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Cu_2O nanosheets: facile synthesis and application in chemical enhancement of surface enhanced Raman scattering

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Instruments

TEM and HRTEM analyses were conducted on a Tecnai G2 F20S-TWIN electron microscope operated at 200 kV. AFM characterization was performed using a Nanoman atomic force microscope (Veeco, Santa Barbara, CA) in tapping mode. XPS measurements were carried out on an ESCAlab 250 system equipped with an Al Kα X-ray source. FTIR spectra were acquired using a Thermo Nicolet 360 FT-IR spectrophotometer, while UV–Vis absorption spectra were recorded on a Persee TU-1950 UV/Vis spectrophotometer (China). XRD patterns were obtained using a Rigaku D/max-3C diffractometer (Japan) with Cu Kα radiation ($\lambda = 1.5406$ Å). SERS spectra were collected on a Renishaw Invia Raman spectrometer equipped with three laser excitation sources (532, 633, and 785 nm). All measurements were performed under consistent conditions, with a laser power of ~8 mW and an accumulation time of 10 s, using a 50× objective lens (numerical aperture = 0.5). Ultraviolet photoelectron spectroscopy (UPS) was performed on a Thermo ESCALAB 250XI UPS system using He I (21.22 eV) photon lines as excitation sources.

Calculation of SERS Enhancement Factors (EF)

The SERS EF was calculated according to the standard equation:

$$\mathrm{EF} = (\mathrm{I}_{\mathrm{SERS}} / N_{\mathrm{SERS}}) / (\mathrm{I}_{\mathrm{bulk}} / N_{\mathrm{bulk}})$$

where $\mathrm{I}_{\mathrm{SERS}}$ and $\mathrm{I}_{\mathrm{bulk}}$ are the SERS intensities of the same vibration mode of the target molecules obtained on the substrates and the normal Raman spectra from solid sample, respectively. N_{SERS} and N_{bulk} represent the numbers of target molecules absorbed on SERS substrates in the focus of the laser beam and the normal Raman sample, respectively.

$$N_{\mathrm{bulk}} = N_{\mathrm{A}} \times \rho \times \mathrm{h} \times \mathrm{S}_{\mathrm{Raman}} / M$$

Where ρ is the density of CV solid (ρ = 1.19 g/cm^3), h is the depth of laster penetration (h = 70 μm), $\mathrm{S}_{\mathrm{Raman}}$ is the laster spot area (the laster spot diameter is 1.26 μm, so $\mathrm{S}_{\mathrm{Raman}}$ = 1.25 μm^2), and M is the molecular weight of bulk CV (M = 407.99 g/mol).

$$N_{\mathrm{SERS}} = C \times V \times N_{\mathrm{A}} \times \mathrm{S}_{\mathrm{Raman}} / \mathrm{S}_{\mathrm{sub}}$$

where C is the molar concentration of CV, V is the volume of CV solution on Si wafer, $\mathrm{S}_{\mathrm{Raman}}$ is the laster spot size ($\mathrm{S}_{\mathrm{Raman}}$ = 1.25 μm^2), and $\mathrm{S}_{\mathrm{sub}}$ is the area of Si wafer. In the experiment, 20 μL of the aqueous CV solution (1.0 × 10^{-6} mol/L) was dropped on the substrate and make it cover the Si wafer (0.5 × 0.5 cm^2) competely. So C = 1.0 × 10^{-6} mol/L, V = 20 μL, and $\mathrm{S}_{\mathrm{sub}}$ = 0.25 cm^2.

As for $\mathrm{I}_{\mathrm{SERS}}$ and $\mathrm{I}_{\mathrm{bulk}}$, the normal Raman spectrum of bulk CV crystals on cleaned SiO_2/Si wafer is recorded, and the SERS spectrum of CV (1.0 × 10^{-6} mol/L) on the substrate is measured under the same laster power, excitation wavenumber, and acquisition time. Then, $\mathrm{I}_{\mathrm{SERS}}$ and $\mathrm{I}_{\mathrm{bulk}}$ are read on the peak intensity of CV molecule at 1619 cm^{-1} in SERS spectrum and normal Raman spectrum.

Thus, EF value can be caculated.

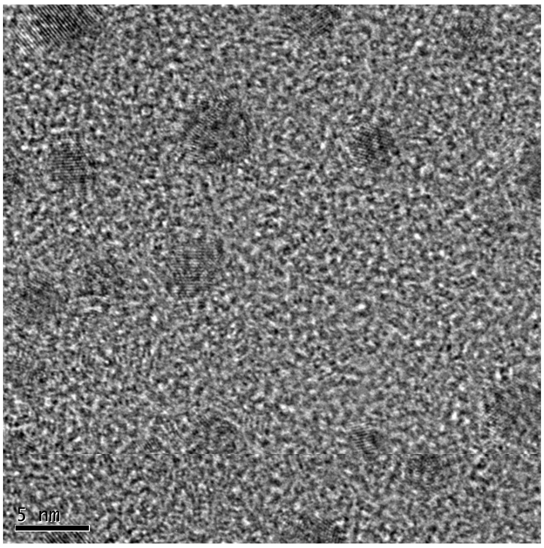

Fig. S1 TEM image of the used s-CDs.

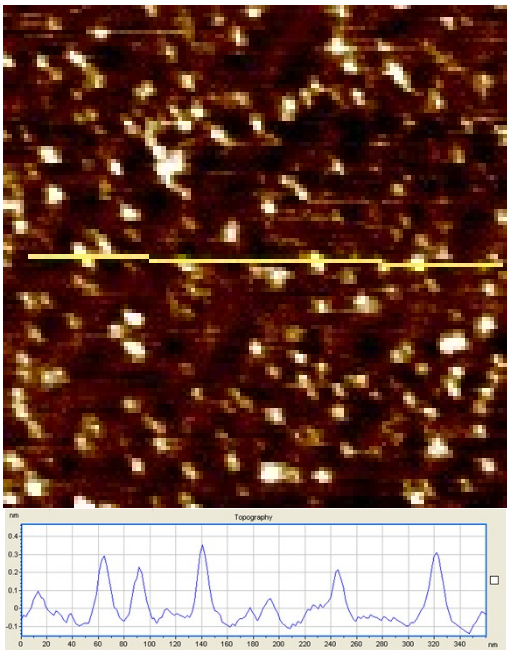

Fig. S2 AFM image of the used s-CDs. The inset shows the correspondingheight profile along the yellow line.

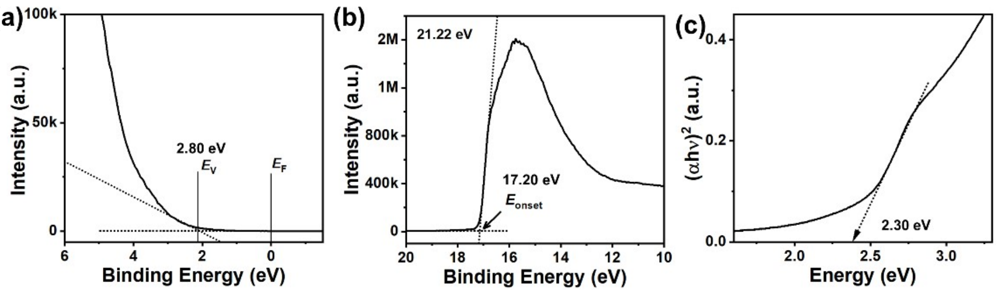

Fig. S3 The valence-band (a) and secondary-edge (b) spectra of the UPS measurement from Cu$_2$O-NSs. Plots of the $(\alpha h\nu)^2$ versus photon energy (hν) for direct inter-band transitions of Cu$_2$O-NSs (c).

UPS measurements are applied to explore the work function and valence band maximum of the obtained Cu$_2$O-NSs. As shown in Figure S1a, the valence band (E_V) for Cu$_2$O-NSs is at 2.80 eV, by linearly extrapolating the leading edge of the spectrum to the baseline. And the work function can be calculated from the difference between the onset level related to the secondary electrons (E_{onset}) and the photon energy of the exciting radiation (21.22 eV). Hence, the work function for the obtained Cu$_2$O-NSs is 4.02 eV (Figure S1b). In addition, the optical band gap (Eg) of Cu$_2$O-NSs based on direct inter-band transitions could be calculated by the absorption coefficient equation:

$$\alpha = B_d\,(hv - E\mathrm{g})^{1/2} / hv,$$

where α is the optical absorption coefficient, B_d is the absorption constant, h is the Planck constant and v is the frequency of the incident photon. Figures S1c shows plot of $(\alpha hv)^2$ versus the photon energy (hv) for the prepared Cu$_2$O-NSs, where the linear fit intercept representing the optical Eg is 2.30 eV, respectively. Based on the results above, the CB and VB of the obtained Cu$_2$O-NSs are calculated to be ~-4.02 and -6.32 eV, respectively.

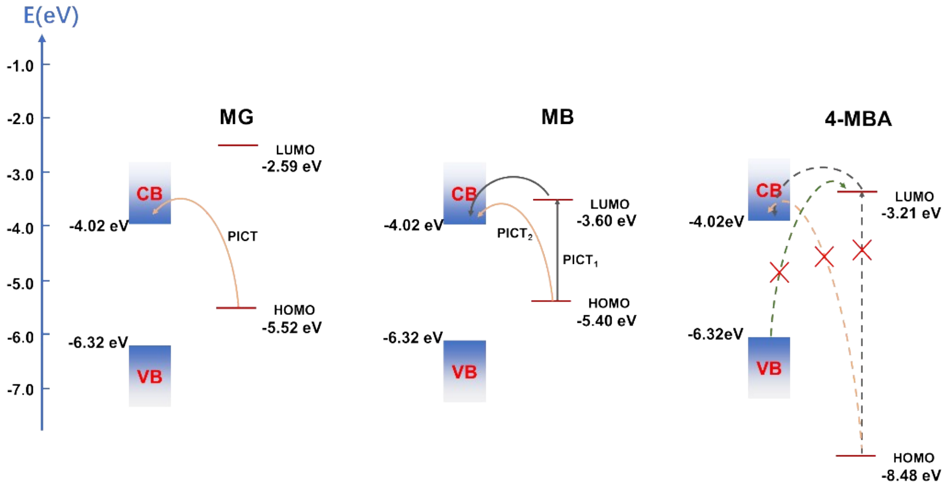

Fig. S4 Schematic energy-level diagram illustrating the electronic states of MG, MB and 4-MBA on Cu_2O-NSs with respect to the vacuum level.

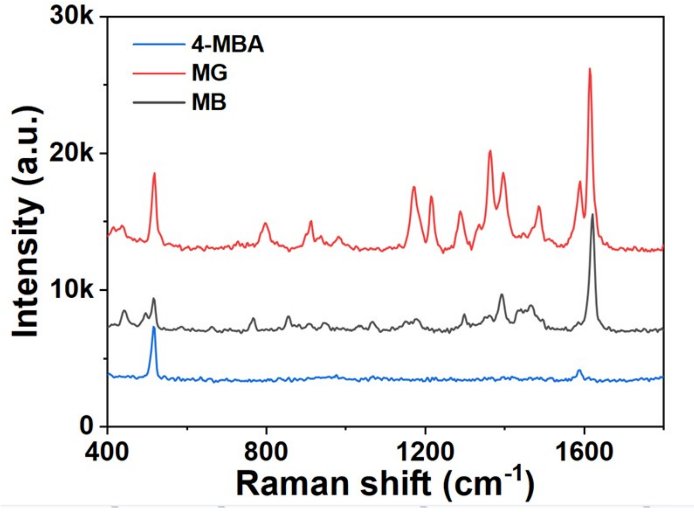

Fig. S5 SERS spectra of 1×10^{-4} mol/L 4-MBA, MG and MB on Cu_2O-NSs under 532 nm laser excitation.

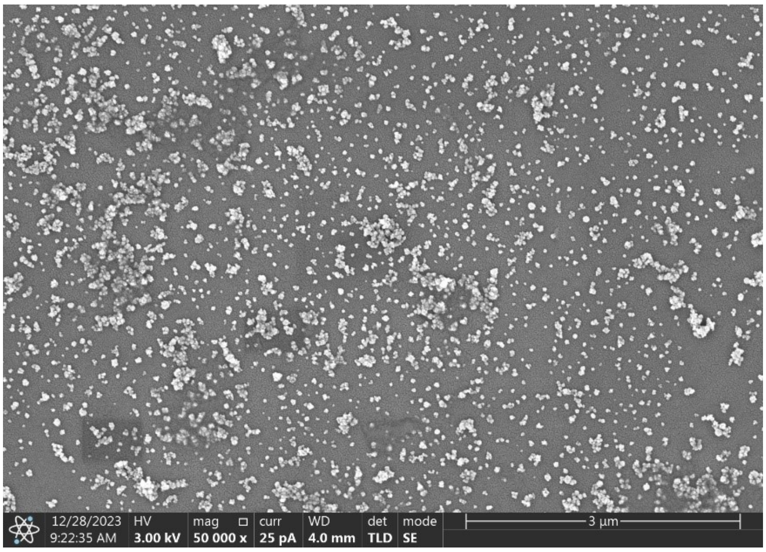

Fig. S6 SEM image of 0.59 µg/cm^2 Cu_2O-NSs on the silicon wafer.

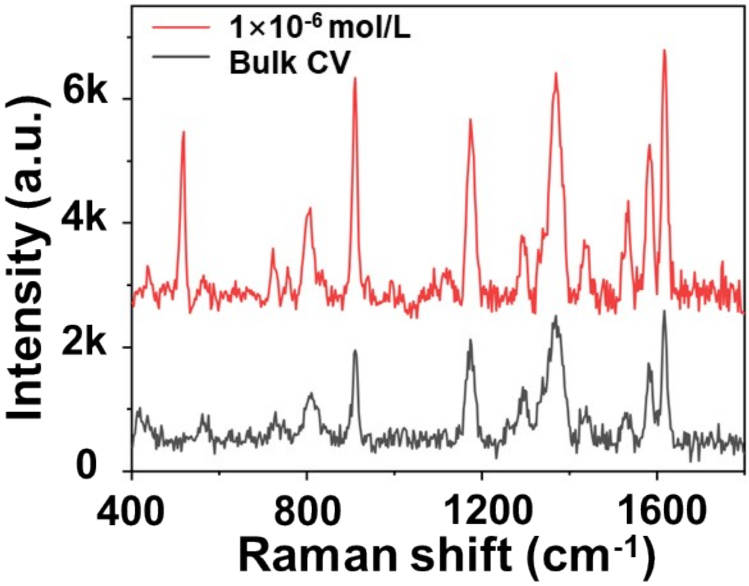

Fig. S7 Raman spectrum of bulk CV and SERS spectrum of 1×10^{-6} mol/L CV on Cu_2O-NSs.