

Portable Surface-Enhanced Raman Scattering Sensor for Multiplex Identification and Quantification of Pesticide Residues in Plant Leaves

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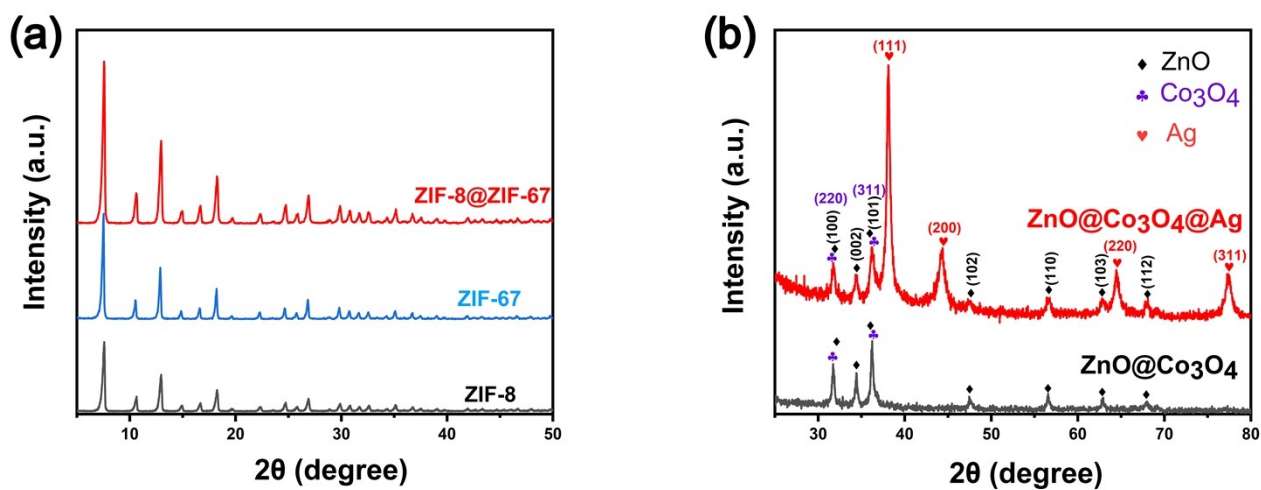


Fig. S1 XRD patterns of different samples: (a) ZIF-8, ZIF-67 and ZIF-8@ZIF-67. (b) ZnO@Co₃O₄ and ZnO@Co₃O₄@Ag.

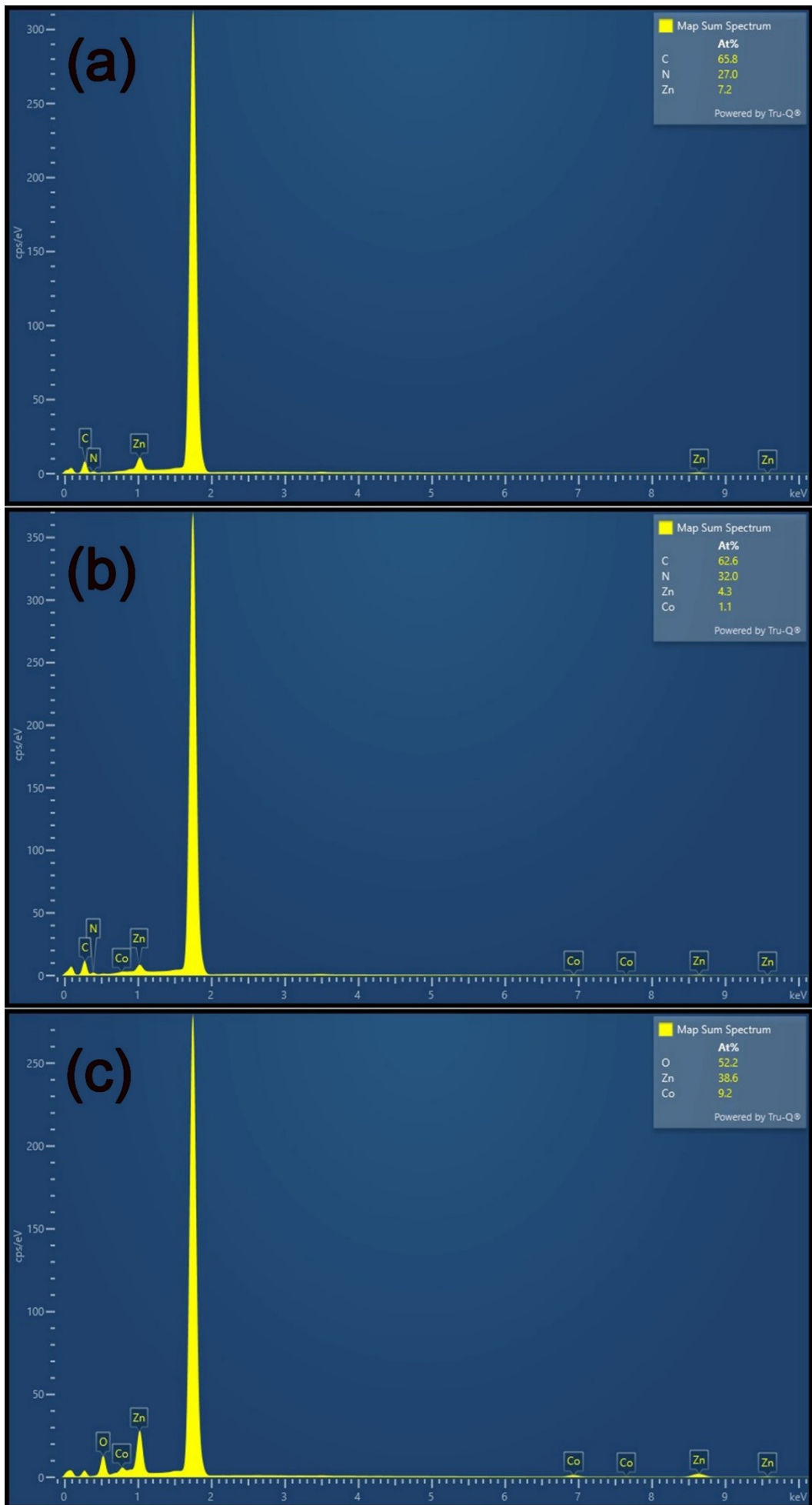


Fig. S2 EDS spectra of (a) ZIF-8, (b)ZIF-8@ZIF-67, and (c)ZnO@Co₃O₄.

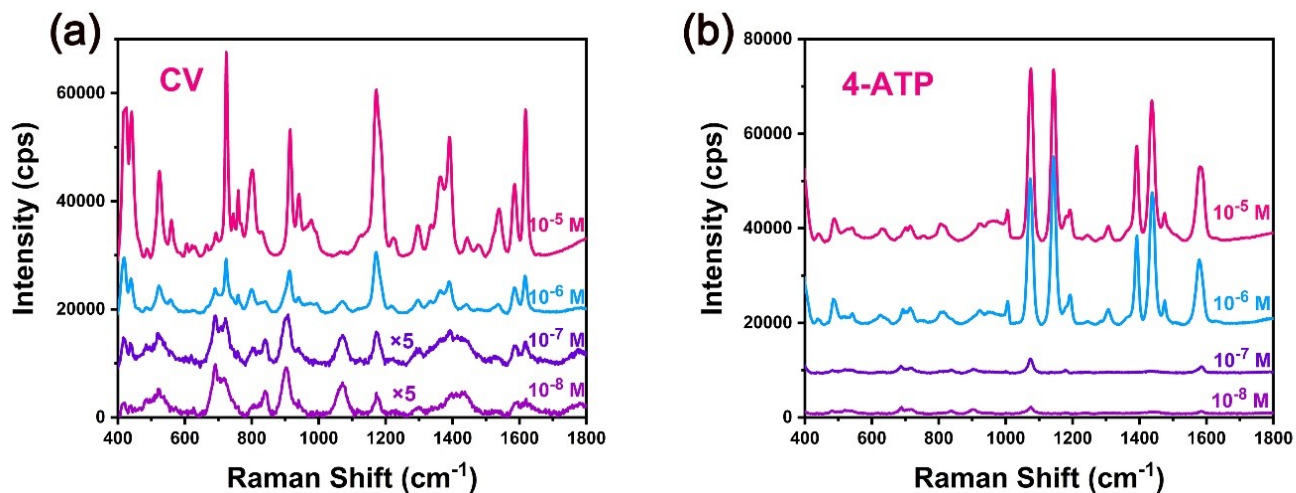


Fig. S3 SERS spectra obtained from different concentrations of (a) CV and (b) 4-ATP dropped on the ZnO@Co₃O₄@Ag substrate.

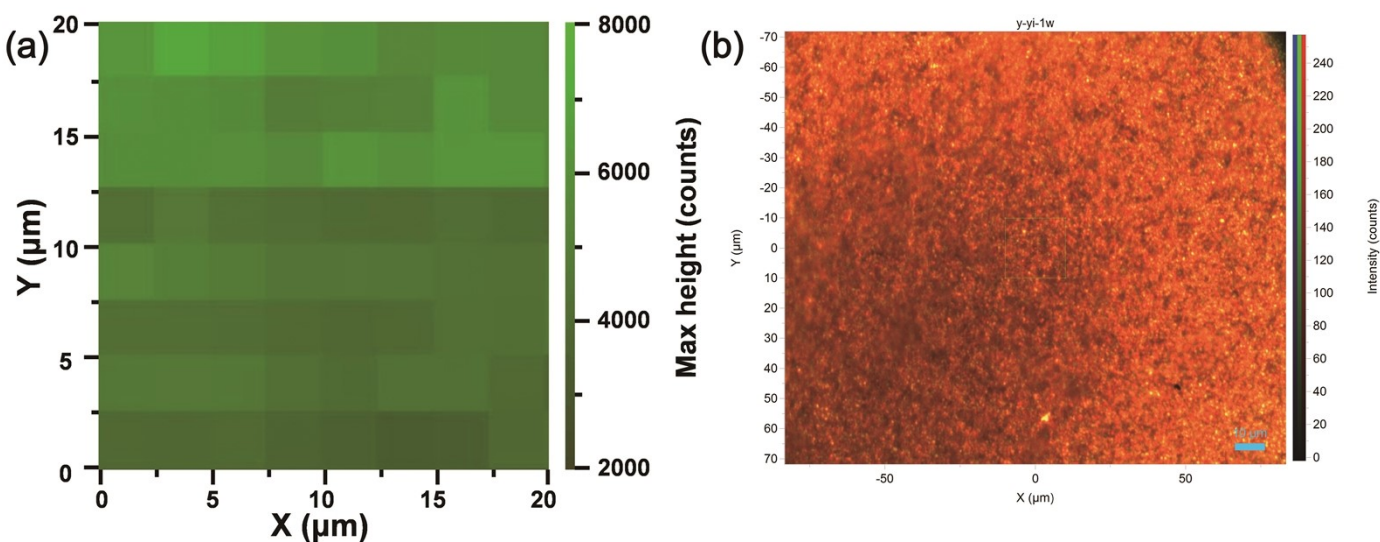


Fig. S4 (a) SERS mapping of the 1172 cm^{-1} peak of CV adsorbed on the ZnO@Co₃O₄@Ag substrate; (b) Electron microscopic image of substrate.

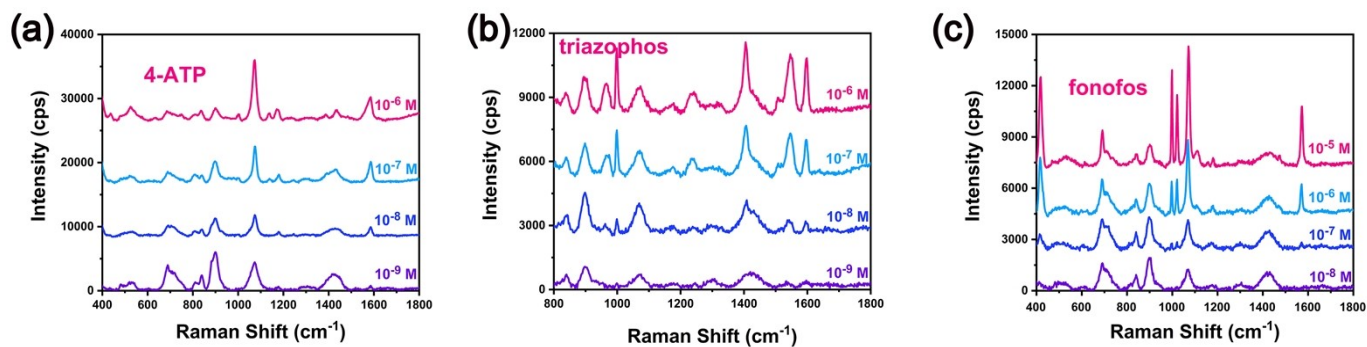


Fig. S5 SERS spectra obtained from the ZnO@Co₃O₄@Ag substrate immersed at different concentrations of (a) 4-ATP, (b) triazophos, and (c) fonofos for 2h.

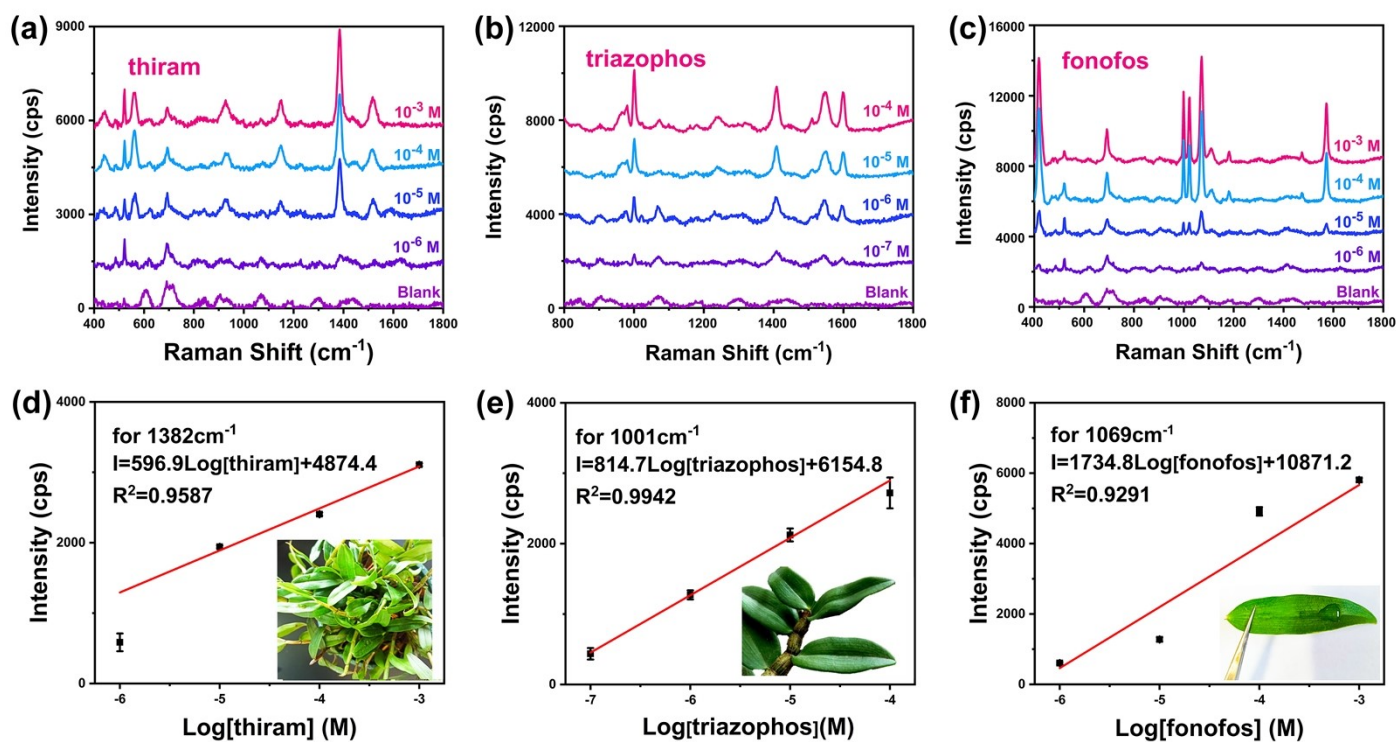


Fig. S6 SERS spectra obtained from dendrobium leaves with different concentrations of (a) thiram, (b) triazophos and (c) fonofos using ZnO@Co₃O₄@Ag sensor. (d-f) Corresponding linear relationship between Raman intensity and detected concentrations.

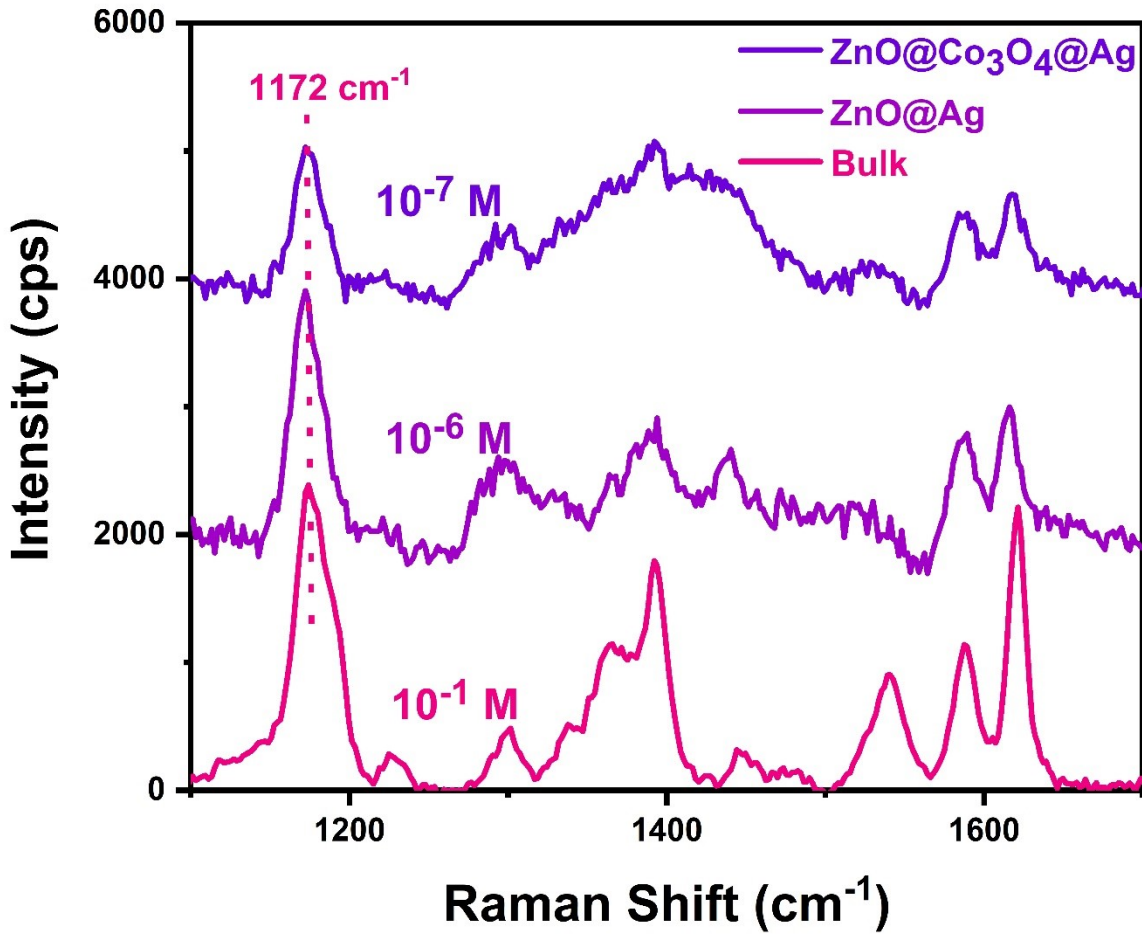


Fig. S7. SERS spectra obtained from bulk CV (10^{-1} M), ZnO@Ag substrate with CV (10^{-6} M) and ZnO@Co₃O₄@Ag substrate with CV (10^{-7} M)

Calculation of SERS enhancement factor (EF)

To quantify the enhancement contribution from ZnO@Ag and ZnO@Co₃O₄@Ag substrates, we calculated their enhancement factor (EF) based on the following formula:

$$EF = (I_{SERS} / I_{BULK}) \times (N_{BULK} / N_{SERS})$$

where I_{SERS} and I_{BULK} represent the intensities of SERS and normal Raman scattering, whereas N_{SERS} and N_{BULK} , respectively, denote the numbers of corresponding CV molecules effectively excited by a laser beam. According to the above formula, the EF for the ZnO@Ag substrate is calculated to be 7.45×10^5 . The EF is calculated to be 4.95×10^6 for the ZnO@Co₃O₄@Ag substrate.

$$N_{BULK} = (\text{Laser spot area} / \text{Diffusion area}) * (N_A * \text{Volume}_{BULK} * \text{Concentration}_{BULK})$$

$$N_{SERS} = (\text{Laser spot area} / \text{Substrate area}) * (N_A * \text{Volume}_{SERS} * \text{Concentration}_{SERS})$$

$$\text{Diffusion area} = \pi(d/2)^2 = 0.5027 \text{ cm}^2$$

$$\text{Substrate area} = 0.25 \text{ cm}^2$$

$$\text{Volume}_{\text{BULK}} = \text{Volume}_{\text{SERS}}$$

$$\text{Concentration}_{\text{BULK}} = 10^6 * \text{Concentration}_{\text{SERS}}$$

$$N_{\text{BULK}} / N_{\text{SERS}} = (0.25/0.5027) \times 10^6 = 5 \times 10^5$$

I = intensity of the 1172 cm⁻¹ peak

$$I_{\text{BULK}} = 29088.9 \text{ a.u.}$$

$$I_{\text{SERS, ZnO@Ag}} = 43493.9 \text{ a.u.}$$

$$I_{\text{SERS, ZnO@Ag}} / I_{\text{BULK}} = 1.49$$

$$\text{EF} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 7.45 \times 10^5$$

$$I_{\text{SERS, ZnO@Co}_3\text{O}_4\text{@Ag}} = 28826.6 \text{ a.u.}$$

$$I_{\text{SERS, ZnO@Co}_3\text{O}_4\text{@Ag}} / I_{\text{BULK}} = 0.99$$

$$\text{EF} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 4.95 \times 10^6.$$