Surface-specific overgrowth of platinum on shaped gold nanocrystals

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Controlling the shape and composition of metal nanocrystals can be beneficial for tuning the optical or catalytic properties in a variety of applications. In this study, surface-specific overgrowth of platinum was found on shaped gold nanocrystals of cubes, octahedra and spheres.

Platinum overgrowth was observed on the planar faces of gold cubes, while the overgrowth occurred at the vertices of gold octahedra, indicating that platinum was selectively reduced on the Au (100) surface for each gold nanocrystal shape. The platinum nuclei covered the entire surface for gold spheres, which don’t have well-defined surfaces. As the Pt/Au ratio increased, a full platinum shell was formed. Solution-based UV-Vis absorption spectra of the composite nanocrystals showed that the absorption peak was red-shifted with increasing platinum coverage. The optical response of a single composite nanocrystal was measured by dark field microscope, which also demonstrated a red shift in the scattering spectrum with increasing platinum coverage. The extent of a red shift depended on the shape and composition of the composite nanocrystals.

Introduction

Controlling the shape and composition of metal nanocrystals enables the development of novel functionalities of nanocrystals that can be applied in a number of applications.1–14 Nanocrystals with a variety of shapes (e.g. cubes, cuboctahedra, octahedra, rods, pyramids, cages and dendrites) have distinct optical properties with unique light absorption or scattering characteristics.15–24 The shaped nanocrystals also have specific surface atomic arrangements (e.g., (100) surface vs. (111) surface) and consequently show distinct reactivity and selectivity for various catalytic reactions.25–27 In addition, the optical or catalytic properties of nanocrystals composed of multiple metals can be tuned to a greater degree than is possible for single-component nanocrystals.28–38 For example, surface plasmon resonance (SPR) peaks of a nanobox made of palladium and silver could be tuned across the entire visible spectrum.39 When palladium was locally overgrown on the surface of platinum cubes, poisoning of the catalytically active sites was greatly reduced for the electrocatalytic oxidation of formic acid.40

In particular, the overgrowth of platinum onto gold has been studied for optical or catalytic applications.41,42 If platinum is overgrown onto the gold rods, the dielectric sensitivity of the Au rod@Pt (where “A@B” represents the overgrowth of B on A) was observed to show a marked increase.43,44 For cases in which platinum nanoparticles were modified with gold clusters, or in which platinum shells were formed on the surface of gold nanoparticles, the catalytic properties of the resultant nanoparticles could be significantly enhanced.45–47 Further control of platinum overgrowth on the surface of shaped gold nanocrystals can provide interesting perspectives for development of multimetallic nanocrystals and their novel applications.

Shape control of metal nanocrystals can be achieved by hindering crystal growth in a specific direction while enhancing growth in another direction.48 In the case of a disparity in interaction energy between a metal surface and the capping agent for different surface structures (e.g., (100) vs. (111)), reduction preferentially occurs on the surface with a weaker interaction.49 Or if one surface is blocked by foreign metals, the other surface would be used preferentially for growth, leaving the blocked surface only in the end.50 The rate of reduction can be controlled by various additives, such as NO2, Fe3+ and OH−.26,51,52 These additives usually lower the reduction rate and magnify the differential growth rate, with the consequence that shaped nanocrystals covered with a specific surface structure are formed. The composition of the metal nanocrystals can be controlled by simultaneously co-precipitating different metal precursors.53 However, the shape of the nanocrystals is rarely controlled in this case. Alternatively, secondary metals can nucleate on the surface of pre-formed nanocrystals.54

In this study, platinum was overgrown on the surface of shaped gold nanocrystals (cubes, octahedra and spheres), and the effect of the underlying nanocrystal shape on the overgrowth mode was evaluated. Platinum overgrowth occurred on the planar faces of gold cubes, but also on the vertices of gold octahedra. Platinum was uniformly overgrown on gold spheres, which have no well-defined surface structure. Unlike cubes or octahedra which have uniform atomic arrangements ((100) surface for cubes and (111) surface for octahedra) on the surface, spheres do not have uniform atomic arrangements. The coverage of platinum was controlled by adjusting the ratio of platinum to gold in the reaction solution. The optical

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properties were measured by ultraviolet-visible spectroscopy (UV-Vis) and dark field microscopy. The properties were found to depend strongly on the shape of the gold core and the coverage of platinum on the gold nanocrystal surfaces.

**Experimental**

**Materials**

Potassium tetrachloroplatinate(II) (K₂PtCl₄; 98%), polyvinylpyrrolidone (PVP, MW 55000), silver nitrate (AgNO₃; 99+%) and l-ascorbic acid (AA; 99+%) were purchase from Sigma-Aldrich. Hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O; 99.99%) was purchased from Alfa Aesar. All chemicals were used without further purification.

**Shape-controlled Au nanocrystals**

Cubic, octahedral and spherical shapes of gold nanocrystals were prepared as reported. A proper amount of AgNO₃ was dissolved in 1,5-pentanediol (96%, Sigma-Aldrich) by sonicating the solution for 50 min. 0.15 mL of AgNO₃ solution was added to 5.0 mL of boiling 1,5-pentanediol. Next, 3.0 mL of PVP (0.15 M in 1,5-pentanediol) and 3.0 mL of HAuCl₄ (0.050 M in 1,5-pentanediol) solutions were alternatively added every 30 s over 7.5 min. The resulting mixture was refluxed for 1 h. The final solution was cooled to room temperature. Different concentrations of AgNO₃ solution were used for the syntheses of octahedra (1.7 mM), cubes (5.0 mM) and spheres (17 mM).

**Synthesis of Au@Pt nanocrystals**

1 mL of each shape-controlled gold nanocrystal sample was washed with 40 mL of DI water several times and the precipitant was finally dispersed in 4 mL of DI water. The exact amount of gold in the washed solution was measured by elemental analysis using inductively coupled plasma (ICP), 1mL of gold nanocrystal solutions for each shape was mixed with proper amounts of 1.7 mM acidic PtCl₄²⁻ solution. 0.07 g of K₂PtCl₄ was dissolved in 2 mL of 0.2M HCl solution and then diluting the solution to 100 mL with DI water. A 12-fold amount of L-ascorbic acid (keeping molar ratio of AA : PtCl₄²⁻ = 12) was added to each sample and the mixture was shaken by a vortex mixer. The total volume of each sample was diluted to 3 mL. Solutions were undisturbed for 14 h at room temperature (except gold octahedra which were at 50 °C) and washed by DI water. The ratio of platinum to gold in the reaction solution was varied in the range of 0–0.5.

**Characterizations**

TEM images were obtained with TECNAI 20 or JEOL 2100, HR-TEM images with JEOL 2100. UV-Vis measurements were performed with Shimadzu UV-2401PC. SEM images were taken using JSM-6500F or JSM-6700F. X-Ray photoelectron spectroscopy (XPS) data were taken using a SIGMA probe (ThermoVG) equipped with a monochromatic Al Kα X-ray source (15 kV, 100 W). The binding energy was calculated with reference to the maximum intensity of the C 1s signal at 285 eV. The obtained spectra were analyzed using XPS PEAK 41 software. Elemental analysis was performed using ICP (IRIS Intrepid II, Thermo Elemental). The dark field images were obtained from an Axio Observer Z1 inverted microscope (Carl Zeiss, Germany) equipped with an oil immersion dark field condenser (NA = 1.4) and LD Plan-neofluar® 63X objective lens (NA = 0.75). The collected scattering light is imaged by a true-colour digital camera (AxioCam MRc 5, Zeiss). Immersion oil (Zeiss Immersol) was used for high index light path. All scattering images were obtained in dark environment which prevents ambient light interference.

**Results and discussion**

In this work, platinum was overgrown on the surface of various shaped gold nanocrystals, and the effect of the shaped core on the nature of platinum overgrowth was evaluated. For face-centered cubic (FCC) metals, cubic nanocrystals are covered by (100) surfaces while octahedra are covered by (111) surfaces. When a secondary metal is overgrown onto the different crystalline surfaces, its growth mode can be variable. Here, we used three different shapes of gold nanocrystals (cubes, octahedra and spheres) as nanocrystalline cores and examined the overgrowth of platinum onto these nanocrystals.

**Overgrowth on Au cubic nanocrystals**

Fig. 1 shows SEM images of Au cube@Pt nanocrystals. As the ratio of Pt/Au increased from 0 to 0.13, 0.21 and 0.5, the overgrowth of platinum onto the gold surface increased. The amount of gold in the aqueous solution was measured by ICP, and the appropriate quantity of platinum salts was added to the reaction solution to control the Pt overgrowth. TEM images were obtained to measure the location, thickness and extent of platinum growth. As in Fig. 2, a dot-type platinum shell was formed on the square planar surfaces of the gold cubes. Interestingly, for Pt/Au ratios of 0.13 and 0.21, the platinum shell was formed only on the plane, not on the corners. When the ratio was higher, platinum was also overgrown onto the corners, forming a full platinum shell. It is also noteworthy that the thickness of the platinum shell showed little variation for different Pt/Au ratios, and only the extent of platinum coverage increased with increasing Pt/Au ratio. Fig. 2(e) shows high resolution TEM image of the corner of Au cube@Pt nanocrystals. Platinum appeared to be epitaxially overgrown on the gold surface, but no overgrowth was observed on the corner, which is characteristic of an Au (111) surface. The optical properties of the Au cube@Pt were observed by UV-Vis spectroscopy. Fig. 3 shows the SPR absorbance changes with increasing Pt/Au ratio. Each spectrum was normalized with respect to the absorbance at 400 nm. The gold cube showed an absorption peak at 557 nm, that red-shifted to 558, 559, 570 and 607 nm with increasing Pt/Au ratio to 0.08, 0.13, 0.21 and 0.5, respectively, with a significant decrease in peak intensity. The overgrown platinum on the gold surface induces a red-shift and damping of the optical response, but the extent of the red-shift was relatively small compared with the red-shift observed from overgrowth onto other gold nanocrystal shapes.
Overgrowth on Au octahedral nanocrystals

Overgrowth of platinum onto gold octahedra is shown in Fig. 4. The overgrowth was achieved at 50 °C. When the reaction was attempted at room temperature, which promoted platinum overgrowth on the gold cube or sphere, platinum nanoparticles were obtained separately. While Au cube@Pt showed a rather smooth covering of platinum, Au oct@Pt yielded bumpy shapes. SEM images of Au oct@Pt with Pt/Au ratios of 0.08 or 0.21 demonstrate that Pt overgrowth occurred mainly on vertices or edges, whereas the overgrowth initially occurred on planes for the Au cube@Pt nanocrystals. As the Pt/Au ratio was increased to 0.5, Pt bumps were still clearly observed. TEM images, shown in Fig. 5, enable a more detailed characterization of the platinum overgrowth onto gold octahedra. Fig. 5(a) shows the octahedral shape of the gold nanocrystals. As platinum salts were reduced in the presence of gold octahedra, the selective overgrowth on vertices was clearly observed for Pt/Au ratios of 0.08 and 0.21. As the Pt/Au ratio was increased to 0.5, platinum dots also covered the planes of gold octahedra. High resolution TEM images, shown in Fig. 5(e) for Au oct@Pt, also showed the epitaxial growth of platinum onto the gold surface. Fig. 6 shows the UV-Vis spectrum for gold octahedra and Au oct@Pt nanocrystals. As platinum was overgrown onto the surface of gold octahedra, the absorption peak was red-shifted from 581 nm (gold octahedra) to 589, 596, 610, and 679 nm (Pt/Au ratios of 0.08, 0.13, 0.21 and 0.5, respectively). The UV-Vis spectrum represents the average optical response of many nanocrystals distributed in the solution. To measure the optical properties of the single nanocrystal, dark field microscopic images obtained from plasmon-meditating scattering were taken for a single gold octahedron or a single Au oct@Pt nanocrystal. The insets in Fig. 5 show the dark field image of the nanocrystal corresponding to each TEM image. The scattered light clearly shows the red-shift of Au oct@Pt with increasing Pt/Au ratio.

Fig. 1  SEM images of gold cubes (a) and Au cube@Pt nanocrystals made with a Pt/Au ratio of 0.13 (b), 0.21 (c), and 0.5 (d).

Fig. 2  TEM images of gold cubes (a) and Au cube@Pt nanocrystals made with a Pt/Au ratio of 0.13 (b), 0.21 (c), and 0.5 (d). High resolution TEM image (edge side) of Au cube@Pt nanocrystal made with a Pt/Au ratio of 0.13 (e).

Fig. 3  UV spectra of gold cubes and Au cube@Pt nanocrystals. Inset shows the ratio of Pt/Au used in the reactant solution.

Fig. 4  SEM images of gold octahedra (a) and Au oct@Pt nanocrystals made with a Pt/Au ratio of 0.08 (b), 0.21 (c) and 0.5 (d).
Overgrowth on Au spherical nanocrystals

In contrast to cubes or octahedra surrounded by (100) or (111) surfaces, the crystalline surfaces of gold spheres are not well-defined. When these spheres were used as cores, platinum was overgrown onto the entire surface of the gold sphere, as shown in the SEM images in Fig. 7. In particular, the TEM image of an Au sph@Pt nanocrystal grown with a Pt/Au ratio of 0.08 (Fig. 8(b)) showed that many Pt nuclei formed on the surface of the gold sphere. As the Pt/Au ratio increased, the platinum shell covered the entire surface. High resolution TEM images of an Au sph@Pt nanocrystal grown with a Pt/Au ratio of 0.08 also revealed that Pt nuclei formed on the surface of the gold sphere epitaxially (data not shown). An increase in platinum overgrowth was accompanied by a corresponding increase in the red shift of the absorption spectrum as shown in Fig. 9. Whereas the gold spheres had a UV-Vis absorption peak at 547 nm, the location of the peak was shifted to 554, 564, 610 and 683 nm with increasing Pt/Au ratio to 0.08, 0.13, 0.21 and 0.5, respectively. The extent of the peak shift was highest for spheres (\(D = 136\) nm) and lower for cubes (\(D = 50\) nm) and octahedra (\(D = 98\) nm).

Surface-specific overgrowth of platinum

The results discussed above are summarized in Fig. 10. When platinum salts were reduced in the presence of gold cubes, which are characterized by (100) planar surface structures, the platinum overgrowth occurred only on the planes, not on the vertices or edges. In contrast, when platinum salts were reduced in the presence of gold octahedra, which are characterized by (111) planar surface structures, the platinum overgrowth was observed only on the vertices, not on the planes. The vertices of FCC cubic nanocrystals have (111) surfaces and those of FCC octahedral nanocrystals have (100) surfaces, as shown in Fig. 10. Platinum overgrowth occurred only on (100) surfaces, not on (111) surfaces. In the case of the gold spheres, which

![Fig. 5 TEM images of gold octahedron (a) and Au oct@Pt nanocrystals made with a Pt/Au ratio of 0.08 (b), 0.21 (c) and 0.5 (d). (Insets show dark field microscopic images of each single nanocrystal.) High resolution TEM image of Au oct@Pt nanocrystal made with Pt/Au ratio of 0.08 (e).](image1)

![Fig. 6 UV spectra of gold octahedra and Au oct@Pt nanocrystals. Inset shows the ratio of Pt/Au used in the reactant solution.](image2)

![Fig. 7 SEM images of gold spheres (a) and Au sph@Pt nanocrystals made with Pt/Au ratio of 0.08 (b), 0.21 (c) and 0.5 (d).](image3)

![Fig. 8 TEM images of gold spheres (a) and Au sph@Pt nanocrystals made with Pt/Au ratio of 0.08 (b), 0.21 (c) and 0.5 (d).](image4)
don’t have well-defined surfaces, platinum nuclei formed on the entire surface, and platinum overgrowth proceeded to form a full shell.

The overgrowth of metals such as palladium, platinum, silver, or gold on anisotropic gold rods has been investigated previously. In these cases, the metal overgrowth usually nucleated on the rod tip rather than the column. This phenomenon was explained by stronger interactions of the column surface ((100) or (110) surfaces) with capping agents (usually CTAB; cetyltrimethylammonium bromide), which hindered the access of gold salts to the surface. Electric-field-directed mechanisms also played a role in gold rod grown in the longitudinal direction. Because the difference in charged potential between AuCl₂–CTAB complex and the gold rod surface was highest at the tip, the flux of gold salts was highest at this location, and reduction occurred more readily at the tip. Another explanation for preferential tip growth focused on the residual silver used in the synthesis of anisotropic gold rods. The silver tended to adhere to the (110) or (100) surfaces of the column, and this residual silver prevented metal salts from depositing on the column surface, thereby inducing overgrowth at the tip.

Unlike the studies using gold rods, this study used a polymer (PVP) with long alkyl chains as a capping agent and platonic crystals with isotropic shapes as gold cores. PVP is known to have a stronger interaction with Au (100) surfaces, producing cubic crystals or long rods covered with (100) surfaces only. Because platinum overgrowth occurred selectively on Au (100) surfaces for various Au@Pt nanocrystals examined in this study, a stronger interaction between the PVP capping agent and Au (100) surface didn’t provide sufficient justification for the observed selective overgrowth. The use of isotropic cores also eliminated the electric-field effect.

X-Ray photoelectron spectroscopy (XPS) results for gold cubes and gold octahedra showed that gold cubes had more residual silver than did gold octahedra (Ag: Au ratio of 7.7% for Au cube and 4.1% for Au octahedra; data shown in Fig. 11). Therefore, the Au (100) surfaces truly had more residual silver than did Au (111) surfaces. In the present study, platinum was more easily overgrown on the Au (100) surfaces, where greater residual silver occurred. During platinum overgrowth on gold crystals, silver can be oxidized, producing electrons that may contribute to reducing the platinum salts. This type of phenomenon has been observed in the transformation of Ag nanocubes to Pt–Ag nanoboxes as well. In this preparation, silver was dissolved out while reducing platinum. For the Au oct@Pt nanocrystals made with a Pt/Au ratio of 0.08, the Ag 3d peak was not observed, indicating that the residual silver on the gold surface was removed during platinum overgrowth. The Ag 3d peaks were still observed for the Au cube@Pt made with a Pt/Au ratio of 0.08, but the Ag 3d peak was not observed, indicating that the residual silver on the gold surface was removed during platinum overgrowth. The Ag 3d peaks were still observed for the Au cube@Pt made with a Pt/Au ratio of 0.08, but the ratio of Ag/(Au + Pt) was greatly reduced to 2.4%. The reduction of platinum occurred more easily on Au (100) surfaces where silver provided extra electrons. In the case of gold octahedra, less residual silver mainly located on the vertices might need higher temperature to be dissolved, having the overgrowth temperature higher (50°C) than cubes or spheres (room temperature). Platinum overgrowth on gold spheres occurred over the entire surface because silver tended to be uniformly distributed over the entire surface, thereby inducing the formation of a full platinum shell.

**Conclusion**

When platinum was overgrown on the surface of gold nanocrystals with cubic, octahedral, and spherical shapes, different modes of overgrowth were observed depending on the shape...
of the gold core. Platinum overgrowth occurred on the planar surfaces of gold cubes, at the vertices for gold octahedra, and over the entire surface for gold spheres. Because FCC metals such as gold have (100) surfaces on the planar faces of cubes or at the vertices of octahedra, the observed overgrowth modes indicate that platinum was selectively overgrown on Au (100) surfaces. Shape modulation of metal nanocrystals has usually been achieved by adding foreign metal ions during synthesis. In the present study, silver was used to control the shape of gold nanocrystals. The residual silver remained preferentially adsorbed to the Au (100) surfaces rather than to the Au (111) surfaces after gold nanocrystal synthesis. When platinum was reduced under these conditions, silver on the Au (100) may have provided additional electrons with the result that silver itself was oxidized. Consequently, the reduction of platinum occurred more easily on Au (100) surfaces where silver provided extra electrons. The optical properties of Au@Pt nanocrystals were modulated by the shape of the gold core and the coverage of the platinum shell. Overall, a red-shift in the UV-Vis absorption spectrum was observed with increasing platinum coverage. The magnitude of the red-shift was largest for gold spheres and smallest for gold cubes. The red shift of a single Au oct@Pt nanocrystal was also observed in the scattering spectrum using dark field microscope. These Au@Pt nanocrystals with overgrown platinum on a specific surface could serve as superior substrates for chemical/biological sensing and catalysis.

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References