Effects of Anions on Oxidation of Au-Ag Core-Shell Nanorods

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1. Introduction

Anisotropic metal nanoparticles have been an attractive research target because of their remarkable spectroscopic properties. We have reported Au-Ag core-shell nanorods of which spectroscopic properties corresponded to those of anisotropic silver nanoparticles [1,2]. Our core-shell nanorods are chemically unstable in the absence of reducing agent. Oxidation of the silver shells gradually proceeded in an aqueous solution and accompanied by changes in their shapes. The shape changes resulted in spectroscopic changes.

In order to allow quantitative evaluation of the shape changes, a constant potential electrolysis, to oxidize the silver shells, coupled with high resolution SEM analysis is herein performed. Oxidation processes of the silver shells in a KCl solution are discussed. Well-controlled oxidation of silver shells is a potential way to give a new class of anisotropic core-shell nanoparticles.

2. Experimental

The anionic poly(styrene sulfonate)-wrapped Au–Ag core–shell nanorods were deposited on an ITO plate which treated with 3-aminopropyltrimethoxysilane, through electrostatic interaction [2,3]. The nanorod-deposited ITO plate (working electrode) was immersed in a KCl solution (0.1 M). Extinction spectral changes during electrolysis, conducted at a constant potential, were monitored using a multichannel spectrophotometer (MCPD-7700, Otsuka, Japan). A potentiostat (HZ-5000, Hokuto, Japan) was used to control the potential. A saturated calomel electrode (SCE) was used as a reference electrode. A scanning electron microscope (JSM-6701F, JEOL) was used to analyze the morphology and to evaluate the size distribution of the deposited nanorods.

3. Results and Discussion

Figure 1 shows the results of the electrolysis in a KCl solution, performed at 0.15 V vs. SCE. Oxidation of the silver shells was observed in the KCl solution. During electrolysis, the peak corresponding to the longitudinal SP band shifted to the shorter wavelength region (Figure 1A). After 10 s of the electrolysis, the longitudinal SP band at 540 nm disappeared, and only the peak at 420 nm remained. This shift indicated a decrease in the aspect ratios of the core–shell nanorods. In a SEM image, oval nanoparticles and thin gold nanorods were observed. In the presence of 0.1 M KCl, silver ions form water-soluble dichloride complexes (AgCl₂⁻) which diffuse in the bulk solution, leaving

core gold nanorods behind.

Figure 1B shows size distribution of the core-shell nanorods at 10 s after electrolysis in the KCl solution. A bimodal size distribution is found in Figure 1B. The smaller portion is associated with the gold nanorods, while the larger group corresponds to the core-shell nanorods. The distribution indicates that the core-shell nanorods remain anisotropic shapes even after the 10 s electrolysis. It should be noted that there are a few spherical particles that are plotted on the line indicating the aspect ratio is one. This indicated that oxidation of silver shells occurred at the corners of the silver shells.



Figure 1. (A) Extinction spectral changes observed in the deposited core–shell nanorods under an applied constant potential (0.15 V vs. SCE) in the KCl solution (0.1 M). (B) size distribution of the deposited core–shell nanorods after a 10 s electrolysis. The scale bar indicates the frequencies of nanoparticles.

4. Conclusions

The spectral changes and the high resolution SEM imaging were used to monitor the shape changes during the electrochemical oxidation of silver shells in Au–Ag core–shell nanorods deposited on an ITO plate. Oxidation of the silver shells proceeds at the corners of the core–shell nanorods in a KCl solution [4].

References

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