Gold Nanohelices: A New Synthesis Route, Characterization, and Plasmonic E-Field Enhancement

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ABSTRACT: Gold nanohelices (AuNHs) are synthesized using surfactant-assisted seed-mediated growth in an aqueous solution. AuNHs with diameters and lengths of 30–150 nm and several micrometers, respectively, are grown in a reaction carried out at 15 °C for 20 h by adding poly(ethylene glycol)(12)tridecyl ether, polyvinylpyrrolidone, and cetyltrimethylammonium bromide as the capping agents in an HAuCl₄(aq) solution. With the addition of gold nanoparticles (AuNPs) in the reaction, the yield of the helical products is considerably increased, which indicates that AuNPs behave as the seeds for AuNH growth. The growth routes of AuNHs in the system are investigated by transmission electron microscopy measurements. Finite-difference time-domain (FDTD) simulations show that total extinction of the AuNH at 660 and 570 nm is dominantly influenced by strong e-field enhancement and the scattering of light incidence. In a practical application, surface-enhanced Raman scattering (SERS) measurements are conducted using AuNHs as the substrates and 4-mercaptobenzoic acid as the probe. A detection limit of 20 ppb is acquired using a micro-Raman spectrometer using a 633 nm He–Ne laser with a power of 3.35 mW which corresponds with the FDTD simulation results and reveals that AuNHs are superior SERS templates with resonance tuning ability in consequence of their unique helical architectures.

1. INTRODUCTION

Over the past two decades, investigations of the unique physical and chemical characteristics of nanoscale materials in comparison to bulk materials have drawn considerable interest from academics and advanced industries. Remarkable reports concerning quantum photonics,¹⁻³ photodynamic therapy,⁴ and the programmable architectures⁵⁻⁹ of nanoscaled gold have revealed that the dimensions, morphologies, and chemical modifications of artificial gold nanomaterials can be tailored for given applications. One-dimensional helical gold nanostuctures, namely, gold nanohelices (AuNHs),¹⁰⁻¹⁶ gold nanospirals (AuNSs),¹⁷,¹⁸ and gold nanosprings¹⁹,²⁰ have been shown to exhibit specific forms of atomic packing, high degrees of surface-enhanced Raman scattering (SERS), and plasmonic responses. In previous studies, several synthesis strategies, including peptide assembly, electrochemical deposition, galvanic displacement reaction, surfactant-assisted reaction, and glancing angle deposition, were utilized for the preparation of AuNHs, and growth pathways were also proposed to interpret the curved morphology of those one-dimensional gold nanomaterials. Our own previous study using a galvanic displacement reaction for aluminum–gold oxidation–reduction provides a new method for creating unique AuNSs.¹⁷ The trunk of the AuNSs thus created has a helical structure, and the outer surface is made up of aggregate granule branches. In this study, we used a similar strategy in order to further control the growth of helical gold nanomaterials, adding three surfactants as the capping agents in combination with the seed-mediated growth to synthesize AuNHs.

Gold nanostructures have attracted considerable attention regarding potential applications because localized surface plasmon resonance (LSPR) is generated by irradiating the metal structures with electromagnetic (EM) waves. It has been observed that such LSPR on metal nanostructures can enhance the e-field near the nanostructures. In addition, the LSPR frequency (wavelength) is strongly related to the shapes and dimensions of the nanostructures. In particular, a metallic nanorod has different LSPR responses at longitudinal and transverse e-field irradiation,²¹,²² that is, longitudinal LSPR is red-shifted compared to transverse LSPR. AuNHs are of interest with respect to LSPR, as the gap originating from their coiled structure would influence both their longitudinal and transverse LSPR responses. Moreover, enhanced EM waves inside of AuNHs would be anticipated because of their resemblance to solenoid coils. In order to characterize the LSPR and enhanced e-field profiles of AuNHs, finite-difference time-domain (FDTD) simulations of AuNHs with changes to the incident direction, polarization, and wavelength of the irradiated light were carried out.

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2. RESULTS AND DISCUSSION

2.1. Synthesis of AuNHs. AuNSs with dendrite structures possess large amounts of surface area and nanoscale space that creates numerous hot spots for superior SERS properties. The degree of field enhancement is greatly dependent on the dimensions of the space between the granule branches at a scale of only a few nanometers. Past studies that used a galvanic displacement reaction to grow AuNSs explored the role of surfactants in the reaction. However, with regard to synthesis, it is difficult to control the sample appearance using a galvanic displacement reaction, which results in the formation of dendrite structures on the surface of synthesized AuNHs and uneven dimensions of the overall product. Therefore, this study used a seed-mediated growth combining with surfactant-assisted method in order to control the growth of AuNHs more precisely. In the solution phase, three types of surfactants were used to provide the confined space for helix growth. Cetyltrimethylammonium bromide (CTAB) absorbed by a gold surface creates a double layer structure, which forces the nanogold to grow in a one-dimensional direction. Polyvinylpyrrolidone (PVP) acts as a capping agent that surrounds the surface of the nanogold. The role of polyethylene glycol (PEG) is to assist in the formation of spiral structures in aqueous solutions. The seed-mediated growth method provides a homogeneous reaction environment, allowing for the control of product appearance. Because of the small quantity of Au nanoseeds that is added, the solution initially appears transparent and gradually becomes rose pink as the reaction time increases. After the completion of the reaction, a centrifugal method can be used to separate the product material from the solid portion in the reaction solution.

Figure 1a shows the scanning electron microscope (SEM) of the products obtained by 14,000 rpm centrifugation. The figure shows two types of product appearances, namely, gold nanoparticles and AuNHs, which were obtained after a 20 h reaction. A different centrifugation speed regarding the weight difference between the two products was then used to remove the gold nanoparticles. After multiple attempts, the centrifugation speed of 1000 rpm was determined to be the most effective. As seen in Figure 1b, a large portion of the nanoparticles were removed, with the few remaining nanoparticles being attached to the helical material. Figure 2 shows the SEM of AuNHs obtained by 1000 rpm centrifugation. The low-magnification SEM image demonstrates the high productivity of helical products. The high-magnification SEM images (Figure 2b,c) clearly show the even structure of the nanohelices; the helices’ diameters range between 30 and 150 nm, and their lengths are several microns. EDS analyses indicated that the helical sample was constructed from gold (Figures S3 and S4). After separation, the sample included two types of structures: AuNHs, which were the main product (Figure 3a,b), and ramified helical structures. The few ideal helical structures formed are shown in Figure 3c. However, the productivity of products with such an appearance was low. Moreover, some products were intertwined because of their structure, forming double helix structures (Figure 3d).

The crystalline phases of the AuNHs obtained by separation were examined using XRD analyses, as shown in Figure 4. The characteristic peaks of the AuNHs at 2θ = 38.1, 44.3, 64.5, and 69.1° belongs to the holder of the Si substrate.
products obtained without the addition of gold nanoseeds in the reaction. After the separation of the solid products and liquids through 1000 rpm centrifugation, it could be clearly observed that few AuNHs were synthesized when gold nanoseeds were not added in the reaction as nucleation points. The number of particles in the product was predominant, and their size was much larger than that of the gold nanoparticles in Figure 1a. According to the above observations, the three types of surfactants form confined helical spaces in a homogeneous aqueous environment, and as a result, gold(III) ions were reduced on the Au nanoseeds and helices are formed through crystal growth. The lack of nucleation points leads to the growth of a large number of gold nanoparticles. Therefore, the addition of Au nanoseeds is necessary for achieving an effective increase in AuNH productivity.

In past studies that used a galvanic displacement reaction, a heterogeneous redox reaction occurred in the interface between the aluminum substrate and the solution containing gold(III) ions, leading to the formation of thicker root ends in AuNSs. In contrast, the tail sections of the AuNSs shrank, forming conic structures. In this study, the gold seeds provided the nucleating points necessary for the growth of a large number of AuNHs. The crystal growth process produced products with even appearances via surfactant confinement. A smaller AuNH was selected in this study for high-resolution transmission electron microscopy (HRTEM) analysis to explore the atomic arrangement of AuNHs, as shown in Figure 6a. The high-magnification TEM in Figure 6b shows the presence of a growth boundary in the structure (marked as R1). The partition line divides AuNHs into two sections, marked as I and II. Figure 6c shows the HRTEM of sections I and II divided by the R1 partition line, where two small figures demonstrate the fast Fourier transform (FFT) analyses of I and II and are marked as FFT-I and FFT-II, respectively. The images show that the (111) plane of FFT-I and FFT-II (blue line) are vertical to R1 (TT1) plane (red line), indicating that the twinning plane corresponding to the R1 partition line is the (TT1) plane and that two (111) planes create a 141° angle. The aforementioned high-resolution atomic images and an FFT conversion chart show that, during the growth of the AuNHs, a mirror-symmetric structure was formed on the (TT1) twinning plane. HRTEM was used to observe the atomic arrangements of the helical nanomaterials, and the results for the AuNHs and the trunks of the AuNSs were similar, indicating that even if different nucleation and crystal growth methods are applied in the confined spaces produced using the surfactants CTAB, PEG, and PVP, the gold(III) ions can effectively directed into a rotation during the restoration process.

A related study proposed that helical gold nanowires were grown by asymmetrical blocking of the organic capping agent, leading to the formation of twin boundaries. Another study observed a phenomenon similar to that in this study and indicated that twin defects are frequently seen in such nanowires owing to the low twin boundary energy for gold. If twin boundaries continue to appear during the process of gold nanowire growth, one-dimensional linear nanomaterials can transform into one-dimensional helical nanomaterials. When two helical nanowires are close to one another, they may be intertwined and form a double helix. To understand the growth routes of AuNHs, TEM was used to observe the changes in the dimension of the products obtained at different reaction time. Two growth modes are observed and shown in Figures 7 and 8. Figure 7 shows the sample obtained in the first 10 min of a reaction performed in an environment that contained gold nanoseeds. An HRTEM analysis (Figure 7c) indicated the absence of twin boundaries or a dislocation in the atomic arrangement. These phenomena were also reproduced in other positions of the sample in Figure 7a and in other small AuNHs, which indicates that this growth mode of AuNHs refers to the topotatic reaction, and there is no structural relationship between the nanoseed and the helix. The elemental mapping and selected area electron diffraction are shown in Figure S4. However, few AuNHs still can be formed without adding gold nanoseeds in the reaction. Therefore, gold(III) ions in the reaction reduced as the
seeds for the helices growth is the minor route of AuNH growth.

Another growth mode of AuNHs is also found in the system, and the TEM images of the samples obtained at 5, 10, and 15 h reaction time are shown in Figure 8. At the initial stage of reaction (Figure 8a, b), short AuNHs grew on the gold nanoparticle aggregates, indicated by the arrow, which suggests that the gold nanoparticle aggregates also play the roles of nucleation points for AuNHs growth. The length and the amount of AuNHs increase with the reaction time lasting to 10 and 15 h, which is shown in Figure 8c, d, respectively. As the oxidation—reduction reaction occurs, the Au(III) ions reducing to gold atoms not only induces the formation of AuNHs but also facilitates the crystal growth of gold nanoseeds. The surfactants in the solution provide confined space leading to the AuNHs growth on these gold nanoparticle aggregates. The observation may explain that the gold nanoparticle aggregates are attached on AuNHs, as shown in Figures 1b and 2b, c, and cannot be removed after ultrasonication and centrifugation. However, this growth route is an obstacle to control the uniformity of the product dimension. In a typical seed-mediated growth reaction, nanoseeds are embedded in the products with the surfactant as the directing agent, leading to the formation of one-dimensional nanowires with uniform diameter. Once one-dimensional nanostructures grew on gold nanoparticle aggregates, as shown in Figure 8, containing AuNHs and gold nanoparticles with different diameters, the AuNHs with different lengths and helical degrees are formed.

2.2. FDTD Simulations of AuNHs. To characterize the optical properties of AuNHs, FDTD simulations in the visible range were carried out with an ideal AuNH model system. In the previous paper, we reported that the wavelength and polarization of incident-light-dependent field enhancement in AuNHs of empirically observed dimensions are characterized by FDTD simulation measurements. Dimensions of the ideal AuNH model were acquired from the perfect AuNH structure shown in Figure 3c. The gap distance between turns and the number of turns of the AuNH were determined to be 500 nm and four, respectively, as shown in Figure 9a. An AuNH approximately 2 μm long and 330 nm wide with a wire thickness of 115 nm was used in the FDTD simulations (Figure 9a, b). Figure 9c shows the spectra of the extinction cross-section of the AuNH obtained from the FDTD simulations.

Figure 7. (a) TEM image of the product obtained in the first 10 min of the reaction. (b) High-magnification image. (c) HRTEM image labeled in (b). Scale bars are 20, 5, and 5 nm in (a–c), respectively.

Figure 8. TEM images of the products obtained in the (a, b) 5, (c) 10, and (d) 15 h of the reaction.

Figure 9. (a, b) Schemes of AuNHs for FDTD simulations: (a) side and (b) top views with denotation of dimensions of the AuNHs and coordination of the simulation system. (c) Wavelength dependent extinction cross-section of the AuNHs with different light incidences of $k_x(E_y)$ (blue), $k_x(E_z)$ (red), and $k_z(E_y)$ (purple). Total extinction cross-section of the AuNHs [$k_x(E_y) + k_x(E_z) + k_z(E_y)$] is displayed as the black symbol. The red and blue dot arrows denote maxima wavelength of the extinction cross-section of $k_x(E_y)$ and $k_x(E_z)$ incidences, respectively.
respectively. In the case of 660 nm incidence, strong e-field enhancement near the outside girth of AuNH is observed with perpendicular incidences of the light polarization with the AuNH, whereas \( k_{\parallel}(E_z) \) represents a parallel incidence \( k_{\parallel} \) of the light with transverse \( E_y \) e-field polarization. While the extinction cross-section of \( k_{\parallel}(E_z) \) showed a relatively minimal intensity and gradually increased as the wavelength of the light increased to 700 nm, the \( k_{\parallel}(E_z) \) and \( k_{\parallel}(E_x) \) incidences showed maxima in spectrum at 660 and 570 nm, respectively, as shown in Figure 9c. These maxima of extinction spectra are also reflected in the total extinction cross-section spectrum of AuNH \( [k_{\parallel}(E_z) + k_{\parallel}(E_y) + k_{\parallel}(E_x)] \) in Figure 9c. UV-vis spectrum of AuNHs suspended in DI water shows the absorption maximum at a wavelength range of 500–700 nm (Figure S5), which corresponds with the FDTD simulation results. Two factors may make a discrepancy in experimental results. Two factors may make a discrepancy in experimental spectrum and simulations. The simulations were carried out with three different incidences of the light. Respectively, \( k_{\parallel}(E_y) \) and \( k_{\parallel}(E_z) \) represent perpendicular incidences \( k_{\parallel} \) of the light with parallel \( (E_z) \) and perpendicular \( (E_y) \) e-field polarization with the AuNH, whereas \( k_{\parallel}(E_z) \) represents a parallel incidence \( k_{\parallel} \) of the light with transverse \( (E_y) \) e-field polarization. While the extinction cross-section of \( k_{\parallel}(E_z) \) showed a relatively minimal intensity and gradually increased as the wavelength of the light increased to 700 nm, the \( k_{\parallel}(E_z) \) and \( k_{\parallel}(E_x) \) incidences showed maxima in spectrum at 660 and 570 nm, respectively, as shown in Figure 9c.

In order to characterize the modes of the plasmonically enhanced e-field in the AuNHs, the e-field profiles in a cross-sectional plane of the AuNH were measured at the maxima wavelength of the extinction spectra (blue and red dot arrows shown in Figure 9c). Figure 10a,b shows maps of the absolute values of the e-fields in the YZ plane at 660 nm with perpendicular \( [k_{\parallel}(E_z)] \) and parallel \( [k_{\parallel}(E_y)] \) incidences, respectively. In the case of 660 nm incidence, strong e-field enhancement near the outside girth of AuNH is observed with \( k_{\parallel}(E_y) \); on the other hand, e-field enhancement inside AuNH is observed with \( k_{\parallel}(E_z) \), which is reasonably understood in light of the parallel e-field formation inside a solenoid coil. In addition, the area of the strong e-field enhancement resulting from the \( k_{\parallel}(E_y) \) incidence was smaller than that resulting from the \( k_{\parallel}(E_z) \) incidence, a result which is highly consistent with the larger excitation cross-section of \( k_{\parallel}(E_y) \) than that of \( k_{\parallel}(E_z) \) at 660 nm, as shown in Figure 9c. According to the e-field profiles of the \( k_{\parallel}(E_y) \) incidence at 570 nm, e-field enhancement near the outside of the AuNH still existed even though its intensity relatively decreased compared to that shown in Figure 10a. Similarly, relatively small e-field enhancement inside the AuNH resulting from the \( k_{\parallel}(E_z) \) incidence at 570 nm in comparison to that at 660 nm (Figure 10b) is shown in Figure 10d. However, the extinction cross-section of \( k_{\parallel}(E_z) \) at 570 nm along with the lowest e-field enhancement inside the AuNH in comparison to that of \( k_{\parallel}(E_z) \) at 570 nm and that of \( k_{\parallel}(E_z) \) at 660 nm (Figure 9c) would be explained by the scattering cross-section of the \( k_{\parallel}(E_z) \) incidence at 570 nm being larger than that of \( k_{\parallel}(E_z) \) at 570 nm and \( k_{\parallel}(E_y) \) at 660 nm. Interestingly, Figure 10d shows stronger e-field propagation from the AuNH to the outside than is shown in the other figures, which is highly consistent with the assumption of relatively a large scattering cross-section in \( k_{\parallel}(E_z) \) at 570 nm.

In terms of results, the peaks of total extinction \( [k_{\parallel}(E_y) + k_{\parallel}(E_x) + k_{\parallel}(E_z)] \) at 660 and 570 nm, as shown in Figure 9c, were dominantly influenced by absorption (strong e-field enhancement near the AuNH) and the scattering of light incidence, respectively. Owing to the e-field enhancement and scattering near the AuNH in the visible range confirmed by the FDTD simulation characterization, the AuNHs can be used as substrates for SERS measurement.

2.3. SERS Measurements Using AuNHs as the Substrate. Based on the results of the FDTD simulations, it can be concluded that the e-field enhancement and scattering

![Figure 10. E-field profiles of AuNHs with (a,b) 660 nm and (c,d) 570 nm of (a,c) \( k_{\parallel}(E_y) \) and (b,d) \( k_{\parallel}(E_z) \) incidences. The centers of the AuNHs were placed at (0,0,0) with the center axis of a given AuNH set along the Z-axis.](https://dx.doi.org/10.1021/acsomega.9b02586)
on AuNHSs are significant at ~660 nm. Therefore, 4-mercaptobenzoic acid (4MBA) molecules were employed as a probe, and He−Ne laser with the wavelength of 632.8 nm was employed as a light source for SERS observation. First, 4 mg of AuNHSs soaked overnight in 1 mL of 4MBA aqueous solution with different concentrations were isolated by centrifugation and then placed on a Si substrate and dried. The 4MBA molecules acted as detection molecules as they carry the −SH functional group on one end and have the ability to form a covalent bond with gold, producing a self-assembly monolayer arrangement on the gold surface. The Raman signals of 4MBA molecules at 1075 and 1590 cm$^{-1}$ are $v_{12C−C\text{ring}}$ and $v_{14C−C\text{ring}}$ respectively. The sample exposure time during the taking of measurements was 5 s. Figure 11 shows that the SERS spectra the AuNHSs soaked in 200 ppm, 2 ppm, 200 ppb, and 20 ppb of 4MBA. At higher concentrations, the −SH functional group in the 4MBA molecules was able to form a strong Au−S covalent bond with the gold surface, replacing the surfactant; therefore, their SERS characteristic peaks were clear. With the reduction of 4MBA concentration, the SERS signals were weakened. When the 4MBA concentration was too low and the surfactant could not be replaced, its characteristic peaks appeared, where ~765, ~1300, and ~1480 cm$^{-1}$ are the C−Br, C−C, and N−C$_3$ stretching modes, respectively, of CTAB. The PEG and PVP characteristics peaks appeared at ~1370 cm$^{-1}$; other signals could not be clearly differentiated because of the overlapping of spectra. The concentration is as low as 20 ppb (~0.13 μmol/L), 4MBA molecule signals can still be discriminated. However, as the number of 4MBA is not sufficient to replace the surfactant, the characteristic signals of the surfactant and 4MBA simultaneously appear in the SERS spectrum. In comparison, a gold monolayer film was prepared as the SERS substrate to detect malachite green with a detection limit of 0.04 μmol/L. The Au@Ag plasmonic chip with the limit of detection of 20 ppb was reported for detecting thiabendazole in food. A similar gold nanostructure, namely, branched gold nanoworms, anchoring onto an ITO substrate was synthesized in an acetamide-based molten solvent possessing low 4MBA detection limit of ~10$^{-2}$ μmol/L. Furthermore, the trace thiram (0.5 ppm) on an orange pericarp was detected with a correlation coefficient of 0.979 using a gold nanoparticle metalfilm as the SERS substrate. The SERS measurements taken in this study confirmed the results of the FDTD simulations. AuNHSs and their helical structures can produce a large number of hot spots. When 4MBA molecules reach the hot spot, they are affected by the coupling effect of an electromagnetic field, which strengthens the detection signals.

3. CONCLUSIONS

In this study, we provide a new solution route for the synthesis of AuNHSs with high yield using a surfactant-assisted method combined with a seed-mediated growth strategy. By precisely regulating the stoichiometry of the reactants and the surfactants, Au(III) ions were reduced and grew on the gold nanoseeds, leading to the formation of AuNHSs in the confined space generated using the three surfactants. The driving force for the helical conformation is the twin growths on the {111} facets with mirror symmetry. The FDTD simulations showed that total extinction at 660 and 570 nm upon light incidences were dominantly influenced by absorption and scattering, respectively, while SERS measurements verified that AuNHSs have superior SERS enhancement with the detection limit in the ppb region.

4. EXPERIMENTAL SECTION

4.1. Synthesis of AuNHSs. Cetyltrimethylammonium bromide ((CH$_3$(CH$_2$)$_{15}$N(CH$_3$)$_3$Br, ≥98%, Sigma-Aldrich, 0.3633 g) was dissolved in deionized water (10 mL). Hydrogen tetrachlorozurate(III) trihydrate (HAuCl$_4$·3H$_2$O, 99.9%, Sigma-Aldrich, 0.02 M 0.0182 mL) was then added and evenly stirred at a room temperature. When the solution cleared up and turned faint yellow in color, sodium borohydride (NaBH$_4$, 99.9%, Sigma-Aldrich, 0.2 M 0.45 mL) was added. The solution was evenly stirred for 5 min and left at room temperature for 2 h, producing a gold nanoseeded solution. The AuNH synthesis method involved the addition of gold nanoseeded solution (0.01 mL) into deionized water (20 mL), followed by the addition of PEG (C$_{12}$H$_{25}$O(CH$_2$CH$_2$)$_n$OH, n = 12, Sigma-Aldrich, 0.0194 mL), PVP ((C$_3$H$_7$NO)$_n$M$_w$ ≈ 55,000, Sigma-Aldrich, 0.736 g, 0.667 mM), and CTAB (0.0242 g, 3.333 mM), after which the solution was stirred. HAuCl$_4$(aq) (0.045 mM 0.0182 mL) and ascorbic acid (C$_6$H$_8$O$_6$, 99.7%, Sigma-Aldrich, 0.1 M 0.056 mL) were then added in the solution. After the solution was evenly mixed, it was left for 20 h at 15 °C. The sample was then separated from the reaction solution using a centrifugal method. Repeated cleaning with deionized water and ethanol was used to remove excessive surfactants and gold nanoseeds.

4.2. Characterizations and Spectroscopic Measurements. Observations of the morphology of the samples were carried out with a scanning electron microscope (Hitachi S-4700) equipped with an energy-dispersive X-ray spectrometer (EDS). The transmission electron microscopy images and electron diffraction patterns were obtained using a transmission electron microscope (JEOL 2100F). The surface-enhanced Raman scattering spectra were acquired from a Raman spectrometer (NTEGRA NT-MDT) using a 632.8 nm He−Ne laser with a power of 3.35 mW as the light source. The laser beam was focused to a spot approximately 1 μm$^2$ with an accumulation time of 10 s.

4.3. FDTD Simulations. The dimensions of AuNHSs for the FDTD simulations (Lumerical Inc.) were assumed from the perfect AuNH structure obtained by the SEM measurement (Figure 3c). The dimensions for the AuNH in the model system were set at a length of about 2 μm, a width of 330 nm, and a wire thickness of 115 nm with four turns (with the gap
between turning being 500 nm) (Figure 9a) with the center axis of the AuNH set along the Z-axis. The refractive index (n) and extinction coefficient (k) of the Au materials based on Johnson and Christy data were used.\(^{40}\) A total-field scattered-field (TFSF) source with a plane monitor (placed at the YZ cross-section in the middle of the AuNH) was used for the simulations. The TFSF source was inlet through parallel (k\(_x\)) and perpendicular (k\(_z\)) directions of the AuNH. The e-field polarization of the perpendicularly inlet source (k\(_z\)) was set as parallel (E\(_z\)) and perpendicular (E\(_x\)) to the center axis of the AuNH, while only one transverse e-field polarization (E\(_x\)) was used in the source inlet in a parallel direction (k\(_x\)) to AuNH because of a rotational symmetry. The mesh size of the simulation was set as 20 nm\(^2\) for an accurate calculation. In terms of results, the extinction cross-section of the AuNH in the visible range (λ: 400–700 nm) corresponded to the three different incidences. In addition, e-field profiles in the YZ cross-section in the middle of the AuNH were also measured to characterize the e-field enhancing mode at the maxima of the extinction cross-section of the AuNH. More details regarding the FDTD simulation works of electrical field enhancement in AuNHs can be found in our previous report.\(^{25}\)

**Notes**

The authors declare no competing financial interest.

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