#### **Supporting Information**

# Plasmonic Molybdenum Trioxide Quantum Dots with Noble Metal-

### **Comparable Surface Enhanced Raman Scattering**

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#### **1. Experimental Procedures**

**Materials:** Ammonium molybdate tetrahydrate ( $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$  AR, product number A116375), bovine serum albumin (product number A116563) and Rhodamine 6G (Biological stain, product number R105623) were purchased from Aladdin. Thiourea (AR, 10022318) was purchased from Sinopharm Chemical ReagentCo. Ltd. All of the chemicals were used as received without further purification.

**Preparation of MoO**<sub>3- $\chi$ </sub>-**QDs.** 100 mmol (NH<sub>4</sub>)6Mo<sub>7</sub>O<sub>24</sub> and 250 mmol thiourea were dissolved in 350 mL distilled water under vigorous stirring until a homogeneous solution was formed. Then, the solution was heated at 110 °C under atmospheric condition for 12 hours. Afterwards, the mixture was dialyzed by dialysis bags with molecular weight cut (MWC) of 3500 for 3 days after it was cooled down to room temperature naturally. After dialysis, the solution was freeze-dried to obtain MoO<sub>3- $\chi$ </sub>-QDs powder.

**BSA testing.** To assess the bio-sensing capability of  $MoO_{3-\chi}$ -QDs, 2 mL of BSA solutions with concentrations of 0, 0.1, 0.2, 0.5, 1, 2, 5 and 10 mg·mL-1 respectively were incubated with 1 mL solutions of the suspended  $MoO_{3-\chi}$ -QDs for 1 h. Their absorption spectra were measured subsequently.

**SERS samples.** The MoO<sub>3- $\chi$ </sub>-QDs dispersion was dropped loaded onto a clean quartz substance and dried at 50 °C for 3 h. R6G solutions with different concentrations were dropped on the substance coated with MoO<sub>3- $\chi$ </sub>-QDs and dried at room temperature before testing.

#### 2. Calculation of the enhancement factor

The EF of  $MoO_{3-\chi}$ -QDs was calculated according to the following formulas:

$$EF = (I_{SERS}/N_{SERS})/(I_{ref}/N_{ref})$$
(1)

$$N_{SERS} = CVN_A A_{Raman} / A_{Sub}$$
<sup>(2)</sup>

$$N_{bulk} = \rho h A_{Raman} N_A / M$$
(3)

I<sub>SERS</sub> and I<sub>ref</sub> represent the intensities of the selected Raman peaks in the SERS and Raman spectra. N<sub>SERS</sub> and N<sub>ref</sub> refer to the number of probe molecules in the scattering areas of SERS and Raman spectra. In the SERS measurements, four Raman peaks, P1 at 612 cm<sup>-1</sup>, P2 at 774 cm<sup>-1</sup>, P3 at 1365 cm<sup>-1</sup> and P4 at 1546 cm<sup>-1</sup> were selected for the calculation of EFs. The peak intensity of R6G on bare quartz substrate was used as I<sub>ref</sub> data. N<sub>SERS</sub> was calculated according to formula 2, where C is the molar concentration of R6G solution, V is the volume of the droplet, N<sub>A</sub> is Avogadro constant, A<sub>Raman</sub> is the laser spot area of Raman scanning, A<sub>sub</sub> is the diffusion area of the substance to be tested on the substrate. In our experiments, 20 µl of the probe solution was spread into a circle with a diameter of 4 mm after solvent evaporation. N<sub>bulk</sub> was calculated according to formula 3, where  $\rho$  is the density of bulk R6G (1.15 g.cm<sup>-3</sup>), h is the confocal depth of the laser beam (21 µm), M is the basis of molecular weight. Since the measurement conditions such as laser power, laser wavelength, and acquiring time are identical, the above formula can be rewritten as:

$$EF = (\rho h A_{sub}) / CVM$$
(4)

#### 3. Characterization

**FETEM characterization.** The morphology of the product was recorded by FETEM technique using JEM-2100F with the accelerating voltage of 200 kV.  $MoO_{3-\chi}$ -QDs dispersion was diluted with distilled water and dropped onto a super-thin carbon film substrate. After vacuum dried at 50 °C for 3 h, the samples were taken out for FETEM testing.

**AFM characterization.** The height of  $MoO_{3-\chi}$ -QDs was confirmed by AFM technique. MoO<sub>3- $\chi$ </sub>-QDs suspensions were diluted with distilled water and dropped onto freshly cleaved mica surfaces. The samples were dried under vacuum condition at 50 °C for 5 h. AFM images were recorded in the tapping mode under air on a multimode 8 model scanning probe microscope. In AFM images, MoO<sub>3- $\chi$ </sub>-QDs show the height below 2 nm, demonstrating the single-layered feature.

**XPS analysis.** The chemical components and electron states of  $MoO_{3-\chi}$ -QDs were investigated by XPS analysis on an AXIS UltraDLD system, operating at 150 W with

Al K $\alpha$  radiation (1486.6 eV). All samples were freeze-dried and saved in a dryer before characterization.

**Raman Spectrometry.** The structure of  $MoO_{3-\chi}$ -QDs was tested by Raman spectrometry on XploRA.  $MoO_{3-\chi}$ -QDs powder was loaded onto a clean quartz substance for measurement. Before sample preparation, quartz substance was washed with ethanol three times and dried in air naturally. Raman spectra were recorded using a 532 nm excitation laser with the integral time of 10 seconds and repeated for 2 times.

**XRD analysis.** The crystal structures were recorded using (X'pert PRO) with 2 $\theta$  scan rate of 10 °/min at operating voltage of 40 kV and operating current of 40 mA with the monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å).

UV-vis-NIR spectra characterization.  $MoO_{3-\chi}$ -QDs suspension was diluted with distilled water for UV-vis-NIR spectrum measurements using Lambda 750. The step size was settled at 1 nm and the testing range was 400 to 1300 nm.



# 4. Supplementary Figures

**Fig. S1.** Growing popularity of the surface enhanced Raman technique. This plot shows citation data in Web of Science for the term "surface enhanced Raman", as accessed on September 28<sup>th</sup>.



**Fig. S2.** The wide application fields of SERS technique. This plot shows citation data in Web of Science for the term "surface enhanced Raman", as accessed on September 28<sup>th</sup>.



**Fig. S3.** Optical image of MoO<sub>3-γ</sub>-QDs dispersion.



**Fig. S4.** Optical image of  $MoO_{3-\chi}$ -QDs powder.



Fig. S5. FETEM image of MoO<sub>3</sub> quantum dots with 100 mmol thiourea.



Fig. S6. Enlarged FETEM image of MoO<sub>3</sub> quantum dots with 100 mmol thiourea.



Fig. S7. AFM image of MoO<sub>3</sub> quantum dots with 100 mmol thiourea.



Fig. S8. FETEM image of MoO<sub>3</sub> quantum dots with 500 mmol thiourea.



Fig. S9. Enlarged FETEM image of MoO<sub>3</sub> quantum dots with 500 mmol thiourea.



Fig. S10. AFM image of MoO<sub>3</sub> quantum dots with 500 mmol thiourea.



Fig. S11. SEM image of MoO<sub>3</sub> without the addition of thiourea.



Fig. S12. Enlarged SEM image of MoO<sub>3</sub> without the addition of thiourea.



Fig. S13. XPS spectrum of  $MoO_{3-\gamma}$ -QDs.



Fig. S14. XPS spectrum of  $MoO_{3-\gamma}$ -QDs-450.



**Fig. S15.** UV-Vis-NIR spectrum of MoO<sub>3</sub> quantum dots with 100 mmol thiourea. The spectrum shows tow SPR peaks centered at 836 and 1088 nm, respectively.



**Fig. S16.** UV-Vis-NIR spectrum of MoO<sub>3</sub> quantum dots with 500 mmol thiourea. The spectrum shows tow SPR peaks centered at 764 and 1084 nm, respectively.



Fig. S17. Raman spectrum of pure R6G powder.



Fig. S18. The SPR peaks as a function of the BSA concentration.



Fig. S19. Raman spectrum of R6G with the concentration of  $10^{-5}$  M.



**Fig. S20.** SERS spectrum of  $MoO_{3-\chi}$ -QDs-450 with the R6G concentration of 10<sup>-5</sup> M. In the SERS spectrum, no typical Raman signals of R6G molecules were observed. The

spectrum displays the characteristic Raman signals of commercial MoO3. Compared with the Raman spectrum of  $MoO_{3-\chi}$ -QDs, the shoulder peaks at 780 and 857 cm<sup>-1</sup> were not observed, implying the repairing of oxygen vacancies after high-temperature treatment.



**Fig. S21.** SERS spectrum of ATP with the concentration of  $5 \times 10^{-9}$  M.

As shown in Fig. S21, the Raman signal of ATP can also be observed when the concentration is as low as 10<sup>-9</sup> M. This result indicates that the main contribution is EM enhancement since CM enhancement leads to different enhancement performances with different detecting molecules.



Fig. S22. FETEM image of MoO<sub>3-χ</sub>-QDs-450.

After thermal treatment,  $MoO_{3-\chi}$ -QDs-450 still retains the feature of QDs with the lateral size smaller than 10 nm. This is in accordance with the previous report, in which molybdenum trioxide was found to maintain its ultra-small feature even after thermal treatment (J. Mater. Chem. C, 2016, 4, 6720-6726).



Fig. S23 O XPS spectra of  $MoO_{3-\chi}$ -QDs and  $MoO_{3-\chi}$ -QDs-450.



Fig. S24 XRD pattern of  $MoO_{3-\chi}$ -QDs-450.



Fig. S25 The amplified Raman spectra of  $MoO_{3-\chi}$ -QDs and commercial  $MoO_3$  between 600 and 950 cm<sup>-1</sup>.

# 5. Comparison of enhancement factors of various SERS materials previously

## reported

Ref.	Substrate material	Enhancement factor	Detection limit	Probe molecule
1	Cu <sub>2</sub> O Superstructure Particle	8×10 <sup>5</sup>	6×10-9	Rhodamine 6G
2	CuTe Nanocrystals	1.5×10 <sup>6</sup>		Nile red
3	W <sub>18</sub> O <sub>49</sub> nanowire	3.4×10 <sup>5</sup>	10-7	Rhodamine 6G
4	ZnO nanocages	6.62×10 <sup>5</sup>		4-mercaptobenzoic acid
5	InAs/GaAs quantum dots	10 <sup>3</sup>		Pyridine
6	Metallic MoO <sub>2</sub>	3.75×10 <sup>6</sup>	10-7	Rhodamine 6G
7	TiO <sub>2</sub> resonators		10-5	methylene blue
8	SnO <sub>2</sub> Octahedral Nanoparticles	10 <sup>3</sup>		4- mercaptobenzoic acid
9	Flower-like Silver Nanoparticles	107	10-10	malachite green isothiocyanate
10	Porous gold membranes	2.62×10 <sup>5</sup>	10-13	benzenethiol

Table S1. Enhancement factors of various SERS materials previously report	ted
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