Electronic Supplementary Information

Crystalline phase induced Raman enhancement on molybdenum carbide

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Contents

Density Functional Theory Calculations

Density Functional Theory (DFT) calculations were performed on the Vienna Ab initio Simulation Package (VASP) by using the PBE exchange-correlation function.[1-3] The interaction between valence electrons and the ionic core was described by the PAW pseudo-potential. The geometry structures were optimized with the cut off energy of 550 eV. All the atomic positions were allowed to relax until the magnitude of all residual forces was less than 0.02 eV. The Monkhorst-Pack k-point mesh of 13 × 13 × 13 was used to calculate the geometry optimization and PDOS. The VASPKIT code was used to analyse data.

Supplementary Figures

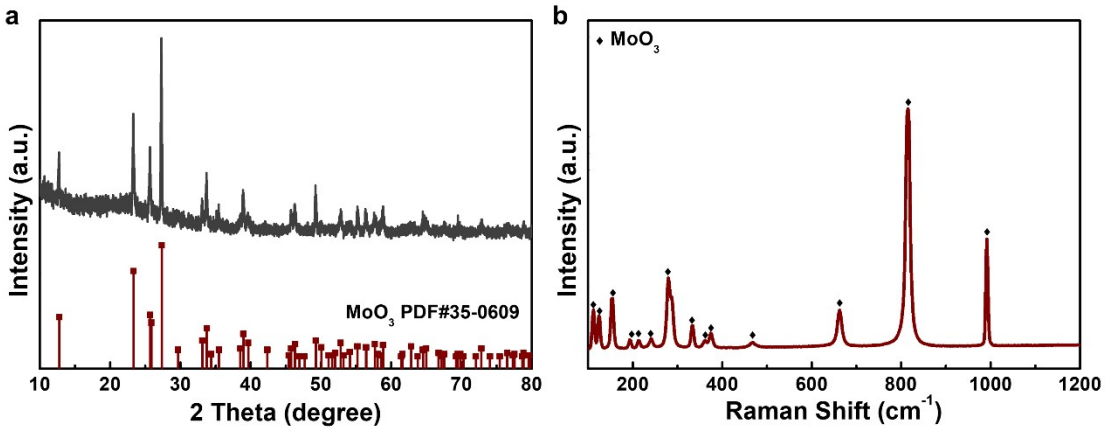

Fig. S1. (a) XRD pattern of the MoO_3 precursor. (b) Raman spectroscopy of MoO_3 precursor.

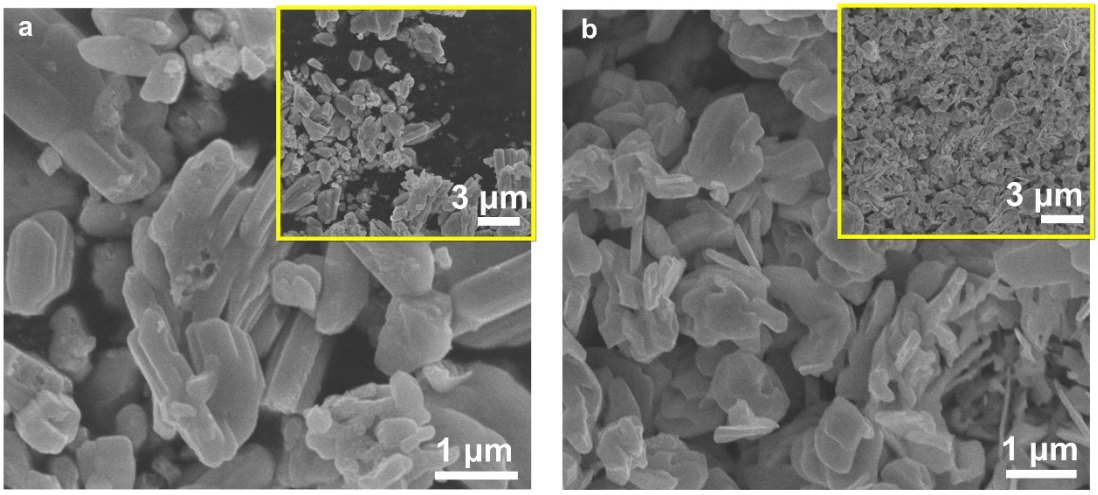

Fig. S2. SEM images of α-MoC and β-Mo_2C.

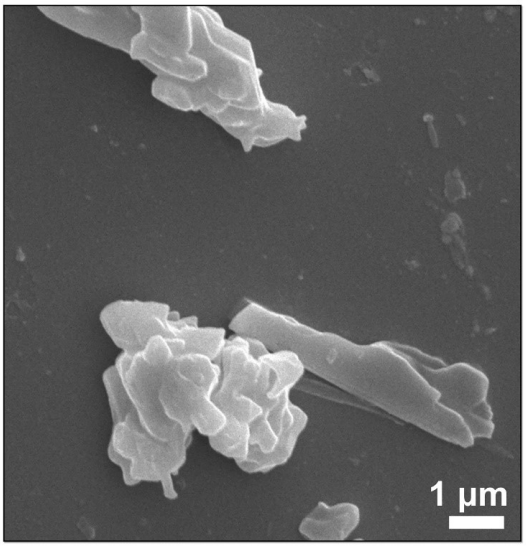

Fig. S3. SEM image of MoO_3 precursor prepared by calcination of $(NH_4)_7Mo_7O_{24}{\cdot}4H_2O$.

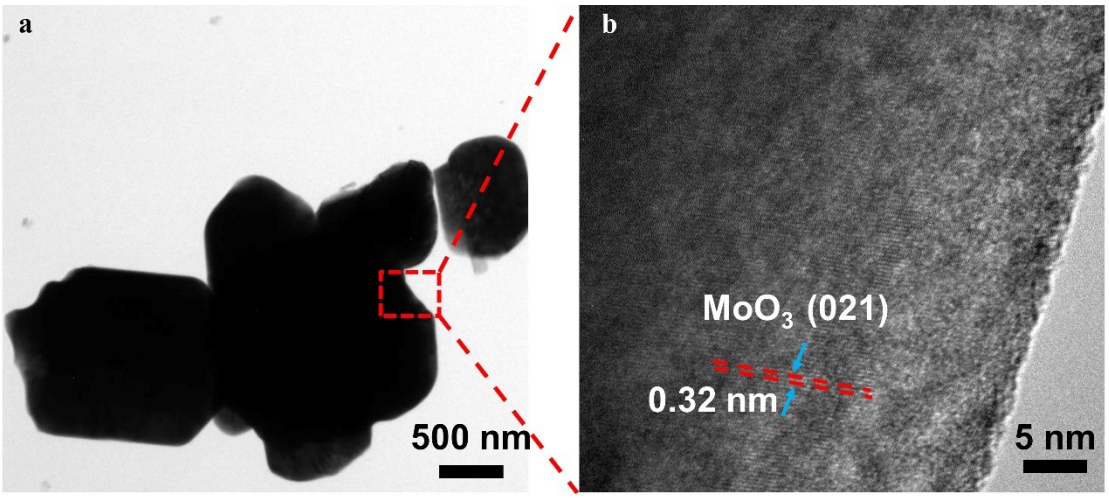

Fig. S4. TEM (a) and HRTEM (b) images of MoO_3 precursor.

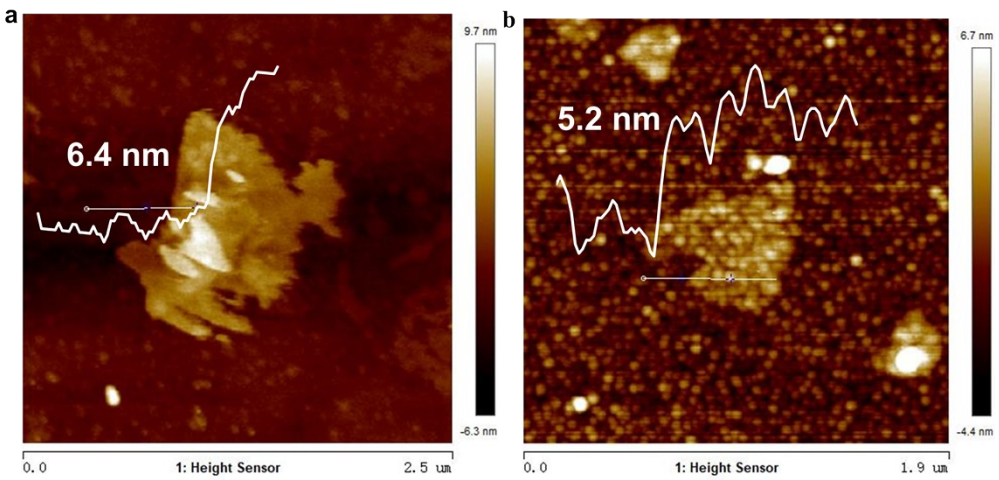

Fig. S5. AFM images of (a) *α*-MoC; (b) *β*-Mo_2C.

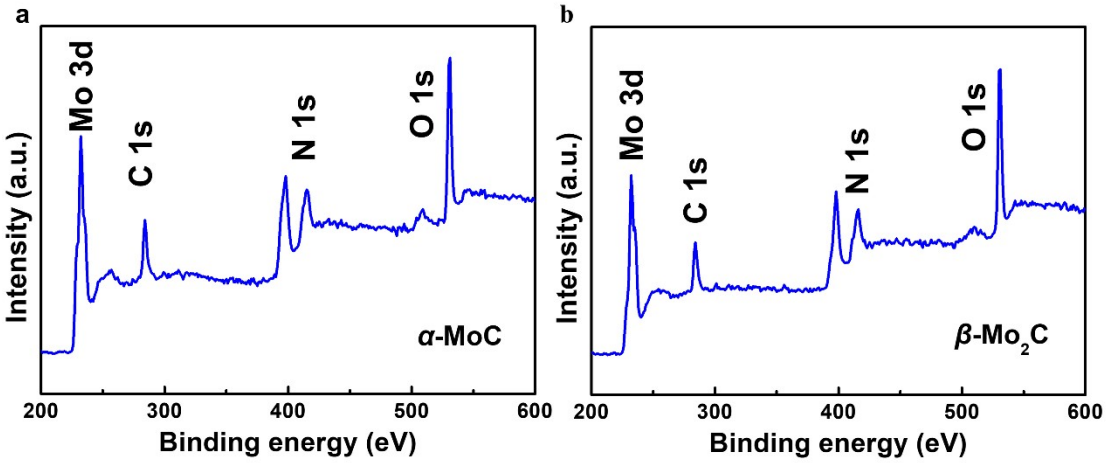

Fig. S6. Survey XPS for (a) *α*-MoC and (b) *β*-Mo_2C.

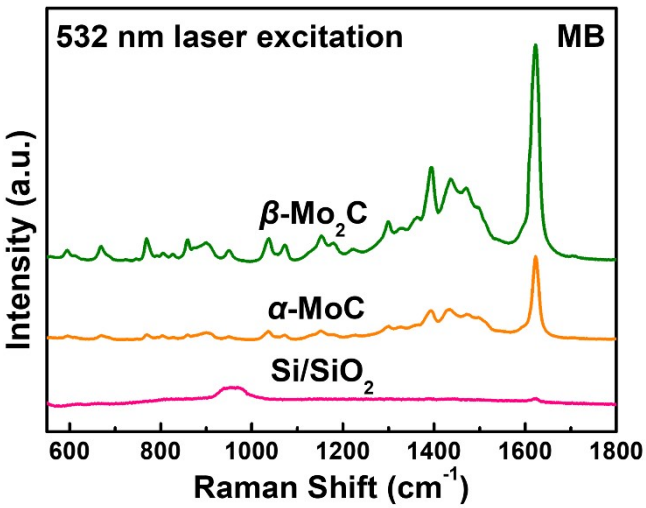

Fig. S7. Obtained SERS signals of MB from α-MoC, β-Mo_2C and SiO_2/Si substrates, respectively.

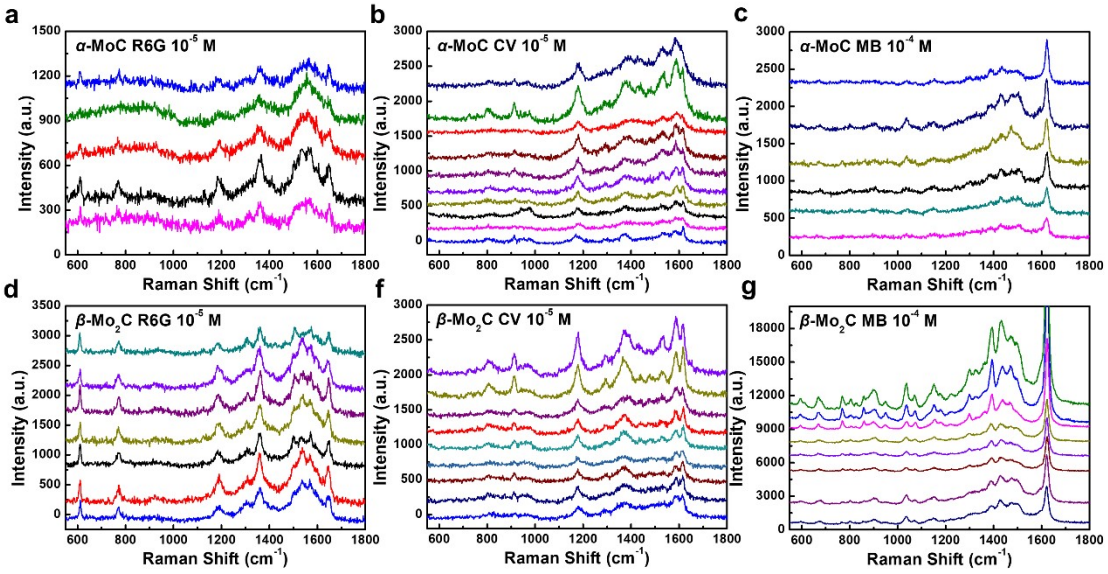

Fig. S8. SERS of (a, d) R6G, (b, f) CV and (c, g) MB molecules obtained from different positions on α-MoC and β-Mo_2C, respectively.

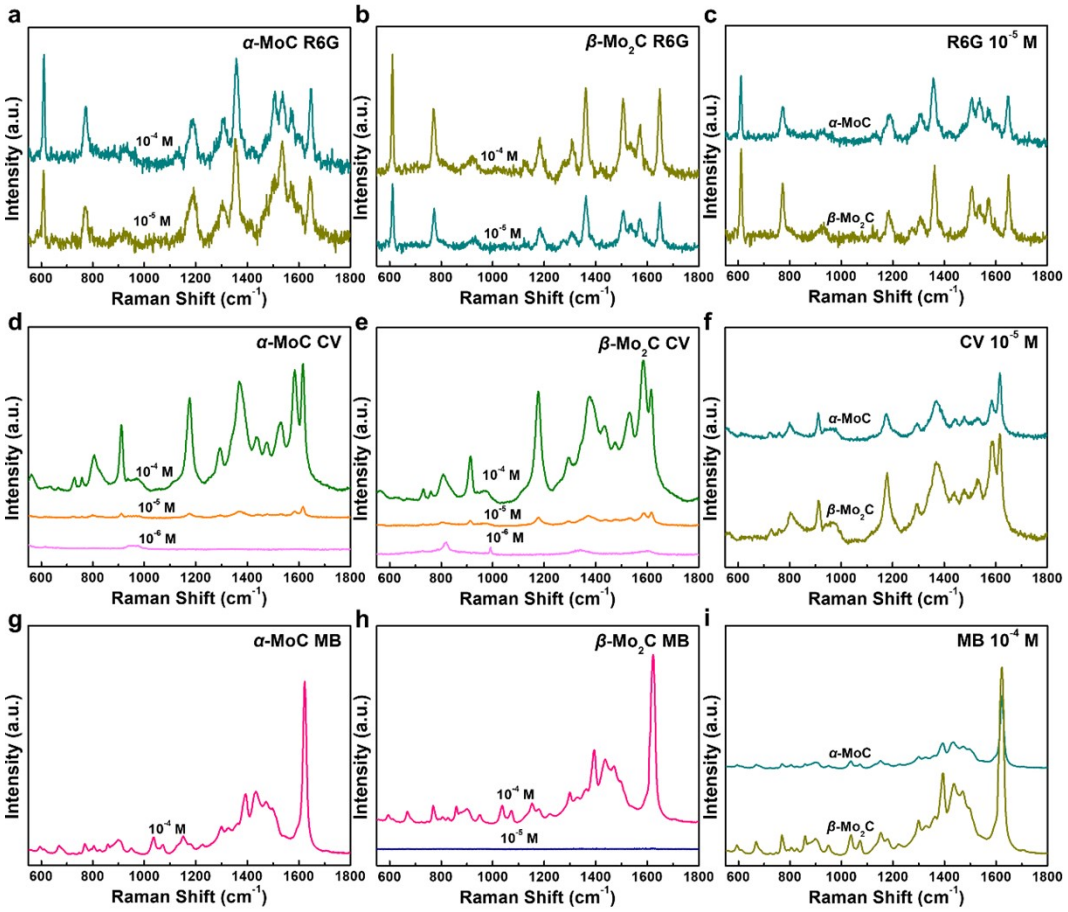

Fig. S9. SERS of different probe molecules adsorbed on α-MoC and β-Mo_2C. (a-c) R6G; (d-f) CV; (g-i) MB.

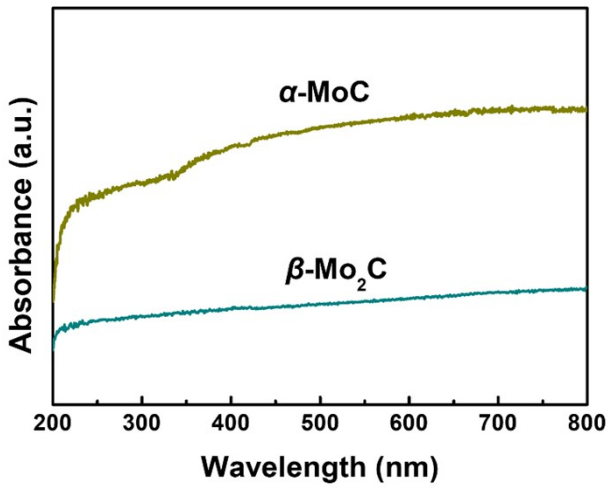

Fig. S10. UV-visible absorption spectra of α-MoC and β-Mo_2C. (During the test, the powder sample was put into a glass groove, and the surface was pressed flat with a glass sheet. The test range was 200-800 nm, and the scanning rate was 300 nm min-

[1].)

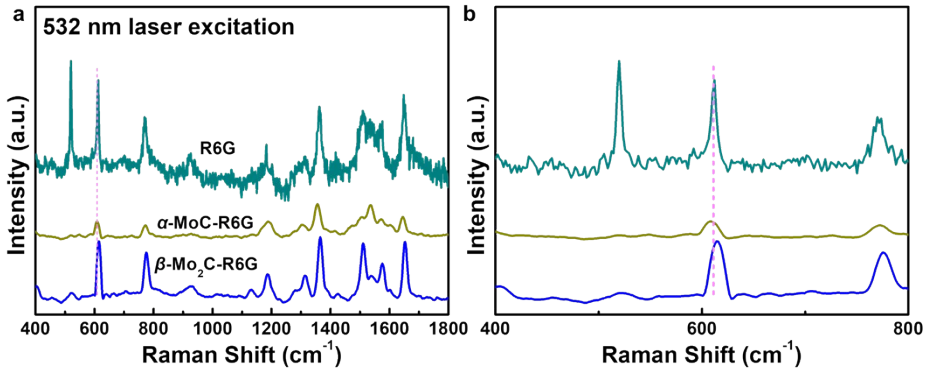

Fig. S11. (a) Raman Spectra of R6G molecules (10^{-3} M) and R6G (10^{-4} M) adsorbed onto α-MoC and β-Mo_2C.[4-7] (b) Enlarged part from 400-800 cm^{-1}.

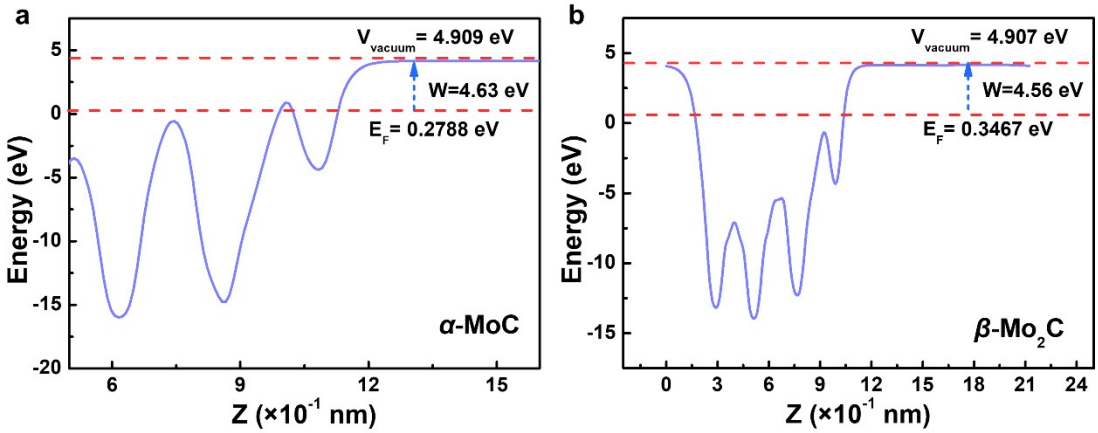

Fig. S12. Work functions of α-MoC (a) and β-Mo_2C (b) by DFT calculations.

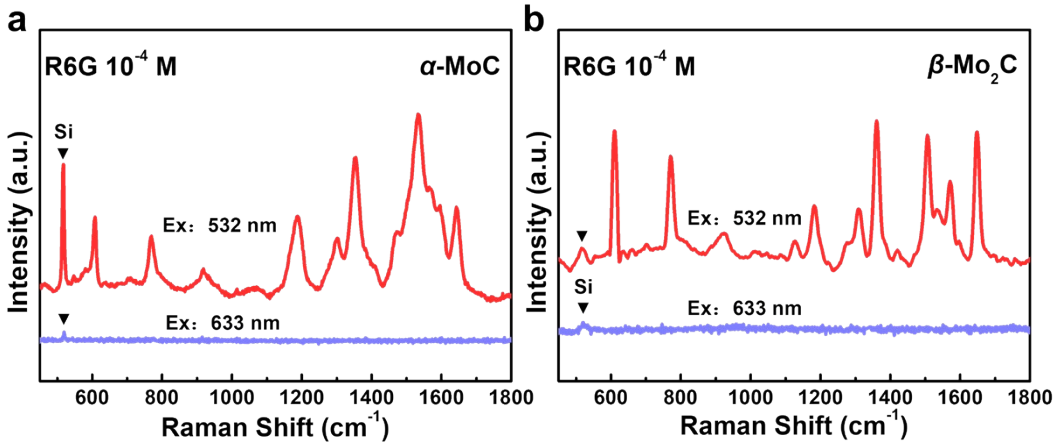

Fig. S13. Influence of changing excitation wavelength on SERS effect (a) α-MoC; (b) β-Mo_2C.

Calculation of enhancement factor

The enhancement factor was calculated according to the following equation[4]:

$$EF = (I_{SERS} / N_{SERS}) / (I_{NR} / N_{NR})$$

where I_{SERS} and I_{NR} are the Raman intensities of MB molecule on substrate and that without substrate (Si substrate in this study). N_{SERS} is the number of molecules absorbed on the molybdenum carbide substrate within the laser spot area, and N_{NR} stands for the number of molecules excited on the Si substrate. In order to obtain the value of N_{NR}, 100 µL of probe molecules solution (1 mM) was dropped onto the Si wafer (0.5 × 0.5 cm^{-2}). N_{NR} can be estimated by the following equation:

$N_{NR} = c_{NR}V (A_{beam}/A) N_A$ where $A_{beam} = \pi(d/2)^2$ is the area of the focal spot of the laser, d is the diameter of the light spot estimated by $d = 1.22 \lambda/NA$, λ is the incident laser wavelength, i.e., 532 nm, and the numerical aperture (NA) of the objective lens NA = 0.75. Thereby, laser spot size is approximately 1.87 μm^2. A is the area of probe molecules layer which equal to the area of Si wafer (0.25 cm^2). NA stands for Avogadro's constant. Therefore, N_{NR} equals to:

N_{NR} =40 µL × 0.001 mol / L × 0.59 μm^2 / 0.25 cm^2 × 6.02 × 10^{23} mol^{-1} =5.68×10^8

Moreover, N_{SERS} is the number of absorbed molecules scattered in the area of laser beam, which can be estimated by the following equation: $N_{SERS} = A_{beam}/\sigma$ where σ is the area occupied by a molecule of adsorbent at monolayer coverage, which is estimated to ~ 0.5 nm^2. It should be mentioned that the surface coverage must remain smaller than one monolayer when using this equation. The concentration of the probe molecules solution was controlled lower than 1×10^{-4} M to prevent the supersaturation adsorption of probe molecule onto molybdenum carbide substrate. N_{SERS} is calculated to be 1.18×10^6.

The intensity at 1626 cm^{-1} of MB molecule on Si and the intensity at 1624 cm^{-1} on molybdenum carbide substrate were used to calculate EF values. Here I_{SERS} =5338 and

13200of α-MoC and β-Mo_2C, respectively, and I_{NR} = 5300 (**Fig. S14**). By substituting these values into the equation, EF of α-MoC and β-Mo_2C are calculated to be 3.6×10^2 and 1×10^3, respectively.

The intensity at 609 cm^{-1} of R6G molecule on Si and the intensity at 609 cm^{-1} on molybdenum carbide substrate were used to calculate EF values. Here I_{SERS} =400 and 1500 of α-MoC and β-Mo_2C, respectively, and I_{NR} = 1800 (**Fig. S14**). By substituting these values into the equation, EF of α-MoC and β-Mo_2C are calculated to be 1.2×10^2 and 4×10^2, respectively.

The intensity at 1176 cm^{-1} of CV molecule on Si and the intensity at 1176 cm^{-1} on molybdenum carbide substrate were used to calculate EF values. Here I_{SERS} =2800 and 4800 of α-MoC and β-Mo_2C, respectively, and I_{NR} = 2400 (**Fig. S14**). By substituting these values into the equation, EF of α-MoC and β-Mo_2C are calculated to be 6×10^2 and 1×10^3, respectively.

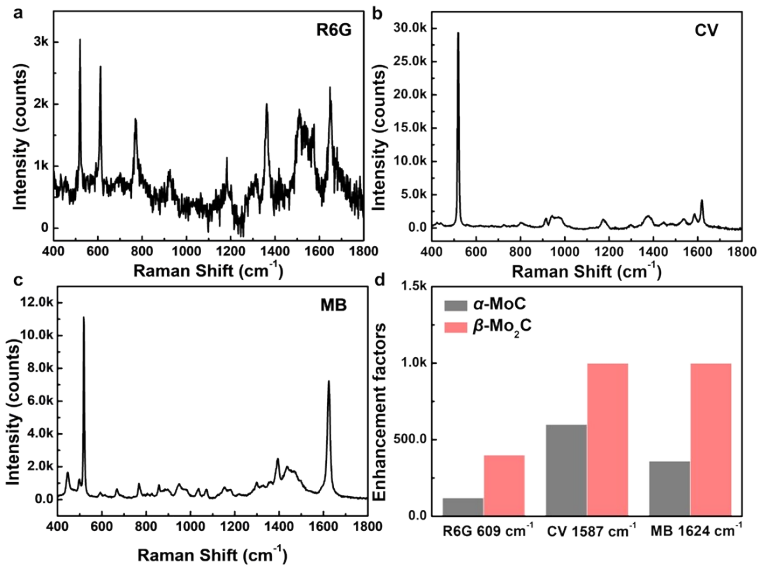

Fig. S14. Raman enhancement factors of α-MoC and β-Mo_2C.

Reference：

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