Supporting Information

Plasmonic MoO_{3-x}@MoO_3 Nanosheets for Highly Sensitive SERS Detection through Nanoshell-Isolated Electromagnetic Enhancing

Xianjun Tan, Lingzhi Wang, Chen Cheng, Xuefeng Yan, Bin Shen, and Jinlong Zhang**

Experimental Section:

Chemicals:

Molybdenum powder, commercial MoO_3 was purchased from Aladdin, hydrogen peroxide (H_2O_2, 30 wt%), methanol, Methylene blue ($C_{16}H_{18}N_3SCl$; MB) was purchased from Yongle Chemic Co. Ltd., China. All chemical reagents were used without any further purification.

Synthesis of MoO_{3-x} nanosheets and core-shell MoO_{3-x}@MoO_3 nanosheets:

The MoO_{3-x} nanosheets were prepared according to previous literature with some modification.[1,2] Briefly, 2 mL of H_2O_2 (30 wt%) aqueous solution was dropwise added into a breaker containing 0.192 g of Mo powder (2 mmol), placed in an ice-water bath. The mixture was magnetically stirred, resulting in the formation of a transparent yellow solution. Subsequently, the solution was transferred into a Teflon vessel (30 mL) containing 20 mL of methanol which maintained at 170 °C for 12 h. After the autoclave was cooled to room temperature, the product was collected by centrifugation and rinsed with methanol for three times. After drying at 60 ^oC in vacuum for 8 h, the MoO_{3-x} nanosheets were obtained. The core-shell MoO_{3-x}@MoO_3 was prepared by annealing the MoO_{3-x} nanosheets at 200 ^oC for 6 h in the air.

Photocatalytic experiments:

The photocatalytic degradation of methylene blue (MB) was carried out in a quartz tube reactor. Typically, 10 mg of the sample was added into 20 mL of 20 mg/L MB

solution. The mixture was irradiated with a 200 W Xe lamp equipped with a 420 nm filter. For different intervals, 1 mL solution was taken out for detection. 1 mL of ethanol and 100 μL of 4 M HCl solution were introduced for desorption. The mixture was centrifuged and the supernate was measured by the UV-visible spectrometer.

Raman spectroscopy measurements:

The as-prepared nanosheets were used as SERS active materials to detect MB molecules with different concentrations. Typically, 5 mg of as-synthesized nanosheets were added to 1 mL of different concentration of MB solution in a centrifuge tube. The mixture was allowed to equilibrate for 1 h. A total of 20 μL of the mixture were transferred to silica slides and allowing it to evaporate naturally.

Characterization:

Scanning electron microscopy (SEM) analysis was performed using a TESCAN nova III scanning electron microscope. Transmission electron microscopy (TEM) analysis was performed using a JEOL 2100 LaB6 TEM, at a 200 kV accelerating voltage. X-ray diffraction (XRD) analysis was performed using Rigaku D/max 2550 VB/PC apparatus. The EPR spectra were collected using a Bruker EMX-8 spectrometer at 9.44 GHz at 298 K.

Raman spectra were recorded on a Renishaw inVia-Reflex Raman microprobe system equipped with Peltier charge-coupled device (CCD) detectors and a Leica microscope. Spectra were collected in Renishaw continuous mode with accumulation times of 10 s and the laser power was maintained at 0.5 mW. Lasers with wavelength 785 nm was used as the excitation light source, and a 50× objective with a numerical aperture (NA) of 0.75 was used to get the laser spot diameter of ~1 μm. To ensure that the obtained spectra were comparable, the settings, including laser power and exposure time, were all kept constant. The silicon line at 520 nm was used to calibrate the observed wavenumbers.

S 1

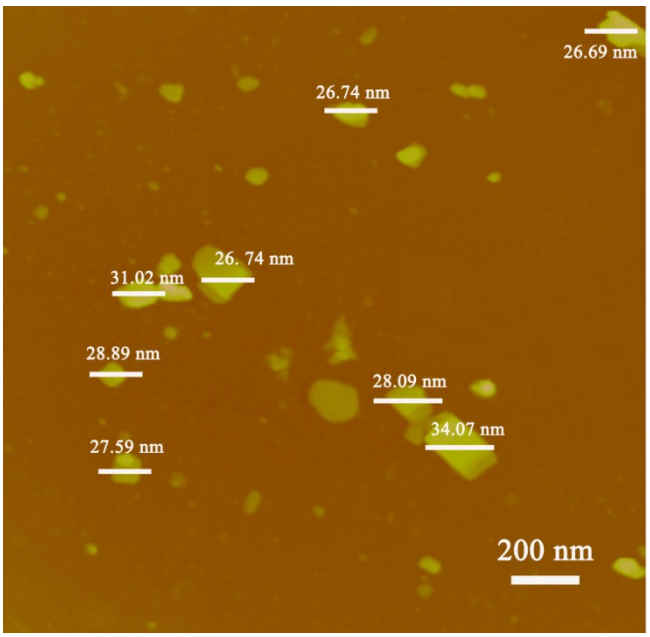

Figure S1 AFM image of the plasmonic MoO_{3-x} nanosheets.

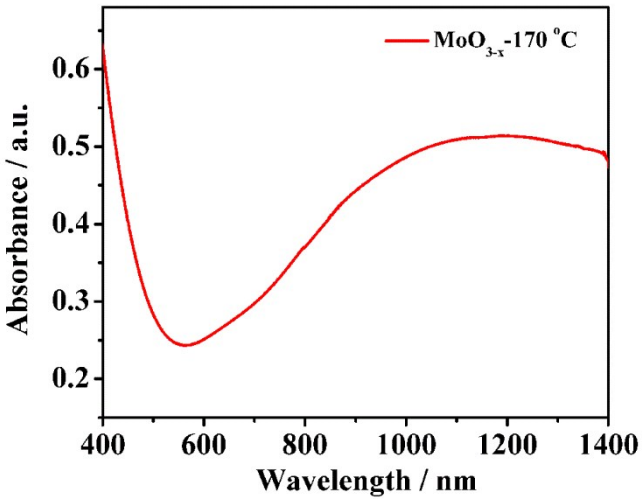

Figure S2 UV-Vis-NIR adsorption spectra of MoO_{3-x}-170 °C nanosheets in water.

The bluk plasmon frenquency (ω_p) was calculated according to Mie scattering theory depending on the UV-vis-NIR spectra data. We used the Mie expression for the polarizability of a spheriod, which can be expressed

$$\alpha = 3\varepsilon_0 V \frac{\varepsilon - \varepsilon_m}{3\varepsilon_m + 3L_j(\varepsilon - \varepsilon_m)} \quad (1)$$

Where V is the nanocrystal volume, ε_0 is free space permittivity, and L_j is the shape factor of the nanoparticles. We set the denominator to zero, then

$$\varepsilon_r = -\frac{(1 - L_j)}{L_j}\varepsilon_m \quad (2)$$

Where ε_r is the real part of ε, and can be expressed by the Drude modal

$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (3)$$

Where ω_p is the bulk plasma oscillation frenquency and the γ is loss associated collision frequency term, and is ω the bulk plasma frequency. From equation (2) and (3), the ω_{sp} can be discribed as

$$\omega_{sp} = \sqrt{(\frac{\omega_p^2}{1 + 2\varepsilon_m} - \gamma^2)} \quad (4)$$

ω_{sp} is the LSPR energy and γ represents the FWHM of the plasmon resonance band.

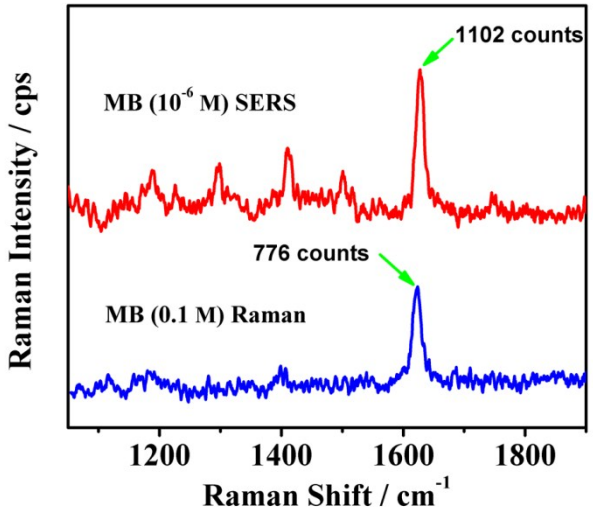

Fig. S3 Comparison Raman and SERS spectra of MB absorbed on the silica slide and slide covered with plasmonic MoO_{3-x} after calcination for 6 h.

We estimated the enhancement factor from plasmonic MoO_{3-x} after calcination for 6 h. In our case, the enhancement factor (EF) was calculated by the following equation.

$$E_F = \frac{I_{SERS} / N_{SERS}}{I_0 / N_0}$$

Where I_{SERS} and I_0 are the intensities of selected Raman peaks in the SERS and normal Raman spectra. N_{SERS} and N_0 are the average number of molecules in scattering for SERS and normal Raman measurement.

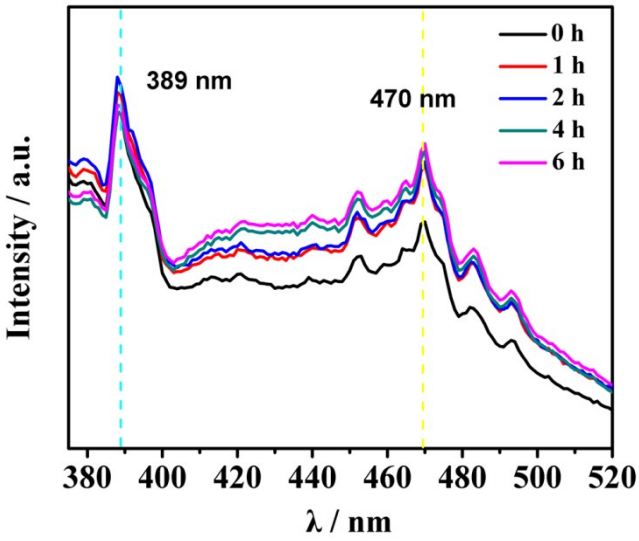

Fig. S4 Photoluminescence spectra of the plasmonic MoO_{3-x} nanosheets after calcination at 200 ^{o}C for different times. Excitation wavelength: 350 nm. The PL emission spectra show emission band at 3.19 eV (325 nm), which corresponding to the band-to-band transition and and 2.64 eV (470 nm) that may originate from the presence of Mo^{5+} and oxygen vacancies.

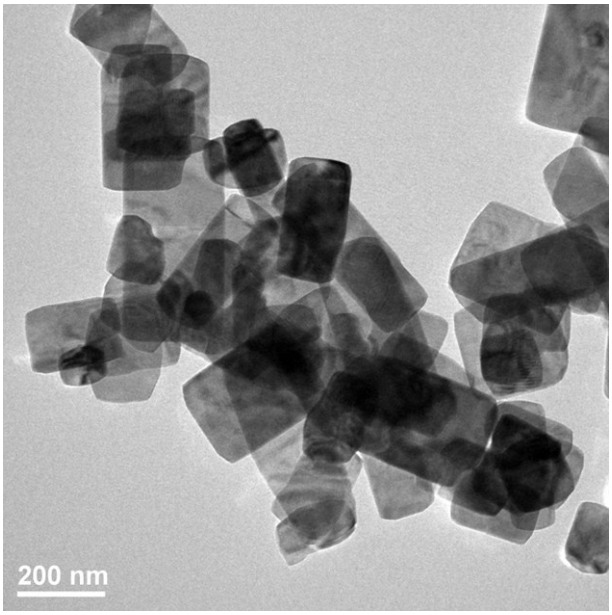

Figure S5 TEM image of the plasmonic MoO_{3-x}-170 ^{o}C nanosheets calcined at 200 ^{o}C for 6 h.

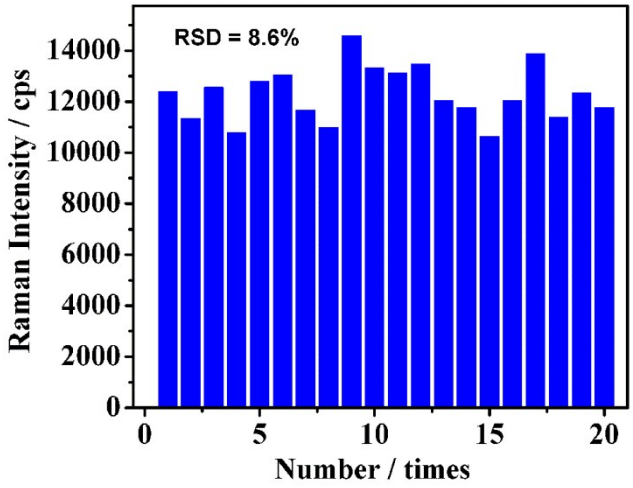

Figure S6 The intensities of the Raman vibration mode (1625 cm^{-1}) of MB on nanosheets. The relative standard deviation (RSD) was calculated to be 8.6 %.

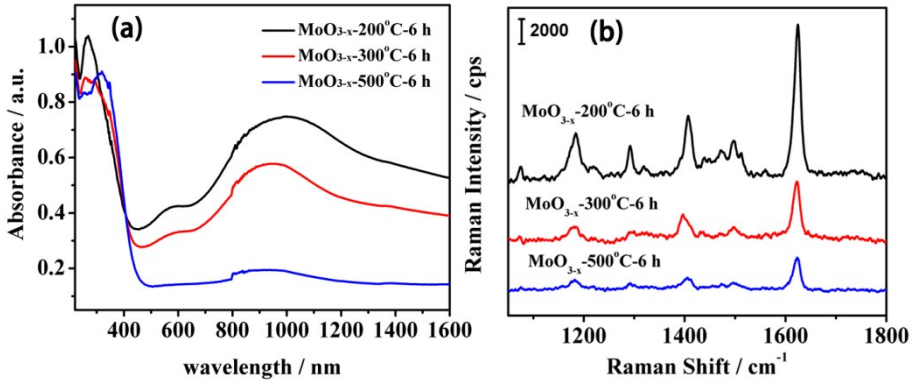

Figure S7 (a) UV-vis-NIR diffuse reflectance and (b) SERS spectra of MoO_{3-x}-170 ^{o}C nanosheets calcined at 200 ^{o}C, 300 ^{o}C and 500 ^{o}C for 6 h, respectively.

References

(1) Song, G.; Shen, J.; Jiang, F.; Hu, R.; Li, W.; An, L.; Zou, R.; Chen, Z.; Qin, Z.; Hu, J. *ACS applied materials & interfaces* **2014**, *6*, 3915.

(2) Cheng, H.; Kamegawa, T.; Mori, K.; Yamashita, H. *Angewandte Chemie International Edition* **2014**, *53*, 2910.