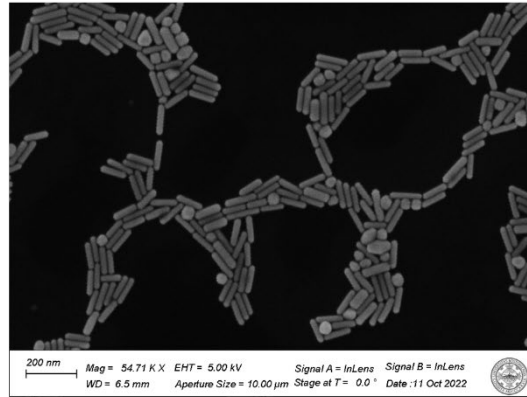


Supplementary information

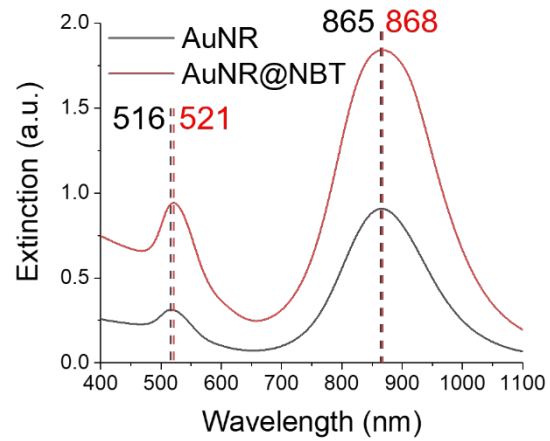
**Gap-enhanced gold nanodumbbells with single-particle surface-enhanced
Raman scattering sensitivity**

Ran Cheng, Danchen Jia, Zhiyi Du, Ji-Xin Cheng and Chen Yang*

a

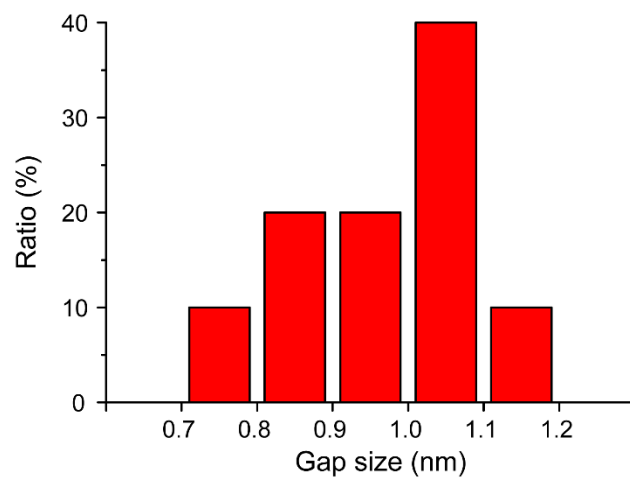


b

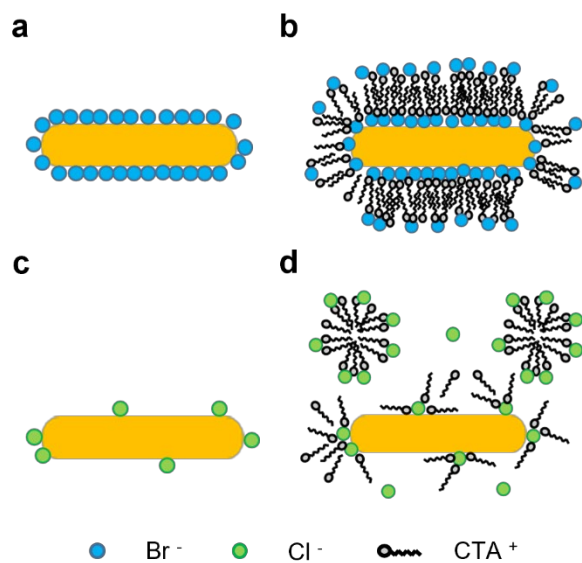


Supplementary Figure S1. Characterizations of AuNRs.

(a) SEM image of AuNRs. Scale bar: 200 nm. (b) Extinction spectra of AuNRs and NBT-functionalized AuNRs (AuNR@NBT). Both were dispersed in the CTAC solution.

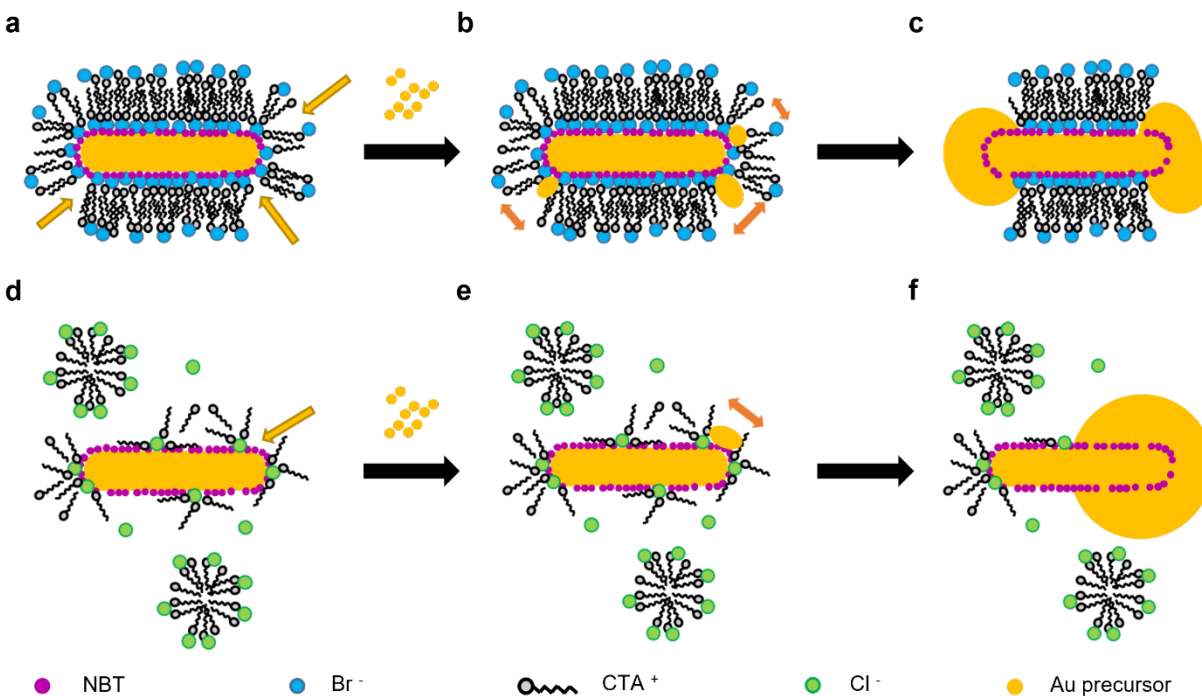


Supplementary Figure S2. Size distributions of the internal gap obtained from 10 gap features in 9 AuNDs.



Supplementary Figure S3. CTA- halide surfactant distributions on AuNR surface.

(a) Facet-dependent absorption of Br⁻ on bare gold nanorod surface. (b) Location-dependent distribution of CTAB on bare gold nanorod surface. (c) Weak absorption of Cl⁻ on bare gold nanorod surface. (d) Distribution of CTAC on bare gold nanorod surface.



Supplementary Figure S4. Potential shell growth mechanisms in different capping agent systems.

(a-c) Potential shell growth mechanism in the CTAB system, from diffusion-limited Au reduction (a), to seed deposition and formation (b) till growing into gap-enhanced AuND (c). The surfactant distribution on newly formed seeds and shells is not drawn in the schematic.

(d-f) Potential shell growth mechanism in the CTAC system, from rapid Au reduction due to less surfactant blockage (d), to rapid seed deposition and formation (e) till growing into AuNL (f). The surfactant distribution on newly formed seed and shell is not drawn in the schematic.

Supplementary Section S1. Calculation of enhancement factor.

1. Concentration of AuNRs@NBT and AuNDs

We firstly calculated the concentration of AuNRs synthesized in CTAB. For the rod solution, the concentration of gold was

$$[Au] = 0.54 \text{ mM}.$$

The molecular weight of Au is 197 g/mol, so the mass of gold in total in 1 mL solution would be:

$$m_{Au} = [Au] * V * M = 1.0638 * 10^{-4} \text{ g}$$

Considering all Au was reduced into AuNRs, the mass of gold could also be calculated this way:

$$m_{Au} = N_{AuNR} * \rho_{Au} * V_{AuNR}$$

$$V_{AuNR} = \pi \left(\frac{d_{AuNR}}{2} \right)^2 * L_{AuNR}$$

According to the SEM measurements, the diameters and lengths of AuNRs were 24 nm and 103 nm.

The density of Au is 19.3 g/mL. Therefore, the total number of AuNRs in 1 mL was around:

$$N_{AuNR} = 1.2 * 10^{11} \text{ NPs/mL}$$

corresponding to $2 * 10^{-13} \text{ mol/mL}$ in particle concentration.

As we mentioned in the method, the peak OD for AuNR@NBT was 1.2 times that of AuNRs in CTAB.

Therefore, the concentration of AuNR@NBT was:

$$[AuNR@NBT] = 2.4 * 10^{-13} \text{ mol/mL}$$

We assumed all the AuNRs@NBT were converted to AuNDs. The total number of AuNDs could be calculated by

$$N_{AuND} = [AuND] * V_{AuND} = N_{AuNR} = [AuNR@NBT] * V_{AuNR}$$

where 0.25 mL of $2.4 * 10^{-13} \text{ mol/mL}$ AuNR@NBT was used for the synthesis of AuNDs in a total volume of 1.94 mL. Therefore, the final concentration of AuNDs was:

$$[AuND] = 3.1 * 10^{-14} \text{ mol/mL}$$

2. Total number of molecules absorbed on the surface of AuNRs@NBT and AuNDs

The topological polar surface area of NBTs is 0.468 nm^2 ¹. We assumed a monolayer of NBT molecules was absorbed on the nanoparticle surface.

AuNR surface area could be calculated by

$$S = \pi dL = 7.76 * 10^3 \text{ nm}^2$$

The total number of NBT molecules per AuNR was

$$N_{NBT} = 1.66 * 10^4$$

Since there were no extra NBT molecules added for AuND synthesis, we expected that all the NBT molecules embedded in AuNDs came from the AuNR cores. The total number of NBT molecules per AuND was also $N_{NBT} = 1.66 * 10^4$.

3. Enhancement factor calculation

The enhancement factor is defined as the ratio of the SERS and normal Raman intensities normalized to the corresponding number of excited molecules and excitation power density,

$$EF = \frac{I_{SERS}/(N_{SERS} * P_{SERS})}{I_{Raman}/(N_{Raman} * P_{Raman})}$$

Since spontaneous Raman measurement of NBT powder sample and SERS measurement of nanoparticles were conducted under the same laser wavelength with the same objective (objective, 20X,

NA 0.4; laser condition, 633nm, 2.4 mW for SERS measurement of nanoparticle colloids, 0.504 mW for spontaneous Raman of NBT powder), the laser spot volume was the same.

The total number of NBT molecules in NBT powder sample under laser irradiation could be calculated by:

$$N_{Raman} = n_{NBT} * N_A = \frac{m_{NBT}}{M_{NBT}} * N_A = \frac{\rho_{NBT} * V_{spot}}{M_{NBT}} * N_A$$

Where the density of NBT (ρ_{NBT}) was 1.4 g/cm³, molecular weight of NBT (M_{NBT}) was 148 g/mol and N_A represents Avogadro's number.

The total number of NBT molecules on nanoparticle surfaces could be calculated by:

$$N_{SERS} = N_{NBT} * N_{NPS} = N_{NBT} * n_{NPS} * N_A = N_{NBT} * [NPS] * V_{spot} * N_A$$

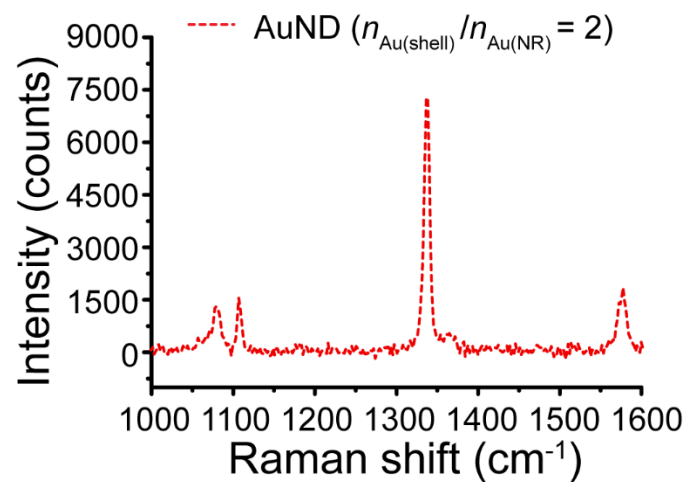
Therefore, the enhancement factor could be calculated as:

$$EF = \frac{I_{SERS}/(N_{SERS} * P_{SERS})}{I_{Raman}/(N_{Raman} * P_{Raman})} = \frac{I_{SERS}/P_{SERS}}{I_{Raman}/P_{Raman}} * \frac{\frac{\rho_{NBT} * V_{spot} * N_A}{M_{NBT}}}{N_{NBT} * [NPS] * V_{spot} * N_A} = \frac{I_{SERS}/P_{SERS}}{I_{Raman}/P_{Raman}} * \frac{\frac{\rho_{NBT}}{M_{NBT}}}{N_{NBT} * [NPS]}$$

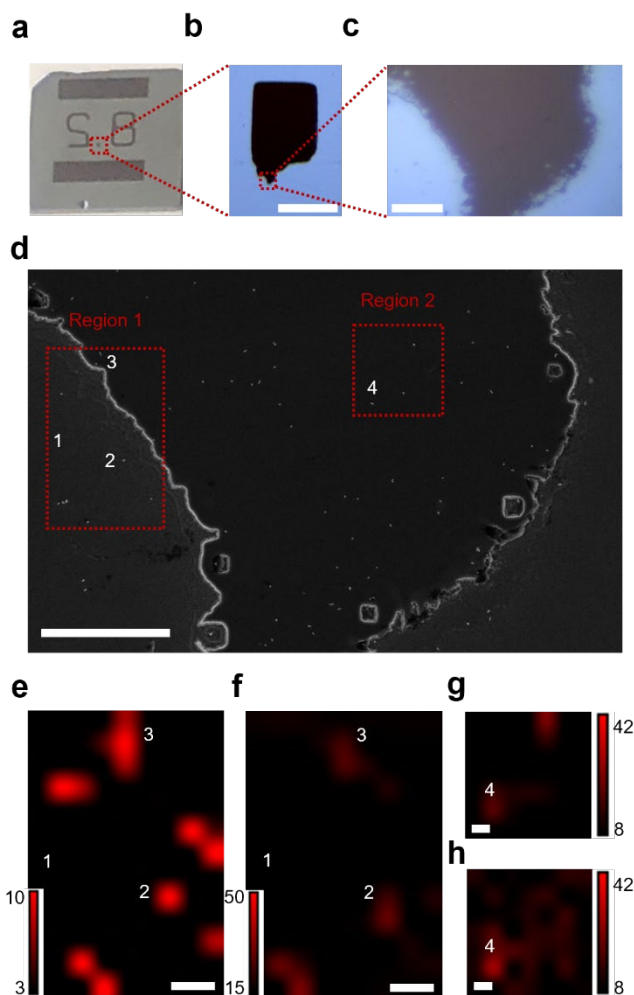
SERS intensities of nanoparticles and spontaneous Raman intensity of NBT powder sample could be found in **Table S1**. Enhancement factors of different nanoparticles could be calculated accordingly and were shown in **Table S1**.

Table S1. SERS intensities of different nanoparticles and corresponding EFs

| Sample | Position of major peak (cm⁻¹) | Averaged intensity (counts) | Experimental EF |
|--|---|------------------------------------|------------------------|
| NBT powder | 1338 | 23248 | |
| AuNRs ($n_{\text{Au(shell)}/n_{\text{Au(NR)}} = 0$) | 1345 | 763 | $1.6 * 10^4$ |
| AuNDs ($n_{\text{Au(shell)}/n_{\text{Au(NR)}} = 2$) | 1338 | 8450 | $1.4 * 10^6$ |
| AuNDs ($n_{\text{Au(shell)}/n_{\text{Au(NR)}} = 4$) | 1338 | 9979 | $1.7 * 10^6$ |
| AuNDs ($n_{\text{Au(shell)}/n_{\text{Au(NR)}} = 8$) | 1333 | 4617 | $7.7 * 10^5$ |



Supplementary Figure S5. Colloidal SERS performances of gap-enhanced AuNDs ($n_{\text{Au(shell)}}/n_{\text{Au(NR)}} = 2$) after storing at room temperature for 3 weeks, under excitation of 633 nm laser.



Supplementary Figure S6. Single-particle SERS study enabled by a labelled silicon substrate.

(a) A photo of the labelled silicon substrate used for the SERS and SEM imaging studies. The middle dot was chosen as the region of interest (ROI), indicated by the red box. (b) A bright-field image of ROI under 5X objective. Scale bar: 200 μm . (c) A bright-field image of ROI under 100X objective to indicate where the SERS and SEM were conducted. Scale bar: 10 μm . (d) A SEM image of ROI. Scale bar: 10 μm . Two regions (Region 1 and Region 2) were chosen for detailed analysis, indicated by the red box. (e-f) SERS mapping image at 1338 cm^{-1} with the acquisition time of 1 s (e) and 0.1 s (f) of Region 1. Scale bar: 2 μm . Location 1-3 were labelled to indicate where the SERS spectra in Figure 5 were taken. (g-h) SERS mapping

image at 1338 cm^{-1} with the acquisition time of 1 s (g) and 0.1 s (h) of Region 2. Scale bar: $1\text{ }\mu\text{m}$. Location 4 was labelled to indicate where the SERS spectra in Figure 5 were taken.

Reference:

1. Khlebtsov, B. N.; Khanadeev, V. A.; Burov, A. M.; Le Ru, E. C.; Khlebtsov, N. G.,
Reexamination of surface-enhanced Raman scattering from gold nanorods as a function of aspect ratio
and shape. *J. Phys. Chem. C* **2020**, *124* (19), 10647-10658.