

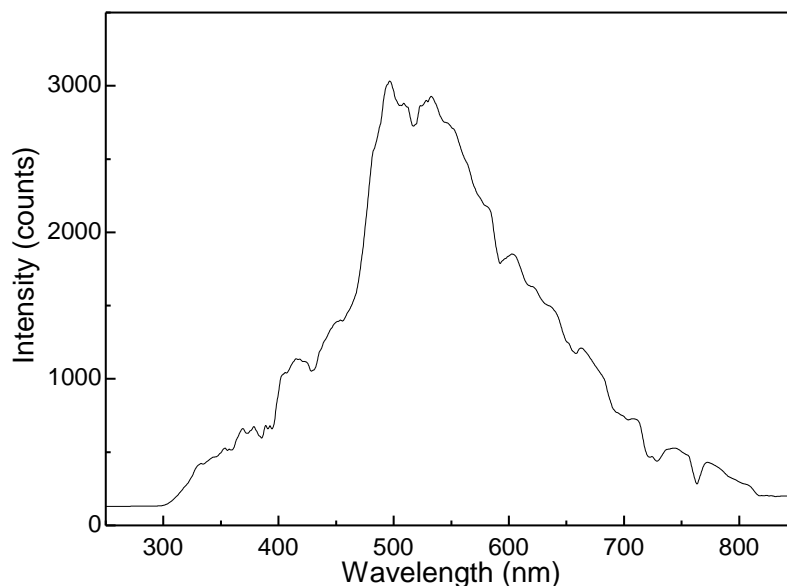
## Electronic Supplementary Information (ESI):

### Micrometer-Sized Gold Nanoplates: Starch-Mediated Photochemical Reduction Synthesis and Possibility of Application to Tip-Enhanced Raman Scattering (TERS)

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**Fig. S1** UV-visible spectrum of sunlight. The spectrum was collected by a fiber-optic portable UV/visible spectrometer (USB2000 UV/visible spectrometer, Ocean Optics). The integration time was 30 ms with 128 accumulation numbers, and the diameter of fiber-optic was 600  $\mu\text{m}$ . A fiber-optic was pointed directly to the sun for collecting an energy profile.

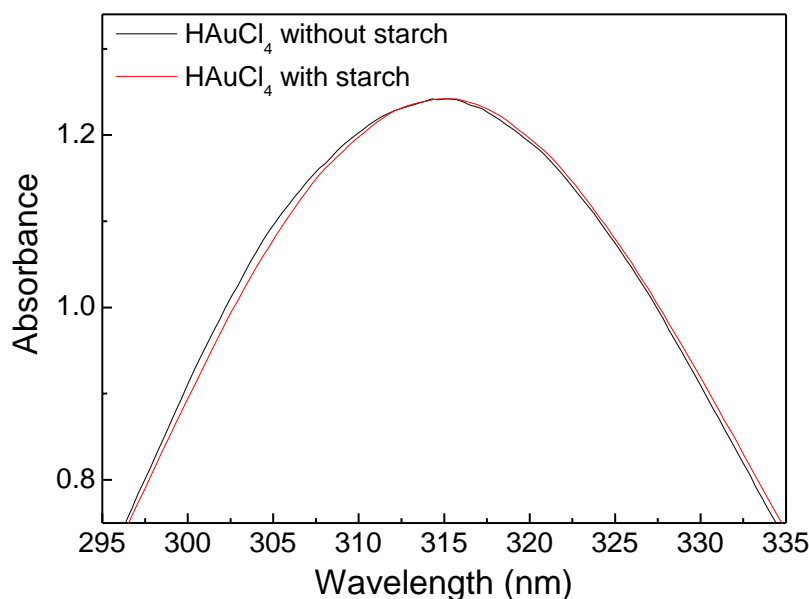


Fig. S2 UV-visible spectra of gold ion mixtures (0.2 M HCl 5 mL + 200 ppm HAuCl<sub>4</sub> (pH 7) 10 mL) in the presence and absence of starch.

The spectrum of gold ion in the presence of starch reveals a small red-shift at the band of charge transfer from Cl<sup>-</sup> to Au<sup>3+</sup> center in AuCl<sub>4</sub><sup>-</sup> (around 315 nm in spectrum) compared to that in the absence of starch. It indicates that the interaction between Cl<sup>-</sup> and Au<sup>3+</sup> in AuCl<sub>4</sub><sup>-</sup> was disturbed and weakened. This red-shift can also be implied that the complex of [Au(III)Cl<sub>4</sub><sup>-</sup>-starch] was formed. However, we cannot confirm the occurrence of [Au(II)Cl<sub>3</sub><sup>-</sup>-starch] and [Au(I)Cl<sub>2</sub><sup>-</sup>-starch] by ourselves. Fortunately, there were many works that discussed and proposed about the mechanism of photochemical reduction. The process of reduction from Au(III)Cl<sub>4</sub><sup>-</sup> to Au(II)Cl<sub>3</sub><sup>-</sup> and Au(I)Cl<sub>2</sub><sup>-</sup> via photoreduction and disproportionation is widely accepted.<sup>1,2</sup> Therefore, the evidence of [Au(III)Cl<sub>4</sub><sup>-</sup>-starch] combined with the reports about the existence of Au(II)Cl<sub>3</sub><sup>-</sup> and Au(I)Cl<sub>2</sub><sup>-</sup> are confidential that starch-mediated photochemical reduction really happens.

### **Reference**

- 1 S. Eustis, H.-Y. Hsu, M. A. El-Sayed, *J. Phys. Chem. B*, 2005, 109, 4811–4815.
- 2 S. Dong, C. Tang, H. Zhou, H. Zhao, *Gold Bull.*, 2004, 37, 187–195.

**Table S1** Raman band assignment for crystal violet.<sup>3</sup>

<b>Raman shift (cm<sup>-1</sup>)</b>	<b>Raman band assignment</b>
330	in-plane Ph–C <sup>+</sup> –Ph bending
433	out-of-plane Ph–C <sup>+</sup> –Ph bending
519	ring skeletal vib radical orientation
554	ring skeletal vib radical orientation
718	out-of-plane ring C–H bending
753	out-of-plane ring C–H bending
799	out-of-plane ring C–H bending
907	ring skeletal vib radical orientation
935	ring skeletal vib radical orientation
1168	in-plane ring C–H bending
1293	ring C–C stretching
1363	N-phenyl stretching
1532	ring C–C stretching
1580	ring C–C stretching
1613	ring C–C stretching

### **Reference**

- 3 E. J. Liang, X. L. Ye, W. Kiefer, *J. Phys. Chem. A*, 1997, **101**, 7330.