Tri-Component Gold–Nickel–Silver Nanorods Leading to Multiple Surface Plasmon Bands

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ABSTRACT: In this work, we demonstrate that surface plasmon resonance coupling can occur on elementally different three-block metal nanorods. The nanorods were composed of three sequential Au–Ni–Ag components prepared with electrochemical deposition and an anodic aluminum oxide template. We investigated the UV–vis–NIR extinction spectroscopy of colloidal nanorods in D₂O liquid phase and found that surface plasmon coupling occurred on optically active Au and Ag motifs in nanorods when the middle Ni block was sufficiently short. As a result, both the longitudinal and transverse plasmon modes appeared clearly in the optical spectra of samples for the total nanorod lengths rather than for individual constituent sub-nanorods. Higher-order modes, such as quadrupole modes, also arose on the longer hybrid nanorods. Nanorods with a Ni portion longer than the corresponding Au and Ag portions could restrain coupling between the Au and Ag segments.

1. INTRODUCTION

Plasmonics is a recently emerging discipline that deals with the interaction between light waves and surface electrons of metallic objects. This field shows great promise in practical applications such as chemical and biochemical sensing, photothermal therapeutics, plasmonic circuits, light generation, and solar energy harvest.1–4 Surface plasmon resonance (SPR) refers to the collective oscillation between conduction electrons on a metal surface and an alternating electric field of incident light. SPR is one of the most critical topics in plasmonics.5 Noble metals are frequently employed as objects of study. The availability of metallic nanostructures provides a way to study SPR because they are comparable in size to light wavelengths. In addition, metallic nanostructures have controlled electron distribution in three dimensions (i.e., morphology control). UV–vis–NIR extinction spectroscopy is the most common means for studying the SPR of a liquid phase suspended colloidal metal nanostructure. Using this method, scientists have discovered that SPR is sensitive to the dielectric constant of the ambient environment as well as the size, shape, and composition of nanostructures.6 Previously, the SPR of colloidal nanostructures with a single component has received extensive attention. The current concern with SPR focuses on complex systems of nanostructures,7 which involves the phenomenon of SPR (or optical) coupling. SPR coupling can occur on two adjacent but disconnected plasmonic metals (or metals with a short spacer between them), resulting in the red-shift of spectral peaks relative to those of individual metals.7–12 Spherical metal nanostructures have previously been used as study subjects in both SPR and SPR coupling. However, they show less plasmonic features and worse spatial controllability because of their zero dimensions. SPR and SPR coupling on rod-like metal nanostructures is more advanced mainly because electrons on the surface of rod-like nanostructures can oscillate along both the short axis (transverse mode) and the long axis (longitudinal mode).13–18 We have previously carried out initiative studies on SPR and SPR coupling of liquid-phase dispersed nanorods. All studied nanorod prototypes showed obvious transverse and longitudinal dipole modes corresponding to their one-dimensional anisotropic nanostructure. Au7,14,15 Ag,19 and Cu19 single-component nanorods, unlike Pd20 and Pt20 nanorods, exhibited distinct higher-order modes (e.g., quadrupole) when their aspect ratios reached an appropriate value. This is due mainly to their excellent optical activity. We also evaluated interesting SPR coupling behaviors on Au–Ni7 and Au–Ag8 two-component nanorods with multiple blocks. These evaluations revealed that Ni blocks in Au played an inhibitory role with SPR coupling as a function of their lengths, but Ag did not. Longer Ni blocks hindered while shorter Ni blocks transmitted SPR coupling between Au nanorods at both ends.7 On the basis of our previously performed systematic studies, it is still unclear whether SPR coupling can occur between different kinds of metals at nanorod ends when a Ni block is placed in the middle. The significance of involving multiplicate metals within a nanorod points to the potential application of nanorods in multipurpose analytic sensing. In other words, the spectral profile can potentially be tuned by selectively modifying the surfaces of individual metals. We herein report an experimental investigation into plasmonic characteristics on three-block Au–Ni–Ag hybrid nanorods. Our theoretical calculation results based on discrete dipole approximation (DDA) matched up well with the obtained experimental findings.
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Scheme 1. Schematic Illustration of the Au–Ni–Ag Hybrid Nanorod Synthesis Procedure

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2. EXPERIMENTAL SECTION

2.1. Chemicals and Apparatus. Au, Ni, and Ag plating solutions (Orottemp 24 RTU) were purchased from Technic Inc. All electrochemical depositions were performed on an Autolab (PGSTAT12) equipped with a three-electrode system (counter electrode, Pt mesh; reference electrode, Ag/AgCl (3 M KCl)). SEM images were acquired by a JEOL JSM-7401F field emission scanning electron microscope (FE-SEM), and TEM images were acquired by a JEOL JEM2100F high resolution transmission electron microscope (HR-TEM). Experimental extinction spectra were measured by a Shimadzu UV-3600 UV–vis–NIR spectrophotometer. Deuterium oxide (D₂O, 99.9%), used as the dispersing solvent, was commercially available from Cambridge Isotope Laboratories, Inc.

2.2. Synthesis of AAO Membranes. Homemade AAO membranes were synthesized using the method established by Masuda et al. In detail, a high-purity (99.999%) thin sheet of aluminum (from Goodfellow Cambridge Limited) was first electro-polished in a mixture of ethanol and perchloric acid (Samchun Chemical, Korea) (7:3, v/v) at 20 V and 0 °C for 3 min. The plate was then anodized in 0.3 M oxalic acid at 40 V and 0 °C for 12 h. The alumina layer was subsequently dissolved using an aqueous mixture of chromic acid (1.8 wt %) and phosphoric acid (Samchun) (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, resulting in a highly ordered porous AAO template. The aluminum sheet residue was removed by immersion into a saturated HgCl₂ aqueous solution for 6 h and then immersion in 8.5 wt % phosphoric acid solution to allow pore widening for 30 min. The resulting pore diameter was 70 (±5) nm.

2.3. Electrodeposition and Nanorod Release. The physical configuration of the cell is similar to that described by Liu et al. Prior to AAO, 400 nm thick Ag film was evaporated on one side as a conducting layer. An AAO membrane (or product) sandwiched between a piece of alumina foil and an insulating O-ring was assembled in a Teflon cell as the working electrode. To block the irregular branch part of AAO nanopores, Ag was predeposited into nanopores of homemade AAO by 1 C/cm² at −0.95 V from a commercial plating solution. For Ni and Au deposition, −0.95 V (vs Ag/AgCl) was applied. Length control was realized by monitoring the charges during electrodeposition. To obtain liquid-phase-suspended nanorods, the Ag conducting layer was dissolved while simultaneously dissolving the predeposited Ag nanorods away from the AAO template using a dilute HNO₃ solution for a short time of ∼1 min. With the protection of the topmost thin layer of Au (∼2 nm) and AAO encapsulation, Ni and Ag segments in hybrid nanorods can avoid being dissolved during the removal of the Ag conducting layer. It is assumed that this protective thin Au layer introduces no obvious influence to optical spectra. The AAO membrane template was then completely removed by 3 M NaOH for 50 min. Released nanorods underwent a repeated three-step rinse process, which includes a nanorod natural sink (12 h), solvent renewal, and ultrasonic dispersing. The rinsing process continued until nanorods were clean under observation by scanning electron microscope.

2.4. Discrete Dipole Approximation (DDA) Calculation. The source code for DDA calculation was obtained from the webpage of Professor Bruce Draine. Johnson and Christy provided optical constants for Ag and Cu. The refractive index dispersion of water was used to generate accurate spectra in the short wavelength region. A cylindrically shaped target of a given diameter and length was subdivided with an array of 4 nm cubic cells. The interaction between polarizable point dipoles in the cells and incident light wave was solved iteratively. Cross sections for extinction and scattering were generated from these calculations. The cross sections of a randomly oriented target under nonpolarized light were obtained by averaging the calculations for seven different incident directions and two mutually perpendicular polarization states of the light wave with respect to target frame.

3. RESULTS AND DISCUSSION

The target hybrid nanorods were fabricated by sequential electrodeposition of Au–Ni–Ag from commercial plating solutions into nanochannels in an anodic aluminum oxide (AAO) template (Scheme 1). The charge amount transported during electrodeposition was used to control the length of compositional segments. SEM images taken using the back-scattered electron (BSE) mode of a field emission scanning electron microscope (FESEM) in Figure 1 show the successful formation of three-block nanorods. Throughout this study, we used 70 (±5) nm diametric nanochannels. It is well-known that the SPR spectral profile of nanorods closely depends on their dimensions and, more precisely, their aspect ratios (defined as the ratio of length/diameter for one-dimensional matters).

Thus, we first prepared short Au–Ni–Ag nanorods with a total length of ∼300 nm (AR ≈ 4.3) and varied the length of individual segments, as displayed in Figure 1A and B. Clearly isolated transverse and longitudinal bands in the extinction spectra of these nanorods facilitate tracing spectral changes when other species are introduced into nanorods. When...
Deionized water was used as solvent, a strong noise was present in the near-infrared region of UV–vis–NIR spectra. To exclude this interference, heavy water (D₂O) was used as the solvent for acquiring spectra. Figure 1C displays UV–vis–NIR spectra of 300 nm nanorods (as shown in Figure 1A and B). The transverse modes for two samples were observed at 410 nm for Ga and 555 nm for Au. Ni had no obvious spectral characteristics, as previously found. The peak intensity difference of transverse modes in the two spectra was caused by a length discrepancy of the metal segments in the two types of nanorods. Transverse mode intensity is positively correlated to the length of nanorods. The peaks at 1530 nm for two samples were assigned to the longitudinal dipole mode of whole nanorods, and were consistent with those (dashed line in Figure 1C) observed on pure Au nanorods of similar length. Pure Au nanorods were used as a reference rather than Au–Ag nanorods because their dipole and higher-order modes arise at the same wavelength when they have the same total length. The spectral features of both nanorod systems matched, confirming that electron oscillation on Au and Ag segments could freely transverse the middle Ni segment under light irradiation. Namely, SPR coupling could occur on the hybrid ~300 nm nanorods when middle Ni segments were relatively short.

In our previous study, Ni segment length could tailor the occurrence of SPR coupling between two Au ends. In this respect, we also checked SPR coupling as a function of the length of Ni segments in the present study. For convenience, typical ~500 nm nanorods (Figure 2A–D) were used as objects in this study. When relatively short Ni segments (80 and 140 nm, Figure 2A and B) were inserted into the nanorods consisting of Au and Ag ends, SPR coupling still occurred with a spectral feature (Figure 2E(a, b)) similar to that of a pure Au nanorod of the same total length (dashed profile in Figure 2E). In comparison, relatively longer Ni blocks (310 and 400 nm, Figure 2C and D) could prevent the occurrence of SPR coupling (Figure 2E(c, d)) between two ends. This resulted in the spectral features of only the Au and Ag segments but not of Au nanorods with identical total length.

We also found that the length of Ni segments affected SPR coupling not only on dipole modes, but also on higher-order modes. For single-component nanorods, higher-order modes are scarcely observed, and only emerge on high-aspect-ratio nanorods. When the lengths of Au and Ag segments were similar (~210 nm) while the Ni portion was ~80 nm (Figure 2A), a quadrupole peak originating from the entire nanorod was distinctly discernible at 1150 nm (Figure 2E(a)). The quadrupole peak position was the same as that of pure Au nanorods with the same length (dashed spectrum in Figure 2E). Spectrum b shown in Figure 2E also displays a quadrupole peak at 1150 nm. The nanorods (Figure 2B) used in this case had total lengths similar to those of Figure 2A, but Ni segments had a length of ~140 nm. The slight mismatch in quadrupole peak positions in spectrum b relative to spectrum a in Figure 2E was caused by a systematic error in the total length of nanorods. After increasing the length of Ni portions up to 310 and 400 nm (Figure 2C and D), the SPR coupling of quadrupole plasmon modes was suppressed, as observed in spectra c and d in Figure 2E. Only the transverse dipole modes of short Au and Ag nanorods could freely transverse the middle Ni segment under light irradiation.
Ag ends appeared below 800 nm in the spectra. There were no obvious spectral features above 800 nm wavelength for these two samples with overlong Ni parts, indicating that the longitudinal dipole, quadrupole modes, and plasmonic coupling failed to arise. This experimental outcome concludes that the Ni block can affect SPR coupling between Au and Ag segments on dipole and higher-order modes depending on its effective length.

To further assess how multiple blocks and physical junctions exert an influence on the SPR coupling in hybrid nanorods, repeating Au−Ni−Ag units in nanorods were investigated. The total length of repeating Au−Ni−Ag nanorods was controlled at ∼750 nm (Figure 3) to examine their plasmonic coupling behaviors. At this length, higher-order modes of pure Au nanorods were readily observed. SPR coupling should happen in this dimension for Au−Ni−Ag−Au−Ni−Ag (210:40:125:125:40:210 nm, Figure 3A) assembled sequentially in a head-to-head fashion, considering that Ni blocks (40 nm) shorter than Au and Ag blocks (210 and 125 nm) cannot inhibit plasmonic coupling. Spectrum a in Figure 3E verified this speculation by comparison with a spectrum (dashed profile in Figure 3E) with the same length of pure Au nanorods. At this longer length, higher-order modes (quadrupole, 1580 nm; higher mode, 1060 nm) were successfully produced. At the same time, longitudinal modes shifted out of range of the spectra window due to increased nanorod aspect ratios. When the segment sequence changed to Au−Ni−Ag−Au−Ni−Ag (170:45:170:45:170 nm, Figure 3B) in head-to-tail fashion, the quadrupole mode at 1580 nm and the higher mode at 1060 nm arose similar to that of the former alignment. The excellent plasmonic signals present in the spectra for repeating nanorods proved that the number of interfacial junctions and arrangement sequence of metal blocks had no significant influence on plasmonic coupling. The tail-to-tail case (Ag−Ni−Au−Au−Ni−Ag) was omitted from study due to an irresolvable experimental limitation. Dissimilar surface areas of the exposed Au and Ag segments induced the peak intensity differences at 410 and 555 nm. To rationally tailor spectral outcome, we fabricated nanorods with three repeating units of similar total lengths (Figure 3C) with Au and Ag segments shorter than those in Figure 3A and B, as was confirmed using element mapping and line analysis in TEM (Figure 4). The quadrupole mode of such nanorods was still obviously noticeable, even though it had a slight attenuated intensity. However, the higher mode completely disappeared (spectrum c in Figure 3E). The reduced length of Au and Ag segments in hybrid nanorods consisting of three repeating units was responsible for the absence of higher modes. This result suggests that the compositional percentage of active and inactive metal blocks, rather than the number of junctions and arrangement sequence...
of individual segments, dominated plasmonic coupling on the overall surface of nanorods.

Since the length of Ni blocks has a critical effect on the SPR coupling, we conclude that the appropriate length proportion of total Ni blocks to the sum of Au and Ag blocks is approximately >1.2. This ratio allowed interruption of the collective oscillation of free electrons on the overall nanorod surface. This result conveys the important information that relatively short Ni spacers can help to tailor the spectral outcome of multimetal nanorods. As further proof, when the longer Ni segments were fabricated into two repeating nanorods (70:210:70 nm, Figure 3D), all higher-order modes were suppressed (spectrum d in Figure 3E) in a manner similar to that of the longer Ni block case described in Figure 2C. Only the transverse modes of Au

Figure 5. Calculated discrete dipole approximation (DDA) extinction spectra of Au–Ni–Ag three-block nanorods with a total length of ~500 nm and varied length of each segment.

Figure 6. Calculated DDA extinction spectra for complex nanorods (~750 nm in total length) used in Figure 3.
and Ag were observed for these complex nanorods. Since Au and Ag segments are shorter than the middle Ni block, the intensities and shapes of the transverse modes of Au at 555 nm and Ag at 410 nm were reduced and broader than segments with higher proportions of Au and Ag. These results are indicated by spectrum d in Figure 3E (as compared to spectra a–c in Figure 3E).

The discrete dipole approximation (DDA) calculation is a useful theoretical method for predicting the spectral outcome that considers scattering and absorption effects. In general, our calculated DDA extinction spectra demonstrated consistent plasmonic properties as achieved in the experimental investigations. The representative length (500 nm) of hybrid nanorods, as shown in Figure 2A–D, was selected as a reference for DDA calculation. The multiplet feature around 400 nm (Figure 5A–D) that corresponds to the transverse mode of Au–Ni–Ag nanorods in DDA spectra is not exactly exhibited in practical experimental spectra (compared to extinction spectra a–d in Figure 2E). This is probably due to the imperfect smooth surface of nanorods. The higher mode at ∼700 nm in the calculated extinction spectra (Figure 5) was not observed in experimental results using ∼500 nm nanorods but was observed for 750 nm nanorods. A small mismatch between calculated results and experimental results is tolerable. It is well-known that the results from ideal theoretical calculations cannot resolve all exogenous influences in actual experimental conditions. The quadrupole mode at 1150 nm, which conveys information on successful surface plasmon coupling, was maintained in both experimental (spectrum a and b in Figure 2E) and calculated (spectrum A and B in Figure 5) extinction spectra when the middle Ni segment was shorter than other segments. In contrast to results from longer Ni segments, the quadrupole peak disappears in experimental results (spectrum c and d in Figure 2E) and decreases greatly in peak intensity in calculated results (spectrum C and D in Figure 5). The calculated DDA extinction spectra (Figure 6) used for samples in Figure 3 also conform to the above analysis. It is reasonable to conclude from experimental and theoretical results that surface plasmon coupling between optically active metal segments can occur. In addition, surface plasmon coupling can be tailored by managing the length of the middle spacer that exhibits no obvious SPR band.

4. CONCLUSIONS

UV–vis–NIR spectroscopy was used to investigate the plasmonic characteristics of liquid phase suspended Au–Ni–Ag three-block nanorods. We found that surface plasmon coupling can occur between optically active metal Au and Ag intranoronds when the appropriate length of Ni spacer is placed between Au and Ag. Higher-order modes, including quadrupole modes, were detected when the total length of multiblock nanorods was more than ca. 500 nm. In addition, calculated DDA extinction spectra agreed with experimental findings. Since noble metals have distinct affinities to specific molecules, the controllable multiple surface plasmon modes on Au–Ni–Ag three-block nanorods show great potential in applications of multiple analyte sensing. Au–Ni–Ag three-block nanorods are believed to be superior to one- and two-component metal nanorods. This study may introduce a way to investigate other spacer materials (e.g., insulators, semiconductors, etc.) for use in controlling the optical responses of designer plasmonic metal blocks.

AUTHOR INFORMATION

Author Contributions

These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The National Research Foundation of Korea supported this work (National Leading Research Lab: 2011-0027911).

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