Thickness-dependent SERS activities of gold nanosheets controllably synthesized via photochemical reduction in lamellar liquid crystals

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1. Experimental details

1.1 Chemicals

HAuCl₄·4H₂O (99%) was obtained from Nanjing Chemical Reagent Co. Ltd (China). Polyoxyethylene sorbitan monopalmitate (Tween 40) was purchased from Sinopharm Chemical Reagent Co. Ltd (China). (1S)-(+) -10-camphorsulfonic acid (99%) (CSA) was purchased from Sigma-Aldrich Chemicals. R6G was received from Aladdin
reagents. All of the chemicals were used without further purification. Millipore purified water was used in all the experiment.

### 1.2 Synthesis of gold nanosheets

In the typical preparation of ultrathin gold nanosheets, HAuCl\(_4\)·4H\(_2\)O (\(x\) mg, \(x\) = 7.41, 22.2, 44.5) was dissolved in H\(_2\)O (1.8 ml) containing camphorsulfonic acid (0.001 mol, 0.23 g). Secondly added Tween 40 (0.001 mol, 1.28 g) into the mixture while keep slowly stirring at 333K. During the stirring by glass rod, small bubbles should be avoided. The precursor was cooled to 293 K and allowed to stand at that temperature for 1 h. The liquid crystal was placed under diffuse reflection sunlight for different periods of time \(t\) (\(t\) = 2 day, 4 days, 6 days) in plastic Petri dishes. The final products were transferred into centrifuge tube and washed alternately with ethanol and hot ultrapure water for each 3 times to remove excess Tween 40 and CSA. Finally the product was dispersed in ethanol for further characterization.

### 1.3 Characterizations

Powder XRD measurements were performed with a Philips X’Pert MPD Pro X-ray diffractometer with graphite-monochromated high-intensity Cu\(_{K\alpha}\) radiation (1.5418 Å) at 40 kV and 40 mA. The diffraction angle covered 20-90 degree with a step size of 0.02 degree. TEM images were recorded with a JEM-1011 Electron Microscope (JEOL) at an accelerating voltage of 100 kV. HRTEM was performed with a JEOL JEM-2010 instrument at an acceleration voltage of 200 kV. Raman spectra were recorded in a Bruker Multi RAM FT-Raman spectrometer. (Laser source: 633 nm, laser power: 6 mW, data collection time: 1 s). The morphology of the gold
nanosheets was analyzed by a scanning electron microscope (SEM, Hitachi S-4800) and optical microscope (Carl Zeiss Axio Scope A1).

Raman spectra were recorded in a Bruker Multi RAM FT-Raman spectrometer (Laser source: 633 nm light of a He-Ne laser). The laser beam diameter was calculated to be 551 nm (D=1.22 λ/NA, λ is the wavelength, NA is the numerical aperture). Rhodamine 6G (R6G) in ethanol was employed as the analyte. Different concentrations (10^{-5} M, 10^{-6} M and 10^{-8} M) were carried out to test the detection limit of R6G on the substrates. SERS samples were prepared by adding ethanol solution of R6G of suitable concentration (1 mL) to 9 mL of AuNSs solution (0.25 mM in gold). After 2 h for thermodynamic equilibrium to be reached, 10 µL analyte together with AuNSs was carefully dropped on the glass slide (25.4 mm × 76.2 mm) and dried under ambient conditions for each measurement. The spectra recorded sequentially in experiments with the same instrumental settings were compared. Thanks to the large size of AuNSs, the laser beam was focused on the middle of a single nanosheet to get the enhanced Raman signal. For the accuracy of experimental data, 20 random Au nanosheets were tested for every kind of nanosheet and presented the representative results.
Figure S1. (a) TEM images of gold nanostructures obtained using different concentrations of HAuCl₄: 0.01 M, 0.03 M, 0.06 M under natural sunlight for 2 days, 4 days and 6 days. (b) Schematic illustration of the Au nanosheets synthesis procedure using 0.01 M, 0.03 M and 0.06 M HAuCl₄.
The reaction systems showed little change in the color after being placed for two weeks under dark conditions, the corresponding SEM/TEM images showed that no product could be detected.

We got the average power density value of diffuse sunlight by collecting 4 days’ data hour by hour in different seasons before. It revealed that low irradiation power density (~420 µW/cm²) was the best condition. Instead, direct sunlight and Xeon light (Fig. S2b and S2c) which had much higher power density were not suitable for slow growth of Au nanosheets. Furthermore, when UV lamps acted as light source, both low (~60 µW/cm²) and high (~3360 µW/cm²) irradiation power densities exhibited a very low yield of Au nanosheets. This might be caused by the thermal effect of UV lamp which was harmful to the stability of lamellar liquid crystals.

**Figure S2.** Irradiation power densities values and products under (a) diffuse sunlight; (b) direct sunlight; (c) Xeon light; (d) 28W UV light; (e) 250W UV light.
Table S1. The final products obtained under sunlight, Xeon light and UV light with different strength.

<table>
<thead>
<tr>
<th>Light condition</th>
<th>Sample a</th>
<th>Sample b</th>
<th>Sample c</th>
<th>Sample d</th>
<th>Sample e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Irradiation Power Density (μW/cm²)</td>
<td>Diffuse sunlight</td>
<td>Direct sunlight</td>
<td>Xeon light (PLS-SXE300)</td>
<td>UV light-1 (28W, 365 nm)</td>
<td>UV light-2 (250W, 365 nm)</td>
</tr>
<tr>
<td>~ 420</td>
<td>~ 6100</td>
<td>~ 39600</td>
<td>~ 60</td>
<td>~ 3360</td>
<td></td>
</tr>
</tbody>
</table>

Products analysis

- Sample a: > 90% AuNSs
- Sample b: Small particles, AuNSs
- Sample c: Large particles, AuNSs
- Sample d: Au particles
- Sample e: Au particles

Figure S3. Optical images of AuNSs obtained under the same natural sunlight (6 days’ irradiation) with different concentrations of HAuCl₄: (a) 0.01 M, (b) 0.03 M, (c) 0.06 M.
Figure S4. An approximate linear relationship between the average side length of AuNSs and the concentration of HAuCl₄. (AuNSs obtained under the same natural sunlight for 6 days)

Due to the large side length (>2.5 μm) of the AuNSs, AFM may not be a good way to give a thickness-distribution. A method using optical image and software proposed by Zhang is suitable to make statistics analysis of the thickness of nanosheets. ¹ Jin reported that the thickness of Au nanoplates has a good linear relationship with the intensity difference in the R channel of optical image. ² So the distribution histograms of transmittance could reflect the general condition of thickness.
Figure S5. (a-b) Optical images of AuNSs-50 and AuNSs-100; (c-d) distribution histograms of transmittance using software of Image J.


Figure S6. AFM images of AuNSs obtained with (a) 0.03 M and (b) 0.06 M HAuCl₄; (c) correlation between the concentration of HAuCl₄ and the thickness of corresponding AuNSs.
Figure S7. Typical phenomena of curling-up near the edges of AuNSs. (a-b) TEM images; (c-d) SEM images.
Table S2. Assignment of selected Raman peaks of R6G.

<table>
<thead>
<tr>
<th>NRS (cm$^{-1}$)$^a$</th>
<th>SERS (cm$^{-1}$)$^b$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>613</td>
<td>609</td>
<td>In plane xanthenes ring deformation</td>
</tr>
<tr>
<td>775</td>
<td>770</td>
<td>Out of plane C-H bending</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In plane xanthenes ring deformation, C-H bending, N-H bending</td>
</tr>
<tr>
<td>1184</td>
<td>1181</td>
<td>In plane xanthenes ring breathing, N-H bending, CH$_2$ wagging</td>
</tr>
<tr>
<td>1312</td>
<td>1309</td>
<td>In plane xanthenes ring breathing, N-H bending, CH$_2$ wagging</td>
</tr>
<tr>
<td>1364</td>
<td>1358</td>
<td>Xanthenes ring stretching, in plane C-H bending</td>
</tr>
<tr>
<td>1512</td>
<td>1507</td>
<td>Xanthenes ring stretching, C-H stretching, C-H bending, N-H bending</td>
</tr>
<tr>
<td>1577</td>
<td>1572</td>
<td>Xanthenes ring stretching, in plane N-H bending</td>
</tr>
<tr>
<td>1651</td>
<td>1644</td>
<td>Xanthenes ring stretching, in plane C-H bending</td>
</tr>
</tbody>
</table>


(b) Experimental data.
**Table S3.** AEF and average AEF values of AuNSs-8, AuNSs-50 and AuNSs-100 (10^{-5} M R6G, signals at 1358 cm\(^{-1}\) and 1507 cm\(^{-1}\) in Figure 5a)

<table>
<thead>
<tr>
<th></th>
<th>AuNSs-8</th>
<th>AuNSs-50</th>
<th>AuNSs-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak (cm(^{-1}))</td>
<td>1358</td>
<td>1507</td>
<td>1358</td>
</tr>
<tr>
<td>AEF</td>
<td>2.26×10^4</td>
<td>2.05×10^4</td>
<td>1.20×10^5</td>
</tr>
<tr>
<td>Average AEF</td>
<td>2.15 × 10^4</td>
<td>1.08 × 10^5</td>
<td>4.61 × 10^3</td>
</tr>
</tbody>
</table>

**Table S4.** AEF and average AEF values of AuNSs-8, AuNSs-50 and AuNSs-100 (10^{-6} M R6G, signals at 1358 cm\(^{-1}\) and 1507 cm\(^{-1}\) in Figure 5b)

<table>
<thead>
<tr>
<th></th>
<th>AuNSs-8</th>
<th>AuNSs-50</th>
<th>AuNSs-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak (cm(^{-1}))</td>
<td>1358</td>
<td>1507</td>
<td>1358</td>
</tr>
<tr>
<td>AEF</td>
<td>3.08×10^4</td>
<td>3.22×10^4</td>
<td>1.50×10^5</td>
</tr>
<tr>
<td>Average AEF</td>
<td>3.15 × 10^4</td>
<td>1.49 × 10^5</td>
<td>1.29 × 10^4</td>
</tr>
</tbody>
</table>

a: AEF Calculation example of AuNSs-50 in Figure 5a.

AEF = \(\frac{I_{\text{SERS}}/C_{\text{SERS}}}{I_{\text{RS}}/C_{\text{RS}}}\)

Calculation for the peak at 1358 cm\(^{-1}\);

\(I_{\text{SERS}} = 4050\) counts, \(C_{\text{SERS}} = 1\times10^{-5}\) M

\(I_{\text{RS}} = 334\) counts, \(C_{\text{RS}} = 1\times10^{-1}\) M

\(\text{AEF} = \frac{I_{\text{SERS}}/C_{\text{SERS}}}{I_{\text{RS}}/C_{\text{RS}}} = \frac{4050/10^{-5}}{334/10^{-1}} = 1.20 \times 10^5\)

Calculation for the peak at 1507 cm\(^{-1}\);

\(I_{\text{SERS}} = 3965\) counts, \(C_{\text{SERS}} = 1\times10^{-5}\) M
\[ I_{RS} = 411 \text{ counts}, \ C_{RS} = 1 \times 10^{-1} \ M \]

\[ AEF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}} = \frac{3965/10^{-5}}{411/10^{-1}} = 0.96 \times 10^5 \]

Average AFE value = \((1.20+0.96)\times10^5/2 = 1.08 \times 10^5\)

b: AFE Calculation example of AuNSs-50 in Figure 5b.

\[ AEF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}} \]

Calculation for the peak at 1358 cm\(^{-1}\);
\[ I_{SERS} = 516 \text{ counts}, \ C_{SERS} = 1 \times 10^{-6} \ M \]
\[ I_{RS} = 334 \text{ counts}, \ C_{RS} = 1 \times 10^{-1} \ M \]

\[ AEF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}} = \frac{516/10^{-6}}{334/10^{-1}} = 1.50 \times 10^5 \]

Calculation for the peak at 1507 cm\(^{-1}\);
\[ I_{SERS} = 608 \text{ counts}, \ C_{SERS} = 1 \times 10^{-6} \ M \]
\[ I_{RS} = 411 \text{ counts}, \ C_{RS} = 1 \times 10^{-1} \ M \]

\[ AEF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}} = \frac{608/10^{-6}}{411/10^{-1}} = 1.48 \times 10^5 \]

Average AFE value = \((1.50+1.48)\times10^5/2 = 1.49 \times 10^5\)