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Rational design and SERS properties of side-by-side, end-to-end and end-to-side assemblies of Au nanorods†

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By taking advantage of the anisotropy of AuNRs, we design different bifunctional PEG molecules to selectively bind to either the end or side face and simultaneously protect other faces of individual AuNRs. In this way, we successfully achieve orientation-controllable assemblies of AuNRs into side-by-side (SS), end-to-end (EE) and end-to-side (ES) orientations based on the electrostatic interaction between carboxylic PEG and CTAB capping on AuNRs. Furthermore, we find that the different orientations of assembled motifs in these three types of AuNRs assemblies exhibited different near field coupling between the surface plasma of the neighboring AuNRs, leading to different surface-enhanced Raman signals. Undoubtedly, the current rational design of oriented assembly can be potentially useful for directing anisotropic nanoparticles into well-defined orientations, which provides a powerful route in designing families of novel nanodevices and nanomaterials with programmable electrical and optical properties.

Introduction

Nowadays, the organization or assembly of nanoparticles is becoming an important research topic in the field of nanoscience because assemblies of nanoparticles may display new or enhanced properties in comparison with the individual nanoparticles *via* coupling effects among nanoparticles.¹ For example, when two metal nanoparticles are placed very close together, near field coupling may occur between their surface plasma due to the transfer and confinement of electromagnetic energy, which greatly enhances the local electromagnetic field between two adjacent nanoparticles.² The excitons of two semiconductor nanoparticles may also couple because of the electron transfer or resonance energy transfer between them, resulting in a red-shift of the adsorption and photoluminescence emission bands of the nanoparticles.³ The collective properties arising from the coupling effects depend not only on the size and shape of the individual building block, but also on the spatial orientation and

alignment among them,⁴ which is particularly interesting when the individual building block is anisotropic. So far, scientists have made great advances in nanoparticle assembly,⁵ and the syntheses of anisotropic nanoparticles have also achieved significant progress.⁶ However, the concept of anisotropic assembly is underdeveloped in most nanoparticle assembly schemes.⁷ Directing anisotropic assembly into well-defined orientations still remains a great challenge.

Gold nanorods (AuNRs) have attracted considerable attention for promising applications including photothermal therapy,⁸ biological imaging,⁹ gene and drug delivery,¹⁰ optical data storage,¹¹ sensing,¹² and surface-enhanced Raman scattering (SERS).^{2c,13} So far, different strategies have been developed for the assembly of AuNRs based on template-directed patterning,¹⁴ polymers,^{1a,15} biomolecular recognition,^{4a,16} solvent evaporation,¹⁷ hydrogen bonding,¹⁸ electrostatic interactions,¹⁹ and seed mediated growth.²⁰ Among these reported strategies, several experiments have been devoted to programming the anisotropic assemblies into the end-to-end (EE) or side-by-side (SS) mode *via* the soft modification of the nanorod face. The EE assemblies were based on modifying the end face with bifunctional molecules while leaving the side faces unaltered.^{4a,16a-c,18,19b,20} For SS assemblies, a typical technique was to coat the entire face of the gold nanorods with functional molecules.^{16c-f,19a} This would induce a general trend of side-side linkage due to increased lateral interaction with the side face, which contains a larger surface area than the end face. However, such an SS assembly was usually accompanied with EE and end-to-side (ES) assemblies because the end faces were also covered with the same functional molecules. Therefore, accurate modification of assembled motifs and control of the uniform ensembles were still

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problematic. Herein, by taking advantage of the anisotropy of AuNRs, we selectively modified different faces of AuNRs with different bifunctional molecules and successfully assembled AuNRs into highly uniform SS, EE and ES ensembles, respectively. Interestingly, we found that the different orientation of assembled motifs in these three types of AuNRs assemblies exhibited different near field coupling between the surface plasma of the neighboring AuNRs, leading to different surface-enhanced Raman signals.

Scheme 1 illustrates the design and fabrication of three types of assemblies of AuNRs. Generally, the AuNRs synthesized through the CTAB-capped seed in the presence of AgNO_3 are enclosed by a $\{110\}$ face on the side and a $\{100\}$ face on the end.²¹ The $\{110\}$ side face is densely capped by CTAB,²² while the $\{100\}$ end face is more exposed and accessible to chemical linkers such as thiol-PEG.²³ Taking advantage of this anisotropic property of AuNRs, we could first use HS-PEG to block the end face and then HS-PEG-COOH to selectively bind to the side face of AuNRs, resulting in the SS orientation assembly as shown in Scheme 1a. We could also let HS-PEG-COOH selectively bind only to the end face in order to obtain the EE orientation assembly (Scheme 1b). If we prepared two different types of modified AuNRs, one with HS-PEG-COOH on the end face and HS-PEG on the side face, and the other one blocked by HS-PEG only on the end face, we could realize ES orientation assembly as shown in Scheme 1c.

Experimental

Chemical reagents

Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.9%), cetyltrimethylammonium bromide (CTAB, 99%), sodium borohydride (NaBH_4 , 99%), L-ascorbic acid (AA, >99%) and silver nitrate (AgNO_3 , >99%) were purchased from Sino-pharm Chemical Reagent Co. Ltd. Thiol carboxylic polyethylene

glycol (HS-PEG-COOH, MW \sim 459 and 5000) and thiol polyethylene glycol ($\text{CH}_3\text{O-PEG-SH}$, MW \sim 2000) were obtained from Rapp Polymere GmbH, Germany. Malachite green isothiocyanate (MGITC) was purchased from Invitrogen Corporation, Carlsbad, CA. Ultrapure water ($18 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout the work.

Synthesis of AuNRs

AuNRs were prepared by the seed-mediated method, as reported by Murphy *et al.* with a slight modification.²⁴ First, we prepared a seed solution by adding a freshly prepared, ice-cold NaBH_4 solution (0.60 mL, 0.01 M) into a mixture solution composed of HAuCl_4 (0.25 mL, 0.01 M) and CTAB (7.50 mL, 0.1 M). This seed solution was used 2 h after preparation. Second, we prepared the AuNR growth solution by adding ascorbic acid (0.032 mL, 0.1 M) into a mixture containing HAuCl_4 (0.20 mL, 0.01 M), AgNO_3 (0.035 mL, 0.01 M), and CTAB (4.75 mL, 0.1 M). Third, 0.020 mL of seed solution was added into the above AuNR growth solution, and the reaction mixture was gently mixed for 30 s and left undisturbed for 5 h. The resulting AuNRs were purified by centrifuging at 8000 rpm for 25 min.

Side-by-side assembly

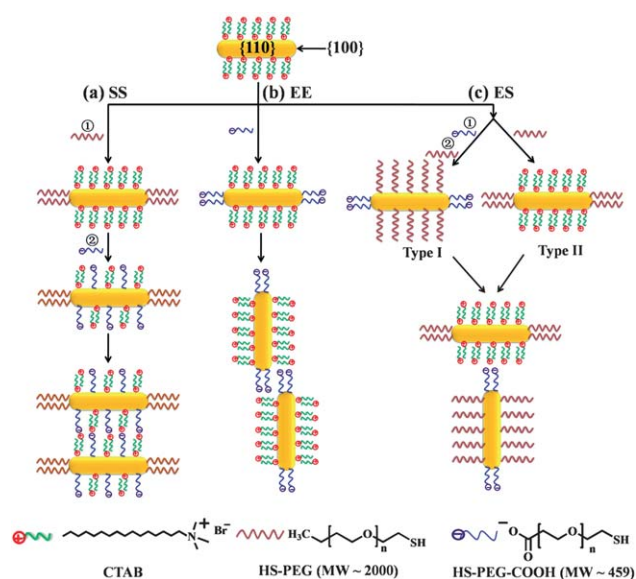
First, PEG-SH (0.30 mL, 1 μM , MW \sim 2000) was added dropwise to the AuNRs (1.50 mL, 0.5 nM) and stirred mildly for 15 min. Second, the solution was centrifuged twice at 7500 rpm for 20 min, followed by redissolving in water to yield a final concentration of 0.5 nM. Then, HS-PEG-COOH (0.10 mL, 10 μM , MW \sim 459) was added dropwise to the above solution (1.00 mL, 0.5 nM), resulting in a gradual color change from reddish to blue-violet, indicating the formation of SS oriented assembly in solution.

End-to-end assembly

First, the AuNRs were centrifuged three times at 7500 rpm for 20 min and redissolved in water to yield a final concentration of 0.5 nM. Next, HS-PEG-COOH (0.25 mL, 1.0 μM , MW \sim 459) was added dropwise to the above AuNRs (1.00 mL, 0.5 nM) and gently stirred. During this treatment, the color of the solution gradually turned from reddish to purple-gray, which indicated the formation of EE-oriented assembly in solution.

End-to-side assembly

We modified two different types of AuNRs. Type I was modified by the following method: first, HS-PEG-COOH (0.15 mL, 0.1 μM , MW \sim 459) was added dropwise to the AuNRs (1.50 mL, 0.5 nM) and stirred gently for half an hour, followed by centrifugation twice at 7500 rpm for 20 min. PEG-SH (0.3 mL, 10 μM , MW \sim 2000) was then added dropwise to the above AuNRs solution (1.00 mL, 0.5 nM) and stirred mildly for 48 h. Type II was modified in a different manner: PEG-SH (0.30 mL, 1 μM , MW \sim 2000) was injected dropwise into the AuNRs (1.50 mL, 0.5 nM) and stirred mildly for 15 min, followed by centrifugation three times at 7500 rpm for 20 min. Finally, we mixed these two types of AuNRs in a molar ratio of 1 : 1.



Scheme 1 Schematic diagram of (a) side-by-side (SS), (b) end-to-end (EE), and (c) end-to-side (ES) assemblies of Au nanorods.

Preparation of dye-modified AuNR assemblies for SERS measurements

EE: MGITC was used as Raman reporter molecules according to our previous report.²⁵ First, we added a freshly prepared MGITC solution (10 μL , 4 μM) dropwise to a rapidly mixing AuNR solution (1.00 mL, 0.5 nM). Second, HS-PEG-COOH (0.2 mL, 1.0 μM , MW \sim 459) was added dropwise to the above AuNRs (1.00 mL, 0.5 nM) to obtain the EE assembly. **SS:** First, PEG-SH (94 μL , 10 μM , MW \sim 2000) was added dropwise to the AuNRs (1.50 mL, 0.5 nM) and stirred mildly for 15 min. Second, we added a freshly prepared MGITC solution (10 μL , 4 μM) dropwise to the above AuNRs solution (1.00 mL, 0.5 nM). Third, HS-PEG-COOH (0.10 mL, 10 μM , MW \sim 459) was added dropwise to the above AuNRs (1.00 mL, 0.5 nM) to achieve the SS assembly. **ES:** We modified the AuNRs into two different types. One is the same as the Type I in ES assembly. The other one is the same as the MGITC-modified AuNRs in SS assembly mode. Then, we mixed these two types of AuNRs to prepare ES assembly.

Characterization

Transmission electron microscopy (TEM) images were obtained using Tecnai F30 operated at 300 kV. TEM samples were prepared according to Murphy's report.^{16d} Briefly, we immersed the TEM grids inside the sample solution for 2 min before removing the solution and using tissue paper to remove any small drops left on the TEM grid. The purpose of this treatment is to rule out any evaporation-related arrangement of AuNRs.^{16d} The UV-vis absorption data was collected on a DU 800 UV/vis spectrophotometer. The zeta potential was measured with a Malvern Zetasizer ZEN3600 instrument. The Fourier transform infrared (FT-IR) spectrum was obtained using a Nicolet Magana 550 FT-IR spectrophotometer. SERS spectra were recorded on a compact Raman system using 785 nm (40 mW) excitation (Advantage Raman Series, DeltaNu).

Results and discussion

Model of thiol-PEG bond to the end or side face of an AuNR

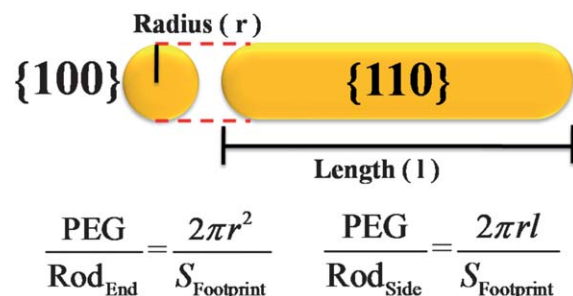
It is well known that thiol molecules can strongly bind to the gold surface. Because the {100} end face of the AuNRs are less densely capped by CTAB, the thiol molecules should preferentially adsorb onto the end face.^{16c,23} If the amount of thiol molecules added is accurately controlled, the majority of the thiols will only adsorb onto the end face of AuNRs. In addition, if more thiol molecules are further introduced, they will start binding to the side face of the AuNRs.^{16c,19b} We can calculate the amount of thiol molecules needed to accurately cover the end {100} or side {110} face by considering the footprint area of a thiol-PEG molecule. HS-PEG (MW \sim 2000) has a footprint of \sim 0.35 nm² according to Nie's²⁶ and Murray's²⁷ reports. HS-PEG-COOH (MW \sim 459) is not a coiled structure, and its footprint is approximated to be \sim 0.25 nm² according to Chen's work.^{13b} Therefore, for the as-synthesized AuNRs (ESI, Fig. S1†), about 500 HS-PEG (MW \sim 2000) and 700 HS-PEG-COOH (MW \sim 459) per AuNR are necessary to achieve complete package on the end face, while 4000 HS-PEG (MW \sim

2000) and 5600 HS-PEG-COOH (MW \sim 459) per AuNR are needed to fully cover the side face. We can then use these values to calculate the amount of thiol-PEG used (Scheme 2).

Side-by-side assembly

For the SS-oriented assembly (Scheme 1a), we first added a controlled number of PEG-SH (slightly below the theoretical value for the end face) to preferentially bind the end face of AuNRs as a barrier to prevent the attachment of other molecules (see the experimental part for details). Since the end has already been blocked by PEG-SH, the HS-PEG-COOH added subsequently is able to selectively bind to the side face of the AuNRs. An important finding is that the number of HS-PEG-COOH should be controlled to be below the theoretical value needed for complete coverage of the side face, such that only part of the CTAB capping molecules on the AuNRs are replaced. This is essential because SS assembly results from the electrostatic interaction between positively-charged CTAB remaining on the side face and negatively-charged HS-PEG-COOH on the side face of neighbouring AuNRs.

Fig. 1a–c shows the TEM images of the AuNRs in SS assembly. A large number of AuNRs are linked SS in parallel like ladders. It is worth mentioning that a space exists between each neighbouring cross-linked AuNRs, which makes the assembly different from the normal "aggregation" typically induced by adding salt. The spacing between each AuNR is measured to be 4.5 ± 0.5 nm as shown in Fig. 1c. Since the thickness of the CTAB bilayer and HS-PEG-COOH (MW \sim 459) layer are evaluated to be 3.2–3.9 nm²⁸ and 1–2 nm²⁶ respectively, the distance between the adjacent surfaces of the SS-assembled AuNRs can be approximately calculated to be 5 nm, which is consistent with that measured from TEM images. In order to rule out the possibility of solvent evaporation by TEM characterization and also to elucidate the dynamics of AuNRs assembly, time-dependent extinction spectra were further recorded at 2 min intervals. As shown in Fig. 1d, for the control sample, the ensemble transverse and longitudinal plasmon wavelengths are 512 and 780 nm, respectively; these originate from the oscillations of free electrons induced by the interacting electromagnetic field.^{5c} After the addition of HS-PEG-COOH into the PEG-SH protected AuNRs, the longitudinal plasmon peak strongly blue-shifts from 780 nm to 690 nm with a decrease in intensity, while the transverse plasmon peak slightly red-shifts with an increase in intensity as a function of time. Such changes in the extinction spectra are attributed to plasmon coupling in the closely spaced



Scheme 2 Model of thiol-PEG bond to the end or side face of an AuNR.

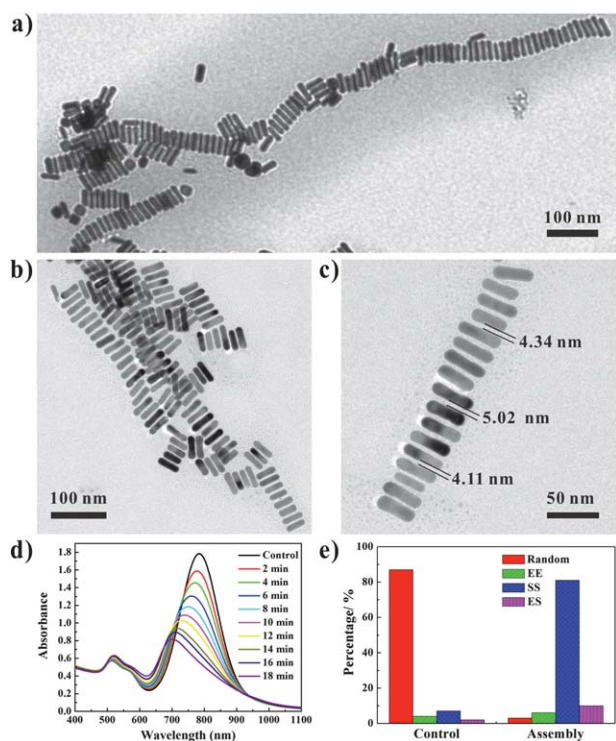


Fig. 1 The TEM images of SS-oriented assembly of AuNRs (a–c). (d) Time evolution of the absorption spectra of the SS-oriented assembly of AuNRs. (e) Proportions of different oriented assemblies of EE, SS, ES, and randomly dispersed AuNRs observed in TEM images. The control sample is subject to the same procedure described for the SS assembly, except that water is used instead of SH-PEG-COOH to eliminate dilution-related influences. In each case 300 AuNRs were counted.

AuNRs in the SS-oriented assembly structure, which qualitatively agrees with the numerical simulations of model systems.²⁹ Although a similar SS assembly pattern formed by biomolecular recognition has been observed in the past, a high degree of control for the assembly orientation was still problematic.³⁰ The design of using PEG-SH to preferentially protect the end face helps rule out random assembly and allows for excellent control over the oriented assembly. The assembly efficiency recorded from multiple TEM images reveals that nearly 81% AuNRs were in the SS assembly (Fig. 1e). In contrast, if we did not add the SH-PEG to preferentially block the end face (later in the text referred to as SS_{end not PEG}), irregular aggregations including SS, ES and EE oriented assemblies were obtained, as seen in the TEM images (Fig. 2a–b). Moreover, the UV-vis absorption spectra in Fig. 2c exhibit many differences from the spectra of the SS assembly sample shown in Fig. 1d. For the SS_{end not PEG} sample, the longitudinal plasmon absorption peak becomes broader and a shoulder peak around 950 nm appears with increasing time, indicating that a complex of SS, EE and ES assemblies exist in this sample, which were also seen in other literatures.^{16d–f} The assembly efficiency showed that only 60% AuNRs can be assembled into the SS orientation (Fig. 2d), which is much lower compared with the 81% yield of SS-oriented assembly by means of utilizing PEG-SH (MW ~ 2000) to block the end face of AuNRs. This process can be summarized in the schematic diagram of SS_{end not PEG} assembly (Fig. 2e).

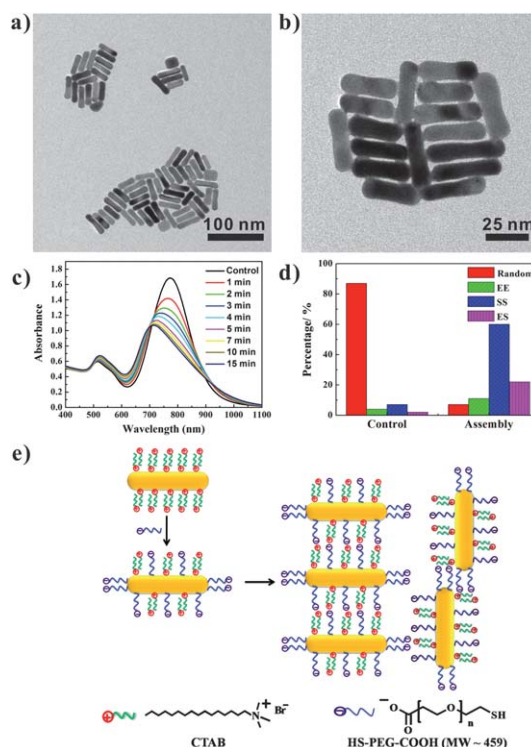


Fig. 2 The TEM images of SS-oriented assembly of AuNRs where PEG-SH was not used to preferentially block the end face of AuNRs (a–b). (c) Time evolution of the absorption spectra of the SS_{end not PEG} assembly of AuNRs. (d) Proportions of different oriented assemblies of EE, SS, ES, and randomly dispersed AuNRs observed in TEM images. (e) Schematic diagram of SS_{end not PEG} assembly of AuNRs. The control sample is subject to the same procedure described for SS_{end not PEG} assembly, except that water is used instead of SH-PEG-COOH to eliminate dilution-related influences. In each case 300 AuNRs were counted.

In order to monitor the assembly process, the zeta potential of the AuNRs in various stages was measured (Fig. 3a). The zeta potential of the original AuNRs (stage I) was 50 ± 4 mV, which originated from the CTAB capping on the side face of AuNRs. After we added PEG-SH (stage II), the zeta potential was almost unchanged, indicating that the PEG-SH just selectively bond to the end face, but did not displace CTAB on the side face. Then, when we added HS-PEG-COOH (stage III), the zeta potential sharply decreased to 5 ± 4 mV in 20 min. Such deep decrease in zeta potential suggests that the added HS-PEG-COOH might bind to the side face and replace the positively-charged CTAB molecules. However, the zeta potential of the final solution did not decrease to a negative value, indicating that HS-PEG-COOH had only replaced part of the CTAB. Through the electrostatic interaction between the negatively-charged HS-PEG-COOH and positively-charged CTAB existing on the side face of neighboring AuNRs, the AuNRs gradually assembled side-by-side. Throughout this process, the charge gradually neutralized and finally decreased to 5 mV. The above assembly process is consistent with that observed in the UV-vis spectra. Moreover, to further demonstrate that HS-PEG-COOH is deprotonated into negatively-charged $-\text{COO}^-$ terminals, the FT-IR spectrum was taken for the final AuNRs. Fig. 3b illustrates a characteristic peak near 1587 cm^{-1} , corresponding to the asymmetric stretching

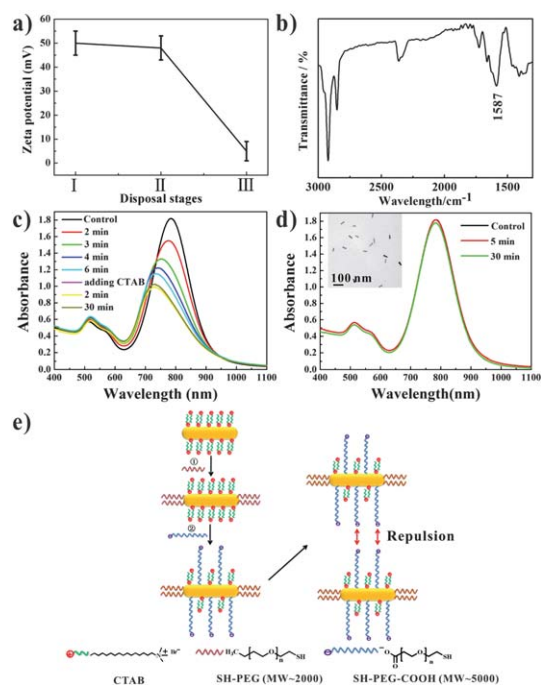


Fig. 3 (a) The zeta potential of AuNRs in various disposal stages: (I) the initial AuNRs, (II) after the addition of PEG-SH (MW ~ 2000) into AuNRs, (III) after the further addition of HS-PEG-COOH (MW ~ 459) into AuNRs. (b) FT-IR spectrum of the final AuNRs. (c) Time evolution of the absorption spectra of the SS-oriented assembly of AuNRs where CTAB was added at a ten-fold excess compared to HS-PEG-COOH (MW ~ 459) after the addition of HS-PEG-COOH (MW ~ 459) for six minutes. (d) the UV-vis absorption spectra of SS-oriented assembly of AuNRs with HS-PEG-COOH (MW ~ 5000) (later in the text referred to as SS₅₀₀₀-oriented assembly) (Inset: The TEM image). (e) Scheme of SS₅₀₀₀-oriented assembly of AuNRs with HS-PEG-COOH (MW ~ 5000).

vibrations of carboxylate ions,³¹ proving that HS-PEG-COOH has been deprotonated into -COO^- terminals with a negative charge in the final AuNRs. To further attest that the SS assembly was mediated through electrostatic interactions, we added free CTAB at a ten-fold excess compared to HS-PEG-COOH into the assembling AuNRs to competitively bind the SH-PEG-COO⁻ on the AuNRs surface. Upon this addition, the assembly was halted and no further shift in plasmon peak could be seen (Fig. 3c), indicating that SS assembly was indeed the result of electrostatic interaction between SH-PEG-COOH and CTAB of the adjacent AuNRs. Moreover, to ascertain whether hydrogen bonding exists in our case, SH-PEG-COOH (MW ~ 5000) with the thickness larger than CTAB²⁶ was used instead of SH-PEG-COOH (MW ~ 500). If any SS-oriented assembly of AuNRs appears under these conditions, the assembly would be the result of hydrogen bonding. However, we did not observe SS assembly (Fig. 3d), confirming that the SS assembly is formed through electrostatic interactions instead of hydrogen bonding.

End-to-end assembly

For the EE assembly, we controlled the amount of HS-PEG-COOH to preferentially functionalize only the end face of the AuNRs. Then, the negatively-charged HS-PEG-COO⁻ on the end face, electrostatically interacted with the positively-charged

CTA⁺ near the end face of neighboring AuNRs, thus inducing the assembly of AuNRs into the EE orientation described in Scheme 1b, as shown in Fig. 4a–b. In this case, we did not find ES assembly, even though electrostatic interaction between positively-charged CTA⁺ on the side face and the negatively-charged HS-PEG-COO⁻ on the end face could be strong. We supposed that the electrostatic repulsion between the CTA⁺ capping on the side faces of neighboring AuNRs (Scheme 3) is strong enough to hinder AuNRs from forming such an assembly.

UV-vis spectroscopy (Fig. 4c) was further utilized to study the assembly process. After HS-PEG-COOH was added to the AuNRs, the transverse plasmon absorption peak (512 nm) was unchanged, while the longitudinal plasmon absorption peak (780 nm) gradually decreased in intensity. Simultaneously, a shoulder peak around 980 nm started to appear and gradually shifted toward the longer wavelength, increasing in intensity with time. The presence of an isosbestic point around 850 nm indicated the existence of both isolated and assembled AuNRs.³² These observations indicate that AuNRs assembled EE, which is consistent with previous reports by Kamat¹⁸ and the numerical simulations of model systems.²⁹ The EE assembly efficiency (Fig. 4d) showed that 65% of AuNRs were assembled into EE assembly, which is higher than previous 30% EE assembly efficiency by bio-recognition.^{16b}

End-to-side assembly

Considering the strong electrostatic repulsion between positively-charged CTAB capping on the side faces of neighboring AuNRs, we prepared two different types of AuNRs for the ES assembly, as shown in Scheme 1c. Type I was first modified with HS-PEG-COOH on the end; then PEG-SH was introduced to the side to completely remove CTAB for the purpose of locally

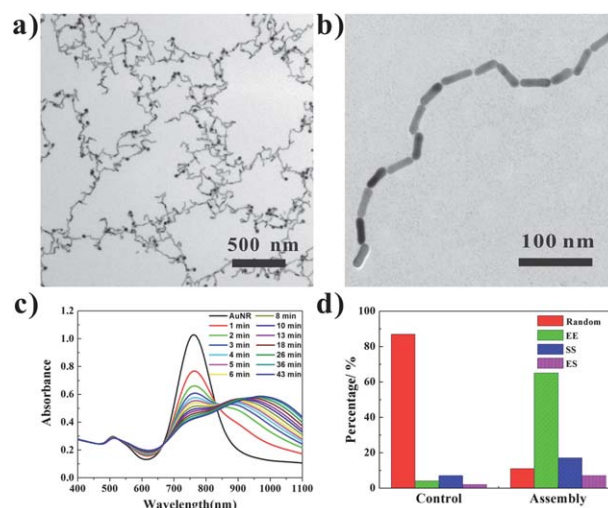


Fig. 4 The TEM images of EE-oriented assembly of AuNRs (a) in low magnification and (b) in higher magnification. (c) Time evolution of the absorption spectra of the EE-oriented assembly of AuNRs. (d) Proportions of different oriented assemblies of EE, SS, ES, and randomly dispersed AuNRs observed in TEM images. The control sample is subject to the same procedure described for EE assembly, except that water is used instead of SH-PEG-COOH to eliminate dilution-related influences. In each case 300 AuNRs were counted.

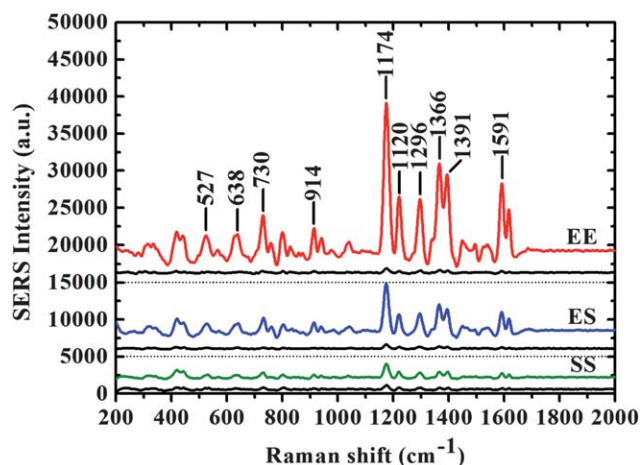


Fig. 6 SERS from different orientations of assembled motifs in these three types of AuNR assemblies. Red curves: EE orientation; blue curves: ES orientation; green curves: SS orientation; black curves: corresponding control sample before assembly. Laser wavelength = 785 nm; laser power = 40 mW; integration time = 10 s. The Raman reporter molecule is malachite green isothiocyanate (MGITC).

with laser light polarized along the assembled axis and the middle column (b, e, h) is taken with laser polarized perpendicularly to the assembled axis. The direction of the electric-field was marked with an arrow in the corresponding figure. It can be seen that the electric-field enhancement is highly dependent on the polarization direction of laser^{2c} and the orientations of assembled motifs. When the laser light is polarized along the assembled axis, the

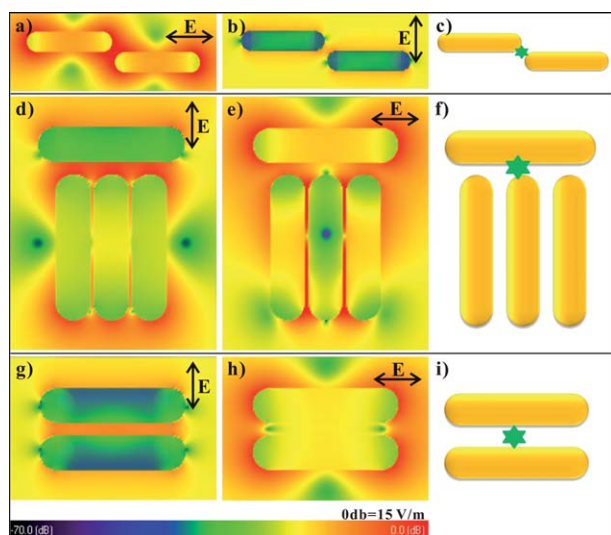


Fig. 7 FDTD simulated electric-field distribution for EE (a, b), ES (d, e) and SS (g, h) assembly motifs taken with 785 nm laser. The left column (a, d, g) is taken with laser light polarized along the assembled axis and the middle column (b, e, h) is taken with laser light polarized perpendicular to the assembled axis. The scale bar is given at the bottom. The direction of the electric-field was marked with an arrow in the corresponding figure. (c, f, i) The diagrams of Raman reporter (star) located at the gaps in EE, ES and SS assembly motifs. For ES assembly, the simulation was carried out on the configuration of one rod connected to three rods since it is the main product in this motif.

highest surface enhancement factors in EE, ES and SS assemblies are about 6×10^5 (a), 2.9×10^4 (d) and 453 (g), respectively. That is to say, the Raman reporter molecules located at the gap between the AuNRs can be differently enhanced in the sequence of EE > ES > SS. In contrast, with the laser polarized perpendicularly to the assembled axis, the electric-fields at the gaps where Raman reporter molecules located are weak, and there would be little contribution to the electric field enhancement. Therefore, our experimental observations agree well with the theoretical predictions that the SERS enhancement is the sequence of EE > ES > SS. Moreover, the experimental enhancements of these assemblies are lower than that of the simulated value. This is because the highest EF in the simulated calculation is taken by the laser light polarized along the assembled axis, which is not the case in our experiment. As a result, the different field enhancement among these three assembly motifs could probably be understood in terms of the “lightning rod” effect,^{34–36} which can increase the local electric field at the highly curved and sharp face. For the EE assembly motif, the antenna effect is stronger and more “hotspots” are generated, thus resulting in the highest SERS intensity, making EE assemblies excellent candidates as SERS substrates.

Conclusions

In conclusion, the present work has demonstrated a facile approach to the fabrication of orientation controlled assemblies of AuNRs into side-by-side, end-to-end and end-to-side motifs by integrating the anisotropy in the assembly of AuNRs. In addition, we observe that the surface-enhanced Raman signals are highly sensitive to the assembled orientation (EE > ES > SS). The assembly was rationally designed based on designing various bifunctional PEG molecules to selectively functionalize designated faces and simultaneously protecting other faces of AuNRs, utilizing the electrostatic interaction between carboxylic PEG and CTAB capping on AuNRs to direct the three types of assembly. Importantly, by means of modifying the different faces of AuNRs in different ways, we notably improve the controllability and accuracy of assembly orientation. Furthermore, the three types of assembly will find use in applications that take advantage of the ability to tune the unique physical properties of these structures, such as plasmonic-based circuitry or waveguides, and photonic bandgap materials, which largely depend on orientation. The present assembly strategy will be widely applicable to directing anisotropic nanoparticles into well-defined orientations, which provides a powerful route in designing families of novel nanodevices and nanomaterials with programmable electrical and optical properties.

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