Supporting information

Ag@Cu_2O-MXene Core-Shell Nanostructures: Plasmonic Coupling and Charge Transfer for Ultra-Sensitive SERS Detection

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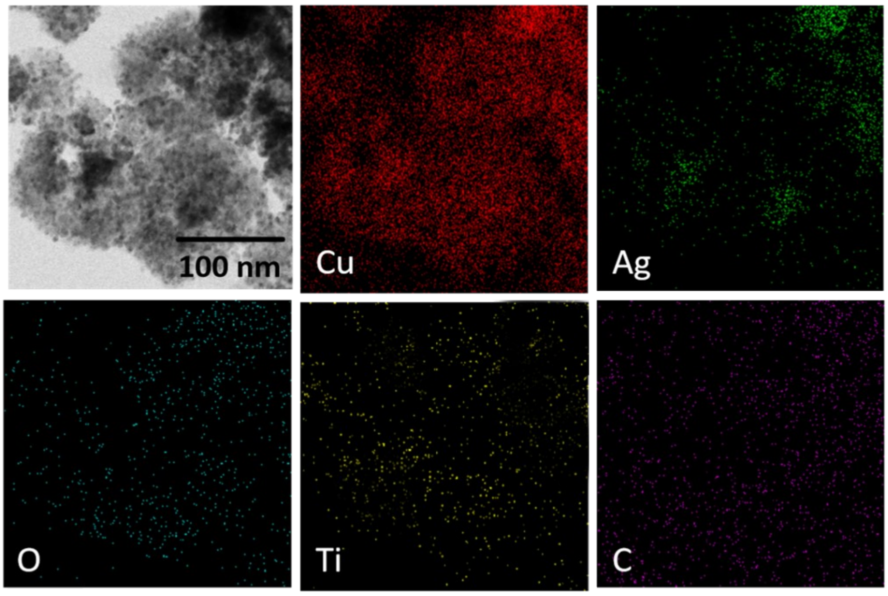

Figure S1. TEM image and EDS mapping of the Ag@Cu_2O-MXene composites, showing the distribution of Cu, Ag, O, Ti, and C.

Table S1. Band assignments of the MBA adsorbed on the Ag@Cu_2O-MXene composites

Wavenumber (cm^{-1})	Band assignments
1012	In-plane ring breathing +ν(C–O), b_2
1075	In-plane ring breathing + ν(C–S), a_1
1138	ν(C–H), b_2
1183	ν(C–H), a_1
1352	β(O–H) + ν(C–ph) + in-plane ν(C–C) + asymmetry ν(O–C–O), b_2
1582	In-plane β(C–H), a_1

[a] *ν*, stretching; *β*, bending. For ring vibrations, the corresponding vibrational modes of benzene and the symmetry species under C_{2v} symmetry are indicated.

[b] Wilson notation is employed.

Calculation of enhancement factor (EF)

To evaluate the SERS activity of the Ag@Cu_2O-MXene composites, the enhancement factor (EF) of MBA adsorbed on the Ag@Cu_2O-MXene composites was calculated. The Raman spectra of MBA obtained under 532 and 633 nm laser excitations are shown in Figure S2. The EFs of the Ag@Cu_2O-MXene composites were determined using the following equation[1]:

$$EF = \frac{I_{SERS}}{I_{Bulk}} \times \frac{N_{Bulk}}{N_{SERS}}$$

where I_{SERS} represents the intensity of the SERS band at 1075 cm^{-1}, and I_{Bulk} denotes the intensity of the Raman band at 1075 cm^{-1} for solid MBA.

$$N_{Bulk} = A_{laser} \mathrm{h} \rho N_A$$

Here, N_{Bulk} is the number of MBA molecules in the solid state irradiated by the laser, A_{laser} is the laser spot area (diameter = 1 μm), h is the effective focusing depth of the laser (19 μm at the excitation wavelength), and ρ is the density of MBA (1.34 g/cm^3).

$$N_{SERS} = N_d A_{laser} A_N / \sigma$$

In this expression, N_{SERS} corresponds to the number of MBA molecules adsorbed on the SERS substrate within the laser spot (diameter = 1 μm), N_d is the density of Ag@Cu_2O particles within the laser spot, A_N is the surface area of an individual Ag@Cu_2O particle, and σ is the area of a single MBA molecule (0.64 nm^2/molecule) adsorbed on the Ag@Cu_2O-MXene composites.

Calculation of charge transfer degree ($\rho_{(CT)}$)

Lombardi et al. proposed that charge transfer degree ($\rho_{(CT)}$) can be used to quantitatively evaluate the CT effect[2]. To elucidate the underlying mechanism of Ag@Cu_2O-MXene composites, $\rho_{(CT)}$ was calculated using the following equation:

$$\rho_{(CT)} = \frac{I^{K}_{(CT)} - I^{K}_{(SPR)}}{I^{K}_{(CT)} + I^{0}_{(SPR)}}$$

Here, K represents the Raman spectrum of a single MBA molecule. $I^{K}_{(CT)}$ and $I^{0}_{(SPR)}$ correspond to the enhanced Raman intensities arising from CT effect and EM effect, respectively. The SERS band intensities of 1075 and 1141 cm^{-1} were selected for the calculation of $\rho_{(CT)}$, corresponding to a_1 mode associated with C–C bond stretching vibration and b_2 mode associated with C–H bending, respectively.

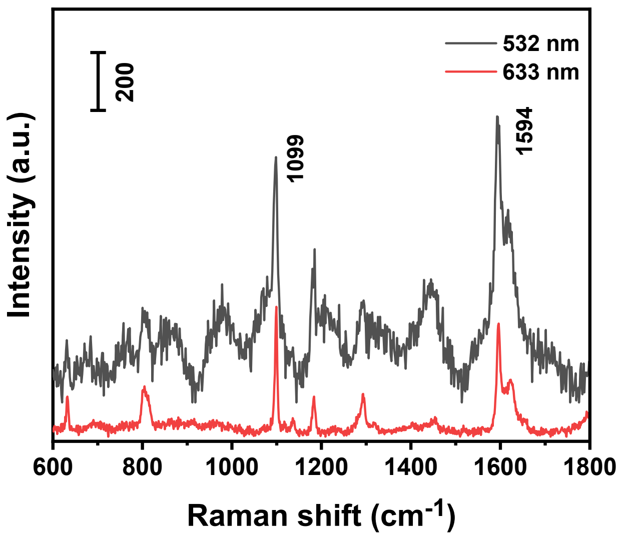

Figure S2. Raman spectra of MBA by using the 532 and 633 nm laser excitation.

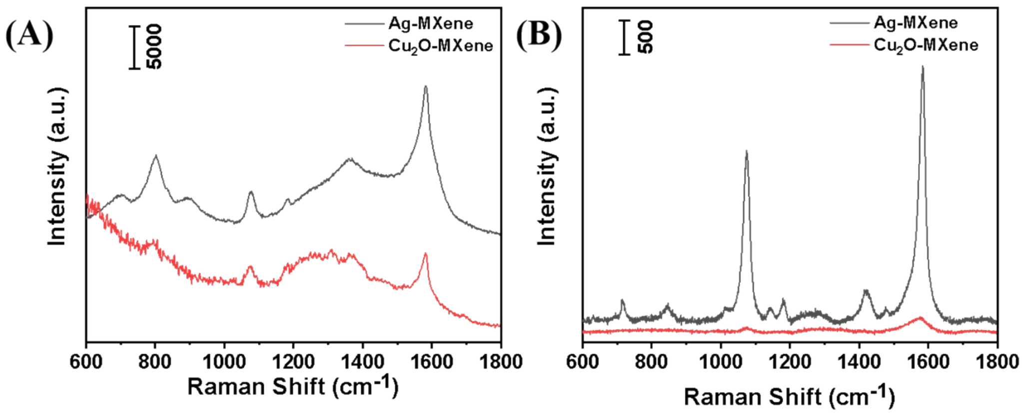

Figure S3. SERS spectra of MBA adsorbed on the Ag-MXene and Cu_2O-MXene substrate under (A) 532 and (B) 633 nm laser excitations.

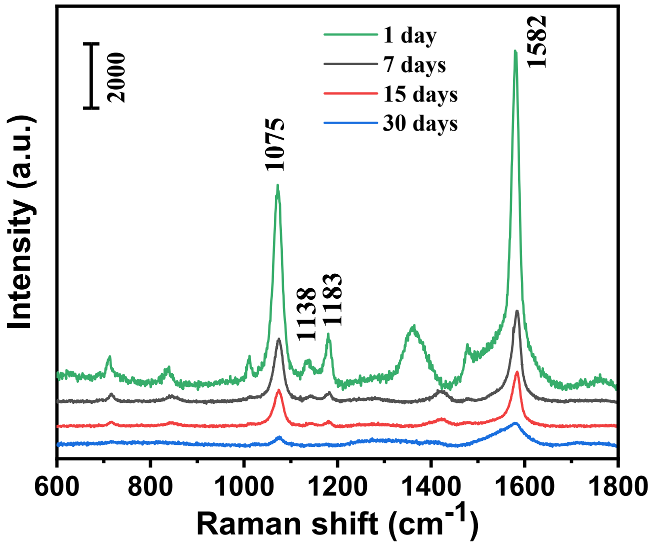

Figure S4. SERS spectra of MBA adsorbed on the Ag@Cu_2O-MXene composites after storage for 1, 7, 15, and 30 days.

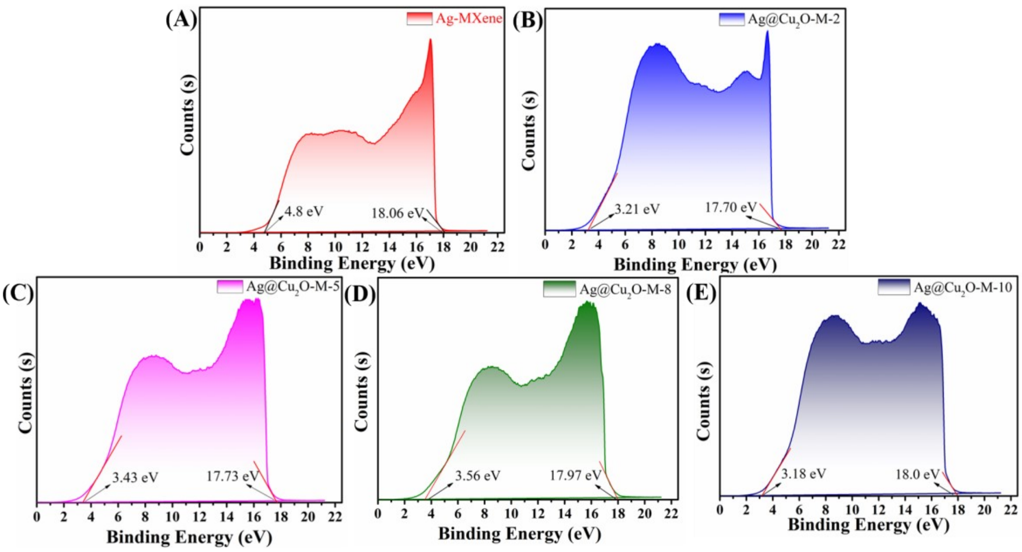

Figure S5. UPS spectra of (A) Ag-MXene and Ag@Cu_2O-MXene composites with varying $Cu(NO_3)_2$ concentrations of (B) 2, (C) 5, (D) 8, and (E) 10 mM.

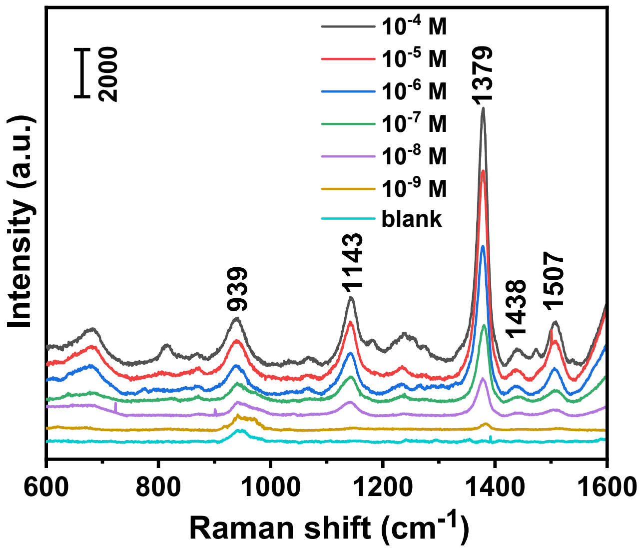

Figure S6. SERS spectra of Ag@Cu_2O-M-8 composites adsorbed with varying concentrations of sodium dimethyl dithiocarbamat under 633 nm laser excitation.

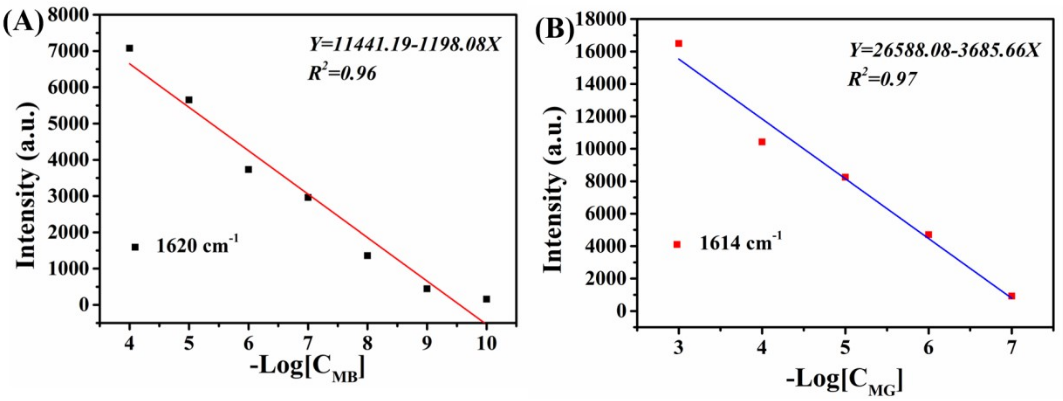

Figure S7. Linear correlation between logarithmic concentration and SERS intensity of the bands at (A) 1620 cm^{-1} (MB) and (B) 1614 cm^{-1} (MG).

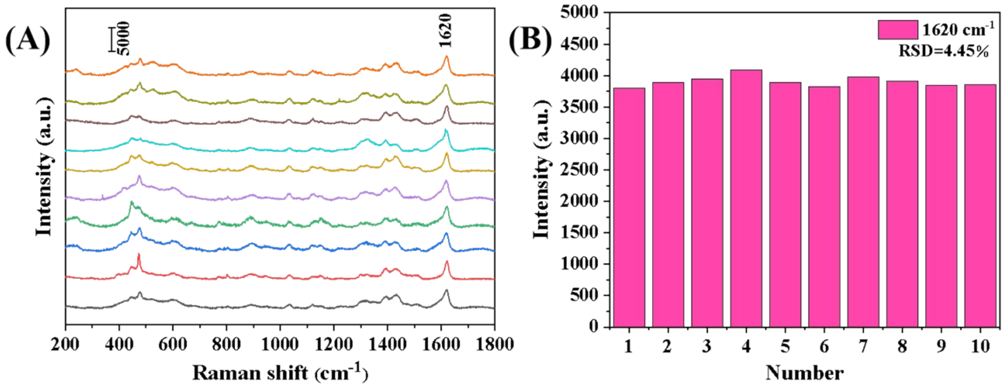

Figure S8. (A) SERS reproducibility of the Ag@Cu_2O-M-8 substrate. SERS spectra of MB (1.0×10^{-6} M) were collected from 10 randomly selected points on the composite surface. (B) Histogram of the intensity distribution for the band at 1620 cm^{-1} across the 10 spectra.

References

1. X. Xue, L. Chen, C. Wang, C. Zhao, H. Wang, N. Ma, J. Li, Y. Qiao, L. Chang, B. Zhao, *Spectrochim. Acta A* 2021, **274**, 119126.

2. J. R. Lombardi, R. L. Birke, *J. Phys. Chem. C*, 2008, **112**, 5605–5617.