Supporting Information

WO$_x$/MoO$_x$ Hybrid Oxide Based SERS FET and Investigation on Its Tunable SERS Performance

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Calculation of enhancement factor

The marked molecule method, commonly employed in SERS studies, establishes a crucial connection between the measured SERS signal and the surface density of the target molecules on the substrate. This technique involves the introduction of a reference or marked molecule with a known concentration. By quantifying the SERS signal of the reference molecule and establishing a standard curve relating signal intensity to concentration, we can then apply this calibration to indirectly estimate the surface density of the target molecules.

The SERS enhancement factor is calculated from the following formula:

$$EF = \frac{I_{SERS} \times N_{bulk}}{I_{bulk} \times N_{SERS}} \#(1)$$

Among them, the I_{SERS} value is the integral intensity of the characteristic peak of R6G measured on the SERS substrate. The I_{bulk} value is the integrated intensity of the characteristic peak of the saturated R6G measured on a non-SERS substrate (silicon substrate). N_{SERS} is the number of molecules adsorbed on SERS substrates, while N_{bulk} is the number of molecules detected on a non-SERS substrate.

To calculate this N_{bulk}, in the first step, the following method is used. R6G powder (9.58 mg) is dissolved in ethanol (30 μL). The solution is dropped on the surface of a Si chip of size 5 × 5 mm² (S) and let it diffuse naturally and dry in air for 2 hrs. Therefore, the coverage area S of R6G can be calculated by the following formula:

$$S = \pi \times R^2 \#(2)$$

Then, the parameters during SERS measurement are set as follows (532 nm excitation source, 1 mW laser power, 10 s integration time, laser spot radius 6.25 μm and 100× objective lens), the N_{bulk} can be calculated based on the following equation:

$$N_{bulk} = c \times V \times N_A \times \frac{\pi r^2}{S} \#(3)$$

Where c is the concentration of R6G, V is the volume of R6G solution dropping on the surface of the silicon surface, r is the radius of the laser spot and N_A is the Avogadro constant, $N_A = 6.022 \times 10^{23}$. These parameters give $N_{bulk} = 5.910 \times 10^{13}$.

N_{SERS} was calculated using the same method, briefly, 10 uL of 0.1 mM R6G ethanol solution was dropped on the SERS substrate and air-dried. The width of the middle channel micro-region of the customized device is L = 12.5 μm, so the Raman spot area is the actual measurement area. Based on the Equation (3), $N_{SERS} = 2.955 \times 10^9$.

In the meanwhile, I_{SERS} corresponding to the different SERS substrates are obtained by integrating the respective SERS spectra and the results are as shown below:

$I_{SERS} = 1.549615 \times 10^6$

For the non-SERS substrate, $I_{bulk} = 8.468 \times 10^2$. Based on Equation (1), the enhancement factors are 3.66×10^7 for the WO_x/MoO_x molecular weight ratio of 1:3. It can reach 6.55×10^7 under 10V voltage modulation. In addition, we also calculated that the enhancement factor of pure WO_x is 8.81×10^6 ($N_{SERS} = 2.955 \times 10^8$, $I_{SERS} = 3.730436 \times 10^4$), and that of pure MoO_x is 1.61×10^7 ($N_{SERS} = 2.955 \times 10^8$, $I_{SERS} = 6.826833 \times 10^4$). This means that the improved enhancement factor is 7.4 times that of the synthesized tungsten oxide and 4.1 times that of the synthesized molybdenum oxide.

EFs for other R6G concentrations and voltages are calculated with the same method.
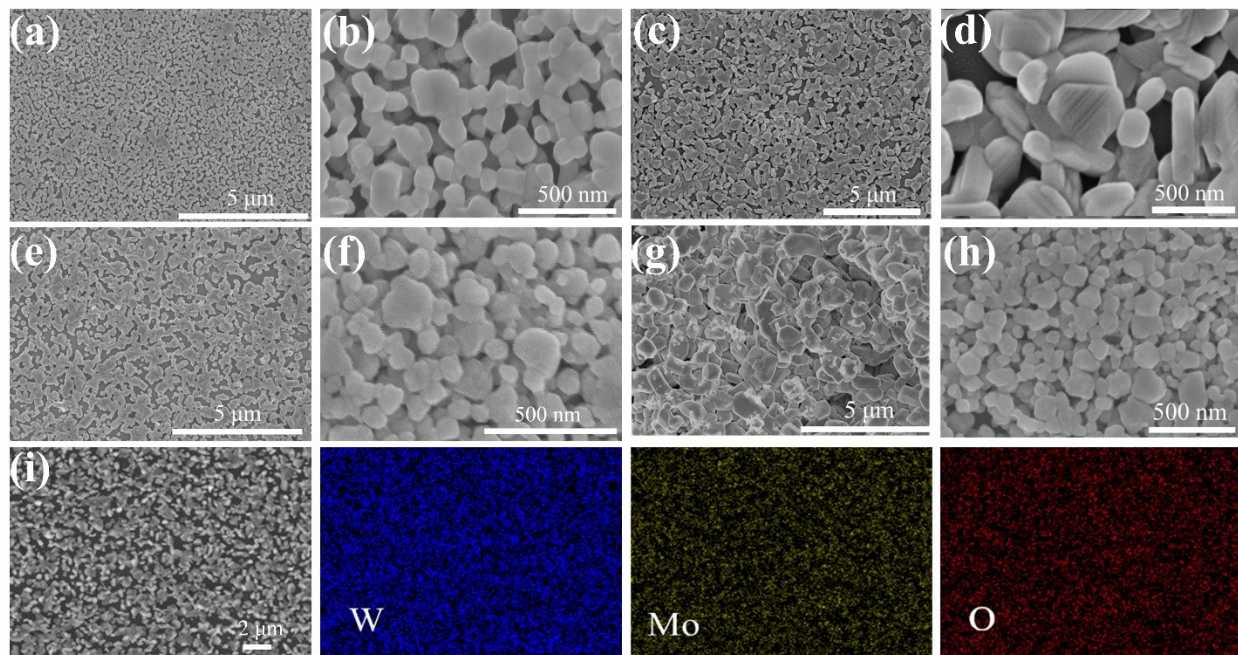
Fig. S1. (a) SEM images of the WO$_x$/MoO$_x$ hybrids with the molar ratio equal to (a)-(b) 1:1; (c)-(d) 1:2; (e)-(f) 2:1; (g)-(h) 3:1; (i) EDS elemental mapping images of WO$_x$/MoO$_x$ hybrid (mole ratio = 1:3).
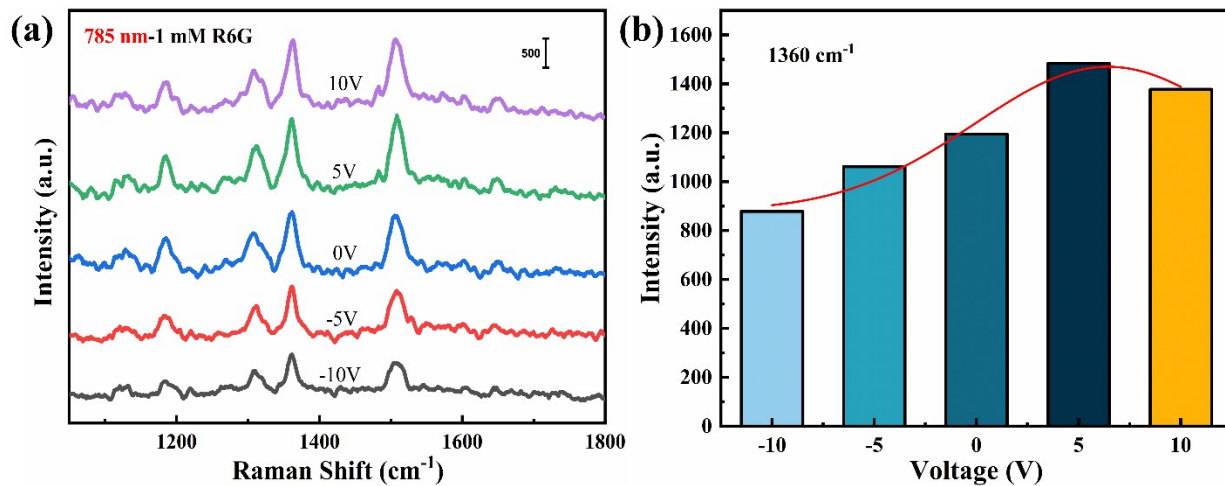
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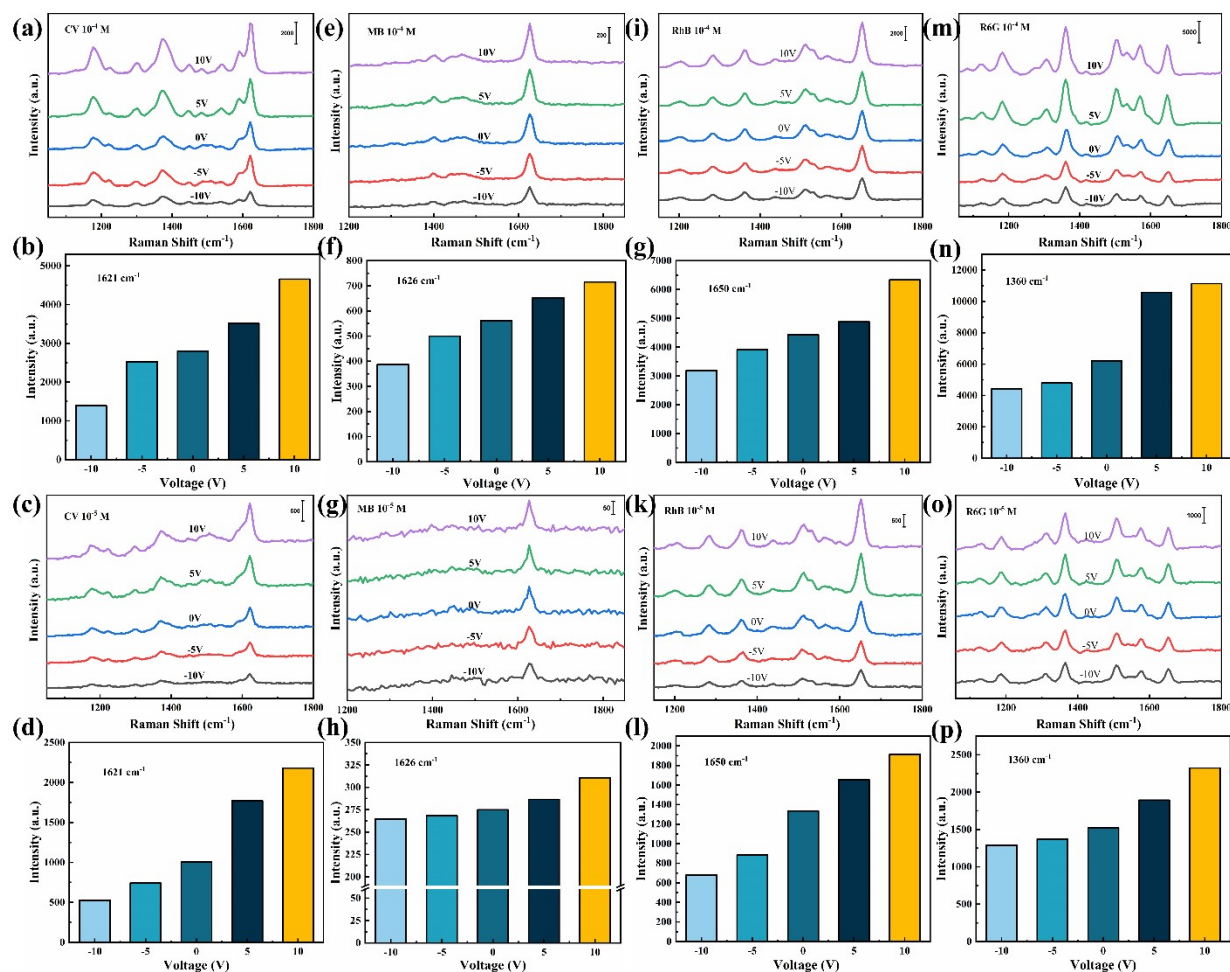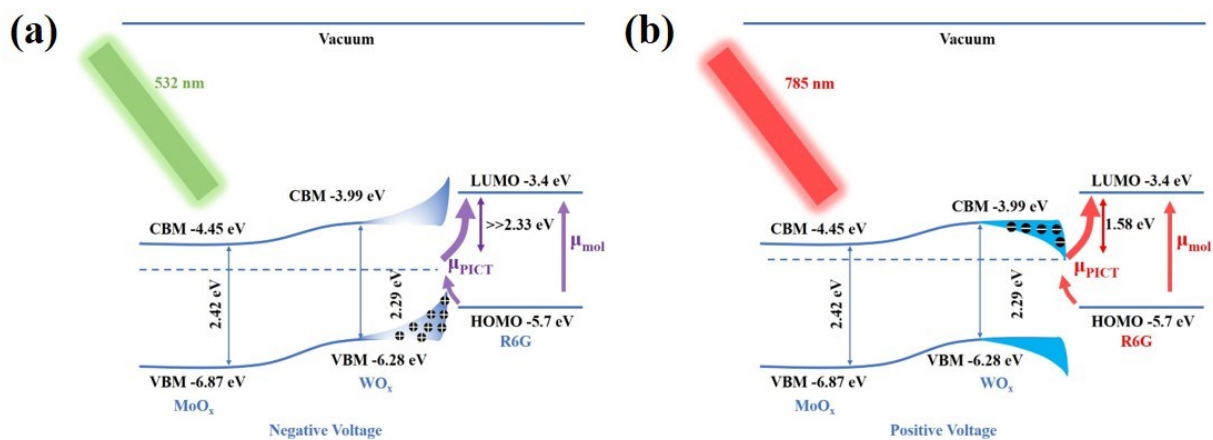
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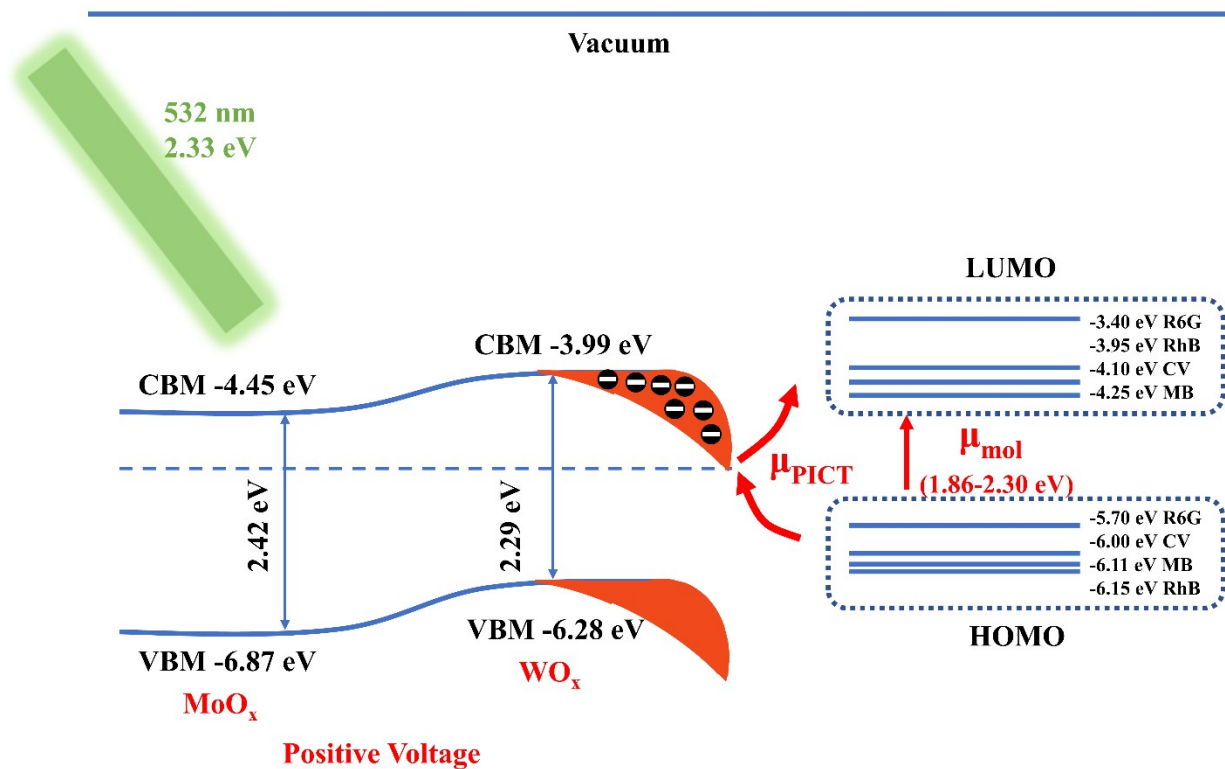
Fig. S4: Energy level alignment between molecular orbits of different molecules and the WO$_x$/MoO$_x$ hybrid under bias voltage while 532-nm laser is used.

Fig. S5: (a) Energy level alignment between molecular orbital energy level and the WO_x/MoO_x hybrid under negative bias while 532-nm laser is used. Inversion holes can be founded near the interface. **(b)** Energy level alignment between molecular orbital energy level and the WO_x/MoO_x hybrid under +5 V bias while 785-nm laser is used.