

Structure and composition-tunable Au-Ag bimetallic nanoparticle synthesis from plasma-driven solution electrochemistry

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Abstract: Plasma-driven solution electrochemistry (PDSE) offers a sustainable and efficient method for synthesizing bimetallic nanoparticles without reducing agents, surfactants, or stabilizers. This study explores the synthesis of Au-Ag bimetallic nanoparticles with tunable core structures by manipulating reduction kinetics with adjusting solution pH and plasma pulse width. We show that this allows to control the composition of bimetallic nanoparticles.

1. Introduction

PDSE has been a promising tool for nanomaterial synthesis due to its capability to bypass the usage of reducing agent, surfactant, and stabilizer. The unique characteristic of PDSE is that the nucleation and continuous growth timescales are much faster than the discontinuous growth such as coalescence, which is even rare due to the stabilizing environment of PDSE [1]. Hence, the particle size is largely determined by the rate of nucleation [2].

Here we show that we can tune Au-Ag bimetallic nanoparticle structure synthesized by PDSE by controlling the relative rate of reduction between Au and Ag precursors, leading to the preceding nucleation of one element to another. We also control the elemental composition of Au-Ag by making an Ag-selective oxidizing environment.

2. Methods

A pulsed-discharge plasma jet treats AgF and HAuCl₄ loaded precursor with helium as a working gas. The solution pH is changed from 3 to 10 by adding NaOH for the structure-tuning experiments. For composition control, pulse width is adjusted from 1 to 50 μ s while keeping electron fluence constant. UV-Vis absorption spectroscopy measures AuCl₄⁻ ion concentration and nanoparticle absorbance spectra. Size and elemental composition are analyzed using scanning electron transmission microscopy (STEM) and energy dispersive X-ray spectroscopy (EDX)

3. Results and Discussion

Figure 1 shows the EDX-mapped images of Au-Ag bimetallic nanoparticles synthesized from different pH environments. The Au-cored nanoparticle is synthesized at pH 3 and Ag-cored nanoparticle at pH 10. The gold complex ions have different forms depending on pH expressed by AuCl_x(OH)_{4-x}, where x is close to 4 in acidic and close to 0 in basic environments. While the reduction potential of Ag⁺ remains constant (~ 0.8 V) regardless of pH, the reduction potentials of AuCl_x(OH)_{4-x} varies from 1 (x=4) to ~ 0.6 (x=0). Therefore, in acidic solution, gold ions are reduced faster than silver ions and form nuclei on which slower reducing silver ions adsorb to. This process becomes opposite at high pH. Contrary to the conventional wet-chemical methods, the control of core element of Ag-Au by adjusting pH is feasible for PDSE, likely due to the suppressed coalescence which can homogeneously re-

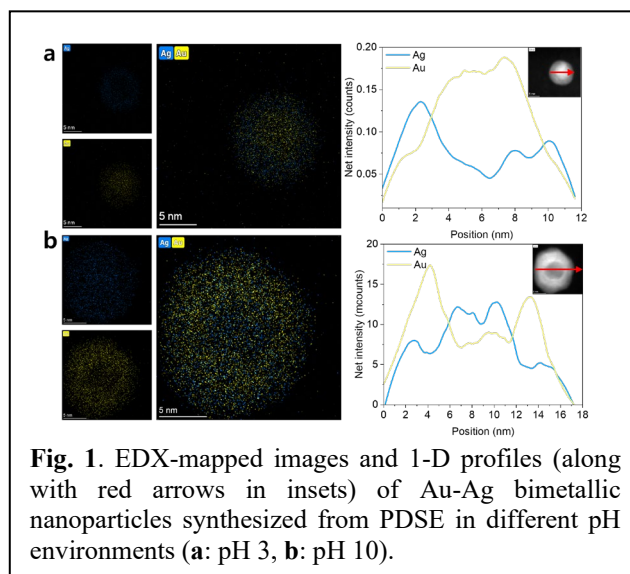


Fig. 1. EDX-mapped images and 1-D profiles (along with red arrows in insets) of Au-Ag bimetallic nanoparticles synthesized from PDSE in different pH environments (**a:** pH 3, **b:** pH 10).

arrange the structure in conventional wet-chemical methods.

In addition to results shown in this abstract, we control the elemental composition of nanoparticles by silver back-oxidation induced by reducing pulse widths for which oxidation behavior becomes more dominant over reduction during the plasma off time.

4. Conclusion

This study demonstrates the ability to tune the structure and elemental composition of Au-Ag bimetallic nanoparticles. Acidic environments favor the formation of Au-cored nanoparticles, while basic conditions lead to Ag-cored structures due to differences in reduction potentials of Au and Ag precursors. Additionally, reducing the plasma pulse width creates an oxidizing environment that enables control of silver content via back-oxidation. These findings highlight the potential of PDSE as a powerful tool for fabricating bimetallic nanoparticles.

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References

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