

# Bimetallic Nanocrystals and Their Optical Properties

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## Abstract and Introduction:

Silver nanocubes exhibit an excellent property known as localized surface plasmon resonance (LSPR) which depends heavily on the composition, size, and geometry of the nanoparticles. LSPR is useful in applications such as surface enhanced Raman scattering (SERS), making silver nanocubes an ideal material for SERS. Although silver nanocubes favor SER, it shows limited catalytic activity towards chemical reactions.

The objective of this project is to improve the catalytic behavior of silver (Ag) nanocubes, but still retain its SERS properties. This can be done by depositing a known catalyst, in this case palladium (Pd), onto the cube in order to create a Ag-Pd bimetallic nanostructure through a widely known process called galvanic replacement reaction. Galvanic replacement reaction destroys the SERS property because one Pd atom deposits onto the cube at the expense of two Ag atoms [1]. In order to combat this, galvanic is done in the presence of reducing agents that will reduce Ag<sup>+</sup> back to Ag atoms to be co-deposited alongside with the palladium which will help in retaining the SERS property.

Through etching the Ag-Pd bimetallic structures with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), Ag-Pd hollow nanoboxes can be created. These hollow nanostructures are more stable than Ag nanocubes, making them more ideal for SERS. The enlarged surface area should also be beneficial to their catalytic activities.

## Experimental Procedure:

The way in which the Ag-Pd bimetallic nanostructure was generated was through galvanic replacement reaction alongside reducing agents, NaOH and ascorbic acid (AA). The palladium precursor, disodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>), was titrated at a rate of 0.02 mL/min into a 20 mL vial that contained 1 mM of 29K polyvinyl pyrrolidone (PVP), which acted as a capping agent, NaOH, ascorbic acid, and silver nanocubes, Figure 1. The amount of NaOH introduced into the solution assisted in tuning the pH of the solution.

Once different volumes of the palladium precursor has been titrated into the mixture a ultraviolet-visible (UV-Vis) spectrum was collected to monitor the change in morphology over time, then the samples were washed three times before being prepared for TEM imaging.

## Results and Discussion:

Experiments were conducted under basic and acidic conditions as well as a control experiment in which no NaOH was added to the solution. In the control experiment, the UV-Vis showed a significant shift indicating that the morphology of the cubes were changing and galvanic was taking place, Figure 1A. After taking TEM images, Figure 2, holes in the cubes were observed which also confirmed that galvanic replacement reaction did in fact take place, and a layer of palladium is present.

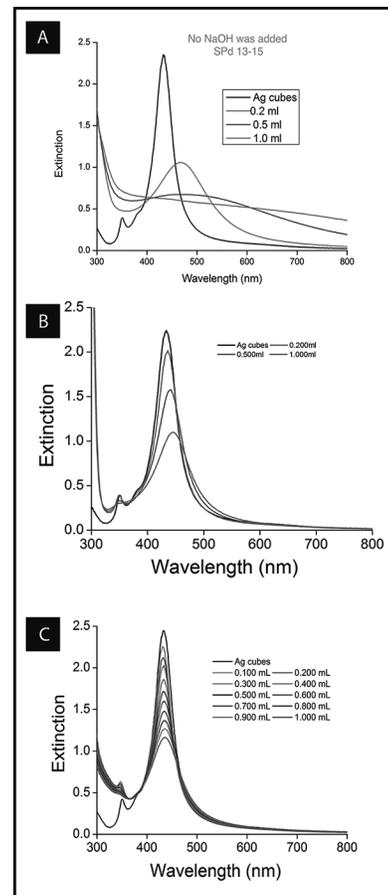


Figure 1: UV-Vis spectra of (A) the control experiment in which no NaOH was added, (B) experiment done under acidic conditions in which 200  $\mu$ L of 200 mM NaOH and 0.5 mL of 100 mM ascorbic acid were used, and (C) experiment done under basic conditions in which 90  $\mu$ L of 200 mM NaOH and 0.5 mL of 100 mM ascorbic acid were used. (See full color version on page xxxvi.)

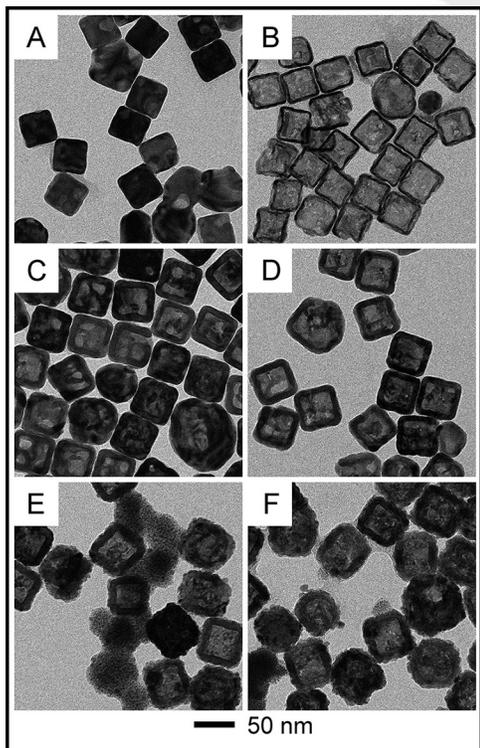


Figure 2: TEM image of control experiment where no reducing agent was added. A, C, and E are images before etching; and B, D, and F are images taken after etching with an excess amount of  $H_2O_2$  solution.

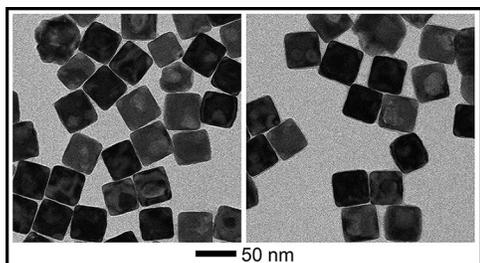


Figure 3: TEM image of sample when 200  $\mu$ L of NaOH and 0.5 mL of 100 mM AA are used.

The experiment was also ran under acidic conditions with a pH of 4.83. In these samples 200  $\mu$ L of 200 mM NaOH and 0.5 mL of 100 mM AA were used to tune the pH. The UV-Vis showed a shift that is characteristic of galvanic, but the shift was not as severe as in the control experiment in which no NaOH was present (see Figure 1B). The TEM images, Figure 3, showed slight holes in the cube, but in comparison with the control these holes were not as intense.

Lastly, under basic conditions with a pH of 10.86, it was noted that the UV-Vis did not have much of a shift indicating the inhibition of galvanic, Figure 1C. After taking TEM images, Figure 4, it was confirmed that the cube somewhat retained their shape, but after etching the sample with a 3% solution of  $H_2O_2$  in order to test the quality of the cubes it was shown that the cubes were unstable, and little to no cubes were left afterwards.

The occurrence of self-nucleation was observed in Figure 1, image E. This was due to the high amount of  $Na_2PdCl_4$  that was being injecting into the solution. Some of the precursor began to form clusters instead of depositing onto the cube which is something that negatively impacted the experiment.

### Future Work:

These preliminary results can assist in furthering the study of the creation of Ag/Pd bimetallic nanostructure that possesses both excellent SERS and catalytic properties. In the future, the conditions could continue to be manipulated to determine if it is indeed possible to create these stable structures that can last under  $H_2O_2$  etching.

### Acknowledgements:

I would like to thank Dr. Dong Qin and my mentor Yin Yang for the opportunity of working in the Qin Lab this summer, Georgia Tech NNIN REU site coordinator Leslie O'Neill, as well as Joyce Allen and Dr. Nancy Healy. I would also like to thank the NSF and NNIN REU Program for their support.

### References:

- [1] "Galvanic replacement-free deposition of Au on Ag for core-shell nanocubes with enhanced chemical stability and SERS activity," Y. Yang, J. Liu, Z. Fu, and D. Qin; JACS, 136, 8153-8156, (2014).

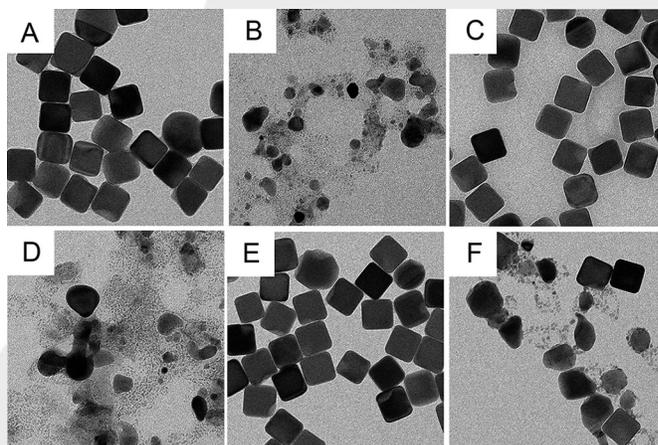


Figure 4: TEM image of product when 90  $\mu$ L of NaOH and 0.5 mL of 10 mM AA is used. A, C, and E are images before etching; and B, D, and F are images taken after etching with an excess amount of  $H_2O_2$  solution.