

Supporting Information

Low Temperature-boosted High Efficiency Photo-induced Charge Transfer for Remarkable SERS Activity of ZnO nanosheets

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Materials: Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), dodecyldimethylammonium bromide (DDAB) and glacial acetic acid were purchased from Aladdin Industrial Inc. (Shanghai, China). Ethylene glycol, tetrabutyltitanate and ascorbic acid was purchased from Xilong Chemical Co. Ltd (Guangzhou, China). $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was purchased from Beijing Chemical Co. Ltd (Beijing, China). De-ionized water (Millipore Milli-Q grade; resistivity = 18.2 M Ω) was used in all experiments. Other reagents were of analytical grades.

Preparation of porous d-ZnO NSs: $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.095 g) and DDAB (0.5 g) were completely dissolved in 50 mL ethylene glycol solution in a 100 mL round bottom flask at room temperature by sonication method (2 min), to obtained a colorless transparent solution. Then, a constant pressure funnel was used to add 5 mL sodium hydroxide (NaOH)-ethanol solution (0.2 mol/L) under stirring, and the solution droplet acceleration was controlled at 2 drops/sec. Magnetic stirring was kept for 40 min till the addition was completed. Afterwards, the sample solution was placed in a heating mantle (rotary knob to 4/5, ~ 300 °C), heated and refluxed with condensed water for 3 h. Then, the reaction was stopping, and the temperature of the sample solution was allowed to return to room temperature. The white sample was then taken out. Finally, the sample was rinsed with de-ionized water and ethanol solution several times, and dried in a vacuum oven at 80 °C for 10 h to obtain the d-ZnO NSs sample.

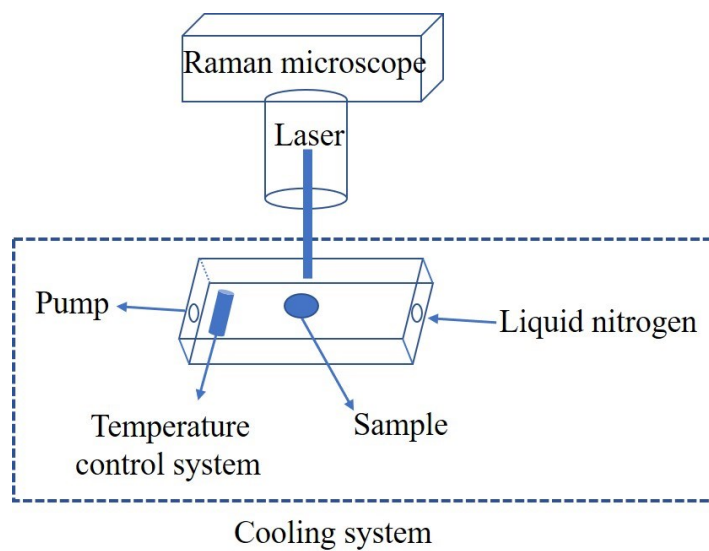
Preparation of d-Cu₂O NPs: 0.171 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was first dissolved in 100 mL de-ionized water at room temperature. Then, 10 mL NaOH (2 M) was added to the solution until it was heated to 55 °C. After 30 min of stirring, 10 mL ascorbic acid (0.6 M) was introduced dropwise into this system. With another 3 h of agitation, a brick-red precipitate was obtained. The precipitate was collected and washed with de-ionized water and ethanol several times by centrifugation and then dried in a vacuum oven at 60°C for 12 h.

Preparation of d-TiO₂ NPs: The d-TiO₂ NPs were prepared by sol-gel method. Typically, tetrabutyltitanate (0.75 mL) was dissolved in a mixture of ethanol (2.0 mL) and glacial acetic (0.075 mL) with stirring at 80 °C. Then, a mixed solution of HNO₃ (0.15 mL), distilled water (0.1 mL) and ethanol (1 mL) was added slowly into the reaction mixture under stirring. Finally, the obtained sample was vacuum dried at 120 °C for 5 h and then calcined at 400 °C for 2 h.

SERS experiment: The solution utilized in SERS experiment is ethanol, d-ZnO NSs ethanol suspension was mixed with different ethanol solutions of probe molecule to obtain a final concentration, and the mixtures were kept for 5 hours. Then, highly diluted material solution adsorbed with different concentrations of molecule were dropped onto a clean Si substrate and thoroughly rinsed with absolute ethanol several times to remove the free probe molecules. The samples were then subjected to SERS characterization. SERS spectra were acquired 30 minutes after the ethanol was completely volatile.

Instrument Characterization:

The Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) images were recorded by JEOL JEM-2100F, with an accelerating voltage of 200 kV. Absorption spectra were recorded on a UV-3600 UV-Vis-NIR spectrophotometer made by Shimadzu, Japan. Raman and SERS spectra were acquired with a Renishaw inVia Reflex instrument, England. Lasers 633 and 532 nm lines from an Ar-Kr ion laser, and laser 785 nm line from semiconductor laser were used as excitation sources. The laser power density was $\sim 10^9$ W/m², and the laser power was ~ 0.5 mW to the surface of the sample. Photoluminescence spectra were collected using a He-Cd laser (325 nm) as excitation wavelength (Lens: 40 × near ultraviolet objective; Laser power: 1 mW). The cooling system utilized in the experiment was THMS600 temperature device (Linkam Scientific; England), composed of THMS600 testbed, T95 control system, and liquid nitrogen refrigeration pump (LNP95). The powder X-ray diffraction (XRD) of the samples were characterized by the Rigaku Rotaflex Dmax2200 diffractometer (Japan) with Cu K α radiation ($\lambda = 1.54056$ Å). Brunauer–Emmett–Teller (BET) surface areas of samples were measured by means of N₂ adsorption over a NOVA 2000e (Quantachrome, Germany) equipment.”



Scheme S1. Schematic diagram illustrating the cooling system combined with the Renishaw inVia Reflex instrument for normal Raman, SERS, and photoluminescent spectrum.

Raman vibration modes of CV¹ and MB² molecules are discussed and shown below:

“For CV molecules, 804 and 1176 cm⁻¹ peaks are assigned to asymmetric C-C stretching modes, 1357 cm⁻¹ peak is assigned to the phenyl-N stretching modes, and 1582 and 1615 cm⁻¹ peaks are assigned to phenyl ring vibration modes. For MB molecules, 769 cm⁻¹ peak is assigned to C-N vibration mode, 1035 and 1066 cm⁻¹ peaks are assigned to C-H vibration modes, 1394 cm⁻¹ peak is assigned to C-N vibration mode, and 1625 cm⁻¹ peak is assigned to phenyl ring vibration mode.

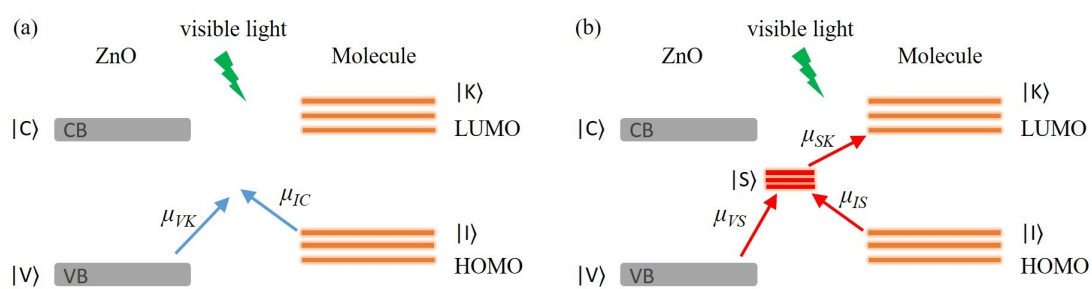


Figure S1. Surface defect states (|S>) can effectively facilitate the exciton transition possibilities between d-ZnO SERS substrate and probe molecule under visible light illumination.

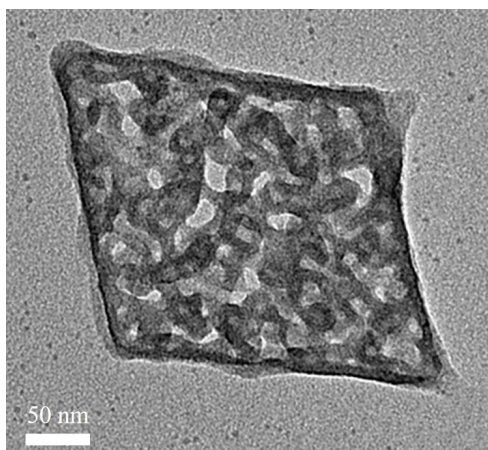


Figure S2. TEM image of porous d-ZnO NSs, which are generated by numerous randomly arranged ZnO NPs (~20 nm).

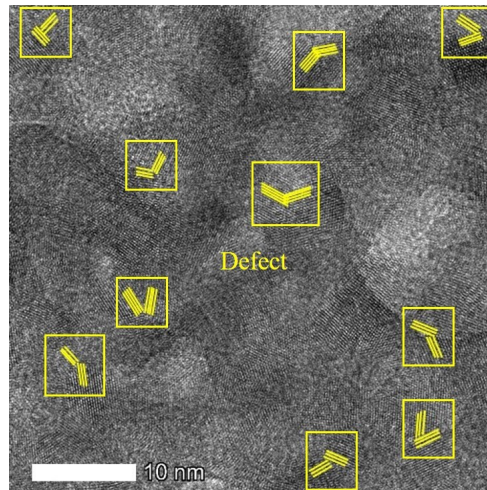


Figure S3. TEM image of abundant surface defect states formed in the porous d-ZnO NSs.

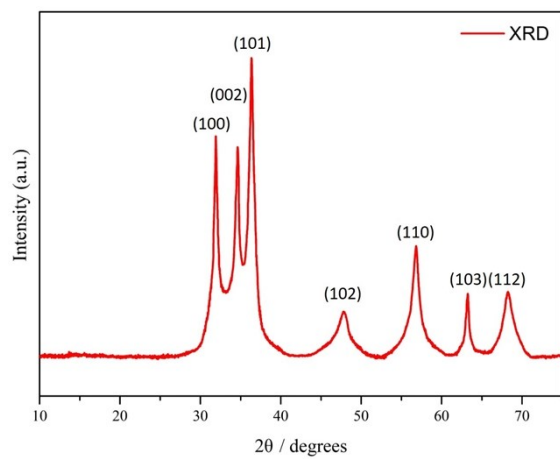


Figure S4. X-ray diffraction (XRD) pattern of the porous ZnO nanosheets.

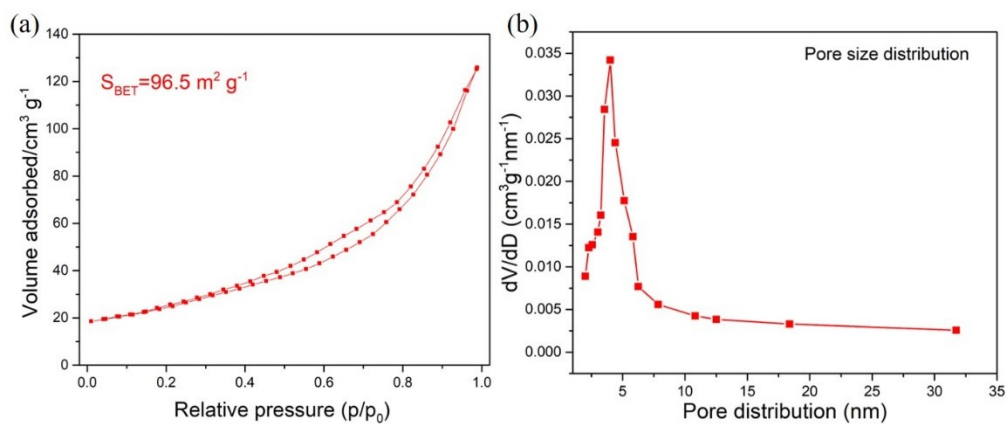


Figure S5. Brunauer–Emmett–Teller N₂ adsorption–desorption curve and the corresponding BJH pore size distribution curve for d-ZnO NSs.

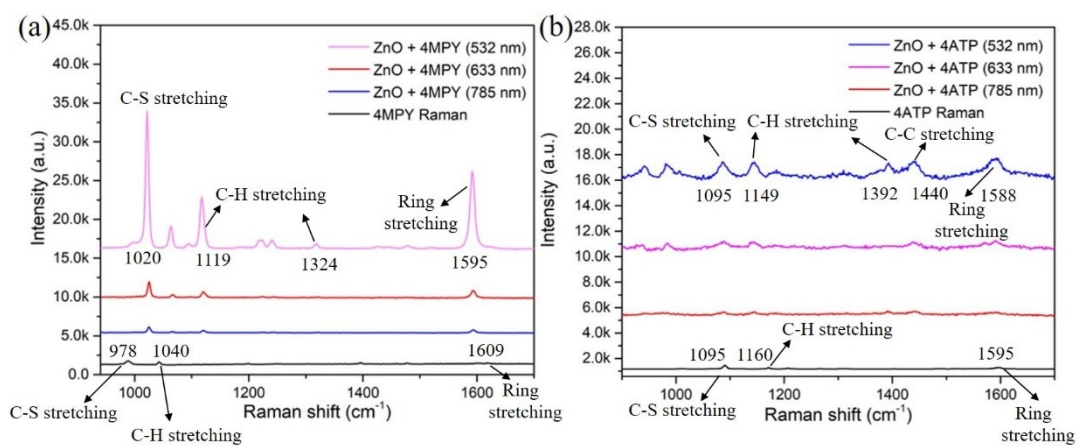


Figure S6. SERS spectra of (a) 4MPY (3×10^{-4} M) and (b) 4ATP (1×10^{-4} M) molecules adsorbed on d-ZnO NSs illuminated by 532, 633, and 785 nm laser, respectively. Laser power: 0.5 mW; lens: $50 \times$ objective; acquisition time: 2 s.

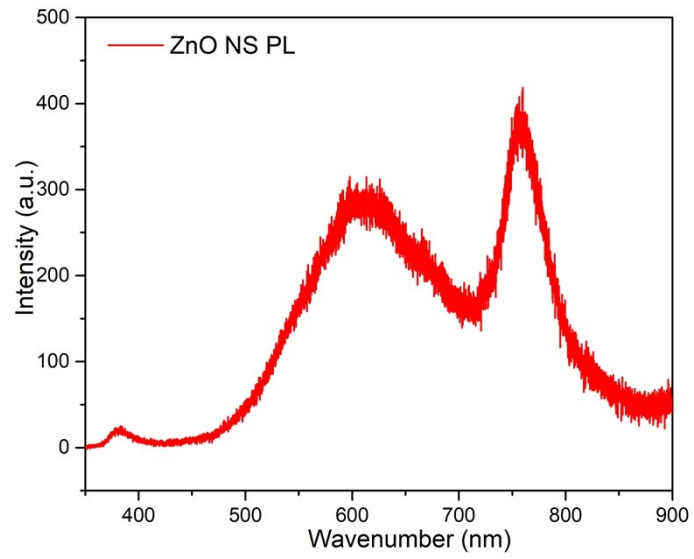


Figure S7. PL emission spectrum of porous d-ZnO NSs. Laser wavelength: 325nm Laser power: 1 mW; lens: 40 × near ultraviolet objective; acquisition time: 2 s.

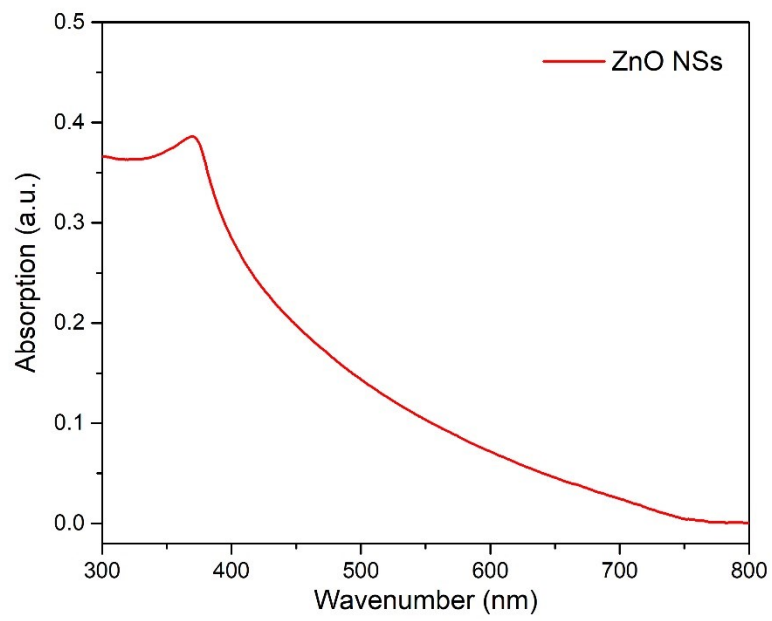


Figure S8. UV-Vis absorption spectrum of d-ZnO NSs.

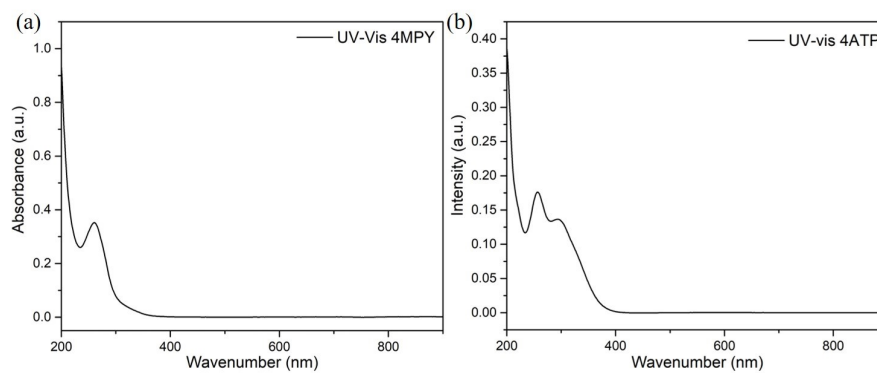


Figure S9. UV-Vis adsorption spectra of 4MPY (a) and 4ATP (b) molecules.

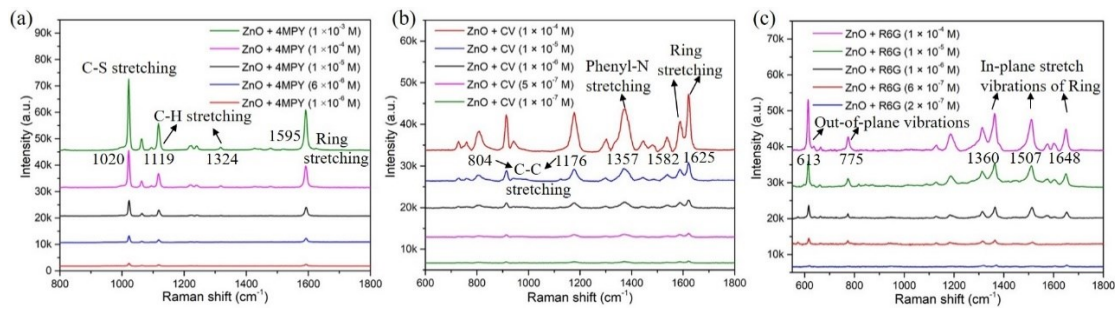


Figure S10. SERS signals of 4MPY (a), CV (b), and R6G (c) molecules adsorbed on d-ZnO NSs at different concentrations. Laser wavelength: 532 nm; Laser power: 0.5 mW; lens: 50 × objective; acquisition time: 2 s.

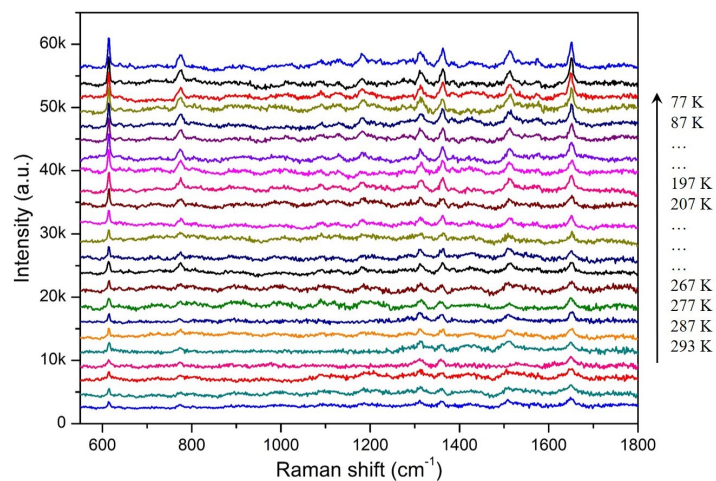


Figure S11. SERS spectra of R6G molecule (5×10^{-5} M) adsorbed on porous d-ZnO NSs under different temperature conditions. Laser wavelength 532nm; Laser power: 0.5 mW; lens: 50 × objective; acquisition time: 2 s.

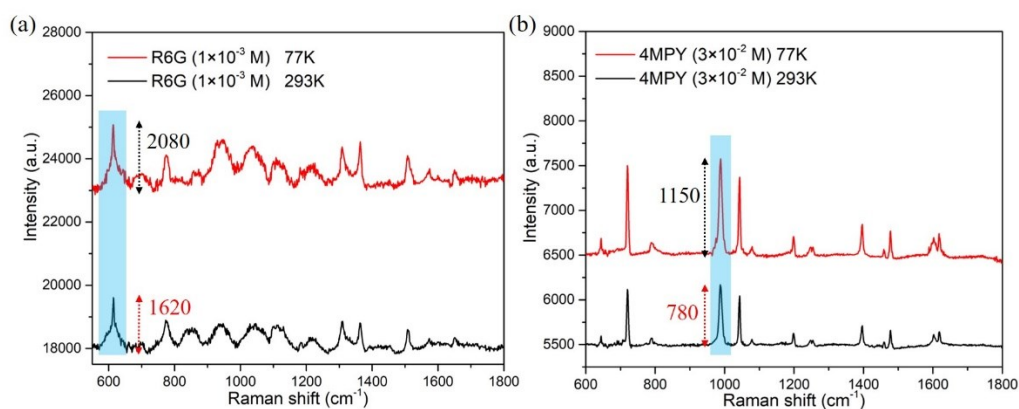


Figure S12. Raman spectrum of R6G and 4MPY molecules at room temperature and low temperature, respectively. Laser wavelength 532nm; Laser power: 0.5 mW; lens: 50 \times objective; acquisition time: 2 s.

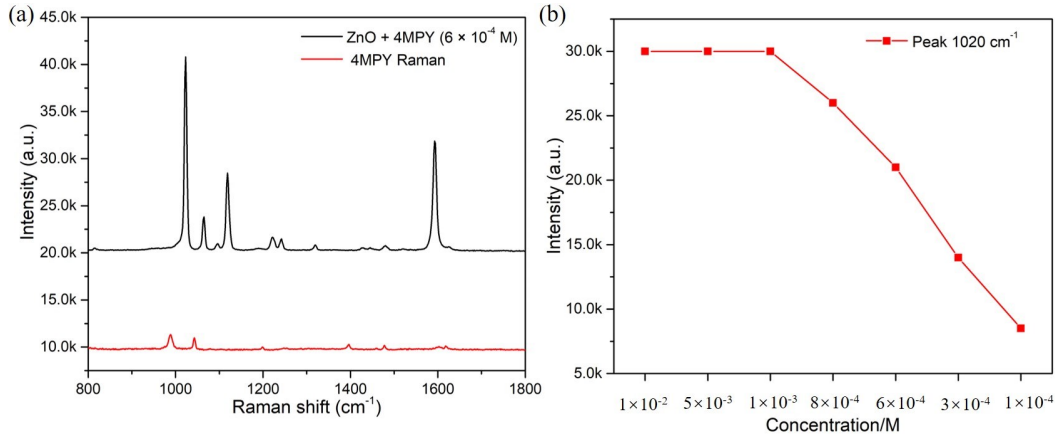


Figure S13. (a) Intensity comparison of 4MPY molecule adsorbed on d-ZnO NSs (SERS spectra) at low-temperature environment (77K) and normal Raman spectra. (b) SERS peak intensity (1020 cm⁻¹) of 4MPY molecule adsorbed on d-ZnO NSs at different concentrations. Laser wavelength 532nm; Laser power: 0.5 mW; lens: 50 × objective; acquisition time: 2 s.

SERS enhancement factor (EF) calculation of porous d-ZnO NSs at low temperature (77K) based on the following equations¹:

$$EF = (I_{SERS} / N_{ads}) / (I_{Raman} / N_{Raman}) \quad (1)$$

$$N = N_A C V S_{scan} / S_{sub} \quad (2)$$

According to the equation (1), N_{ads} and N_{Raman} are the number of 4MPY molecules adsorbed on the d-ZnO NSs SERS substrate and acted as normal Raman sample under laser illumination, respectively. I_{SERS} and I_{Raman} are the SERS peak (1605cm⁻¹) intensity of 4MPY probe molecule adsorbed on d-ZnO NSs and normal Raman vibration signal of 4MPY molecules, respectively. In the Raman experiment, 60μL 4MPY ethanol solution (6×10^{-2} M) was dropped on 0.5 cm × 0.5 cm silicon wafer. The laser spot was determined by laser wavelength (532 nm) and numerical

aperture of objective (50 ×; N.A: 0.5) $Spot\ size = \frac{1.22\lambda}{N.A}$, hence, the 532 nm laser spot size is ~ 1.30 μm²,

$$N_{Raman} = 60\mu L \times 6 \times 10^{-2} M \times 6.02 \times 10^{23} \text{ mol} / L \times 1.30 \mu m^2 / 0.25 \text{ cm}^2 \quad (2)$$

Based on equation (2), N_{Raman} is estimated as ~ 1.12×10^{11} . N_{ads} is determined by laser spot size and the density of 4MPY molecules adsorbed on the d-ZnO NSs (~ 0.5 nM cm⁻²)³, N_{ads} is estimated as ~ 3.9×10^6 . I_{SERS} and I_{Raman} are the SERS and Raman peak intensities at 1605 cm⁻¹ of 4MPY molecules shown in Figure S11 (a). The spectra intensity comparison is based on the average of 10 different laser spots in SERS experiments, $I_{SERS} = \sim 11800$ and $I_{Raman} = \sim 300$. Substituting above values into equation (1), EF is concluded about 1.13×10^6 .

In addition, the temperature effect on Raman intensity of investigated 4MPY molecule without ZnO NSs is carefully performed as shown in Figure S12, where the enhancement factor contributed by low temperature is 1.47. Hence, the real enhancement factor dominated by d-ZnO NSs SERS substrate at low-temperature environment (77K) is estimated to be 7.7×10^5 .

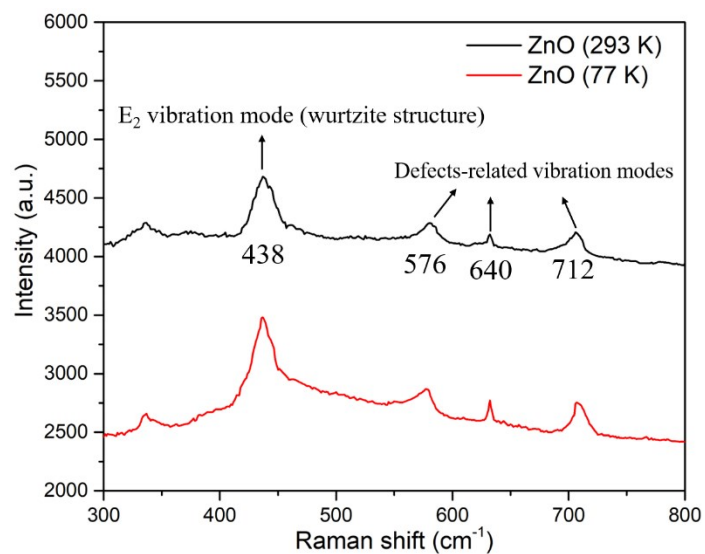


Figure S14. Raman spectrum of d-ZnO NSs at room temperature and low temperature, respectively. Laser wavelength: 532 nm; Laser power: 0.5 mW; lens: 50 × objective; acquisition time: 5 s.

Raman vibration modes of d-ZnO NSs: 438 cm^{-1} is assigned to E_2 vibration mode (wurtzite structure), 576, 640, and 712 cm^{-1} peaks are assigned to defects-related vibration modes.⁴

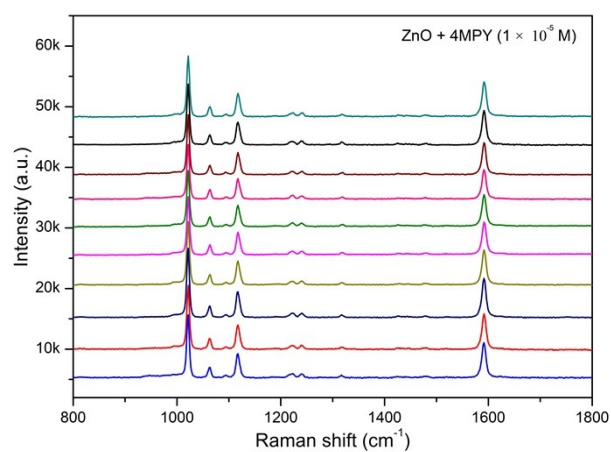


Figure S15. SERS spectra of 4MPY molecule (1×10^{-5} M) adsorbed on d-ZnO NSs collected on 10 different laser spots, respectively.

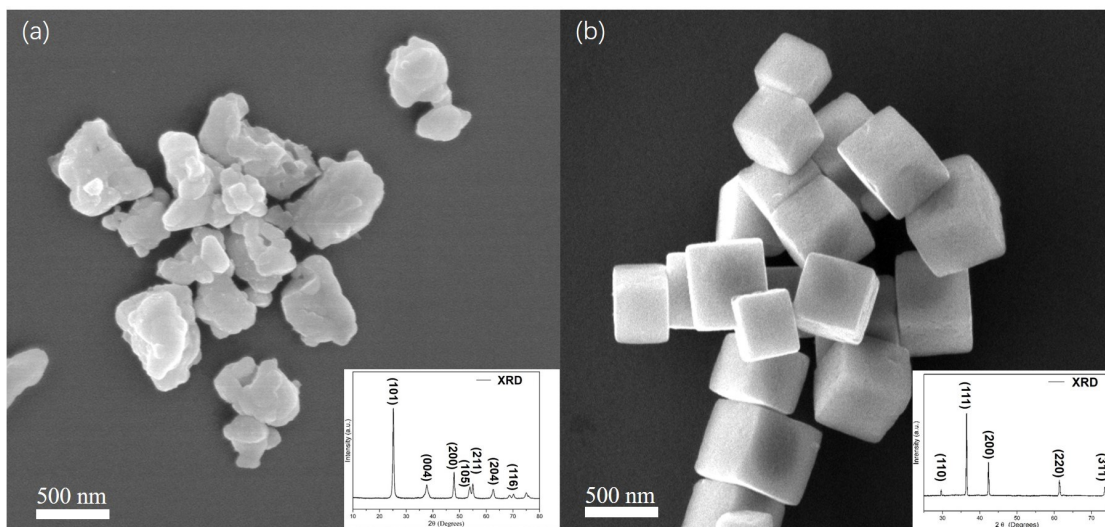


Figure S16. SEM image and XRD pattern of d-TiO₂ (a), and d-Cu₂O (b) NPs, respectively.

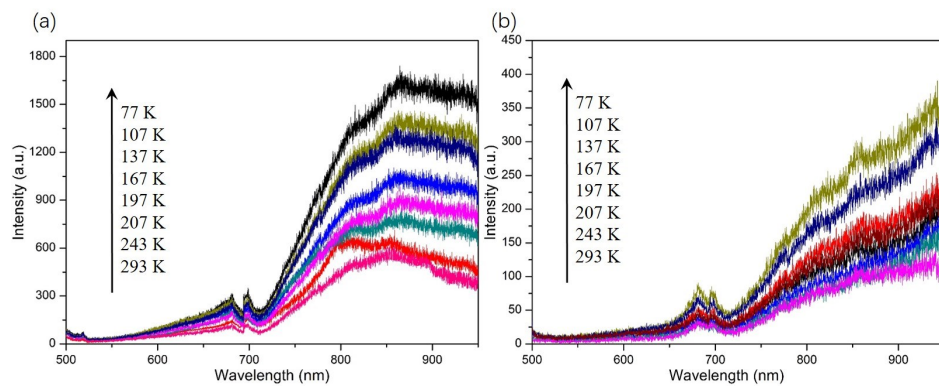


Figure S17. PL emission spectra of d-TiO₂ (a), and d-Cu₂O (b) NPs at different temperatures.

Reference:

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