Supporting Information for

Enhanced Sensing Performance of Carbaryl Pesticide by empolying MnO_2/GO/e-Ag-based Nanoplatform: Role of Graphene Oxide as Adsorbing Agent on SERS Analytical Performance

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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 Carbaryl (480 cm^{-1}), h = 2 μm = 2×10^{-4} cm, ρ = 1.2 g/cm^3, M = 201.22 g/mol, $A_{substrate}$ = 4 π 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/GO 0.1%/e-Ag were estimated using the spectra in Figure S5.

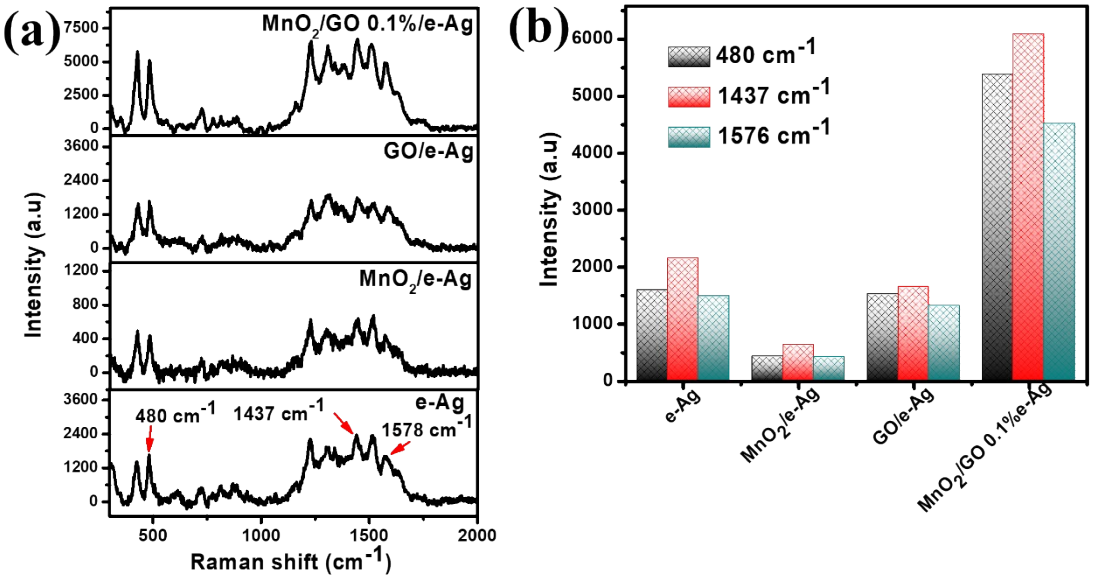


Figure S1: (a) SERS spectra of CBR (10^{-3} M) on e-AgNPs, MnO_2/e-Ag, GO/e-Ag, and MnO_2/e-Ag nanocomposites. (b) SERS intensities of MB (10^{-5} M) at 480 cm^{-1}, 1437 cm^{-1}, and 1576 cm^{-1} on e-AgNPs, MnO_2/e-Ag, GO/e-Ag, and MnO_2/e-Ag nanocomposites.

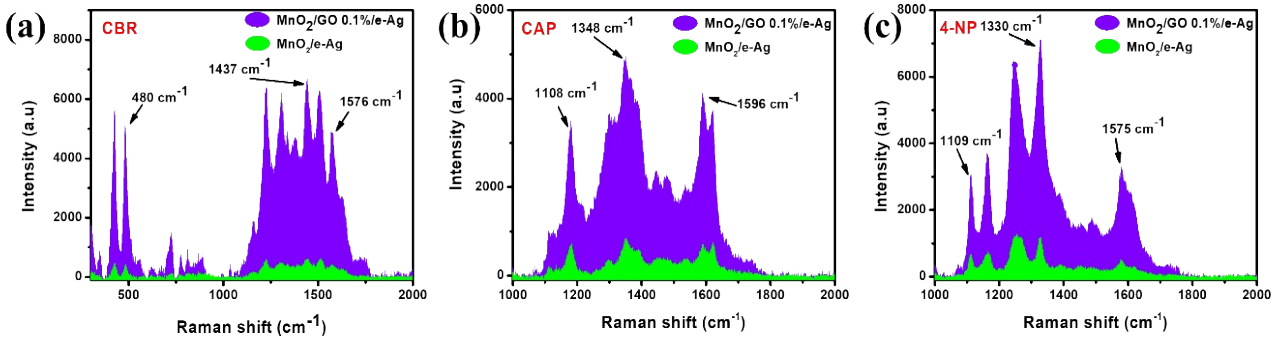


Figure S2: SERS intensities of (a) CBR (10^{-3} M), (b) CAP (10^{-3} M), and (c) 4-NP (10^{-3} M) at characteristic peaks on MnO_2/e-Ag, and MnO_2/GO 0.1 wt%/e-Ag nanocomposites.

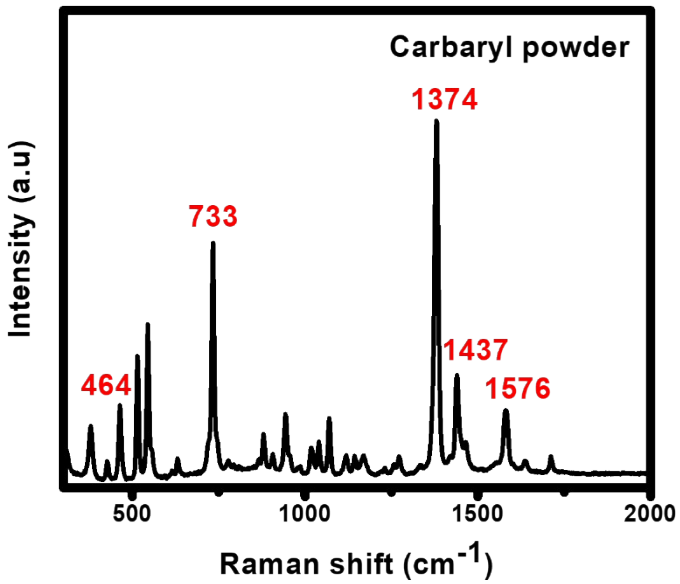


Figure S3: Raman spectrum of Carbaryl.

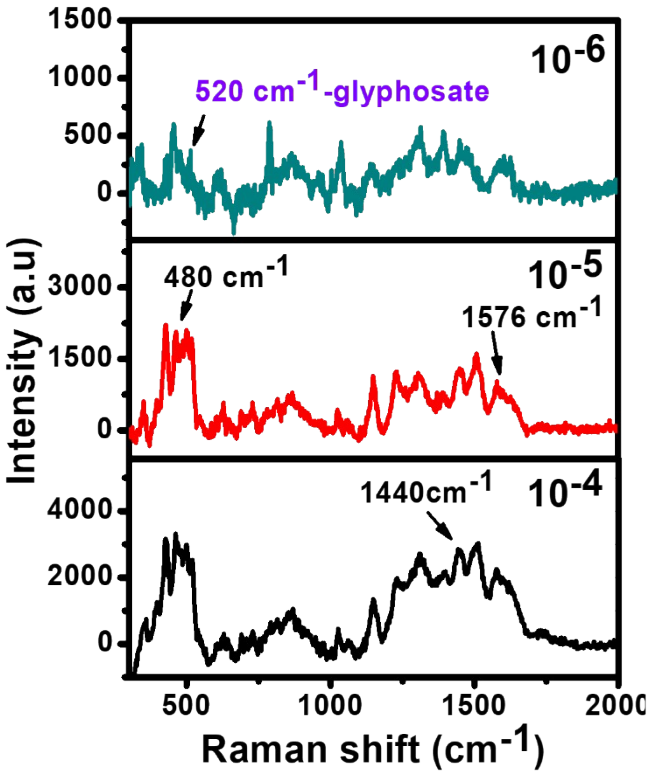


Figure S4: SERS spectra of the mixture of Carbaryl, 4-Nitrophenol, and Glyphosate (10^{-4} M – 10^{-6} M) in the real sample of the cucumber on the MnO_2/GO 0.01 wt%/e-Ag substrate.

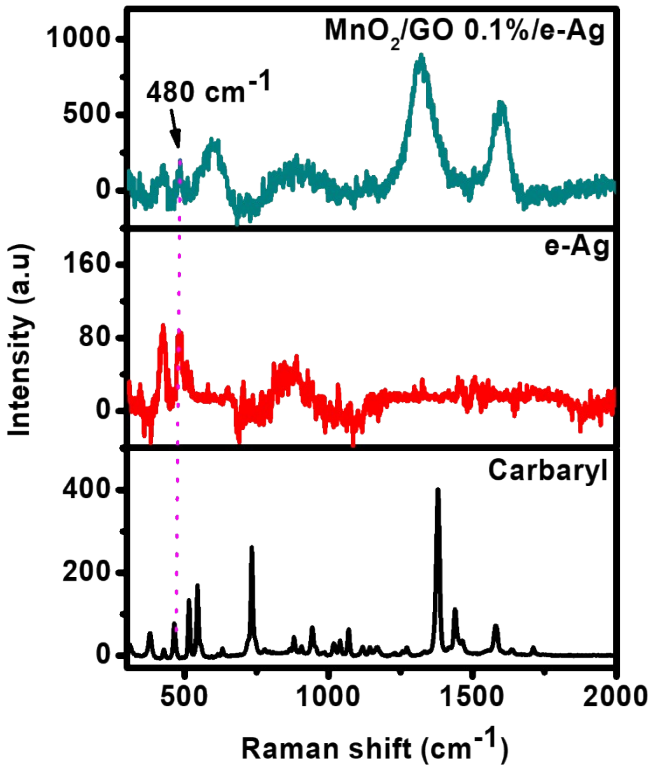


Figure S5: Raman of CBR; and SERS spectrum of e-Ag and MnO_2/GO 0.1 wt%/e-Ag for CBR (10^{-7}M).

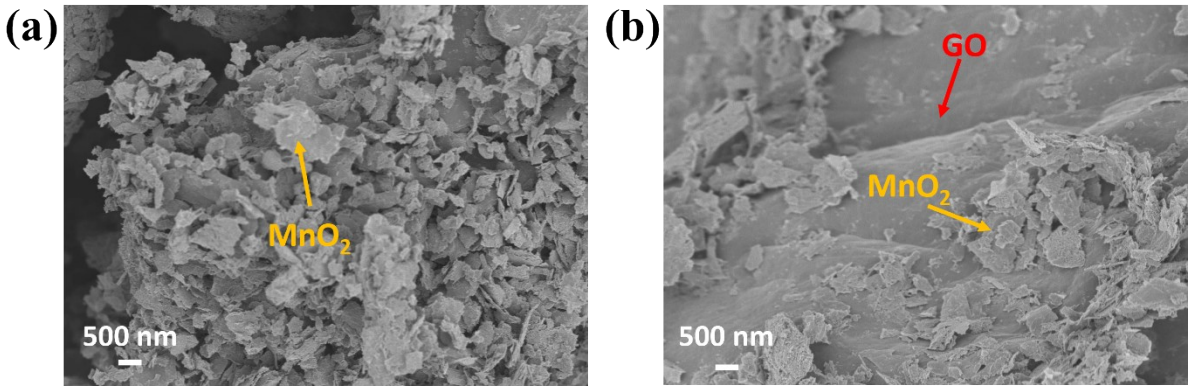


Figure S6: SEM images of MnO_2/GO with GO contents of (a) 0.1 wt% (to become 0.4 wt% in MnO_2/GO/e-Ag) and (b) 0.5 wt% (to become 2.0 wt% in MnO_2/GO/e-Ag).

Table S1: Molecular structure and assignments of vibrational bands in Raman and SERS spectra of some chemicals.

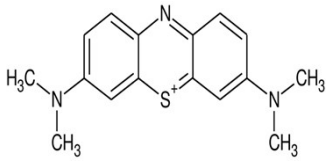
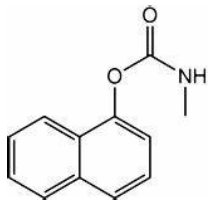
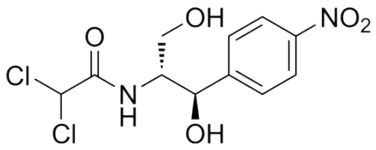
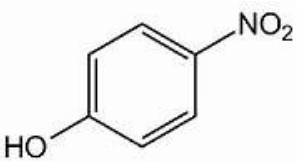
	Group 1		**Group 2**		
	TCZ	**MB**	**CBR**	**CAP**	**4-NP**
Molecular structure					
Vibrational band	**(1)** 431 cm^{-1}: C-N-C deformation vibration **(2)** 595 cm^{-1}: C-S-C deformation vibration **(3)** 1372 cm^{-1}: C-N stretching vibration	**(1)** 453 cm^{-1}: C–N–C skeletal deformation mode **(2)** 1397 cm^{-1}: C–N symmetrical stretching **(3)** 1622 cm^{-1}: C–C ring stretching	**(1)** 480 cm^{-1}: C–C bending mode **(2)** 1437 cm^{-1}: C–H wagging mode **(3)** 1576 cm^{-1}: C=C stretching mode in naphthalene ring	**(1)** 1108 cm^{-1}: Ring in-plane bending **(2)** 1348 cm^{-1}: $N–O_2$ symmetric stretching **(3)** 1596 cm^{-1}: Ring stretching	**(1)** 1109 cm^{-1}: C-H ip bend **(2)** 1330 cm^{-1}: NO_2 symmetric stretching **(3)** 1575 cm^{-1}: Ring stretch

Table S2: The recovery values for four concentrations of CBR in the tap-water and cucumber samples.

Real sample	Analyte	Concentration of CBR (M)	Recovery (%)	RSD (%)
Tap-water	CBR	10^{-4}	106.98	9.70
		10^{-5}	95.47	11.18
		10^{-6}	89.44	11.03
		10^{-7}	84.65	13.46
Cucumber	CBR	10^{-4}	111.64	13.57
		10^{-5}	98.23	12.27
		10^{-6}	93.12	7.42
		10^{-7}	87.61	9.34

Table S3: The recovery values for three concentrations of CBR in the cucumber samples containing extra-two pesticides (4-nitrophenol and glyphosate).

Real sample	Analyte	Concentration of CBR (M)	Recovery (%)	RSD (%)
Cucumber	CBR	10^{-4}	109.86	11.54
		10^{-5}	93.75	14.52
		10^{-6}	98.39	13.49

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.