Electronic Supplementary Information (ESI)

Pressure-induced SERS enhancement in MoS_2/Au/R6G system by a two-step charge transfer process

Huanhuan Sun,[a] Mingguang Yao,*[a] Yanping Song,[a] Luyao Zhu,[a] Jiajun Dong,[a] Ran Liu,[a] Peng Li,[b] Bing Zhao[b] and Bingbing Liu*[a]

[a]*State Key Laboratory of Superhard Materials, College of Physics, Jilin University, No. 2699 Qianjin Street, Changchun 130012, China*

E-mail: yaomg@jlu.edu.cn, liubb@jlu.edu.cn

[b]*State Key Laboratory of Supramolecular Structure and Materials, Jilin University, No. 2699 Qianjin Street, Changchun 130012, China*

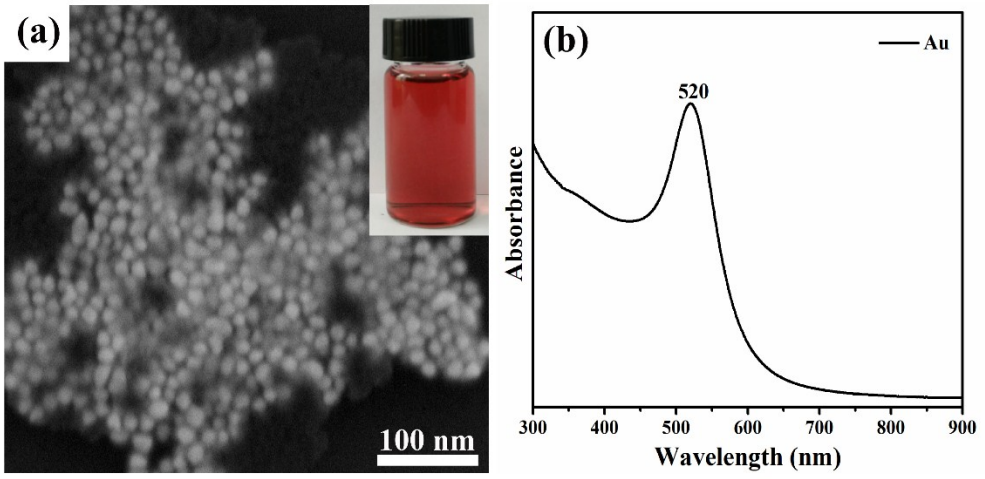

Fig. S1 (a) SEM image of pure Au NPs. The inset shows the photo image of gold solution. (b) UV-Vis spectrum of Au colloid NPs.

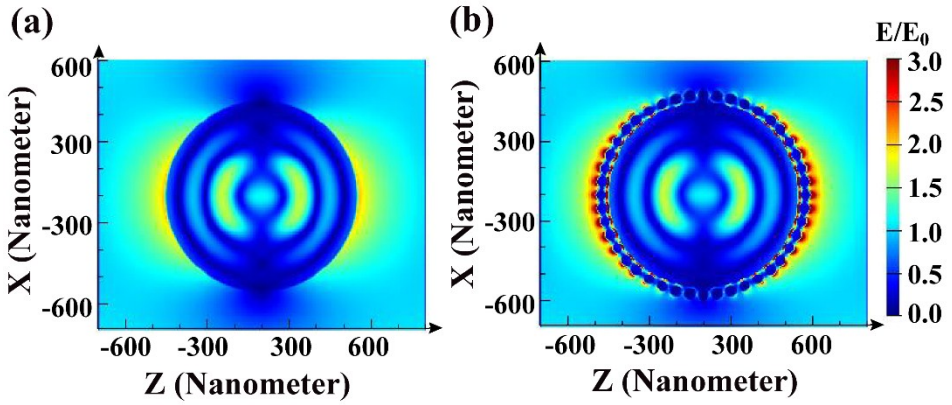

Fig. S2 The electric field distributions of (a) MoS_2 and (b) MoS_2/Au composite.

The electromagnetic field distribution based on numerically simulated method was performed using finite-difference time-domain (FDTD) Solutions. Fig. S2a shows the electric field distribution of single MoS_2 NFs, in which the size of MoS_2 NFs was set to 700 nm according to the SEM images. The X, Y and Z directions were enclosed by perfect match layers. As shown in Fig. S2b, the distance between Au NPs was set to 2 nm, and the incident electric field was polarized in-plane with a wavelength of 473 nm.

Calculation of enhancement factor (EF)

The enhancement factor was estimated by the equation (2) in the manuscript. Take the R6G molecules adsorbed on MoS_2/Au composite as an example, the Raman peak of the in-plane vibration mode (613 cm^{-1}) in the Raman spectrum was selected to calculate EF values. The 613 cm^{-1} Raman intensity of MoS_2/Au composite is 11864.7 counts with 50 s acquisition time, and that of MoS_2 NFs is 447.5 counts with 160 s acquisition time. The Raman intensity ratio is estimated as below

$$\frac{I_{\mathrm{SERS}}}{I_{\mathrm{bulk}}} = \frac{11864.7}{447.5} \times \frac{160}{50} = 84.8$$

$$N_{\mathrm{SERS}} = \frac{cVN_{\mathrm{A}}A_{\mathrm{Raman}}}{A_{\mathrm{sub}}}$$

$$N_{\mathrm{bulk}} = \frac{\rho hN_{\mathrm{A}}A_{\mathrm{Raman}}}{M}$$

c is the molar concentration of the analyte molecules, V is the volume of the droplet, N_{A} is avogadro's constant (6.023×10^{23}), A_{Raman} is the area of laser spot (diameter in 1 μm), A_{sub} is the effective area of the substrates, 20 μL of the droplet on the substrate was spread into a circle of about 3 mm in diameter to form the effective area of the substrate (A_{Sub}). ρ is the density of R6G molelcules (1.15 $g\cdot cm^{-3}$), h is the confocal depth of laser (23.64 μm), M is the molecular weight of R6G (479 g/mol).

Taking all the measurement parameters into consideration, the EF value can be estimated based on the following equations:

$$EF\left(\mathrm{MoS_2/Au}\right) = \frac{I_{\mathrm{SERS}}N_{\mathrm{bulk}}}{I_{\mathrm{bulk}}N_{\mathrm{SERS}}} = \frac{84.8 \times 1.15 \times 23.64 \times 15^2 \times \pi}{10^{-3} \times 479 \times 20} = 1.69 \times 10^7$$

$$EF(\mathrm{MoS_2}) = 2.05 \times 10^4$$

Therefore, we calculated the EF for R6G molecules on MoS_2/Au and MoS_2 substrates to be 1.69×10^7 and 2.05×10^4, respectively. By the similar method, the EFs for MB and CV dye molecules adsorbed on MoS_2/Au substrate were calculated to be 6.53×10^7 and 2.13×10^7, respectively.

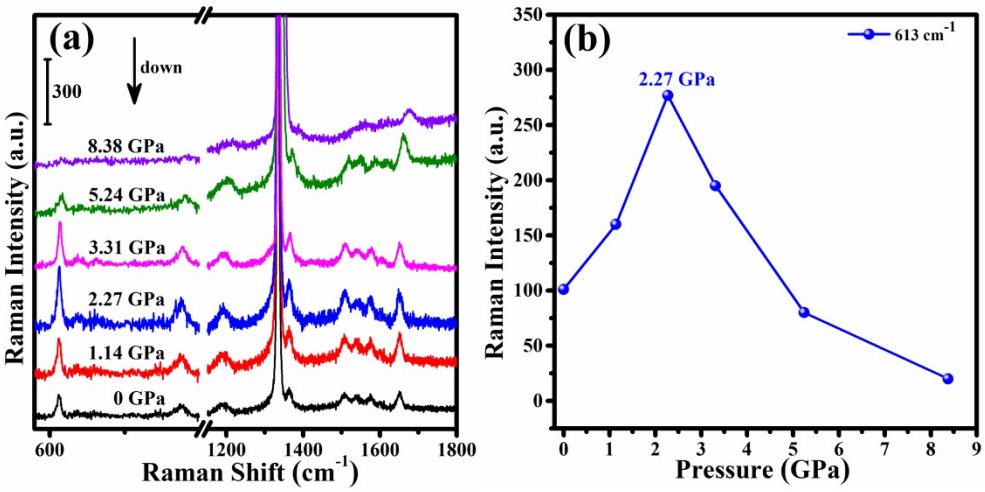

Fig. S3 (a) PI-SERS spectra of R6G molecules adsorbed on MoS_2/Au composite under releasing pressure. (b) The change trend of Raman intensity of R6G molecules as a function of pressure. The strongest Raman peak at ~1333 cm^{-1} is originated from the diamond.

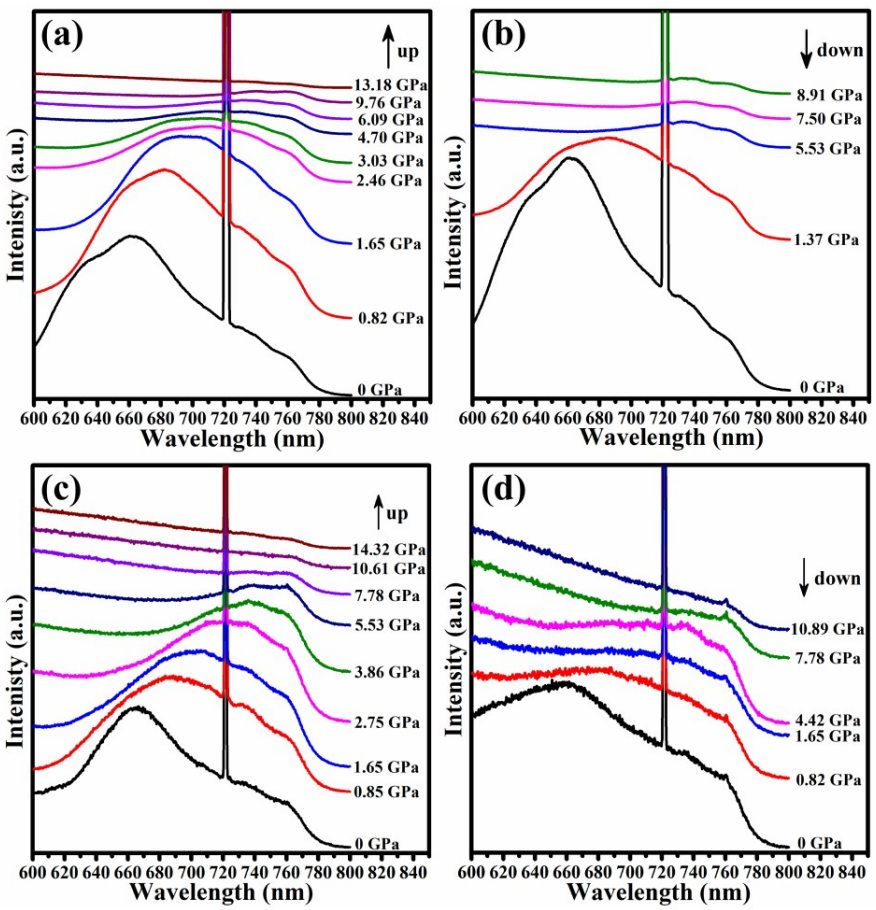

Fig. S4 PL spectra of pure R6G molecules as a function of pressure along the compression (a) and decompression (b) path. PL spectra of R6G molecule (10^{-1} mol/L) adsorbed on MoS_2/Au composite as a function of pressure along the compression (c) and decompression (d) path. The strongest PL band at ~720 nm belongs to the frequency multiplier of 365 nm laser.

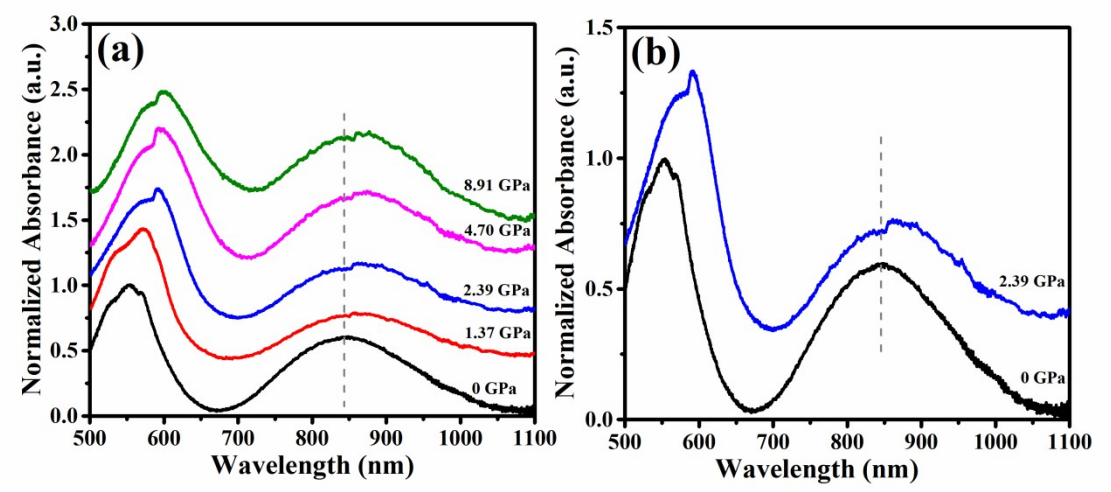

Fig. S5 (a) the pressure-dependence UV-VIS spectra of the MoS_2/Au/R6G system and (b) the UV-VIS spectra of the MoS_2/Au/R6G system at ambient pressure and at 2.39 GPa.