Supporting Information for

Manganese Dioxide-Silver Nanostructure-based SERS Nanoplatform for Ultrasensitive Tricyclazole Detection in Rice Samples: Effects of Semiconductor Morphology on Charge Transfer Efficiency and SERS Analytical Performance

Dao Thi Nguyet Nga[a,1], Quan Doan Mai[a,1], Nguyen Le Nhat Trang[a], Minh Khanh Pham[a], Nguyen Quang Hoa[b], Vu Dinh Lam[c], Hoang Van Tuan[a], Ha Anh Nguyen[a,*], Anh-Tuan Le[a,d,**]

[a]*Phenikaa University Nano Institute (PHENA), Phenikaa University, Hanoi 12116, Vietnam*

[b]*Faculty of Physics, VNU University of Science, Vietnam National University, Hanoi, 334 Nguyen Trai, Thanh Xuan, Hanoi, Viet Nam*

[c]*Institute of Materials Science (IMS) and Graduate University of Science and Technology (GUST), Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi 10000, Vietnam*

[d]*Faculty of Materials Science and Engineering (MSE), Phenikaa University, Hanoi 12116, Vietnam*

Corresponding authors:

*anh.nguyenha@phenikaa-uni.edu.vn (H.A.Nguyen)

**tuan.leanh@phenikaa-uni.edu.vn (A.T.Le)

[1] D.T.N. Nga and M.Q.Doan contributed equally to this work

Calculation of limit of detection (LOD)

The standard curve of linear detecting range was given as:

$$Y = A + B \times Log(X) \quad (1)$$

where A and B are intercept and slope of regression equation obtained through the plot of the logarithmic SERS intensity (Y) – logarithmic concentration (X).

The LOD is calculated using the following equation [1]:

$$LOD = 10^{\left[(Y_{blank} + 3SD)/Y_{blank} - A\right]/B} \quad (2)$$

where Y_{blank} and SD are the SERS signal and the standard deviation of blank sample, respectively.

SD is calculated via the well-known formula:

$$SD = \sqrt{\frac{1}{n-1} \times \sum_{i}^{n} (x_i - x_{average})^2} \quad (3)$$

where x_i if the "i" sample of the series of measurements, $x_{average}$ is the average value of SERS signal obtained from the blank sample repeated n times.

Calculation of relative standard deviation (RSD)

The RSD value of repeatability and reproducibility is calculated via the well-known formula:

$$\text{RSD} = \frac{SD \times 100}{x_{average}} \quad (4)$$

where SD is the standard deviation that calculates using equation 4 and $x_{average}$ is the average value of SERS signal obtained from each measurement.

Calculation of enhancement factor (EF)

The EF value is calculated according to the well-established equation, which was employed in several published studies [2, 3]:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{bulk}}{N_{surface}} \quad (5)$$

where I_{SERS} and I_{Raman} are Raman signal intensity of the analyte with and without SERS from the substrate, respectively; and N_{bulk} is the number of analyte molecules that are probed on the Raman spectrum, while $N_{surface}$ is the number of analyte molecules probed using SERS.

N_{bulk} can be calculated following:

$$N_{bulk} = \frac{A_{laser} \times h \times \rho}{M} \times N_A \quad (6)$$

where A_{laser}, h, ρ and m are the laser spot area, the focal length, the density of the solid analyte and its molecular weight, respectively; and N_A is the Avogadro number.

$N_{surface}$ can be expressed as:

$$N_{surface} = \frac{C \times V}{A_{substrate}} \times N_A \times A_{laser} \quad (7)$$

where C, V, $A_{substrate}$ are the concentration, the volume drop-casted of the analyte, and the area of the substrate, respectively; N_A is the Avogadro number; and A_{laser} is the laser spot area.

Thus, EF can be calculated as:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{bulk}}{N_{surface}} = \frac{I_{SERS}}{I_{Raman}} \times \frac{h \times \rho \times A_{substrate}}{M \times C \times V} \quad (8)$$

In our case, I_{SERS} and I_{Raman} is Raman signal intensity with and without SERS substrate of Tricyclazole (431 cm^{-1}), h = 2 μm = 2×10^{-4} cm, ρ = 1.5±0.1 g/cm^3, M = 189.24 g/mol, $A_{substrate} = 4\pi$ $mm^2 = 4\pi \times 10^{-2}$ cm^2, C = 10^{-7} mol/L, V = 5 μL = 5×10^{-6} L.

I_{SERS} and I_{Raman} values of e-AgNPs and MnO_2-s/e-Ag were estimated using the spectra in Figure S6.

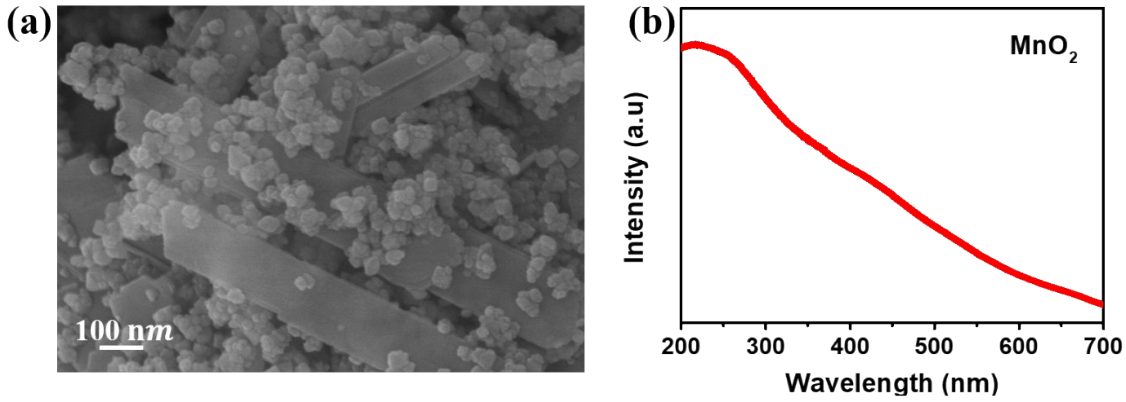

Figure S1: (a) SEM image, and (b) UV-vis absorption spectrum of MnO_2.

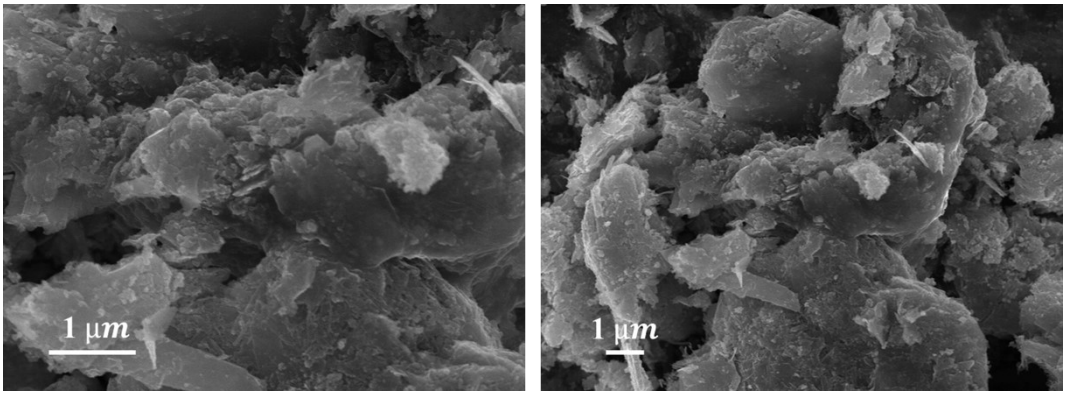

Figure S2: SEM images of MnO_2-s.

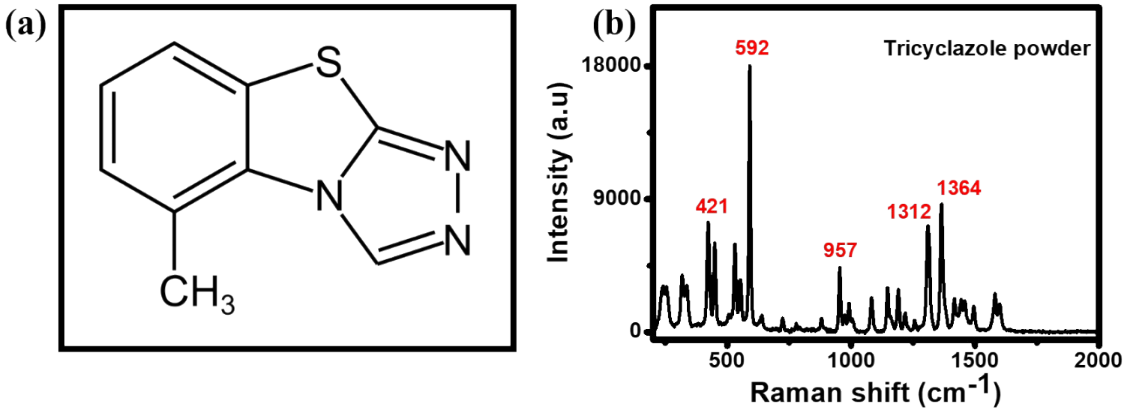

Figure S3: (a) Molecular structure of TCZ, (b) Raman spectrum of TCZ powder.

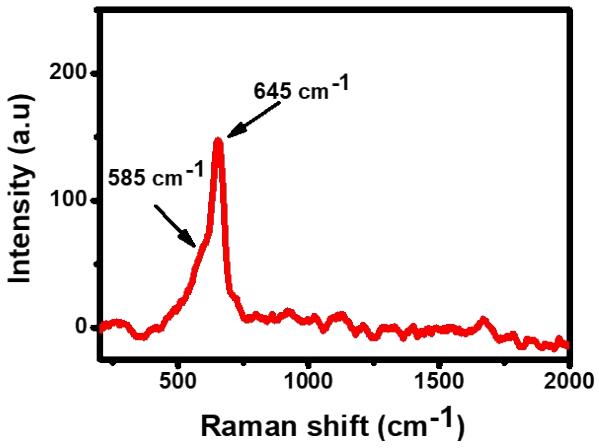

Figure S4: SERS spectrum of MnO_2-s for TCZ (10^{-3}M).

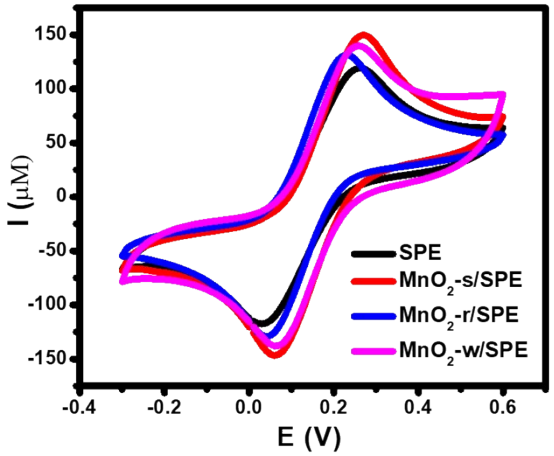

Figure S5: (a) CV profiles of various modified electrodes at scan rate 50 mV/s in in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$.

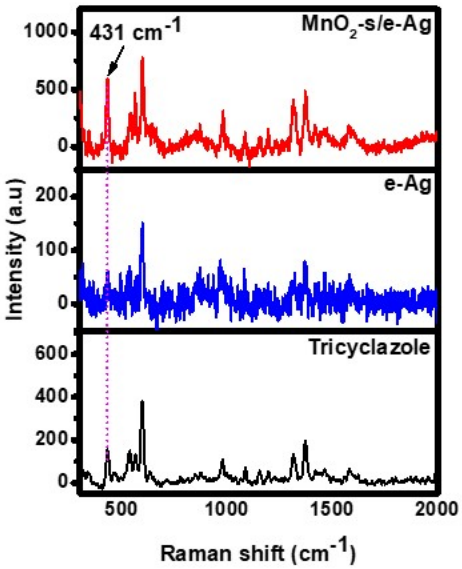

Figure S6: Raman spectrum of TCZ; and SERS spectra of e-Ag and MnO_2-s/e-Ag for TCZ (10^{-7}M).

Table S1: The enhancement levels of MnO_2/e-Ag nanocomposites at those peaks.

Substrate	Level of enhancement compared to e-Ag substrate (times)		
	431 cm^{-1}	**595 cm^{-1}**	**1372 cm^{-1}**
MnO_2-s/e-Ag	6.66	7.90	5.15
MnO_2-r/e-Ag	2.18	1.66	1.50
MnO_2-w/e-Ag	1.81	1.54	1.31

Table S2: The recovery values for five concentrations of TCZ in the ST25 rice samples.

Real sample	Analyte	Concentration of TCZ (M)	Recovery (%)
ST25 rice	TCZ	10^{-7}	108.05
		10^{-8}	102.09
		10^{-10}	100.63
		10^{-11}	99.11

References

(1) Chen, R.; Shi, H.; Meng, X.; Su, Y.; Wang, H.; He, Y. Dual-Amplification Strategy-Based SERS Chip for Sensitive and Reproducible Detection of DNA Methyltransferase Activity in Human Serum. *Anal. Chem.* **2019**, *91* (5), 3597–3603. https://doi.org/10.1021/acs.analchem.8b05595.

(2) Le Ru, E.C.; Blackie, E.; Meyer, M.; Etchegoin, P.G. Surface Enhanced Raman Scattering Enhancement Factors: A Comprehensive Study. *J. Phys. Chem. C*, 2007, **111**, 33, 13794-13803. https://doi.org/10.1021/jp0687908.

(3) Fu, W. L.; Zhen, S. J.; Huang, C. Z; One-pot green synthesis of graphene oxide/gold nanocomposites as SERS substrates for malachite green detection. *Analyst*, 2013, **138**, 3075-3081. https://doi.org/10.1039/C3AN00018D.