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Editor's Choice

Site Specific Deposition of Ag on the Corners of Pt Nanocubes

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Novel heterostructured nanoparticles were synthesized by the deposition of Ag on Pt nanocubes by overcoming lattice mismatch, where Ag deposition preferentially occurred at corners of Pt nanocubes during the initial stage of deposition, and position and amount of Ag deposition were controlled by tuning of reaction conditions. The mechanism of such site-specific deposition of Ag is discussed in relation to I^- (shape forming agent) and succinate (organic protective agent).

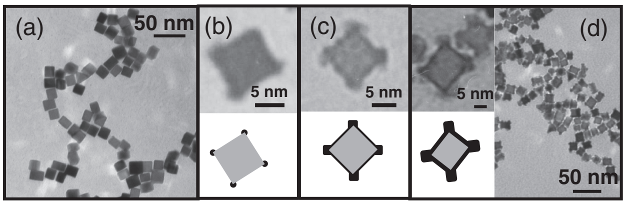

Figure 1. TEM images of Pt nanocube without (a) and with (b)–(d) addition of $AgNO_3$. Time evolution after addition of $AgNO_3$; (b) 1, (c) 3, and (d) 15 h. Insert of (b)–(d) shows schematic drawing of Pt nanocube with deposits.

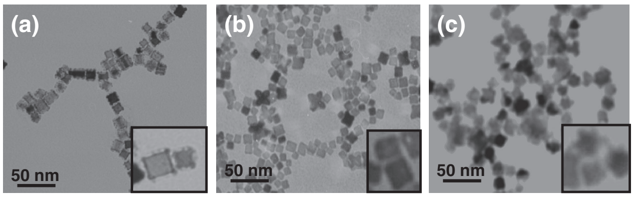

Figure 2. TEM images of Pt nanocube with deposits prepared under different amounts of $AgNO_3$ and succinate; (a) 0.2 mM of $AgNO_3$, (b) 1 mM of succinate, and (c) 4 mM of succinate. Concentration of $PtCl_4^{2-}$, succinate, $AgNO_3$, and NaI was fixed to 1, 2, 1, and 10 mM, respectively, under otherwise stated.

Fabrication of shape-controlled heterostructured nanoparticles has received increasing interest because of their tunable properties, depending on combinations of different components, in addition to the shape effects, e.g., work function[1] and surface energy,[2] and they have potential applications in areas such as catalytics,[3a] magnetics,[3b] plasmonics,[3c] and electronic devices.[3d,3e] Although metallic nanoparticles have achieved significant success in controlling shape,[4] only limited reports[5] appear for shape-controlled heterostructured nanoparticles, especially for site specific deposition of second component.[5d,6] Site-specific deposition has been performed by the aid of difference in adsorption densities of organic protective agents at different sites, e.g., deposition of Pd on Pt cubes,[6a] Au on Ag cubes,[6b] and Au on Ag nanorods.[5d] Several bimetallic nanoparticles including core–shell structures have been prepared so far,[7,8] and the number of combinations is restricted for epitaxial growth because of the essential regulations.[5a,8] Lattice mismatch is an important factor to retard the epitaxial growth of second components. Although several approaches have been studied to obtain Pt–Ag core–shell nanoparticles by liquid reduction, only a physical mixture of two kinds of metal nanoparticles has been obtained.[9] No report has appeared yet for the preparation of Pt–Ag core–shell metallic nanoparticles, since Ag and Pt have a large lattice mismatch of 4.1%.[5a,8]

Here, we demonstrate site-specific deposition of Ag at corners of Pt nanocubes. The degree of deposition and coverage of Ag on Pt nanocube can be controlled by tuning the reaction conditions. Such controlled deposition of a second component on a shape-regulated core will lead to unique physical and chemical properties not realized so far, e.g., masking or creating active sites at the corner as a catalyst model and creating new functional materials having special physical properties due to electron-rich or deficient sites. The most plausible mechanism for site specific Ag deposition on the corners of Pt nanocubes is discussed in relation to I^- and succinate added as shape-forming agent and protective agent, respectively.

Preparation of heterostructured Pt nanocube with Ag deposits was carried out by a modified seed-mediated growth method, without isolation of seed Pt nanoparticles throughout the reaction. Typically, a seed Pt nanocube was prepared by hydrogen reduction of K_2PtCl_4 (1 mM) in aqueous solution in the presence of sodium succinate (protective agent: 2 mM) and NaI (shape forming agent: 10 mM) for 20 min,[4e] followed by addition of aqueous $AgNO_3$ solution (5 mL, 20 mM) and further stirring under hydrogen atmosphere up to 15 h.[10]

Figure 1 shows TEM images of the obtained nanocrystals (NCs) with and without addition of $AgNO_3$. Without addition of $AgNO_3$, monodispersed Pt nanocubes with average size of ca. 15 nm were obtained with high shape selectivity as shown in Figure 1a. For the product obtained by the addition of $AgNO_3$, another component with different contrast from Pt nanocubes was observed on Pt nanocubes by TEM, especially at the corners of Pt nanocubes (Figure 1b). Such site-specific deposition of another component is also confirmed by high-resolution TEM (HRTEM) observation.[10] The amount of the second component increased with an increase in the reaction time (Figures 1b–1d). It should be noted that amounts of $AgNO_3$ and sodium succinate also caused increased deposition of second component as indicated by TEM observation (Figure 2) and EDX analysis (Table 1). Table 1 also indicates that the increase in amount of $AgNO_3$ is accompanied by an increase in the amount of I. Thus, the possibility of AgI formation is briefly discussed later. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and EDX line-scan profiles of a single Pt nanocube with Ag deposits along the diagonal (indicated by red line) are shown in Figure 3. The EDX line-

Table 1. EDX analysis of Pt nanocube with deposits prepared under different amounts of $AgNO_3$ and succinate

$AgNO_3$ /mM	Succinate /mM	Pt /atom %	Ag /atom %	I /atom %
0.1	2.0	93.5	6.0	0.5
0.2	2.0	83.8	7.5	8.7
1.0	2.0	47.7	27.3	25.0
4.0	2.0	3.5	42.6	53.9
1.0	1.0	73.9	24.9	1.2
1.0	4.0	11.7	67.7	20.6

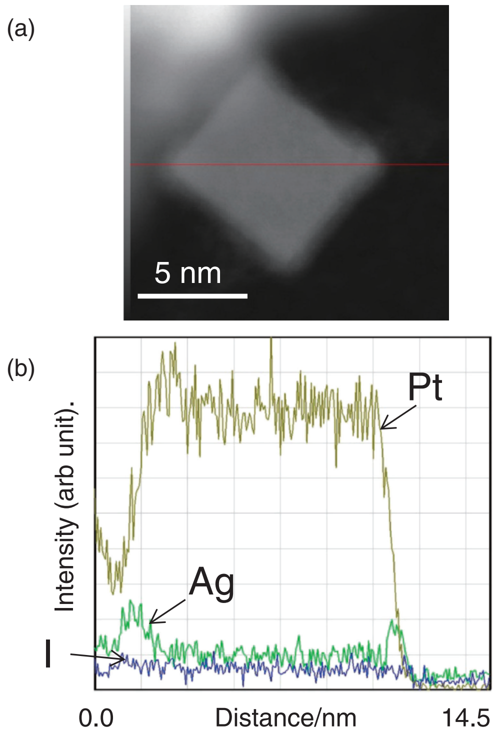

Figure 3. (a) HAADF-STEM image of Pt nanocube with deposits. (b) EDX line-scan profiles of Pt (brown), Ag (green), and I (blue) recorded along the red line on a Pt nanocube with deposits shown in the HAADEF-STEM image in (a).

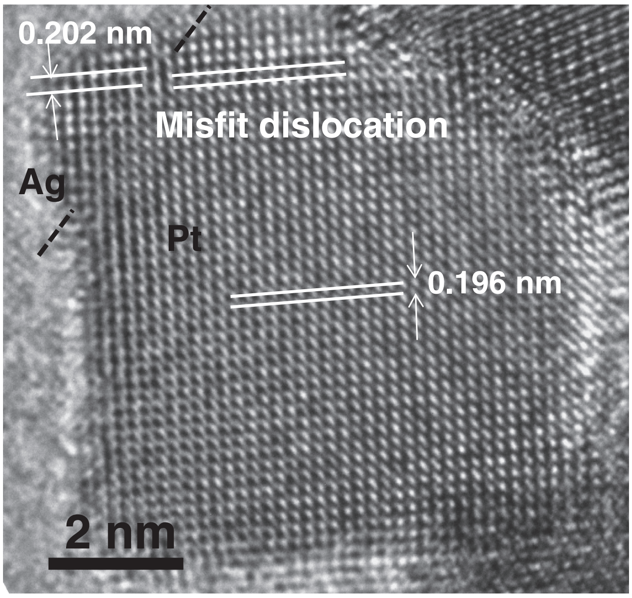

Figure 4. HRTEM image of Pt nanocube with deposits. Observed fringe spacing of 0.196 nm at center and 0.202 nm at corner almost coincide with those of Pt{200} and Ag{200}, respectively. A misfit dislocation is observed at boundary between atomic arrangements of Pt and Ag.

scan profiles on a single Pt nanocube with Ag deposits confirm the preferential deposition of Ag at corners of Pt nanocubes.

It is well known that lattice mismatch has a significant impact on the epitaxial growth of heterostructure. Silver seems to be difficult for coherent growth on Pt since Ag and Pt metals have a large lattice mismatch of 4.1%.[5a,8] Figure 4 shows a HRTEM image of Pt nanocube with Ag deposits along with the [001] axis of core Pt nanocube. Analysis of fringe spacing in the center of nanoparticle (0.196 nm) corresponds to Pt{200} planes. At the corners of the nanoparticles, the fringes with lattice spacing (0.202 nm) were observed, which almost coincide with Ag{200} planes (0.204 nm) of fcc Ag metal structure, accompanied with misfit dislocation at Ag–Pt boundary to release lattice distortion energy. A reason for successful epitaxial growth of Ag on Pt is not clear at present. One possibility is that some Ag derivative such as AgI deposits as a precursor, followed by transformation to Ag metal, since I content increases by an increase in Ag content by EDX analysis of Pt nanocube with deposits as shown in Table 1. Such transformation of AgI to Ag metal has been reported by electron beam irradiation during TEM observation.[11]

In order to discuss the mechanism for site specific deposition of Ag on Pt nanocubes, we need to consider the growth process of Pt nuclei (Figure 5a). This is because when the isolated Pt nanocubes (the same sample shown in Figure 1a) were treated in solution with $AgNO_3$ in the presence of NaI and succinate, not the deposition of Ag on Pt nanocubes but the wrapping of Pt nanocube aggregates with Ag foil was observed by TEM, indicating that the Pt seed (truncated cube) (Figure 5b) is an important precursor for the formation of the Pt nanocube with Ag deposition.[10] Several groups have already reported the importance of surface structure of seed particles on the growth of second materials.[5c,12] A cuboctahedron nucleus, known as stable structure for fcc metal nanoparticle, should be formed at first by the reduction of $PtCl_4{}^{2-}$ under the present experimental conditions. The nucleus may grow, via truncated cube seeds, to finally cube under kinetically controlled conditions in the presence of I^- used as shape-forming agent, which adsorbs preferentially on (100) facet, while the (111) facet grows the faster, resulting in formation of Pt nanocube. The shape of Pt seed, just before $AgNO_3$ addition, was confirmed as truncated cube by TEM observation of the reaction mixture.[10] The surface of Pt seed is known to be mostly electron-deficient[13] and should be adsorbed by anionic species, such as I^- and succinate (Figure 5b). We should stress that succinate has free carboxylate in addition to one used to adsorb on Pt seed. Thus, succinate may play an important role to accumulate Ag^+ around the Pt seed with the aid of free carboxylate,[14] while accumulation of anionic Pt precursor ($PtCl_4{}^{2-}$) should be retarded. It should be

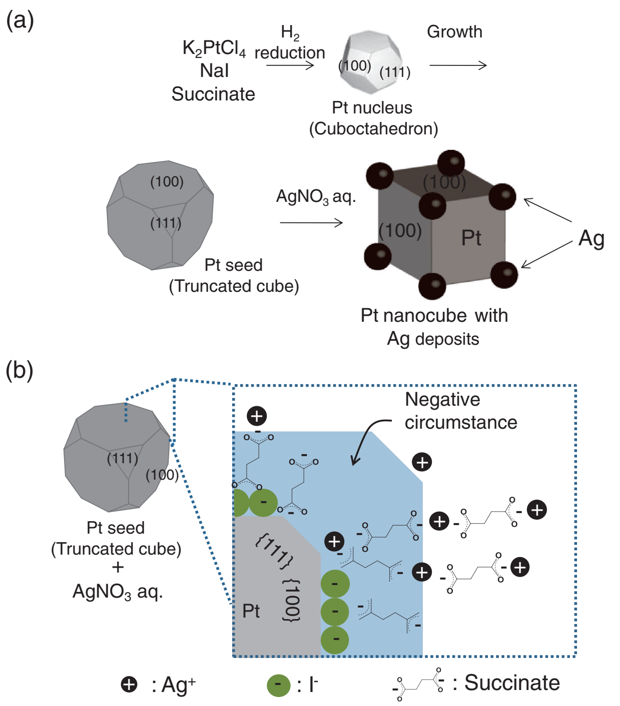

Figure 5. Plausible mechanism for site-specific deposition of Ag on Pt nanocube. (a) During the reduction of $PtCl_4^{2-}$, cuboctahedral Pt nucleus grows first, via truncated cube seed, to cube under a kinetically controlled conditions due to preferential adsorption of I^- (shape forming agent) and succinate (protective agent) on Pt{100}. After addition of $AgNO_3$, Ag deposits principally on corners of Pt cube. (b) Schematic image of Pt seed and Ag accumulation. The negative circumstance around Pt nanocube is formed by the adsorption of succinate and iodide because of the electron deficiency of Pt nanocube surface. Adsorption of Ag^+ on Pt{111} precedes to Pt{100} because of preferential adsorption of I^- and succinate on Pt{100}. Succinate provides free carboxylate group to form complex with Ag^+ even when one group is used to adsorb on Pt nanocube.

mentioned that an increase in succinate in the reaction system causes increased deposition of Ag on Pt nanocubes (Figure 2 and Table 1). Discussion of the mechanism of site-specific deposition of Ag on Pt nanocube should include consideration of chemical species adsorbed on different facets; {111} and {100} of truncated cube seed. Iodide has been reported to be adsorbed stronger on Pt{100} compared with Pt{111} by surface X-ray diffraction analyses of several Pt bulk single crystals adsorbed by iodine.[15] Furthermore, adsorption energy of propionic acid estimated by DFT calculations suggests that the Pt{111} facets are less protected by carboxylate groups than Pt{100} facets.[16] A succinate adopted in the present study also has carboxylate groups and is predicted to adsorb advantageously on the Pt{100} facets. Thus, accumulated Ag^+ may adsorb on Pt{111} with vacant space of truncated cube because Pt{100} is preoccupied by I^- and succinate resulting in site-specific deposition of Ag on corners of Pt nanocube.

In conclusion, we have successfully synthesized heterostructured Pt nanocube with Ag deposits by overcoming lattice mismatch. Deposition of Ag occurred preferentially at corners of Pt nanocubes, and amount and sites of deposition were tuned by the reaction conditions. Negative circumstance formed by I^- (shape forming agent) and succinate (protecting agent) around Pt seeds induces site-specific deposition of Ag^+ on Pt seeds. Thus, skillful selection of adosorbents on Pt NCs is essential. The proposed method has potential to open new ways to prepare various shape-controlled heterostructured NCs.

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