium/platinum nanocubes were obtained when palladium chloride (PdCl$_2$) and platinum(II) chloride instead of acetylacetonates were used as the metal precursors (Supporting Information, Figure S7). While critical to the development of the cube morphology, the presence of iodide ions in the solution of [Pt(acac)$_2$]/[Pd(acac)$_2$] also significantly alters the dominating forms of the metal precursors and therefore the reduction kinetics of metal precursors. When iodide ions were introduced into DMF solutions of [Pd(acac)$_2$] and [Pt(acac)$_2$] respectively, the [Pd(acac)$_2$] solution became much darker and the [Pt(acac)$_2$] one remained almost unchanged (Supporting Infirmation, Figure S8). Since [PtI$_4$]$^{2-}$ and [PdI$_4$]$^{2-}$ are both colored much darker than their acetylacetonate counterparts, this observation indicates the stability of [Pt(acac)$_2$] over [PtI$_4$]$^{2-}$, and [PdI$_4$]$^{2-}$ over [Pd(acac)$_2$]. The additon of iodide ions to the [Pd(acac)$_2$]/[Pt(acac)$_2$] mixture results in [PdI$_4$]$^{2-}$ and [Pt(acac)$_2$] becoming the dominating precursors. In DMF, we found evidence that the reduction of [PdI$_4$]$^{2-}$ is more favorable than [Pt(acac)$_2$] (Supporting Information, Figure S9 and S 10). Therefore, it is not surprising that the dense palladium nanocubes formed before deposition of the platinum is the prerequisite to create hollow structure.

Following the formation of the dense nanocubes, the galvanic replacement between palladium cubes and the platinum(II) is the main driving force for the palladium atoms to diffuse outwards to create the palladium/platinum hollow structure. In addition to facilitating the formation of palladium nanocubes, an important role of the iodide ions in the galvanic replacement process was also evidenced. To identify the role of the iodide ion in the process of formation of the hollow nanocubes, we prepared and purified palladium nanocubes to remove the iodide ions. The purified palladium nanocubes were then reacted with [Pt(acac)$_2$] for eight hours in a DMF solution of PVP containing different halides. While the presence of iodide ions in this reaction produced uniform

hollow nanocubes, the absence of iodide ions led to no formation of hollow particles (Figure 4). Based on EDX analysis, only trace amount of platinum was observed on the obtained solid particles. Similarly, when the iodide ions were
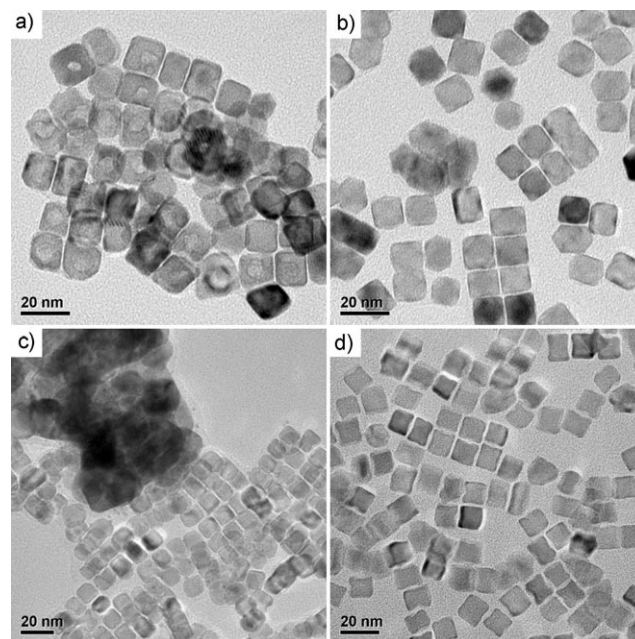

Figure 4. TEM images of the Pd/Pt nanoparticles prepared a) with and b) without the I$^-$ ions; nanoparticles collected after 8 h of reaction at c) 180°C and d) 120°C, respectively.

substituted with other halides (i.e., Br$^-$, Cl$^-$, and F$^-$), the formation of hollow cubes was not observed either. The yielded solid particles contained mainly palladium and a small amount of platinum (Supporting Information, Figure S11). This result might be ascribed to the strong coordination of iodide ions to palladium(II) ions, which facilitates the galvanic replacement between palladium nanocubes and [Pt(acac)$_2$] and therefore fast diffusion of palladium atoms for the creation of the hollow structure. This observation is somewhat consistent with the findings in dealloying studies. For example, Corcoran and co-workers reported that the iodide ions enhance surface diffusion compared to other halides during the dealloying of gold/silver alloys.[24]

In addition to the coordinated use of iodide ions and the acetylacetonates, the selection of the reducing agent and temperature is important to distinguish the reduction of palladium(II) and platinum(II) in two steps, so that their co-reduction can be prevented. When a stronger reducing agent (i.e., ascorbic acid) was added to the system, the reduction of palladium(II) and platinum(II) occurred simultaneously, leading to a phase separation (Supporting Information, Figure S12). A similar situation happened when the reaction temperature was elevated from 150°C to 180°C. The reactions at 180°C led to formation of palladium nanocubes and large platinum nanoparticles separately (Figure 4c; Supporting Information, Figure S13). In comparison, much longer time, 48 hours, was required to obtain the hollow cubes at

120°C (Supporting Information, Figure S14). While four hours at 150°C was long enough to obtain the hollow cubes, reactions at 120°C for four hours yielded only solid cubes of palladium. At 120°C, the etching of the solid palladium cubes by platinum(II) species was observed only when the reaction was extended beyond eight hours (Figure 4d). This result implies that the diffusion rate of palladium atoms caused by the galvanic reactions is much slower at lower temperatures. Therefore, there is a particular temperature window in which the production of the hollow structure can be optimized.

As a galvanic reaction is involved during the formation of the hollow structures, the void space inside each hollow palladium/platinum nanocube is interconnected with its external surface (Figure 2). The inner void space can therefore be considered as internal indentation of the nanocubes. Such a structural feature increases the overall surface area accessible by small molecules (e.g., carbon monoxide, formic acid), which is expected to be beneficial to their catalytic applications. To demonstrate the increased surface area resulting from the hollow structure, carbon monoxide stripping voltammetry studies were performed on both hollow and solid palladium/platinum nanocubes. Both types of nanocubes are of similar sizes (ca. 12 nm). The hollow nanocubes show a current density that is twice that of the solid cubes (Supporting Information, Figure S15). This observation is consistent with the increased accessible surface area caused by the hollow structure discussed above. Such a surface-area increment in the hollow cubes might explain the enhanced performance of the hollow nanocubes in the electrooxidation of formic acid (Supporting Information, Figure S15).

In summary, a simplified synthetic strategy has been developed to prepare single-crystalline hollow palladium/platinum nanocubes with both palladium and platinum precursors present at the same time. Together with the use of iodide ions as the shape regulator, the use of acetylacetonate precursors is demonstrated to alter the reduction kinetics of metal cations and therefore critical to the one-pot formation of hollow palladium/platinum nanocubes. Compared to the solid palladium/platinum nanocubes, the hollow palladium/platinum nanocubes increase accessible surface area and therefore improve electrocatalytic activity in formic acid oxidation.

Experimental Section

Chemicals: [Pd(acac)$_2$] (99%), [Pt(acac)$_2$] (99%), PdCl$_2$ (99%), and PtCl$_2$ (99%) were purchased from Alfa Aesar, PVP (MW = 30000, AR), NaX (X = F, Cl, Br, I) and DMF were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The water used in all experiments was ultrapure with a resistivity of 18.2 MΩ cm. All reagents were used as received without further purification.

Synthesis of Pd multiply twinned nanoparticles: Pd(II)acetyl-acetonate ([Pd(acac)$_2$], 50.0 mg), PVP (160.0 mg), and water (2 mL) were mixed together in DMF (10 mL). The resulting homogeneous yellow solution was transferred to a teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 150°C for 8 h before it was cooled to room temperature. The black nanoparticles were precipitated by acetone, separated using a centrifuge, and further purified by an ethanol/acetone mixture.

Synthesis of palladium nanocubes: [Pd(acac)$_2$] (50.0 mg), PVP (160.0 mg), and an NaI solution (2 mL, 0.15 g mL^{-1}) were mixed together in DMF (10 mL). The resulting homogeneous brown solution was then treated under the same conditions as those used in the preparation of multiply twinned nanoparticles.

Synthesis of hollow palladium/platinum nanocubes: [Pd(acac)$_2$] (25.0 mg), [Pt(acac)$_2$] (30.0 mg), PVP (160.0 mg), and an NaI solution (2 mL, 0.15 g mL^{-1}) were mixed together in DMF (10 mL). The resulting solution was transferred to a teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 150°C for the desired time before it was cooled to room temperature. The black nanoparticles were precipitated by acetone, separated using a centrifuge, and further purified by an ethanol/acetone mixture.

Synthesis of solid palladium/platinum nanocubes: PdCl$_2$ (13.3 mg), PtCl$_2$ (20.0 mg), PVP (160.0 mg), and an NaI solution (2 mL, 0.15 g mL^{-1}) were mixed together in DMF (10 mL). The resulting homogeneous brown solution was then sealed and heated at 150°C for 8 h to yield the solid nanocubes.

Electron microscopy characterization: The high-resolution transmission electron microscopic (HRTEM) observations were performed on a FEI TECNAI F30 microscope operated at 300 kV.

Electrochemical measurements: An ethanol dispersion of purified nanoparticles was deposited on a glassy carbon electrode to obtain the working electrodes after evaporation of the solvent under an IR lamp. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. For the CO stripping voltammetry measurements, CO gas (99.99%) was bubbled for 20 min through a 0.5 M H$_2$SO$_4$ solution in which the electrode was immersed. The electrode was quickly moved to a fresh solution and the CO stripping voltammetry was recorded at a sweep rate of 50 mV s^{-1}. For the electrooxidation of formic acid, the cyclic voltammograms were recorded at a sweep rate of 50 mV s^{-1} in a solution (25 mL) containing H$_2$SO$_4$ (0.5 M) and formic acid (0.25 M). Before the cyclic voltammetry measurements, two cycles of potential sweeps between −0.2 V and 1.2 V at a sweep rate of 250 mV s^{-1} were applied.

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