Synthesis and Characterization of Pd-Based Bimetallic Twinned Nanocubes

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Abstract

The generally high cost of noble metals paired with an increase in demand necessitates the maximization of their efficiency in their target applications. This can be accomplished through controlled synthesis of noble metal nanocrystals with well-defined morphologies. For bimetallic nanocrystals, understanding the interactions between two metals is critical for achieving desired structures with optimized properties.

In this work, we use Pd nanoplates as seeds/substrates to investigate their interactions with different metals (Cu, Ag and Au) under various reaction conditions. When a sufficient amount of metal precursor is added to the system, the final morphology of the nanocrystals is determined by the presence of defects on the Pd plate, the use of a capping agent, and the intrinsic metal properties such as lattice mismatch. By reducing the concentration of metal precursor added to the system to a varying degree, the growth behavior of the nanocrystals can be observed, revealing how the interaction between the Pd plates and each metal differs. Using UV-vis spectroscopy and transmission electron microscopy (TEM), we are able to observe the layer by layer growth pattern and the island growth pattern of Ag and Au, respectively, on the Pd plates.

Background

Noble metals are valued for their catalytic and plasmonic properties. This is due to their high specific surface area, therefore, a large number of exposed atoms on their surfaces. As many of these metals are very expensive, maximizing the efficiency of the catalysts is important. This can be achieved through the engineering of their shape and compositions. For bimetallic nanocrystals, understanding the shape evolution process and the bimetallic interaction is of great significance because this knowledge can help people better design catalysts desired for target reactions.

Methods and Results

Palladium nanoplates were formed by reducing Na_2PdCl_4 using poly(vinyl pyrrolidone) (PVP, MW=55,000) and $NH_2OH{\cdot}HCl$ (hydroxylamine hydrochloride). Citric acid (CA) was introduced both as reducing agent and capping agent to stabilize Pd {111} facets. This solution mixture was heated at 100 °C for 3 hours [1]. Figure 1 shows a TEM image of the hexagonal Pd nanoplates.

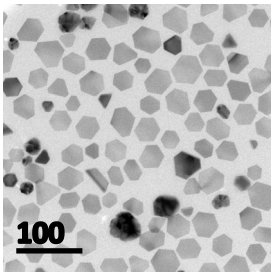
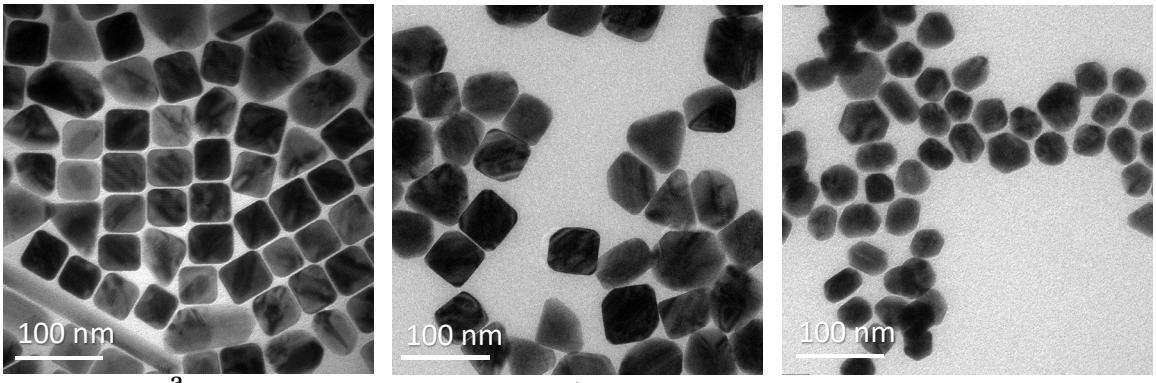


Figure 1. *Pd nanoplates.*

Bimetallic nanocrystals were synthesized by adding additional metal precursor into a solution containing Pd nanoplates as seeds/substrate. When a sufficient amount of the second metal precursor was added to into solution with the seeds, the newly reduced atoms can completely cover the Pd plate seeds and the final crystal morphology of the bimetallic nanocrystals was determined by additional controls, such as the use of a capping agent.

For the purposes of this project, we have successfully employed different capping agents for different second metals introduced on the Pd plates. Here we used hexadecylamine and Cl^- for Cu {100}, PVP for Ag {100} and cetyltrimethylammonium chloride (CTAC) for Au {100}, respectively. The final morphologies of the bimetallic products are shown in Figure 2. From Figure 2, Cu on the surface of the Pd nanoplates yields a relatively high purity of Pd-Cu twin cubes as a final product. When the metal precursor changed from $CuCl_2$ to $AgNO_3$, the products were a mixture of twin cubes and right bipyramids. For the case of Au, only few twin cubes could be resolved under the TEM image, the majority of the products are larger Pd@Au core-shell nanoplates.



a. b. c.

Figure 2 *a) Pd-Cu twin cubes, b) Pd-Ag right bipyramids/twin cubes and c) Pd-Au nanocrystals obtained through seed-mediated growth using Pd plates as seeds.*

In order to understand how the deposition initiated for different second metals on the Pd plate seeds, we decreased the amount of the second metal precursor injected to resolve the bimetallic interactions. This set of experiments was performed for Ag and Au due to their strong characteristic signals in UV-vis spectroscopy, which allows us to quantifiably track the growth of our sample. Figure 3- Figure 6 show the TEM images of these nanocrystals and their corresponding UV-vis spectra.

From Figure 3, when the concentration of $AgNO_3$ was 0.005 mM, only very small amount of Ag deposition can be seen on the surface of the Pd plate due to the difference in contrast. When the concentration of the Ag precursor increased to 0.05 mM, the Ag coverage were extended to entire surface of the plate and vertical growth was observed as shown with a side view of a plate. At a concentration of 0.5 mM, the plate was entirely covered by silver precursor and cubic shapes developed due to the presence of PVP as Ag{100} capping agent. Because deposition was uniform and thin at the very beginning, this growth behavior was grouped as layer by layer growth.

Figure 4 gives the UV-vis spectra of each of these samples. Samples with 0.005 Mm and 0.5 mM $AgNO_3$ were too dilute so that no notable peaks were detected after the samples were washed to removed impurities, though a visible color difference could be detected before washing.

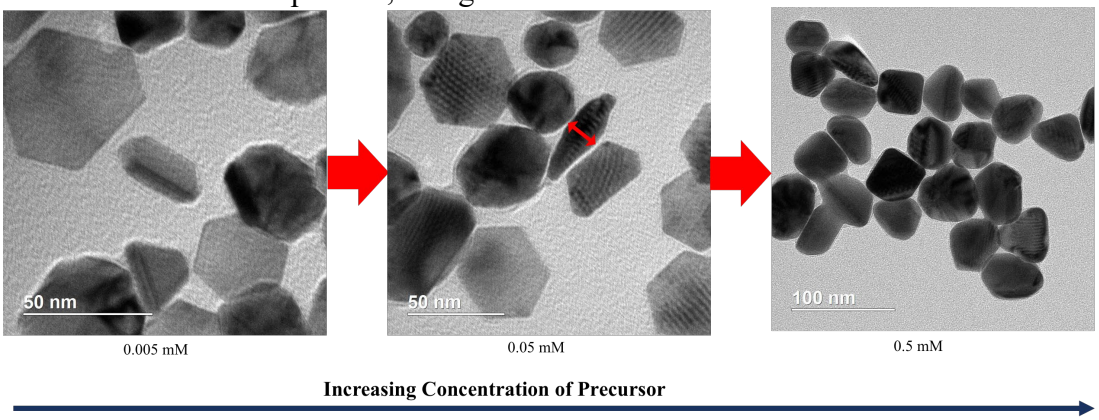


Figure 3 *Growth of Ag on Pd nanoplates.*

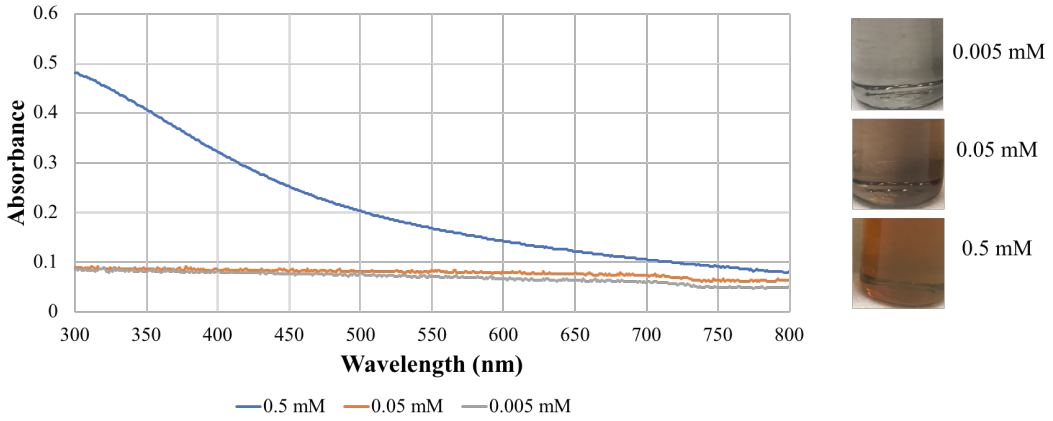


Figure 4 *UV-vis spectrum for Pd-Ag nanoplates with different concentration of $AgNO_3$ in the solution. The right panel shows the color of the solution after reaction before washing to remove impurities.*

Figure 5 shows results from a similar experiment using $HAuCl_4 \cdot 3H_2O$ as a second metal precursor. At a concentration of 0.005 mM of Au precursor, a few small pockets of deposition can be seen on the plate surfaces. As the concentration increased to 0.05 mM, these pockets of deposition have grown larger, more defined, and more numerous. At a concentration of 0.5 mM, these pockets have coalesced to form a total coverage of the plate surface. This can be considered characteristic of an island growth mode.

In addition, in Figure 6, there is observable shift in peak positions in the UV-vis spectra for these samples. The peak shifts from 570 nm at a precursor concentration of 0.005 mM to 530 nm at a concentration of 0.5 mM. This allows us to use a facile technique to the quantify the growth of our samples.

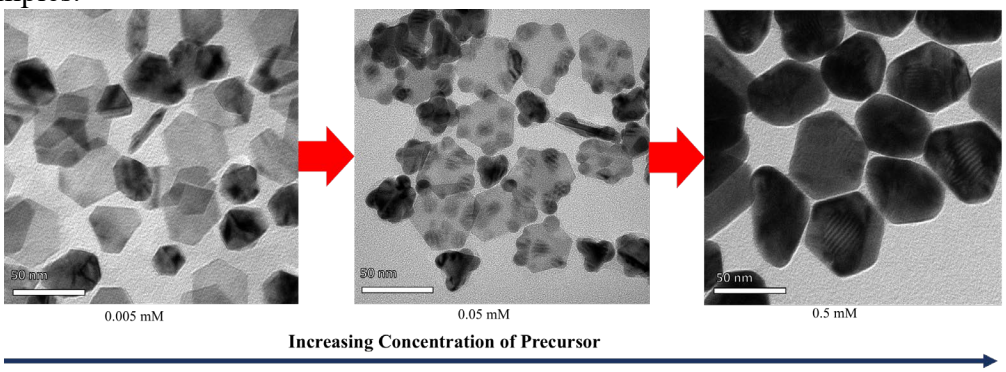


Figure 5 *Growth of Au on Pd nanoplates.*

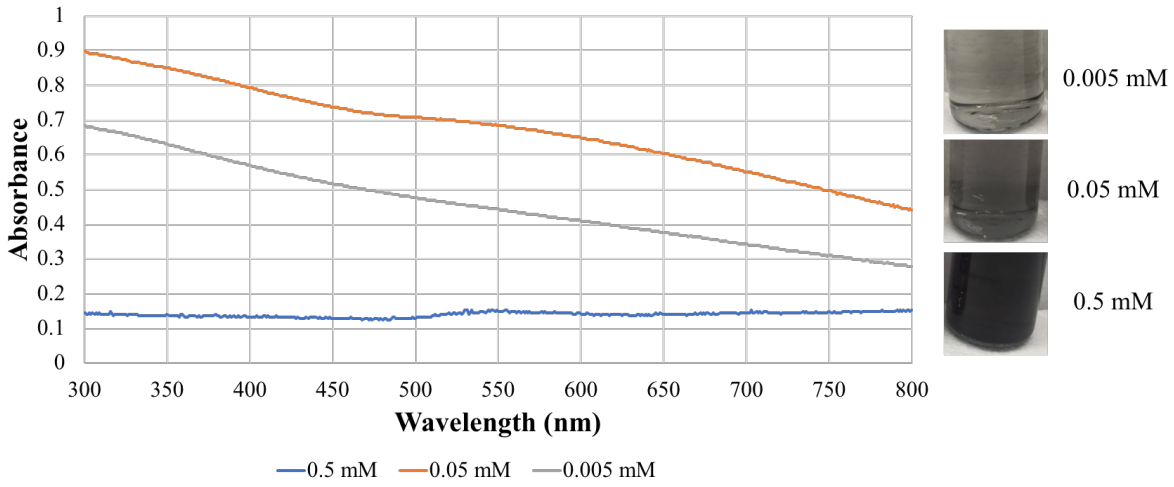


Figure 6 *UV-vis spectrum for Pd-Ag nanoplates with different concentration of $AgNO_3$ in the solution. The right panel shows the color of the solution after reaction before washing to remove impurities.*

Future Research

In the future, growth mode analysis using larger plates will be performed. This will allow us to better image the deposition of metal precursor on the plate surface. In addition, other metals can also be tested.

References

[1] L. Figueroa-Cosme, Z. D. Hood, K. D. Gilroy, Y. Xia, J. Mater. Chem. C 2018, 6, 4677.

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