

Supporting Information

Investigating the effect of MnO₂ band gap in hybrid MnO₂-Au materials over the SPR-mediated activities under visible light

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Experimental Section

Materials and instrumentation

Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 50 % Au, Adamas), polyvinylpyrrolidone (PVP, adamas, $M=58000$ g/mol), p-aminothiophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{SH}$, >97.0%, Sigma-Aldrich), potassium permanganate (KMnO_4 , >99.5% Adamas), sodium citrate dehydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$, Aladdin), hydrate manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\geq 99.0\%$, Sigma-Aldrich), ethanol (Vetec) were used as received. All the chemicals were grade reagents and used without any further purification. De-ionized (DI) water (18.2 M Ω) was used throughout the experiments.

SEM Images were obtained with a field-emission scanning electron microscopy (FESEM, Hitachi S-4800) worked at 5 kV. To prepare the samples of SEM, the aqueous suspension including the nanoparticles (NPs) was dripped on a Si wafer, followed by drying under the air condition. HRTEM images were obtained with a high-resolution transmission electron microscopy (HRTEM, TECHAI G2S-TWIN) operated at 200 kV. To prepare the samples of HRTEM, the alcoholic suspension including the nanoparticles was dripped on a copper grid, followed by drying under the air condition. The sizes of Au NPs were determined by measuring about 50 nanoparticles. UV-VIS spectra were obtained from the powder containing the MnO_2 NPs with a Shimadzu UV-3600 spectrophotometer. The samples for XRD were characterized by X-ray powder diffraction (XRD, Rigaku D/Max-2550). The samples for XPS were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Science, ESCALAB 250Xi, USA). The binding energy (BE) was scaled regarded the C 1s line at 284.6 eV as the standard for calibration. All data were processed by using the CasaXPS software.

SERS spectra were obtained on a Renishaw Raman InVia provided with a CCD detector and coupled to a Leica microscope permitting a rapid accumulation of Raman spectra with a spatial resolution of about 1 μm . The laser beam was focalized on the sample with a 50 \times lens. The processes of experiments were operated under ambient conditions in a back-scattering geometry. The samples were irradiated with a He-Ne laser (Renishaw RL633) exciting the 633 nm line or a solid-state laser (Renishaw RL532C)

exciting the 532 nm line, respectively. All Raman spectra were acquired with 60 s accumulation time.

Preparation of Au NPs

Typically, 1.5 mL sodium citrate aqueous solution (1 wt%) was added into 50mL DI water. This mixture was heat to boil for 5 min with the magnetic stirring. Then, 62.5 μL of 200 mM AuCl_4^- (aq) was added slowly for a rate of $\sim 5 \mu\text{L/s}$ with the magnetic stirring and the reaction was allowed to proceed for 0.5 h, and then cooled to the room temperature. The obtained Au NPs were washed three times with ethanol and three times with DI water by successive cycles of centrifugation and removal of the supernatant and re-suspended in water for further use.

Synthesis of MnO_2 nanoflowers

The synthesis of MnO_2 nanoflowers was followed by previous report.¹ 1.2, 1.0, 0.8, 0.6 and 0.4 g KMnO_4 were added into the Teflon-lined stainless steel autoclave with 0.4 g MnSO_4 stirring in 30 mL water, respectively. The Teflon-lined stainless steel autoclave was heat and stirred at 140 °C for 1 h. Then, cool down to the room temperature. The obtained MnO_2 nanoflowers were washed three times with ethanol and three times with DI water by successive cycles of centrifugation and removal of the supernatant. Finally, the materials were dried at 80 °C for 6 h in air for further use.

Synthesis of MnO_2 nanoflowers decorated with Au NPs (MnO_2 -Au NPs)

Briefly, 50 mg of MnO_2 nanoflowers were added into 50 mL DI water. Then, 108 mg PVP and 1 mL sodium citrate aqueous solution (1 wt%) was added into the solution which was heated with the magnetic stirring. After boiling, 62.5 μL of 200 mM AuCl_4^- (aq) was mixed slowly for a rate of $\sim 5 \mu\text{L/s}$ in the solution which were kept boiling for 1h. The obtained MnO_2 -Au NPs were washed three times with ethanol and three times with DI water by successive cycles of centrifugation and removal of the supernatant. Finally, the materials were dried at 80 °C for 6 h in air.

Preparation of Raman substrates

An 1.5 mL suspension containing Au NPs, MnO₂ or MnO₂-Au were centrifuged, respectively. The supernatant was removed and the corresponding solid re-suspended in 10 µL of H₂O. The 10 µL of suspension was then drop-cast onto a 1×1 cm Si wafer and followed by dried in air. Then, 40 µL of an 1.0 mM ethanolic solution of p-aminothiophenol was drop-cast on the corresponding Si wafer and dried in air. The Si wafers were used for SERS measurements and all samples need to be used immediately after preparation. All spectra were normalized with respect to the Raman band at 1081 cm⁻¹ for the comparison.

The calculation of atomic ratios

The atomic ratio between Mn and K was obtained with the quantitative analysis of high-resolution XPS spectra.² We regarded the I^{Mn} and I^K as the Mn and K intensities from Mn and K atom. The total intensities of Mn 2p_{3/2} and K 2p_{3/2} can be explained with the following expression:

$$I_{(TOT)}(\text{Mn } 2p) = I^{Mn} k^{Mn} / (1 - k^2) \quad (1)$$

$$I_{(TOT)}(\text{K } 2p) = I^K k^K / (1 - k^2) \quad (2)$$

Where the layer-by-layer attenuation factor is given by $k = \exp(-c / \lambda \sin\theta)$. The c is the depth of atoms, λ is the photoelectron inelastic mean free path^{3,4} and θ is the takeoff angle relative to the sample surface. Owing to the isotropic property of nanoparticles, k must should be integrated to obtain the average. Thus, the layer-by-layer attenuation factor is given by the follow expression:

$$k = \frac{\int_0^\pi \exp\left(-\frac{c}{\lambda \sin\theta}\right) d\theta}{\int_0^\pi d\theta} \quad (3)$$

The parameter c can be obtained by XRD. And the photoelectron inelastic mean free path ($\lambda_{Mn}=1.73$ nm, $\lambda_K=2.25$ nm) was calculated by the NIST .

Thus the atomic ratios of K/Mn are 1:4.2, 1:6.6 and 1:19.5 corresponding to 1.2, 1.0 and 0.8 g KMnO₄, respectively.

References

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- 2 M. P. Seah, I. S. Gilmore, and S. J. Spencer, *J. Electron Spectrosc. Relat. Phenom.*, 2001, **120**, 93-111.
- 3 C. J. Powell and A. Jablonski, *J. Electron Spectrosc. Relat. Phenom.*, 2010, **178**, 331-346.
- 4 C. J. Powell and A. Jablonski, *Surf. Sci.*, 2010, **604**, 3-4.

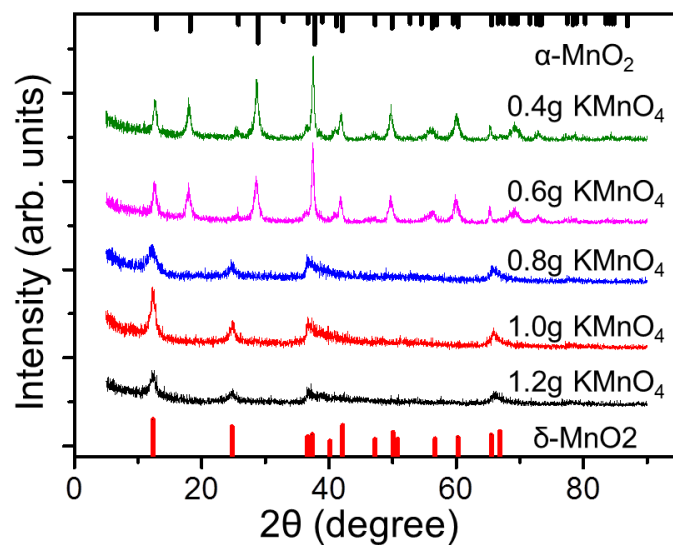


Figure S1. XRD patterns of MnO₂ materials synthesized with different amount of KMnO₄. The standard XRD pattern of α-MnO₂ (JCPDS No.29-1020) and δ-MnO₂ (JCPDS No.52-0556) are presented on the top (black trace) and bottom (red trace) for comparisons. When the amount of KMnO₄ employed in our synthesis was more than 0.8 g, all the diffraction peaks of the samples were assigned to the δ phase. Meanwhile, when the amount of KMnO₄ employed in the synthesis was less than 0.6 g, all the diffraction peaks of the samples can be corresponded to the α phase.

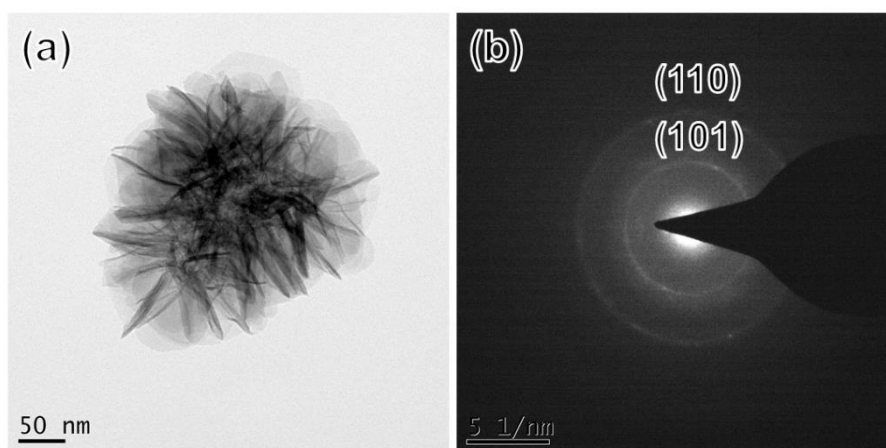


Figure S2. TEM image (a) and SEAD patterns (b) for MnO₂ nanoflowers obtained with 1.0 g of KMnO₄ during the synthesis.

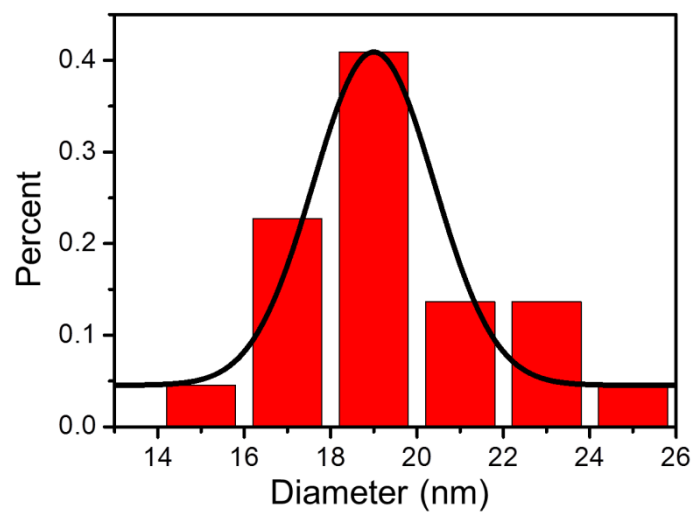


Figure S3. Size distribution for Au nanoparticles in the Au-MnO₂ material.

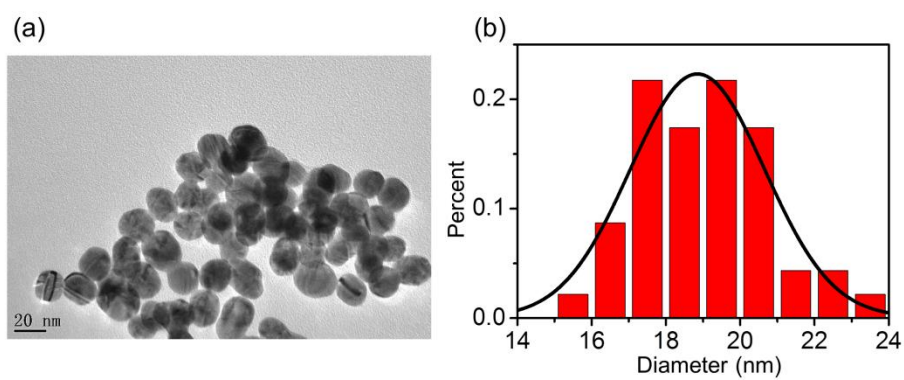


Figure S4. TEM image (a) and histogram of size distribution for unsupported Au nanoparticles.

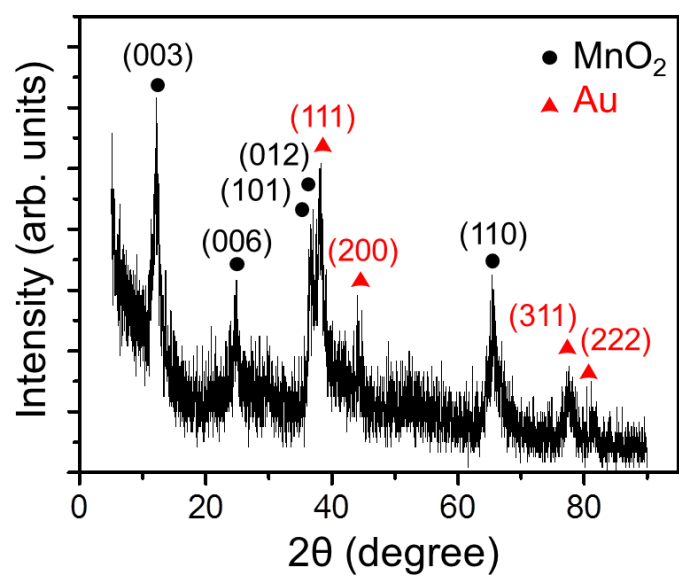


Figure S5. XRD pattern for MnO₂-Au that were obtained employing the MnO₂ nanoflowers prepared with 1.0 g of KMnO₄ as physical templates for the deposition of Au NPs at their surface.

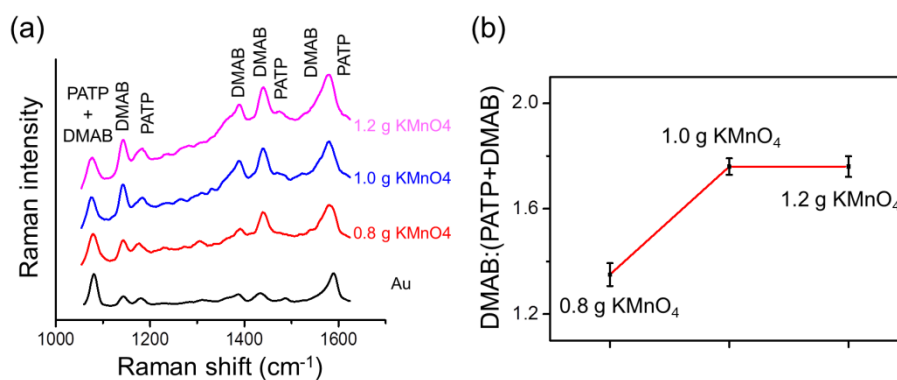


Figure S6. (a) SERS spectra for Au NPs and MnO₂-Au obtained with 1.2, 1.0 and 0.8 g of KMnO₄ in the synthesis that had been functionalized with PATP employing 60 s as the exposure time and 532 nm as the excitation wavelength. All spectra were normalized with respect to the band at 1081 cm⁻¹. **(b)** 1433:1081 cm⁻¹ DMAB:(PATP+DMAB) intensity ratios on MnO₂-Au prepared by different K-doped MnO₂ as substrates for Au deposition. The laser power corresponded to 0.700 mW in all cases.

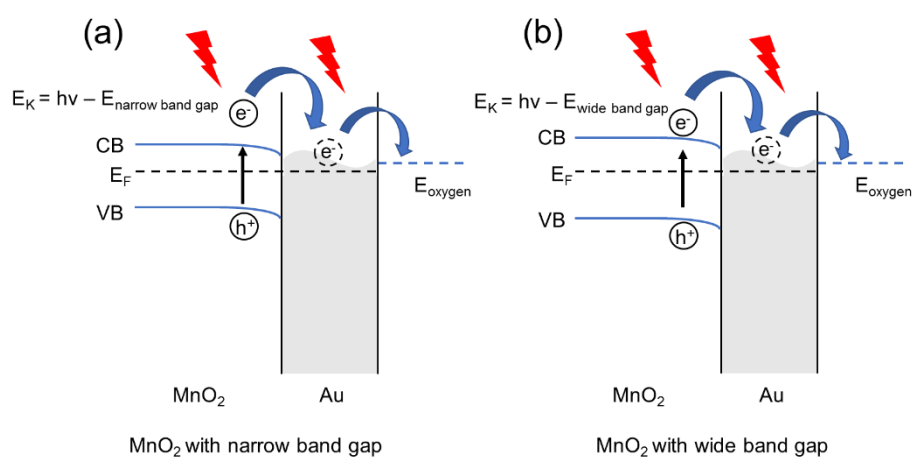


Figure S7. Schematic for the energy-level diagrams and charge transfer pathways in MnO₂-Au where the MnO₂ support displays a narrow (a) and wide (b) band gap under visible light excitation.