

## Electronic Supplementary Information

### Rational Design and SERS properties of Side-by-Side, End-to-End and End-to-Side Assemblies of Au Nanorods

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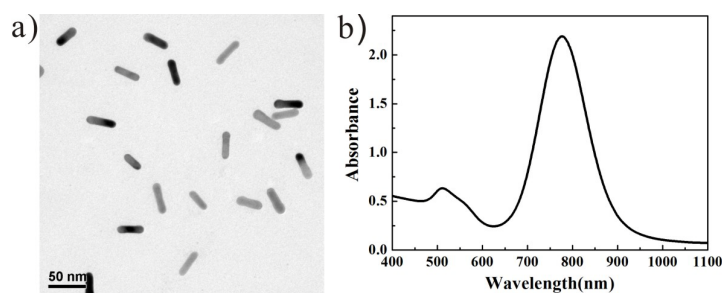
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#### Section 1. Synthesis of AuNRs

Fig. S1a shows the TEM image of the as-prepared AuNRs, which are isolated and randomly dispersed. The average length, diameter, and aspect ratio, determined from  $\approx 300$  AuNRs on TEM images, are  $38 \pm 4$  nm,  $11 \pm 2$  nm, and  $3.5 \pm 0.5$ , respectively. The zeta potential of the AuNRs was measured to be around +50 mV due to CTAB capping on the side face of AuNRs. The AuNRs concentration is estimated to be  $\approx 0.8$  nM according to previously determined molar extinction coefficients.<sup>1</sup> Fig. S1b shows the UV-vis spectra of the prepared AuNRs. The ensemble transverse and longitudinal plasmon wavelengths are 512 and 780 nm, respectively.



**Fig. S1** The TEM image (a) and the UV-vis absorption spectra (b) of AuNRs.

## Section2. Determination of SERS enhancement factor

The surface enhancement factor (EF) was calculated based on Eq 1<sup>2</sup>:

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{NRS} / N_{NRS}} = \frac{I_{SERS} / (C_{SERS} \times V_{SERS})}{I_{NRS} / (C_{NRS} \times V_{NRS})} = \frac{I_{SERS} / C_{SERS}}{I_{NRS} / C_{NRS}} \quad (1)$$

Where  $I_{SERS}$  and  $I_{NRS}$  denote the integrated intensities for the strongest band of the measured SERS and normal Raman scattering (NRS), from MGITC dissolved in water.  $N_{SERS}$  and  $N_{NRS}$  represent the number of MGITC excited by a laser beam in SERS and NRS, respectively.  $V_{SERS}$  and  $V_{NRS}$  is the volume irradiated by a laser beam in SERS and NRS, respectively.  $C_{SERS}$  is the concentration of MGITC in SERS-AuNRs solution, where we assumed all MGITC was bound.  $C_{NRS}$  is the concentration of MGITC in water. The strongest Raman peak at  $1174 \text{ cm}^{-1}$  ( $\nu_9$  benzene in plane)<sup>3</sup> was chosen for EF calculation.

The ratio of surface enhancement factors between assembled AuNRs and a single AuNR was calculated based on Eq 2:

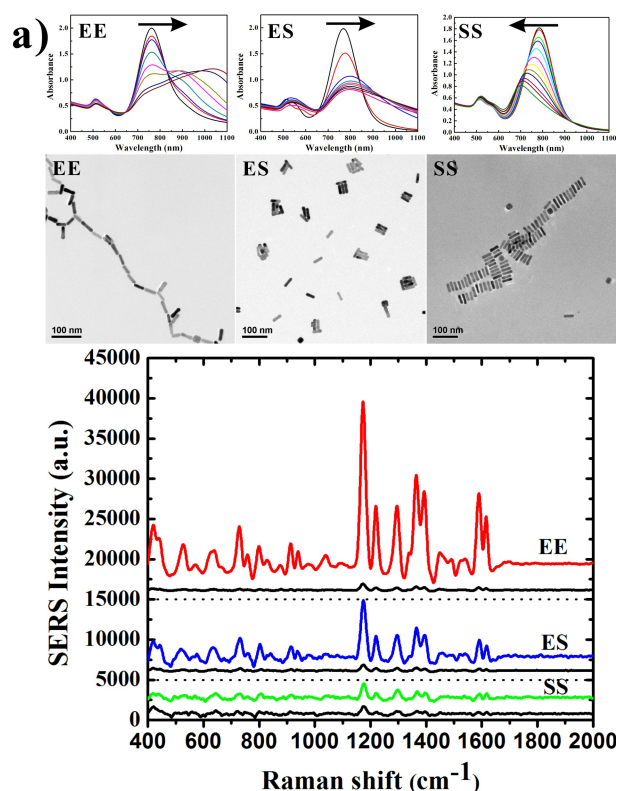
$$R_{EF} = \frac{EF_{Assembly}}{EF_{Single}} = \frac{\frac{I_{SERS^{Assembly}} / N_{SERS^{Assembly}}}{I_{NRS} / N_{NRS}}}{\frac{I_{SERS^{single}} / N_{SERS^{single}}}{I_{NRS} / N_{NRS}}} = \frac{I_{SERS^{Assembly}}}{I_{SERS^{single}}} \quad (2)$$

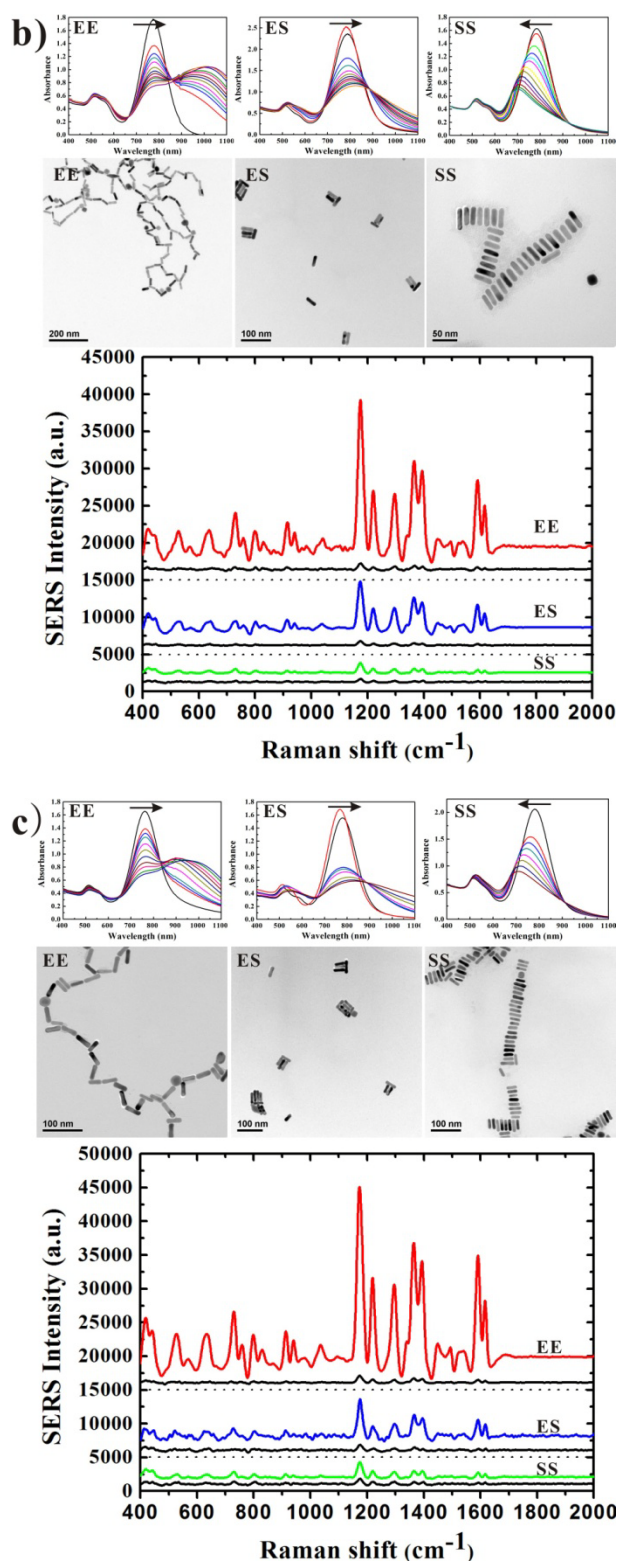
$R_{EF}$  represents the ratio of surface enhancement factors between assembled AuNRs and a single AuNR.  $EF_{Assembly}$  and  $EF_{Single}$  represent the surface enhancement factor of assembled AuNRs and a single AuNR (no assembly), respectively.

### Section 3. Reproducible experiments of AuNR assemblies in different orientations and their corresponding SERS properties

In order to ensure reproducibility of our own results, all measurements were performed over three repeats for each AuNR assembly motif. Figure S2 shows the UV-vis absorption spectra, TEM images and SERS from separately prepared AuNRs assembly. Both the assembly behavior and their corresponding SERS properties which include the position and intensity of all the observed modes showed a remarkable reproducibility.

Enhancement in signal intensity was further quantified by estimating the signal enhancement factor (EF). As shown in Table S1, the EF for EE, ES and SS motifs are about  $4\sim 5 \times 10^4$ ,  $1.4 \times 10^4$  and  $0.3 \times 10^4$  respectively, and the reproducibility of this work is good enough.





**Fig. S2** Reproducible experiments (a, b, c) from different, independently prepared AuNR assembly samples in EE, ES and SS orientations. The UV-vis absorption spectra (top), TEM images (middle) and SERS spectrum (bottom). The arrow represents the direction of the transverse plasmon peak shift.

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**Table S1** SERS enhancement factor for separately prepared AuNRs assembly in different orientations. Abbreviations:  $R_{EF}$  = the ratio of surface enhancement factors between assembled AuNRs and a single AuNR

Sample	Assembly motif	EF	$R_{EF}$
a	EE	$4.0 \times 10^4$	26.96
a	ES	$1.4 \times 10^4$	10.48
a	SS	$0.32 \times 10^4$	1.75
b	EE	$4.0 \times 10^4$	29.64
b	ES	$1.2 \times 10^4$	12.45
b	SS	$0.26 \times 10^4$	3.73
c	EE	$5.0 \times 10^4$	26.32
c	ES	$1.4 \times 10^4$	7.88
c	SS	$0.4 \times 10^4$	3.50

#### References:

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