

Synthesis and Galvanic Replacement Reaction of Silver Nanocubes in Organic Medium

Kaylie Young
Chemistry, Brown University

NNIN REU Site: Center for Nanotechnology, University of Washington

NNIN REU Principal Investigator: Younan Xia, Department of Chemistry, University of Washington

NNIN REU Mentor: Xianmao Lu, Department of Chemistry, University of Washington

Contact: Kaylie_Young@brown.edu, xia@chem.washington.edu

Abstract:

Silver nanocubes 30-50 nm in diameter have been synthesized using a polyol process in which silver nitrate is reduced by ethylene glycol in the presence of a capping agent, poly(vinylpyrrolidone) (PVP). A ligand exchange reaction was used to replace the PVP with another capping agent, allowing the nanocubes to be soluble in chloroform. Oleylamine, oleic acid, and decane-thiol were among the ligands investigated. The silver cubes were then used as sacrificial templates to generate hollow gold nanocages using a galvanic replacement reaction during which the silver cubes were titrated with chloroauric acid. The use of different capping agents allows us to further understand the role of the ligand in the galvanic replacement reaction.

Introduction:

The properties and applications of metallic nanostructures are mainly determined by their size, shape, composition, crystallinity, and structure (solid versus hollow). Optical properties of nanomaterials are of importance for the detection and treatment of cancer, particularly a phenomenon known as surface plasmon resonance (SPR), which refers to the characteristic wavelength at which free electrons in a nanomaterial collectively oscillate and scatter/absorb an incident electromagnetic wave [1].

The ability to tune the SPR of gold nanocages, which are hollow nanostructures with porous walls, into the infrared region promises uses as both contrast agents for optical imaging in early stage tumor detection and as therapeutic agents for photothermal cancer treatment [2].

The Xia group developed a process to synthesize gold nanocages with smaller dimensions than previously reported using a galvanic replacement reaction between silver templates and chloroauric acid [3]. This galvanic replacement reaction had previously been done in aqueous conditions with polyvinylpyrrolidone (PVP). Here we extended the replacement reaction to an organic

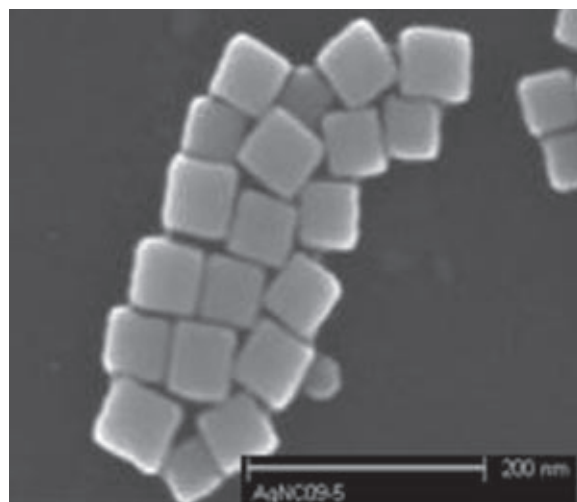


Figure 1: SEM of silver nanocubes.

medium, chloroform, for Ag nanocubes passivated with various capping ligands.

Experimental Procedures:

Silver cube synthesis: Silver nanocubes were prepared using the polyol process, during which ethylene glycol serves as both the reducing agent and the solvent. After heating ethylene glycol in a vial in an oil bath for one hour, the silver precursor, the capping ligand (PVP), and an etching agent were added. The reaction was stopped when the solution turned a grayish-silver color and appeared to be opalescent, which took about 15-25 minutes. The vial was submerged in cold water and the samples were washed once with acetone and twice with water to remove the excess PVP and ethylene glycol. The resulting silver nanocubes are shown in Figure 1.

Ligand exchange reaction: Before the ligand exchange reaction was performed, a small amount of PVP was added to the silver nanocubes to ensure their stability in chloroform. The silver cubes were then transferred from water into chloroform by evaporating off the water using a vacuum chamber and adding chloroform. The desired ligand was added in excess and the solution was briefly stirred and then allowed to sit for one hour.

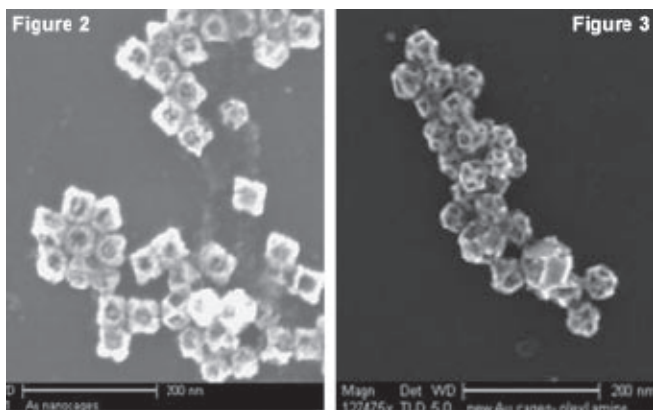


Figure 2:
SEM of gold nanocages with
{100} faces etched.

Figure 3:
SEM of gold nanocages with
{111} faces etched.

Galvanic replacement reaction: A dilute solution of chloroauric acid (HAuCl_4) in chloroform was added slowly to the newly-capped silver nanocubes using a syringe pump. The reaction, which was done at an elevated temperature, proceeded through a number of color changes and was stopped at a grayish color. The resulting gold nanocages, shown in Figures 2 and 3, were washed with ethanol and stored in chloroform.

Results and Conclusions:

A galvanic replacement reaction has been demonstrated as a means for preparing gold nanocages using silver nanocubes as sacrificial templates. Since the standard reduction potential of $\text{AuCl}_4^-/\text{Au}$ (0.99 V vs standard hydrogen electrode, SHE) is larger than that of Ag^+/Ag (0.80 V vs SHE), silver is oxidized to Ag^+ when gold ions (HAuCl_4) are added to the silver nanocubes [3]. The SPR peak was significantly shifted toward the infrared region for the gold nanocages versus the silver nanocubes. This is evident in the absorption spectra of the nanocubes and nanocages in Figure 4.

The morphology of the resulting gold nanocages was found to depend strongly on the capping ligand of the silver nanocubes used in the galvanic replacement reaction. The capping agent oleylamine gave the best nanocages with the highest yield. PVP-capped silver nanocubes resulted in some gold nanocages, although they were often found in large clumps and in low yields. In the cases of oleic acid and 1-decane thiol, no nanocages were formed. The thiol was thought to have bound so strongly to the silver nanocubes that it prevented the galvanic replacement reaction from occurring, leaving

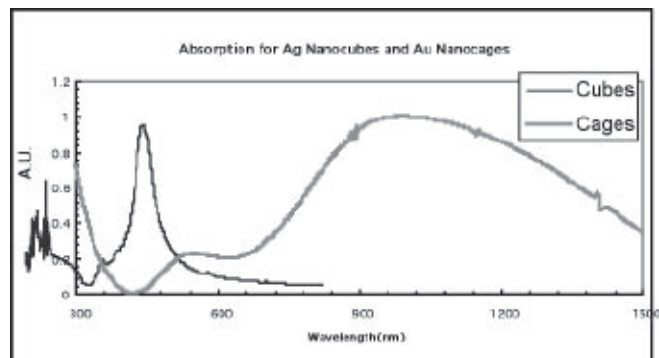


Figure 4: Absorption of silver nanocubes and gold nanocages.

the silver nanocubes as they were before the reaction. The oleic acid was thought to have strongly etched the silver nanocubes before the galvanic replacement reaction took place, resulting in tiny spheres and amorphous clumps. Neither nanocubes nor nanocages were visible after the galvanic replacement reaction.

Interestingly some batches of nanocages formed with oleylamine had the {100} faces of the cube etched while other batches had the {111} faces etched. This is illustrated by Figures 2 and 3. The difference between the batches was the amount of time that passed between the ligand exchange reaction and the galvanic replacement reaction. This suggests possible control over the face of the nanocube that etches. The possibility of selective etching of nanocubes needs to be further investigated in future work.

Acknowledgements:

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References:

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