Multiple Surface Plasmon Modes for Gold/Silver Alloy Nanorods

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Alloy nanorods consisting of bimetallic gold and silver are synthesized by employing the electrochemical codeposition of Au/Ag alloy materials into the pores of anodized aluminum oxide templates. This paper presents the variation of localized surface plasmon resonance (LSPR) modes of the Au$_x$/Ag$_{1-x}$ alloy nanorods as a function of relative compositions of Au and Ag. Transverse and multiple longitudinal modes were observed when the length was longer than ca. 300 nm. For a given length, the transverse LSPR mode systematically blue-shifted as the Ag portion increased, while there was little variation in peak positions of the longitudinal LSPR modes. The optical properties of the Au$_x$/Ag$_{1-x}$ alloy nanorods were calculated using the discrete dipole approximation and showed a good agreement with the experimental measurements.

1. Introduction

Noble metal nanoparticles and their optical properties originating from localized surface plasmon resonance (LSPR) absorption constitute many ongoing studies, especially on their controlled synthesis and photonic applications.1–4 LSPRs are essentially light waves that are trapped on the surface due to the interaction with the free electrons of the metal. The free electrons oscillate in a collective fashion when the light wave meets the resonance conditions.5,6 The LSPR modes depend on the physical dimensions of the nanoparticles, dielectric constant of the surrounding medium, and compositions.5–8 Among them, the control of shape has been regarded as a key factor in order to tailor the optical properties of nanoparticles. Isotropic nanostructures with a spherical shape have attracted a lot of interest due to their relatively simple optical characteristics compared to anisotropic nanoparticles. Now, one can readily synthesize other anisotropic nanostructures such as nanorods (NRs) and nanoprisms. Because NRs have an anisotropic shape, they support more complicated LSPR modes than spherical nanoparticles.13,14 The noticeable feature with higher-order LSPR modes is that quadrupole resonances are known to extend to longer wavelength with increasing aspect ratio but with a shallower slope (for peak position versus aspect ratios) than dipole resonances.3,11,13 While most studies have focused on single-composition noble metal nanoparticles, there are a few on alloy nanoparticles that investigate how variations in the relative composition affect the optical properties. For example, El-Sayed et al. prepared spherical Au/Ag alloy nanoparticles and showed that the maximum of the LSPR mode blue-shifts linearly with increasing Ag content.15 Later, this group extended their theoretical work to NRs to investigate the optical spectra of Au/Ag alloy metal NRs as a function of Ag concentrations.16 It was found that the aspect ratio plays a key role in the sensitivity of plasmon response to variations in the medium dielectric constant. Very recently, Evans et al. reported the optical properties of a vertical array of Au/Ag alloy NRs as a function of incident light angles and relative compositions.17 As observed in the previous optical studies with spherical nanoparticles, they found the linear dependence of transverse LSPR mode on Ag content.

Herein, we report the first experimental observation of multipole LSPR modes for colloidal, Au$_x$/Ag$_{1-x}$ alloy NRs with various compositions of Au and Ag. The optical properties vary as a function of length as well as Au$_x$/Ag$_{1-x}$ compositions. When compared to the analogous single-component Au NRs, the transverse LSPR mode of Au$_x$/Ag$_{1-x}$ NRs consistently blue-shifted as the Ag component became dominant, while the longitudinal modes were much less sensitive to composition variation for a given length.

2. Experimental Section

AAO Fabrication. An AAO template with diameter of 81 (±5) nm was prepared by using a two-step anodization process.9,11,12,18 Aluminum served as the anode while graphite

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served as the cathode in the two-electrode electrochemical cell. A high-purity (99.999%) thin aluminum sheet (from Goodfellow Cambridge Limited) was electropolished in a mixture of ethanol (Sigma-Aldrich) and perchloric acid (Samchun Chemical) (7:3, v/v) at +20 V for 5 min, creating a smooth aluminum surface. The shiny aluminum was anodized in 0.3 M oxalic acid (Sigma-Aldrich) at 40 V and 0 °C for 12 h. The alumina layer was removed in a mixture of chromic acid (Sigma-Aldrich) (1.8 wt %) and phosphoric acid (Samchun Chemical) (6 wt %) at 60 °C for 12 h. A second anodization step followed in 0.3 M oxalic acid at 40 V and 0 °C for 24 h to grow ordered porous alumina. The remaining aluminum was next removed by immersing in a saturated HgCl₂ (Samchun Chemical) aqueous solution for 6 h. These AAO templates were immersed in phosphoric acid solution (8.5 wt %) for 30 min for pore widening.

**Au/Ag Alloy NRs Synthesis.** The Au/Ag alloy NRs were synthesized by using the electrochemical codeposition of Au and Ag materials into the pores of anodized aluminum oxide (AAO) templates, as illustrated in Figure 1. A thin layer of silver (∼300 nm) was thermally evaporated on one side of nanoporous AAO templates and served as a working electrode in a three-electrode electrochemical cell. The Pt wire and Ag/AgCl electrode were used as a counter and a reference electrode, respectively. Next, Au/Ag alloy materials were electro-deposited into the empty interior of an AAO template at a constant potential of ∼0.95 V. The value of x in the Auₓ/Ag₁₋ₓ alloy NRs was controlled by varying the mole fraction of Au⁺ and Ag⁺ ions in homemade plating solutions. A solution containing Au⁺ was prepared by using 0.05 M solution of KAu(CN)₂ (from Alfa) and 0.25 M Na₂CO₃ (from Samsun Chemicals). A Ag⁺ solution was prepared by using 0.05 M of KAg(CN)₂ (from Alfa) and 0.25 M Na₂CO₃. The relative mole fraction in an alloy plating solution was varied by changing the volume fraction of two solutions. The length (L) of the alloy NRs could be controlled by monitoring the total amount of charge passed during the electrochemical deposition. Typically, 0.08 C yields approximately 300 nm Au/Ag alloy NRs when the exposed apparent surface area is ca. 0.98 cm². Then, the evaporated Ag film was selectively etched with diluted nitric acid. The thermally evaporated Ag is a pure form of Ag, and it is less resistant to acid etching than when it is in the alloy form with Au. If we immerse the sample in concentrated acid for an extended period of time, then it also affects the Au in the alloy; however, the use of dilute acid and careful sample handling minimizes the dissolution of Ag in the Au/Ag alloy nanorods (Supporting Information Figure S1). Subsequently, the AAO templates were dissolved by using an aqueous 3 M NaOH solution. The resulting NRs were rinsed with distilled water until the pH was ∼7 and then redispersed in D₂O for extinction spectrum characterization.

**Material Characterization.** The morphology of the resulting nanorods was investigated by a field emission scanning electron microscope (JEOL 7000F). Experimental extinction spectra were measured using the Shimadzu UV-3600 UV–vis NIR spectrophotometer.

### 3. Results and Discussion

We synthesized Auₓ/Ag₁₋ₓ alloy NRs with different Au fraction (x) ranging from 1 to 0.4 and analyzed their morphology and compositions with field emission scanning electron microscopy (FESEM) and energy-dispersive spectrometer (EDS), respectively. The Au/Ag alloy NRs were synthesized by using the electrochemical codeposition of Au and Ag materials into the pores of anodized aluminum oxide (AAO) templates, as illustrated in Figure 1. The representative FESEM images of the resulting Auₓ/Ag₁₋ₓ alloy NRs reveal their narrow size distribution and homogeneous morphology, as illustrated in Figure 2. The length of all of the synthesized Auₓ/Ag₁₋ₓ alloy NRs was fixed to ∼325 nm regardless of compositions. The composition of Auₓ/Ag₁₋ₓ alloy NRs could be systematically controlled by varying the relative concentration of Au⁺ and Ag⁺ ions in a plating solution. When x is 1, the resulting NRs are pure Au NRs without any Ag component. A smaller value of x indicates an increase in the Ag fraction of the NRs. The four representative Auₓ/Ag₁₋ₓ alloy NRs contain different compositions of Au and Ag. The measured x values from EDS analysis are 1.00, 0.75, 0.65, and 0.40, as shown in Figure 2A, B, C, and D, respectively.

Figure 3A shows the corresponding extinction spectrum of the four Auₓ/Ag₁₋ₓ alloy NRs represented in Figure 2. Of particular interest is the optical behavior change of Auₓ/Ag₁₋ₓ alloy NRs with different compositions for a given length - that is, how the transverse and longitudinal modes of Au NRs are perturbed by mixing Au with Ag, and how the higher-order, longitudinal modes behave in comparison to the dipole mode. The NR diameter depends on the pore diameter of the AAO template utilized, and here, templates with a pore diameter of 81 (±5) nm have been used. In this size regime, we previously showed that Au NRs exhibit higher-order, longitudinal LSPRs as well as a transverse dipole mode. As expected, pure Au NRs (x = 1) have three distinct peaks at 528, 748, and 1470 nm corresponding to the transverse dipole, longitudinal quadrupole, and dipole mode, respectively. When the molar ratio of Au in the Auₓ/Ag₁₋ₓ alloy NRs is 0.75, the corresponding visible–near-IR extinction spectrum shows a transverse mode appearing at 492 nm (Figure 3A, spectrum b). The longitudinal dipole mode and a quadrupole mode appear at 1482 and 736 nm, respectively. There are no additional peaks observed in the given spectrum range. When the Ag fraction was further increased up to 0.35 and 0.60, the transverse mode blue-shifted considerably, while there was little variation in peak position of the longitudinal LSPR modes, showing only a very slight blue shift. We plotted the peak positions of the transverse dipole modes (circles), longitudinal quadrupole modes (squares), and longitudinal dipole modes (triangles) as a function of compositions in Figure 3B. As is clearly displayed, the peak position of the transverse dipole modes consistently blue-shifted as the Au fraction decreased from 1.00 to...
0.40 with a slope of 149 nm/Au mole fraction. Because the lengths of all of the synthesized Au\textsubscript{x}/Ag\textsubscript{1-x} alloy NRs were fixed to ∼325 nm, the transverse dipole peak position is solely attributed to the variation in the relative material composition. Taking into account the observation that Ag NRs show a transverse mode at ca. 410 nm under the given conditions, the blue shift of the peak position in the alloys is consistent. The magnitude of the peak position shift is dependent on the weight contribution of Au and Ag, which is directly related to the dielectric constant of the alloy metal.\textsuperscript{19–22} The optical constants of Au and Ag are similar at IR wavelengths, so altering the relative amounts of the alloy components generates much less dramatic shifts of the plasmon resonances in this region. This is indicated by the relative insensitivity of the longitudinal peak positions to the amount of Ag found experimentally and supported by discrete dipole approximation (DDA)\textsuperscript{23,24} simulations, which also show a slight blue shift in the longitudinal resonance peaks upon increasing the Ag component.

Figure 2. FESEM images of (A) pure Au NRs (L = 326 (±27) nm), (B) Au\textsubscript{0.75}/Ag\textsubscript{0.25} alloy NRs (L = 323 (±22) nm), (C) Au\textsubscript{0.65}/Ag\textsubscript{0.35} alloy NRs (L = 328 (±23) nm), and (D) Au\textsubscript{0.40}/Ag\textsubscript{0.60} alloy NRs (L = 320 (±20) nm). The diameter of AAO templates is 81 (±5) nm for all the samples. Insets are the corresponding EDS spectrum of the NRs.

Figure 3. (A) Visible–near-IR extinction spectra for Au\textsubscript{x}/Ag\textsubscript{1-x} alloy NRs with different Au mole fraction. (a), (b), (c), and (d) were obtained from the corresponding samples shown in Figure 2A,B,C, and D, respectively. All the spectra were measured in D\textsubscript{2}O and normalized to have the same extinction for the transverse modes. (B) Plot of LSPR modes vs Au mole fraction of alloy NRs. The circles, squares, and triangles correspond to transverse dipole, longitudinal quadrupole, and longitudinal dipole modes, respectively. Open symbols are the corresponding peak positions obtained from DDA calculations.

Figure 4. (A) Experimental visible–near-IR extinction spectra of the Au\textsubscript{0.65}/Ag\textsubscript{0.35} alloy NRs in D\textsubscript{2}O with different lengths (L ∼ (a) 123 (±11) nm, (b) 328 (±23) nm, (c) 410 (±33) nm, (d) 501 (±35) nm, (e) 542 (±52) nm, (f) 615 (±45) nm, and (g) 740 nm (±50) nm). (B) Calculated extinction spectra corresponding to experimental results as shown in panel A. Triangle symbols indicate the peak position of longitudinal quadrupole modes.

observed with Au$_{0.65}$/Ag$_{0.35}$ alloy NRs. When more than the transverse LSPR mode. A similar trend was observed in the 500 nm range with a sharp maxima adjacent to the red in the 525–575 nm range. This resonance shape is evident in trace c of Figure 4B at 625 nm, which red-shifts to ~950 nm in trace g. Initially, this resonance is unresolved experimentally but is in good agreement as the excitation becomes resolved (Figure 4A, trace g).

Our simulations do a poorer job of describing the transverse dipole mode present in alloy nanorods. The resonance structure typically displays a broad feature in the 350–500 nm range with a sharp maxima adjacent to the red in the 525–575 nm range. This resonance shape is present in all of the traces in Figure 4B (the transverse mode blue-shifts slightly but is much less sensitive to increases in rod length, so all traces are representative). Increasing the Ag mole fraction as is discussed in Figure 3—yielded blue shifts that were comparable to experiment, but the resonances were always shifted to slightly longer wavelengths due to the asymmetric line shape. Interestingly, if we were to report the plasmon peak as the center of the transverse resonance structure, the effective dielectric constant of the alloy was generated by taking a linear combination of the Au and Ag components with weights determined by the relative amount of the metals in the alloy.15,16

Figure 4A, spectrum g.

We have calculated the optical properties of the Au$_{0.65}$/Ag$_{0.35}$ alloy NRs with different lengths ranging from ca. 123 to 740 nm and measured their corresponding visible–near-IR extinction spectra, as shown in Figure 4A. FESEM images show their narrow size distribution and homogeneous morphological features (Figure 5). Because of the constant width, the transverse dipole modes at 469–473 nm are largely insensitive to the increase of aspect ratio; however, the longitudinal dipole modes red-shift considerably from 716 nm for L ∼ 123 to 1467 nm for L ∼ 328 nm. It is well-known that the aspect ratio of pure Au NRs affects the longitudinal LSPR modes more than the transverse LSPR mode. A similar trend was observed with Au$_{0.65}$/Ag$_{0.35}$ alloy NRs. When L is greater than 500 nm, the longitudinal dipole resonances shift well into the IR region. Another noticeable feature is the appearance of the longitudinal quadrupole mode at 737 nm when L ∼ 328 nm. The peak position systematically red-shifts as the aspect ratio increases and is highlighted with triangle symbols in Figure 4A. The agreement with experiment is good for the longitudinal plasmon resonances, which reside beyond 600 nm. Theory and experiment are in excellent agreement on the dipole modes that occur at ~750 and 1450 nm for traces a and b, respectively. Panels A and B also show the same evolution of the quadrupole mode (labeled by triangles) as the aspect ratio is increased. The simulations are able to predict the correct resonance wavelengths for the quadrupole modes of most nanorods yet slightly overestimate the red shift for some structures, such as the 740 nm rod (Figure 4g). In general, the longitudinal peak positions are in very good agreement, but the resonance widths are consistently narrower in the simulations. This likely results from the calculations being performed on a single nanorod, while the true experimental samples contain many particles with slightly different dimensions and alloy compositions, which result in peak broadening. The broadening observed experimentally obscures some of the less intense, fine structure predicted theoretically. For example, a higher-order longitudinal mode is evident in trace c of Figure 4B at 625 nm, which red-shifts to ~950 nm in trace g. Initially, this resonance is unresolved experimentally but is in good agreement as the excitation becomes resolved (Figure 4A, trace g).

We have calculated the optical properties of the Au$_{0.65}$/Ag$_{0.35}$ alloy NRs with different lengths using the discrete dipole approximation (DDA).23,24 For all of the simulations, we created an alloy dielectric constant by appropriately weighting the experimentally determined components;25 that is to say, the effective dielectric constant of the alloy was generated by taking a linear combination of the Au and Ag components with weights determined by the relative amount of the metals in the alloy.23,24 For all of the simulations, we created an alloy dielectric constant by appropriately weighting the experimentally determined components;25 that is to say, the effective dielectric constant of the alloy was generated by taking a linear combination of the Au and Ag components with weights determined by the relative amount of the metals in the alloy.

In addition to blue shifts, we also find that the Au$_{x}$/Ag$_{1-x}$ alloy NRs have broader resonance widths that obscure the quadrupole resonance structure at ~737 nm. The larger widths imply an increase in the damping rate likely resulting from small variations in the mole fraction of the alloy from particle to particle and slight particle inhomogeneities. Compared to pure Au NRs, the Au$_{x}$/Ag$_{1-x}$ alloy NRs generate plasmon excitations over a slightly broader distribution of oscillator frequencies that may lead to a faster decay of LSPRs. However, further study is necessary to clarify the nature of band broadening in Au/Ag alloy systems.

We synthesized Au$_{0.65}$/Ag$_{0.35}$ alloy NRs with different lengths ranging from ca. 123 to 740 nm and measured their corresponding visible–near-IR extinction spectra, as shown in Figure 4A. The agreement with experiment on the transverse mode will be discussed in more detail below.

The peak position systematically red-shifts as the aspect ratio increases and is highlighted with triangle symbols in Figure 4A. The agreement with experiment is good for the longitudinal plasmon resonances, which reside beyond 600 nm. Theory and experiment are in excellent agreement on the dipole modes that occur at ~750 and 1450 nm for traces a and b, respectively. Panels A and B also show the same evolution of the quadrupole mode (labeled by triangles) as the aspect ratio is increased. The simulations are able to predict the correct resonance wavelengths for the quadrupole modes of most nanorods yet slightly overestimate the red shift for some structures, such as the 740 nm rod (Figure 4g). In general, the longitudinal peak positions are in very good agreement, but the resonance widths are consistently narrower in the simulations. This likely results from the calculations being performed on a single nanorod, while the true experimental samples contain many particles with slightly different dimensions and alloy compositions, which result in peak broadening. The broadening observed experimentally obscures some of the less intense, fine structure predicted theoretically. For example, a higher-order longitudinal mode is evident in trace c of Figure 4B at 625 nm, which red-shifts to ~950 nm in trace g. Initially, this resonance is unresolved experimentally but is in good agreement as the excitation becomes resolved (Figure 4A, trace g).

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and not the maximum, then theory and experiment would agree well. Moreover, the magnitude of the broad hump increased in proportion to the sharper feature when the amount of Ag in the alloy was increased. These findings appear to emphasize a shortcoming in the prescription used to generate the alloy dielectric functions, as has been suggested previously for certain wavelength regimes.\textsuperscript{15} In the 350–550 nm range, the real portion of the refractive index of Ag is approximately zero, while the real part for Au is significantly larger. A linear combination of the optical constants in this regime likely over-represents the Au character in the alloy even when the mole fraction is small. We believe that the method of producing the alloy dielectric data for the calculations generated the unusual shape of the transverse mode, which is dominated by Au in this spectral region. At longer wavelengths, the optical constants of Ag and Au are very similar, and both components contribute to the alloy data in the prescribed proportions. As such, the agreement with experiment is significantly better. Therefore, these results suggest that using the linear combination method for producing alloy dielectric data is reasonable beyond the interband transition regions for Au and Ag (i.e., $\lambda > 550$ nm for the Au).

Future work will involve a systematic study using experimentally determined values for the alloy permittivity in the appropriate mole fractions. This will allow us to directly compare simulation results using true alloy dielectric data to that of the weighted component model and test our hypothesis regarding the discrepancies in the shape of the transverse mode. In general, this study will elucidate how the optical constants of alloys may vary from the components that compose them and how this affects nanoparticle optics.

### 4. Conclusions

In conclusion, the template-assisted method allowed the synthesis of Au\textsubscript{x}/Ag\textsubscript{1-x} alloy NRs with a fine control over the relative compositions. We have demonstrated that one can straightforwardly synthesize Au\textsubscript{x}/Ag\textsubscript{1-x} alloy NRs with different x by controlling the mole fraction of two metal ions in a plating solution. The resulting Au\textsubscript{x}/Ag\textsubscript{1-x} alloy NRs exhibited a transverse mode as well as multiple longitudinal LSPRs, as in the case of pure Au NRs with the same dimensions. The transverse mode consistently blue-shifted as the Ag fraction increased in the alloy NRs, close to the wavelength for the transverse mode of pure Ag NRs. However, the absorption bands of longitudinal modes were largely insensitive to the change of composition for a given aspect ratio, showing only very slight blue shifts. In contrast, for a given Ag mole fraction, the longitudinal modes of Au\textsubscript{x}/Ag\textsubscript{1-x} alloy NRs were very sensitive to changes in aspect ratio, but the transverse mode was insensitive in this case. This experimental observation was similar to the case of pure Au NRs. Theoretical studies using DDA confirmed the experimental findings that the longitudinal plasmon resonances in Au\textsubscript{x}/Ag\textsubscript{1-x} alloy NRs are much less sensitive to the mole fraction of Ag than the transverse modes for a given aspect ratio, and that for a given Ag mole fraction, the longitudinal modes are very sensitive to rod length, while the transverse mode is insensitive to this property.

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**Supporting Information Available:** Figure S1. TEM image of Au\textsubscript{0.65}/Ag\textsubscript{0.35} alloy NRs (A) before and (B) after chemical etching. This material is available free of charge via the Internet at http://pubs.acs.org.