Control over the Morphology and Plasmonic Properties of Rod-like Au-Pd Bimetallic Nanostructures

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Abstract. Bimetallic nanostructures are interesting materials for many applications ranging from plasmonics to catalysis. However, synthesizing bimetallic nanorods with good control over composition, morphology and maintaining an anisotropic shape is challenging. Here, we have shown a reproducible approach to the synthesize the bimetallic core-shell nanorods within a stabilizing mesoporous silica shell and with an Au core and a Pd metal shell with excellent control over their properties. Specifically, we demonstrate that the thickness and morphology of the Pd metal shell (rough/smooth) can be precisely tuned and studied the plasmonic properties of the resulting bimetallic nanostructures in detail. Our approach can be naturally extended to different or more than two metals leading to rod-shaped metal particles with highly tunable materials properties that are of interest in their use in optical and catalytic applications.

1. Introduction

Localized surface plasmon resonances (LSPRs) are oscillations of conduction electrons of metallic nanostructures which arise from the interaction with an electromagnetic field resulting in strong local electromagnetic field enhancements close to the nanoparticle’s surface, especially at sharp corners and edges. Noble metallic nanoparticles like Au and Ag have been extensively studied due to their strong localized SPR, and the many SPR-related applications [1-2]. Advances in wet chemical methods enabled the preparation of gold nanoparticles with various shapes and structures [3,4], and fundamental studies on the effect of these parameters on the plasmonic properties. Among these different shapes, gold nanorods (AuNRs) exhibit better properties due to their antenna-like shape, especially compared to spherical particles [5-6]. In addition, next to a transverse LSPR AuNRs (perpendicular to the length of the rods) exhibit a shape/symmetry-induced longitudinal mode in the direction of the length of the rods as well which is found at lower energies and that can be extended into the near-infrared region to be used in biological applications as well, as biological cells and tissues have significant less absorptions in this region of the spectrum.

However, single-component Au-nanostructures are not always the ideal choice for practical applications [7]. Compared to single-component Au nanoparticles, bimetallic Au-metal nanostructures...
offer additional control over size, shape, composition and morphology of the resulting particles, leading to unique optical properties and functionality [8-9]. In particular, Au-Ag [10-13], Au-Pd [14-16], and Au-Pt [17-20], nanostructures have attracted much attention because of their broad range of applications in fields ranging from plasmon driven photocatalysis (enhancing the rates of chemical transformation using light) [20], electrocatalysis [17,18,19], sensing [13,14,15], SERS (surface enhanced Raman scattering) [11] and light harvesting [16]. As Pd have desirable catalytic properties for several reactions, combing Au with Pd can lead to better catalytic activities; under certain conditions it has been demonstrated that the catalytic reaction can be simultaneously followed using SERS.

Here, we show that we can systematically and precisely control the morphology and thickness of this second Pd metal layer. We heat the AuNRs@meso-SiO$_2$ in methanol with HCl resulted in reproducible oxidation of the AuNRs by dissolved O$_2$ specifically at the rod ends, which can precisely control over the aspect ratio of the rods. The etched-AuNRs@meso-SiO$_2$ were used as a template, then the second metal Pd can regrowth on it.

2. Materials and Methods

2.1. Synthesis of Au-metal bimetallic nanorods in meso-SiO$_2$ shell

AuNRs were synthesized using the seed-mediated method as optimized by the group of Murray et al. [22], and coated with a mesoporous layer of silica [23]. For part of the oxidative etching of the AuNRs in a meso-SiO$_2$ shell we used the procedure as described before in our previous work with some small modifications. Briefly, it was carried out by heating the AuNRs@meso-SiO$_2$ aqueous solution (15 mL in methanol) in a 40 mL glass vial in an oil bath to 70 °C. To start the etching process, 0.3 mL HCl was added. The cap of the glass vial was closed to prevent evaporation of HCl. After 8 min, the color of the solution changed from brownish to green-yellow. The oxidation process was monitored by measuring extinction spectra in a 10 mm cuvette. The spectra were measured by taking samples from the etched-AuNRs@meso-SiO$_2$ solutions and mixing them with same volume of methanol to rapidly cool down the temperature. The LSPR peak of the AuNRs@meso-SiO$_2$ before etching was at 829 nm, and had an intensity of 1.74. The etching was stopped by adding large amount of cool methanol and centrifugation at 7000 rpm for 15 min. The precipitate was re-dispersed into 1.1 wt% PVP (K29-32) aqueous solution. Then the solution was centrifuged again and re-dispersed in 1.1 wt% PVP/H$_2$O as a stock solution. The LSPR peak of the etched-AuNRs@meso-SiO$_2$ dispersion was at 740 nm, and had an intensity of 0.76.

For the growth of Au-Pd nanostructures, Na$_2$PdCl$_4$ (0.5 mM, 0.03 mL) was added into the etched-AuNRs@meso-SiO$_2$ solution (0.3 mL), followed by the addition of ascorbic acid (20 mM, 0.03 mL). The mixture was gently shaken for 20 min. To control the morphology, the precursor concentration was changed. The whole experimental parameters can be found in Table 1.

The resulting particles were centrifuged at 8000 rpm for 10 min and re-dispersed in water for further characterization. It must be noted that the overgrowth could be done in water without PVP as well, yielding ligand-free Au-metal nanorods.

2.2. Characterization

Extinction spectra were measured using a vertex 70 FT-IR Spectrometer and 10 mm cuvettes. Transmission electron microscopy (TEM) images were acquired with a Tecnai 12 microscope (FEI) operating at 120 kV. The particle sizes were measured from TEM images, whereby 300-400 particles were measured for each sample. HAADF-STEM and EDX elemental mapping on Au-metal nanorods were performed using a FEI Talos F200X operated at 200 kV, and HRTEM imaging were carried out on a cubed Titan microscope (FEI) with spherical aberration correction operated at 300 kV.
3. Results and Discussion

Figure 1. Control over the Pd overgrowth on AuNRs by changing the Na$_2$PdCl$_4$ concentration. (a) Schematic of Pd overgrowth on etched AuNRs within mesoporous silica shells. The morphology of the Pd shell changed from smooth to rough with increasing Na$_2$PdCl$_4$ concentration; (b) extinction spectra of Au-Pd NRs with Na$_2$PdCl$_4$ concentrations ranging from 0 to 10.0 mM; HAADF-STEM images of Au-Pd rods with Na$_2$PdCl$_4$ concentration of (c) 1.0 mM and (d) 10.0 mM; (e) and (f): EDX mapping (left, Au: red, Pd: green, Si: blue) and HAADF-STEM images (right) of the Au-Pd rods in (c) and (d); HRTEM images of Au-Pd nanostructures showing (g) smooth and (h) rough surfaces after Pd overgrowth. The arrows show the lattice orientation of the Au core. The Pd layers were smooth when the Na$_2$PdCl$_4$ concentration used was lower than 2.0 mM, and became rough when the Na$_2$PdCl$_4$ concentration was higher than 2.0 mM.
Table 1. Reaction conditions for Au-Pd bimetallic nanostructures

| Sample No. | Na$_2$PdCl$_4$ (mM) | Ascorbic acid (mM) | Reaction time (min) |
|------------|---------------------|--------------------|---------------------|
| 01         | 0.03 mL 0.5 mM      | 0.03 mL 2 mM       | 20 min              |
| 02         | 0.03 mL 1 mM        | 0.03 mL 4 mM       | 20 min              |
| 03         | 0.03 mL 2 mM        | 0.03 mL 8 mM       | 20 min              |
| 04         | 0.03 mL 3 mM        | 0.03 mL 12 mM      | 20 min              |
| 05         | 0.03 mL 4 mM        | 0.03 mL 16 mM      | 20 min              |
| 06         | 0.03 mL 5 mM        | 0.03 mL 20 mM      | 20 min              |
| 07         | 0.03 mL 6 mM        | 0.03 mL 24 mM      | 20 min              |
| 08         | 0.03 mL 10 mM       | 0.03 mL 40 mM      | 20 min              |

Because of larger differences in materials properties affecting the overgrowth the morphologies that were achievable for Pd. Figure 1 shows the overgrowth of Pd on etched AuNRs within meso-SiO$_2$ shells. The schematic in Figure 1a shows the effect of the Na$_2$PdCl$_4$ precursor concentration on the final morphology of the Au-Pd NRs that were obtained. With increasing Na$_2$PdCl$_4$ concentration, the Pd shell morphology changed from smooth to rough. Figure 1b presents experimental extinction spectra of Au-Pd NRs for increasing Na$_2$PdCl$_4$ concentrations from 0 mM to 10.0 mM. The LSPR broadened, decreased in intensity and red-shifted after coating the AuNRs with a Pd layer. These effects increased with increasing Pd deposition and can be partially explained by the strong plasmonic damping of Pd compared to Au or Ag.

Two typical samples with a smooth and rough Pd shell are shown in Figures 1c and 1d and their corresponding EDX maps and HRTEM images are displayed in Figures 1e to 1h. In the HRTEM images, the smooth Au-Pd NR looks similar to a single AuNR, while for the rough Au-Pd NR, a few atomic Pd layers can be seen on the AuNR surface, and then Pd nanoparticles were grown, which is most likely due to the large lattice mismatch between Au and Pd. Depending on the precursor concentration, the morphologies of Au-Pd nanorods were quite different. The structure appeared (atomically) smooth when the concentration was less than 2.0 mM, and rough surfaces started to appear at the tips of the NRs when the concentration was larger than 2.0 mM.

4. Conclusions
In conclusion, we have demonstrated a simple and reproducible method to precisely control the composition, morphology, as well as the plasmonic properties of rod-like Au-Pd bimetallic nanostructures by using seeded metal growth onto monodisperse single-crytalline gold nanorod cores which were obtained by etching the Au NR cores inside thin ~ 30 nm thick mesoporous silica shells. The morphology of Au-Pd NRs can be tuned from smooth to dendritic via the precursor concentration or reaction time. The plasmon peak of the Au NR cores broadened after a Pd coating, and the LSPR blue-shifted, stayed unchanged, or red-shifted, depending on the morphology and amount of metal deposited on the AuNR surface. Comparison with the experimental spectra made it likely that even thin shells of Pd that appeared smooth in the TEM images were not continuous. The strong control over the morphology of the rod-like bimetallic nanostructures allows their properties to be optimized strongly in the many fields that make use of their plasmonics response, but also in applications where this is now case like in catalysis. Moreover, the mesoporous silica coated Au-Metal NRs presented in this work can also be used as a starting material to make alloyed NRs as is the subject of follow up work, adding a further dimension in the tunability of their properties.

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