

## Supplementary Information

### **Building of lateral/vertical 1T-2H MoS<sub>2</sub>/Au heterostructure for enhanced photoelectrocatalysis and surface enhanced Raman scattering**

Xiaoli Zheng, Zhihua Guo, Guoyuan Zhang, Hao Li, Jianan Zhang and Qun Xu\*

College of Materials Science and Engineering, Zhengzhou University, Zhengzhou  
450052, P. R. China

\* Corresponding author, Email: qunxu@zzu.edu.cn

## 1. Experimental Section

**Materials.** Commercially available MoS<sub>2</sub> powder was purchased from Sigma-Aldrich (Fluka, product number 69860). H<sub>2</sub>SO<sub>4</sub> (Analytical reagent). 1-amino-9-octadecene (CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>8</sub>NH<sub>2</sub>, 70%, technique grade, Sigma-Aldrich). Hexane (≥97%, technique grade). Ethanol in all experiments was purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used without further purification. CO<sub>2</sub> with purity of 99.99% was provided by the Zhengzhou Shuangyang Gas Co. and used as received. Aqueous solution was prepared with deionized water.

**Synthesis of exfoliated MoS<sub>2</sub>.** In a typical process, 500 mg commercial MoS<sub>2</sub> powder were added into 5:5 ethanol/water mixtures (100 ml). The mixture was continuously sonicated in an ice bath for 8 h. Then the sonicated dispersion was centrifuged at 3000 rpm for 45 minutes to acquire supernatant. Finally, the supernatant was dried at 60 °C in the vacuum oven to obtain exfoliated MoS<sub>2</sub>.

**Synthesis of MoS<sub>2</sub>/Au.** 1 mg of the exfoliated MoS<sub>2</sub> was dispersed in the 0.5 mL of ethanol, and then the dispersion was added to the 2 ml mixture of hexane and ethanol (v/v = 7:1) containing 4 mM of H<sub>2</sub>SO<sub>4</sub> and 220 μL of 1-amino-9-octadecene. The mixed solution in a 10-ml glass bottle was heated in a water bath at 58 °C for 16 h. The final reacted solution was centrifuged at 5,000 rpm for 10 min and washed at least three times with hexane. Finally, the product was dissolved in hexane and dried at room temperature.

**Synthesis of 1T-2H MoS<sub>2</sub>/Au.** In a typical process, 500 mg commercial MoS<sub>2</sub> powder were added into 5:5 ethanol/water mixtures (100 ml). The mixture was continuously

sonicated in an ice bath for 8 h. Then the sonicated dispersion was centrifuged at 3000 rpm for 45 minutes to acquire supernatant. The supernatant was quickly added into the supercritical CO<sub>2</sub> apparatus composed mainly of a stainless steel autoclave (50 ml) with a heating jacket and a temperature controller. The autoclave was heated to 373.2 K, and CO<sub>2</sub> was subsequently charged into the autoclave to the desired pressure (16 MPa) under stirring. After a reaction time of 6 h under SC CO<sub>2</sub>, the gas was slowly released. Finally, the dispersion was collected and dried at 60 °C in the vacuum oven to obtain the 1T-2H MoS<sub>2</sub>. The 1T-2H MoS<sub>2</sub>/Au was prepared as the same as the procedure for MoS<sub>2</sub>/Au by replacing the exfoliated MoS<sub>2</sub> by 1T-2H MoS<sub>2</sub>.

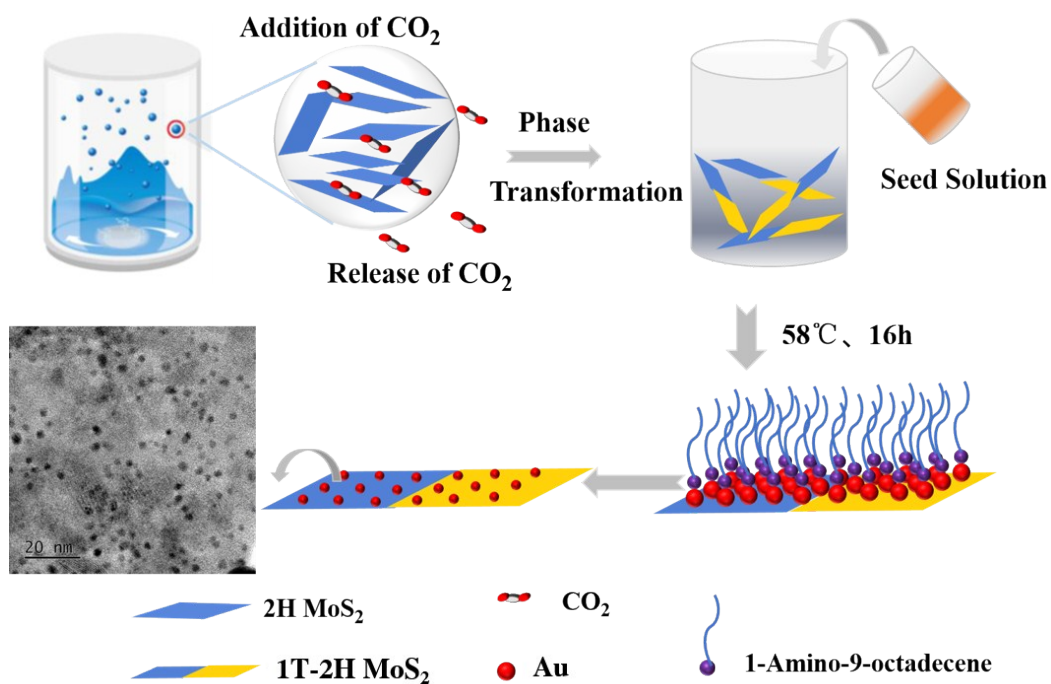
**Characterization.** The morphology and structure of the materials was characterized by Field-emission scanning electron microscope (FE-SEM, JSM7500F) and transmission electron microscopy (TEM) (JEM-2100). X-ray diffraction (XRD) patterns of samples were measured on a Y-2000 X-ray Diffractometer with copper K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). UV–vis spectra were measured on Shimadzu UV-240/PC. Raman measurements were carried out on a LabRAM HR Evolution with laser wavelength of 532 nm. X-ray photoelectron spectroscopy was performed using AXIS Supra system. Femtosecond pump-probe transient absorption spectroscopy were conducted in a setup with pump and probe beams derived from a femtosecond amplifier laser system (Spitfire Ace, Spectra Physics, 800 nm, 35 fs, and 1 kHz repetition rate). The Mid-IR probe light was then dispersed in a polychromator (iHR320, HORIBA) and detected by a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) array detector.

**Photoelectrochemical (PEC) measurements.** The PEC measurements were taken using an electrochemical workstation (CHI660E) with a typical three-electrode cell. The as-prepared sample was used as the working electrode, a Ag/AgCl electrode and a platinum wire were used as reference and counter electrode, respectively. 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> (pH = 6.8) was used as the electrolyte. The working electrodes were prepared by dropping the suspension onto the surface of a clean fluorine-doped tin oxide (FTO) conductive glass substrate. The reversible hydrogen potential can be converted from the Ag/AgCl reference electrode potential as RHE= E vs Ag/AgCl + E° Ag/AgCl+0.059 \* pH, where E° Ag/AgCl is 0.1976 V at 25 °C. The electrochemical impedance spectroscopy (EIS) measurement was conducted under 0 V vs. RHE with 100 mV amplitude in a frequency range from 1 Hz to 100 kHz.

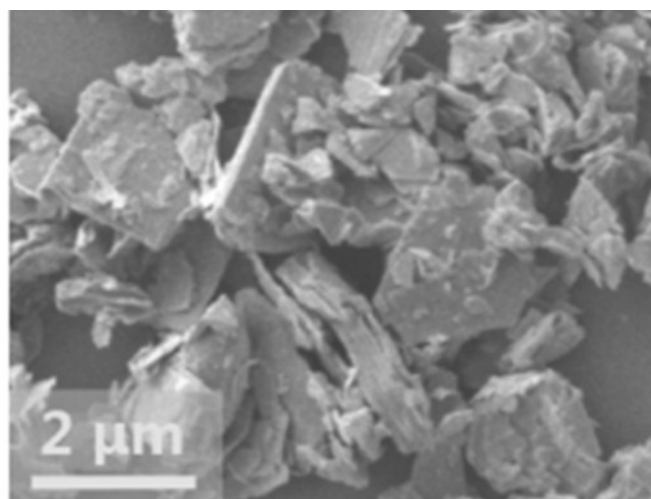
**Raman Measurement.**

Raman spectra of R6G deposited on the as-prepared samples as substrates were characterized under laser excitation at 514.5 nm. 1 mL of R6G solution with given concentration was mixed with 500 μL of sample dispersion (1 mg mL<sup>-1</sup>) followed by 2 h storage in dark for an adsorption equilibrium. Finally, 20 μL suspension was extracted and dropped onto a cleaned silicon wafer (3 mm × 3 mm) followed by drying at 60 °C. Raman spectra of all samples were measured under same conditions afterward. Raman measurement parameters setting: laser wavelength: 514.5 nm; power: 0.5 mW; lens: 50 × long distance objective; acquisition: 10 s.

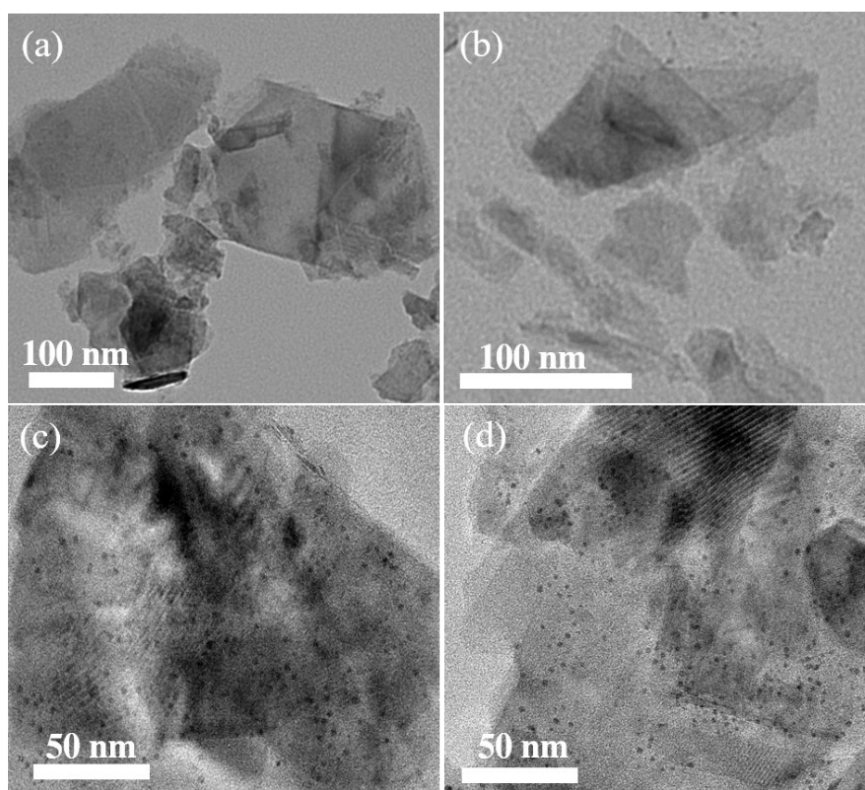
## 2. Supplemental Figures and Tables



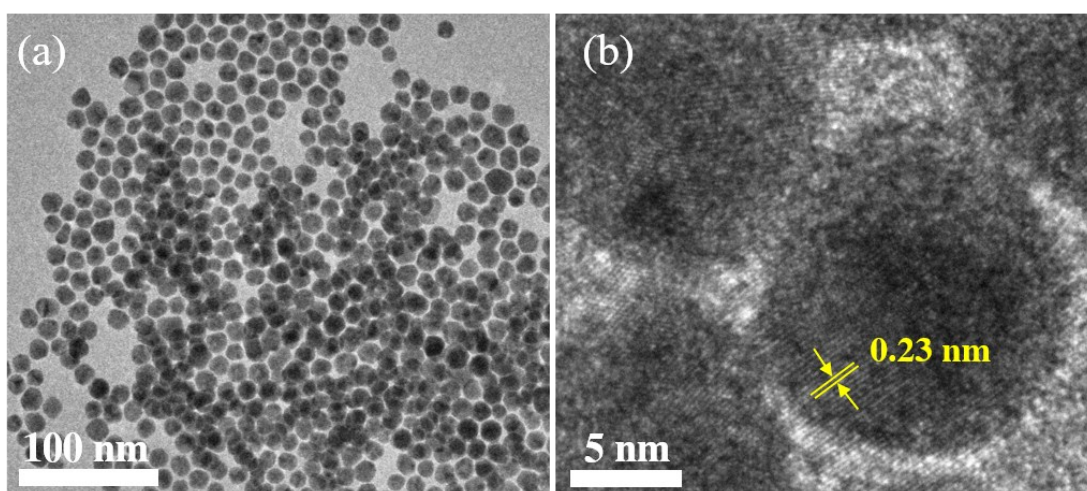
**Figure S1.** Schematic illustration of the fabrication process for lateral/vertical 1T-2H MoS<sub>2</sub>/Au heterostructures.



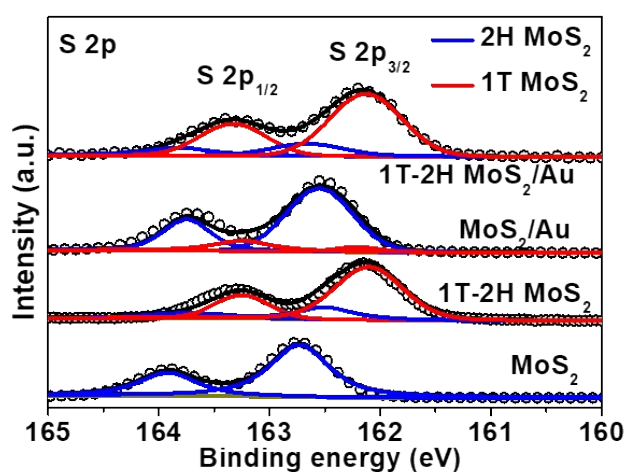
**Figure S2.** SEM image of bulk MoS<sub>2</sub>.



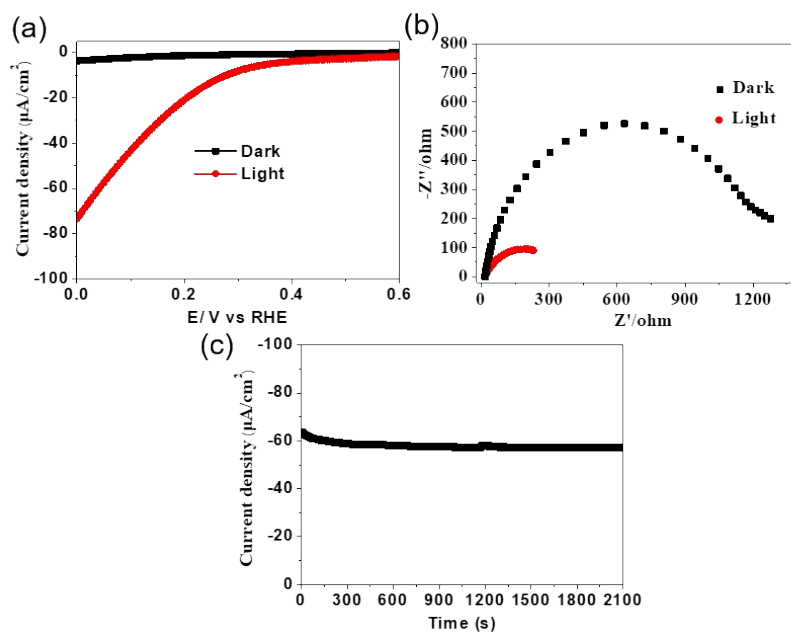
**Figure S3.** TEM images of (a) exfoliated MoS<sub>2</sub> (MoS<sub>2</sub>), (b) 1T-2H MoS<sub>2</sub>, (c) exfoliated MoS<sub>2</sub>/Au (MoS<sub>2</sub>/Au), (d) 1T-2H MoS<sub>2</sub>/Au.



**Figure S4.** (a) Low-magnification and (b) HRTEM images of pure Au nanoparticles without the addition of MoS<sub>2</sub>.



**Figure S5.** High-resolution S 2p XPS spectra of exfoliated MoS<sub>2</sub>, 1T-2H MoS<sub>2</sub>, MoS<sub>2</sub>/Au and 1T-2H MoS<sub>2</sub>/Au heterostructure.



**Figure S6.** (a) LSV curves and (b) EIS Nyquist plots of the 1T-2H MoS<sub>2</sub>/Au heterostructure electrode in dark and under visible light ( $\lambda > 420$  nm, AM 1.5, 100 mW cm<sup>-2</sup>) irradiation. (c) Photocurrent density stability of the 1T-2H MoS<sub>2</sub>/Au heterostructure electrode under visible light ( $\lambda > 420$  nm, AM 1.5, 100 mW cm<sup>-2</sup>) irradiation.



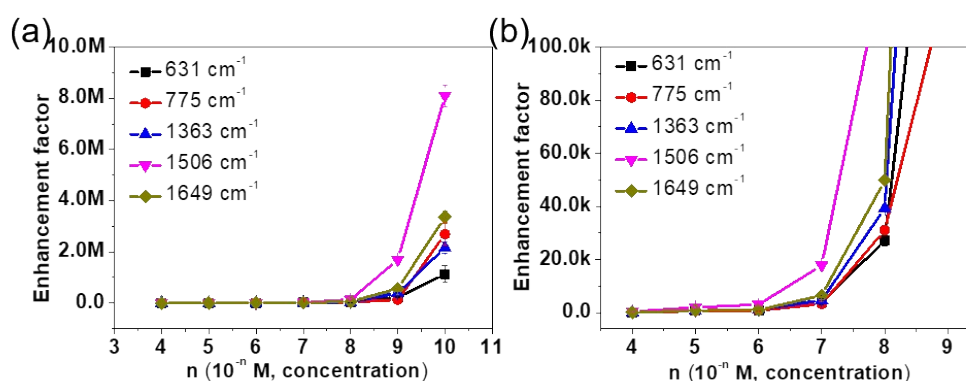
## The Calculation Equation of Enhancement Factor (EF)

The Raman signal data for Rh6G ( $10^{-3}$  M) is used as non-SERS-active reference. Specifically, the intensity was obtained by taking average from measurements of several spots, and the EF was calculated as the following equation:<sup>1,2</sup>

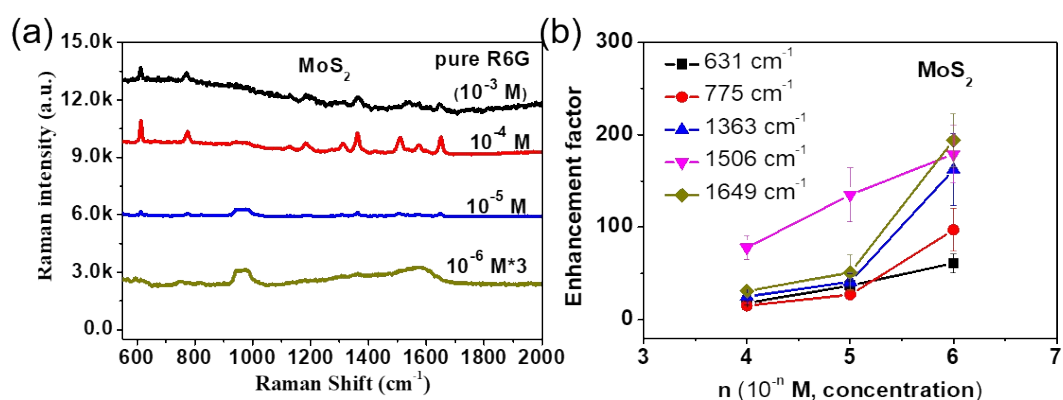
$$EF = (I_{SERS}/I_{Bulk})(N_{Bulk}/N_{SERS}) \quad (1)$$

$$N = CVN_A S_{Raman}/S_{sub} \quad (2)$$

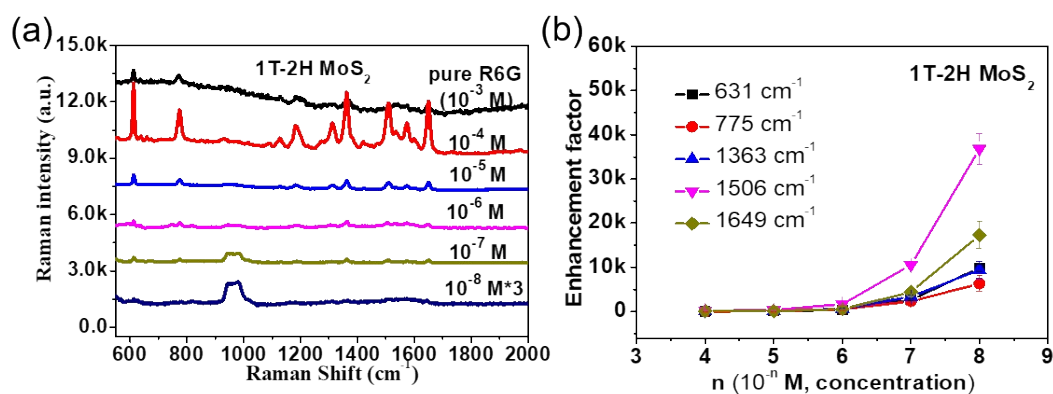
Where  $I_{SERS}$  is the Raman intensity of R6G on the SERS-active substrate and  $I_{Bulk}$  is the intensity of the same Raman band under non-SERS conditions, used as reference. A  $10^{-3}$  M R6G solution was employed as the reference.  $N_{SERS}$  is the number of R6G molecules absorbed on the SERS-active substrate under the laser spot area and  $N_{Bulk}$  is the number of molecules illuminated within the volume of the laser waist for the R6G bulk solution.  $C$  is the molar concentration of the probe molecule solution,  $V$  is the volume of the droplet,  $N_A$  is Avogadro constant.  $S_{Raman}$  is the laser spot area ( $1\mu\text{m}$  in diameter) of Raman scanning, and  $S_{Sub}$  is the area of the substrate ( $3\text{ mm} \times 3\text{ mm}$ ). This equation is based on the assumption that the probe molecules were distributed uniformly on the substrates.



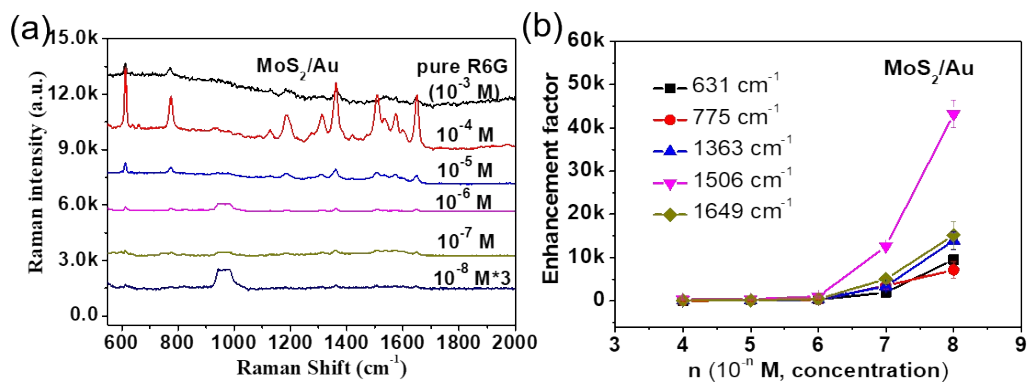
**Figure S7.** EF of the SERS signal peaks as a function of R6G concentrations based on 1T-2H  $\text{MoS}_2/\text{Au}$  heterostructure SERS substrate.



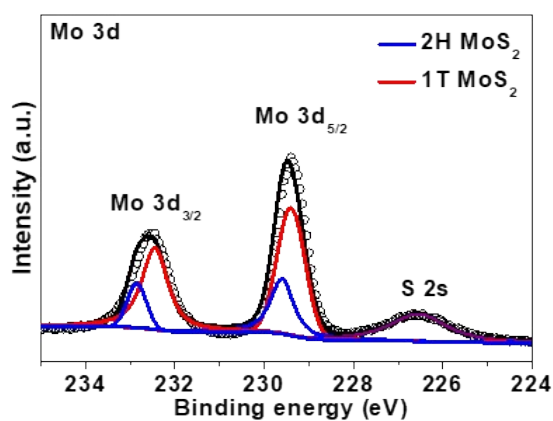
**Figure S8.** (a) Raman spectra of pure R6G ( $10^{-3}$  M) and MoS<sub>2</sub> as an enhancement substrate with different concentrations of R6G. (b) The corresponding EFs of the SERS signal peaks as a function of R6G concentrations based on MoS<sub>2</sub> as SERS substrate.



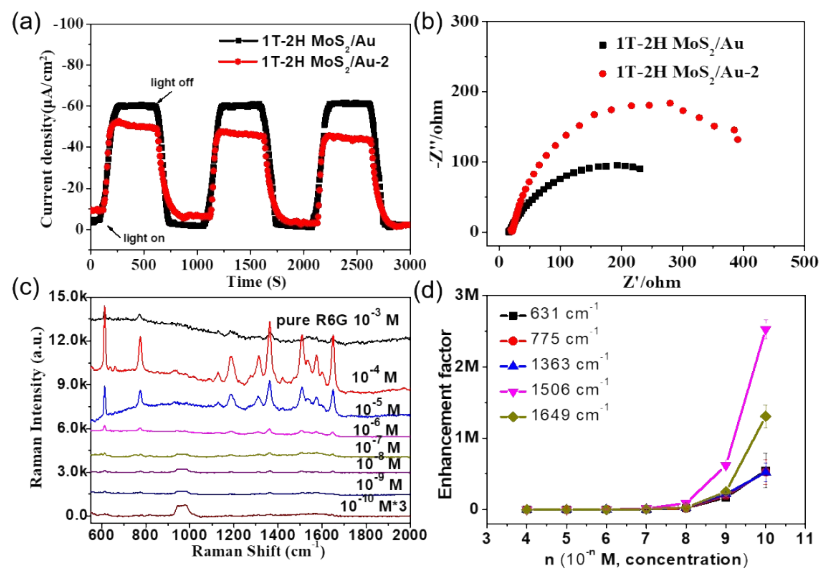
**Figure S9.** (a) Raman spectra of pure R6G ( $10^{-3}$  M) and 1T-2H MoS<sub>2</sub> as an enhancement substrate with different concentrations of R6G. (b) The corresponding EFs of the SERS signal peaks as a function of R6G concentrations based on 1T-2H MoS<sub>2</sub> as SERS substrate.



**Figure S10.** (a) Raman spectra of pure R6G ( $10^{-3}$  M) and MoS<sub>2</sub>/Au as an enhancement substrate with different concentrations of R6G. (b) The corresponding EFs of the SERS signal peaks as a function of R6G concentrations based on MoS<sub>2</sub>/Au heterostructure as SERS substrate.



**Figure S11.** High-resolution Mo 3d XPS spectra of 1T-2H MoS<sub>2</sub>/Au-2 heterostructure.



**Figure S12.** (a) Photocurrent responses and (b) EIS Nyquist plots of the 1T-2H MoS<sub>2</sub>/Au and 1T-2H MoS<sub>2</sub>/Au-2 heterostructure in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at 0 V vs. RHE. (c) Raman spectra of pure R6G (10<sup>-3</sup> M) and 1T-2H MoS<sub>2</sub>/Au-2 heterostructure as an enhancement substrate with different concentrations of R6G. (d) The corresponding EFs of the SERS signal peaks as a function of R6G concentrations based on 1T-2H MoS<sub>2</sub>/Au-2 as SERS substrate.

**Table S1.** The fit results of femtosecond pump-probe transient absorption kinetic traces of MoS<sub>2</sub>, 1T-2H MoS<sub>2</sub>, MoS<sub>2</sub>/Au and 1T-2H MoS<sub>2</sub>/Au heterostructure.

Samples	Time constant (ps)
MoS <sub>2</sub>	$\tau_1 = 0.20 \pm 0.04$
	$\tau_2 = 1.16 \pm 0.15$
	$\tau_3 = 7.29 \pm 1.20$
1T-2H MoS <sub>2</sub>	$\tau_1 = 0.08 \pm 0.01$
	$\tau_2 = 0.49 \pm 0.04$
	$\tau_3 = 1.58 \pm 0.21$
MoS <sub>2</sub> /Au	$\tau_1 = 0.11 \pm 0.03$
	$\tau_2 = 0.77 \pm 0.12$
	$\tau_3 = 2.39 \pm 0.36$
1T-2H MoS <sub>2</sub> /Au	$\tau_1 = 0.06 \pm 0.01$
	$\tau_2 = 0.36 \pm 0.03$
	$\tau_3 = 1.47 \pm 0.15$

**Table S2.** SERS property comparison with previous works.

Substrate	Detection limit (M)	EF	Molecules	References
Ag NW-Ag NP- MoS <sub>2</sub>	10 <sup>-11</sup>	5.6 × 10 <sup>6</sup>	R6G	<i>Nano Res.</i> , 2018, <b>11</b> , 2181 <sup>3</sup>
AuNPs@MoS <sub>2</sub>	10 <sup>-7</sup>	8 × 10 <sup>5</sup>	R6G	<i>ACS Appl. Mater. Interfaces</i> , 2014, <b>6</b> , 18735 <sup>4</sup>
3D MoS <sub>2</sub> -Au NPs	10 <sup>-9</sup>	—	R6G	<i>Chem. Phys. Lett.</i> , 2017, <b>682</b> , 64 <sup>5</sup>
1T'-ReS <sub>2</sub>	10 <sup>-9</sup>	—	R6G	<i>Small</i> , 2018, <b>14</b> , 1704079 <sup>6</sup>
W <sub>18</sub> O <sub>49</sub> nanowire	10 <sup>-9</sup>	3.4 × 10 <sup>5</sup>	R6G	<i>Nat. commun.</i> , 2015, <b>6</b> , 7800 <sup>7</sup>
H <sub>x</sub> MoO <sub>3</sub> quantum dots	10 <sup>-8</sup>	5.5 × 10 <sup>4</sup>	R6G	<i>Small</i> , 2018, <b>14</b> , 1801523 <sup>1</sup>
1T-2H MoS <sub>2</sub> /Au heterostructure	10 <sup>-10</sup>	8.1 × 10 <sup>6</sup>	R6G	This work

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