Engineering the Optical Properties of Gold Nanocages for Biomedical Applications

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***Abstract* - The galvanic replacement reaction has been shown to be a robust method to produce a wide variety of nanostructures with complex shapes and compositions. This reaction is highly tunable, allowing for precise control of the properties of the final material. Gold nanocages, one exciting structure made with the galvanic replacement reaction, are particularly interesting for their use in biological applications such as photothermal therapy and contrast enhancement in optical imaging.**

I. Introduction

Metal nanostructures have been the focus of extensive research in recent years due to the fascinating connections between their structures and properties and the potential to harness these properties for numerous applications including biomedical imaging, trace detection of biomarkers, catalysis, and drug delivery [1, 2]. Of the many synthetic techniques that have been developed, galvanic replacement is particularly interesting due to its ability to be easily tuned and the chance to study the intricacies of alloying and dealloying in nanostructures. The galvanic replacement method relies on a remarkably simple reaction to create highly complex systems. When a metal salt is in the presence of a metal of a lower electrochemical potential, the electrons from the solid metal will be spontaneously transferred to the dissolved metal, forcing dissolution of the template and reduction/deposition of the metal salt, creating a new nanostructure. This process is depicted in Figure 1 for the reaction between silver nanocubes and chloroauric acid, creating gold nanocages [3].

II. Discussion

A. Effect of Shape and Morphology

The most important factor in controlling the morphology of the final structure in a galvanic replacement reaction is the shape/morphology of the template [4]. As the newly formed metal atoms will deposit on the surface of the template, the final structure is closely related to the original template. In a typical galvanic replacement reaction the final structure is a hollow shell of the same shape and of similar size to the template.

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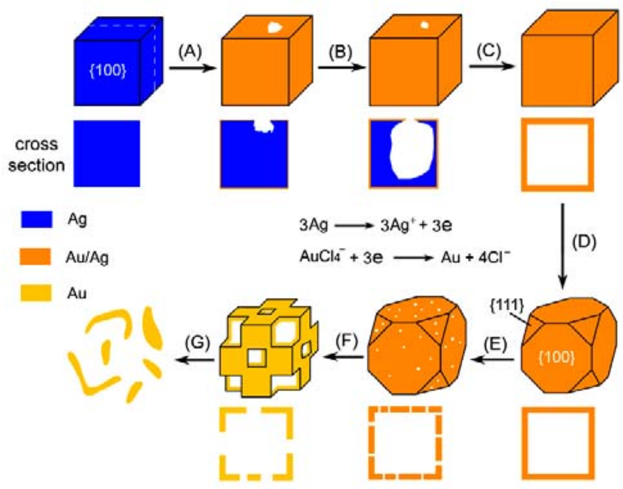

Fig. 1. Schematic showing the galvanic replacement reaction between silver nanocubes and chloroauric acid to form gold nanocages. The solid silver interior is gradually dissolved away while gold is plated on the surface, forming a gold-silver alloy. After all the pure silver is dissolved, silver atoms are selectively removed from the gold-silver alloy, forming pores in the walls [3].

Yet as with many areas, the most interesting observations come from the exceptions. It has been shown, for example, that the susceptibility of different facets of fcc crystals to a galvanic reaction can vary due to differences in coverage by a polymer capping agent [5]. This allows for the synthesis of structures with controlled pores on selected facets, an important property for drug delivery vessels. The size and shape of nanostructures can also play unexpected roles. One such example is the galvanic replacement reaction between palladium rods and chloroauric acid. Instead of the anticipated shell uniformly surrounding the rod, the gold is instead found primarily in a ball at one tip. The rod-shape of the template is thought to cause this unusual tadpole-like shape as electrons repel, forcing deposition to be more favorable at the tips [6]. By adjusting the templates, complex structures such as multi-walled tubes and rattles can also be produced.

B. Alloying and Dealloying

The alloying and dealloying processes involved in galvanic replacement reactions also have a strong effect on the structure and properties of the final products. For example, when multiple metal precursors are added during a single reaction, the order of addition is found to be critical in determining the optical, morphological, and catalytic properties of the final material. This difference can be explained by the different abilities of the two metal precursors in the dealloying phase of the reaction, where one type of metal is selectively removed from the combined structure. By understanding how different metals interact in the nanoscale, we will be better able to engineer their properties for catalytic applications.

The choice of precursor also has an effect on the evolution of the galvanic replacement reaction. When gold (I) chloride is substituted for gold (III) chloride in the galvanic replacement of silver cubes, the morphology of the final product changes and frame-like structures can be produced [7].

C. Applications

Finally, there are many promising applications using structures created through the galvanic replacement method. Because of the tunability of this reaction, the optical absorption due to surface plasmon resonance can be shifted into the near-infrared region, where absorption from biological tissues is low. This property has been exploited in the production of gold nanocages (hollow, porous boxes of gold created from silver cube templates) to enhance the contrast in biomedical optical imaging and in photothermal therapy investigations [2, 8]. Figure 2A and B shows a circular region of cell death after SK-BR-3 breast cancer cells were incubated with gold nanocages and then exposed to a laser. Green indicates live cells and red indicates dead cells. Figure 2C and D shows a control experiment with no nanocages, showing that the strong optical absorption and consequent heat generation from the nanocages is responsible for the selective destruction of cancer cells. In addition to biomedical applications, alloyed materials also show great promise for catalysis - it has been shown that alloyed materials are superior to any of their individual components for certain catalytic applications. Galvanic replacement is a simple and controllable way to create alloys, and is thus well-suited for such applications.

III. Conclusion

Galvanic replacement reactions are a robust way to engineer highly tunable nanostructures for a variety of applications. A number of templates have been used for this reaction and the structure (shape, size, defects, etc) has interesting effects on the ultimate product, beyond serving as a simple site for deposition. We can manipulate the processes of alloying and dealloying to produce interesting structures and precursor choice has a strong effect on the final properties. Gold nanocages made through a galvanic replacement reaction between chloroauric acid and silver nanocubes show great promise for biomedical applications, and the bimetallic structures are potentially interesting for their catalytic abilities.

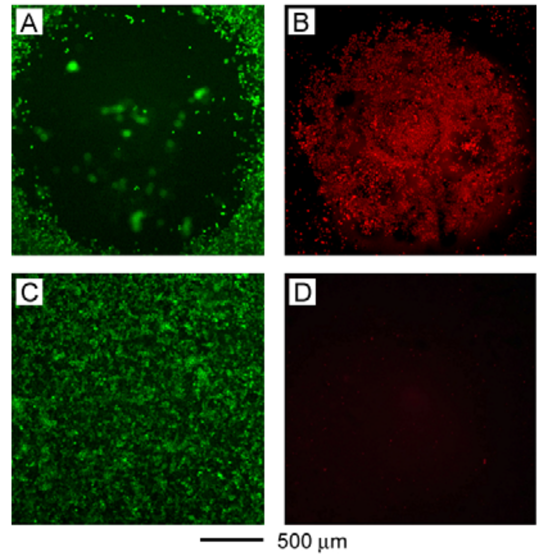

Fig. 2. SK-BR-3 cells after illumination with an 810 nm laser for 5 min with a power density of 1.5 W/cm^2. Cells in (A) and (B) were incubated with immuno gold nanocages prior to laser treatment while those in (C) and (D) were not. (A, C) Calcein AM assay, where green indicates live cells. (B, D) ethidium homodimer 1 assay, where red indicates cells with irreversibly damaged membranes (dead cells). A circular region of damaged cells is clearly visible for the cells incubated with immuno gold nanocages, while no such region is visible in the control experiment [8].

Acknowledgment

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References

[1] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, "One-Dimensional Nanostructures: Synthesis, Characterization, and Applications," *Adv. Mater*., vol. 15 pp. 353-389, 2003

[2] S. E. Skrabalak, J. Chen, Y. Sun, X. Lu, L. Au, C. M. Cobley, Y. Xia, "Gold nanocages: synthesis, properties, and applications," *Acc. Chem. Res*., vol. 41, pp. 1587-1595, 2008

[3] Y. Sun and Y. Xia, "Mechanistic study on the replacement reaction between silver nanostructures and chloroauric acid in aqueous medium," *J. Am. Chem. Soc*. vol. 126, pp. 3892-3901, 2004

[4] X. Lu, J. Chen, S. E. Skrabalak, Y. Xia, "Galvanic replacement reaction: a simple and powerful route to hollow and porous metal nanostructures," *Proceedings of the Institution of Mechanical Engineers, Part N: Journal of Nanoengineering and Nanosystems* vol. 221 pp. 1-16, 2008

[5] J. Chen, J. M. McLellan, A. Siekkinen, Y. Xiong, Z.-Y. Li, Y. Xia, "Facile synthesis of gold-silver nanocages with controllable pores on the surface," *J. Am. Chem. Soc*. vol. 128, pp. 14776-14777, 2006

[6] P. H. C. Camargo, Y. Xiong, L. Ji, J. M. Zuo, Y. Xia, "Facile synthesis of tadpole-like nanostructures consisting of Au heads and Pd tails," *J. Am. Chem. Soc*. vol. 129, pp. 15452-15453, 2007

[7] L. Au, X. Lu, Y. Xia, "A Comparative Study of Galvanic Replacement Reactions Involving Ag Nanocubes and AuCl2 or AuCl4," *Adv. Mater*. vol. 20, pp. 2517-2522, 2008

[8] J. Chen, D. Wang, J. Xi, L. Au, A. Siekkinen, A. Warsen, Z.-Y. Li, H. Zhang, Y. Xia, X, Li, "Immuno gold nanocages with tailored optical properties for targeted photothermal destruction of cancer cells," *Nano Lett.* vol. 7, pp. 1318-1322, 2007