

Semiconductor Heterojunction-AgNPs Mediated Surface-Enhanced Raman Spectroscopy (SERS) Sensor for Portable Miniaturized Detection Platform

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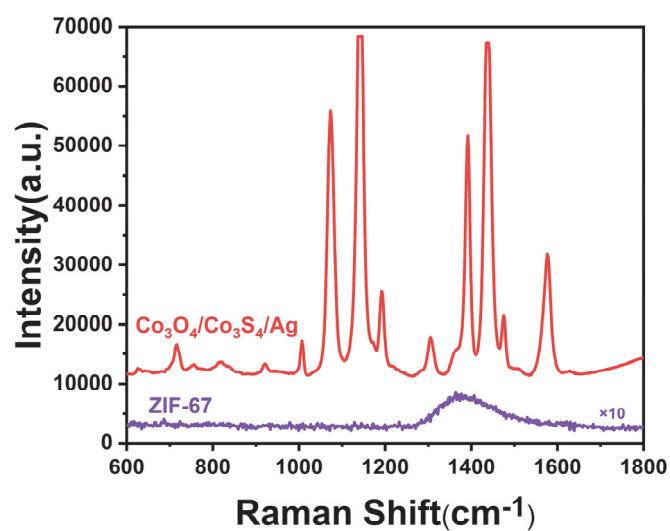


Figure S1. SERS spectra of $\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{Ag}$ and ZIF-67.

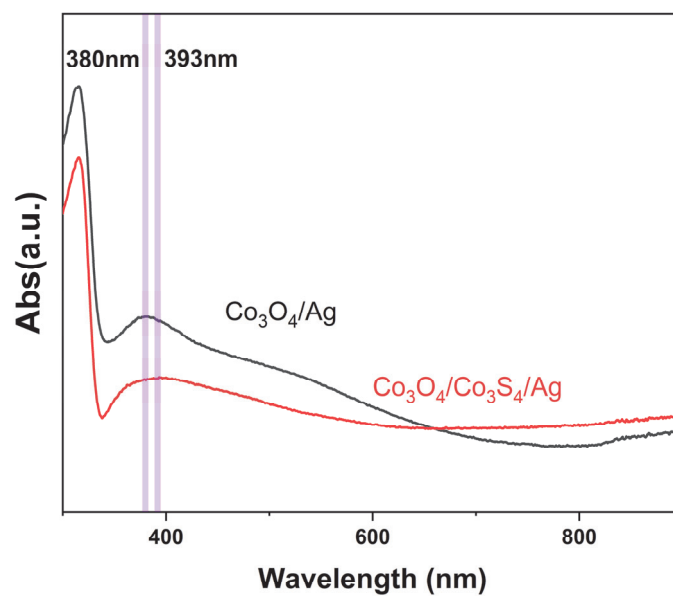


Figure S2. Ultraviolet absorption spectra of $\text{Co}_3\text{O}_4/\text{AgNPs}$ and $\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}$.

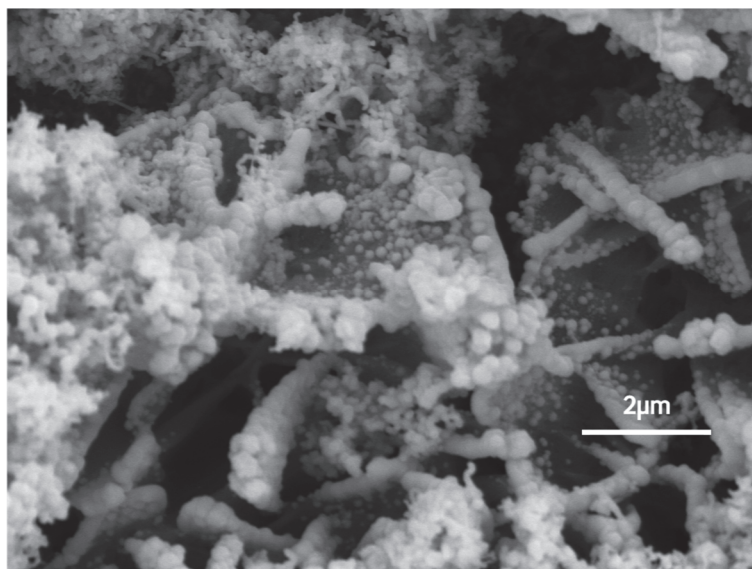


Figure S3. SEM images of $\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}$.

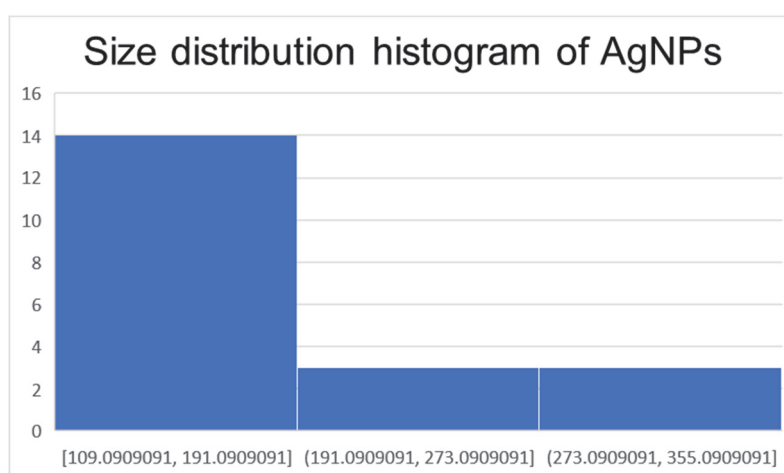


Table 1. Size distribution histogram of AgNPs.

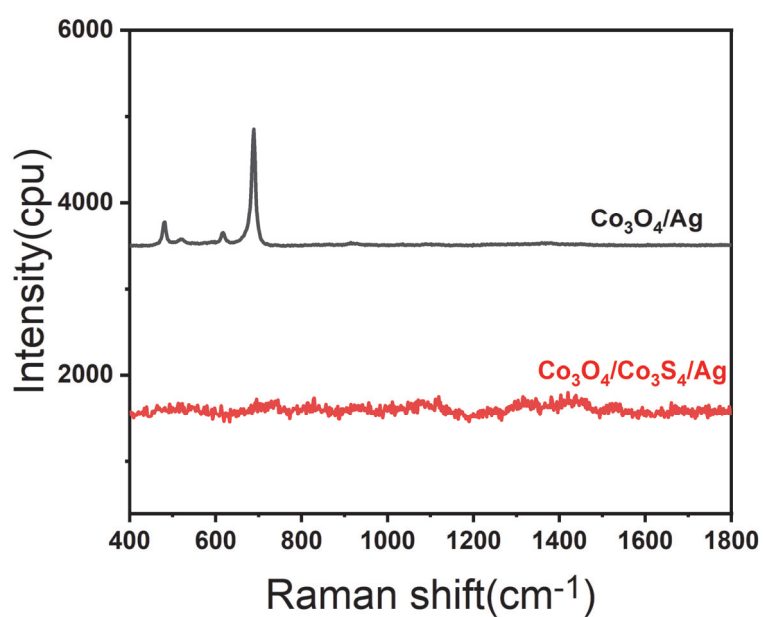


Figure S4. Raman spectrum for $\text{Co}_3\text{O}_4/\text{AgNPs}$ and $\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}$ substrates without analyte.

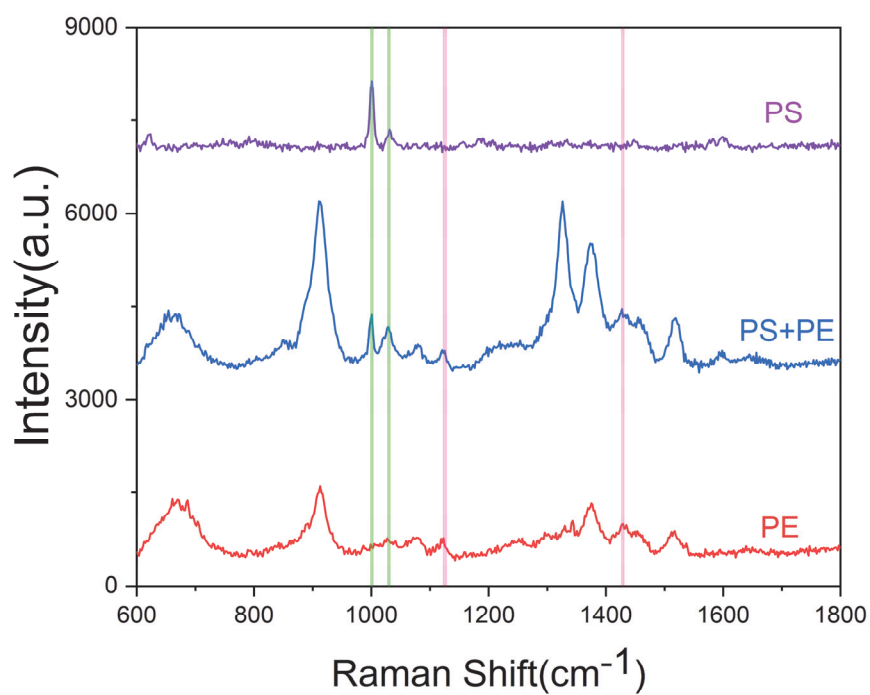


Figure S5. SERS spectra of PS and PE mixture.

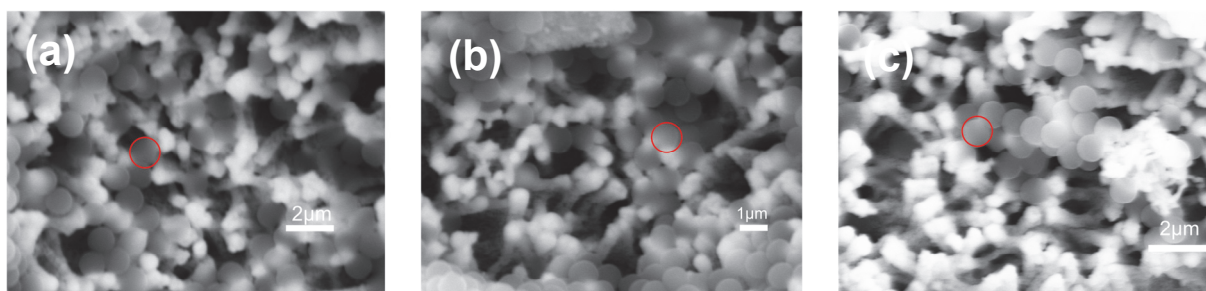


Figure S6. SEM images of plastic particles with diameters of (a) $1\mu\text{m}$, 2.5mg/mL , (b) $1\mu\text{m}$, 2mg/mL and (c) $800\mu\text{m}$, 2.5mg/mL .

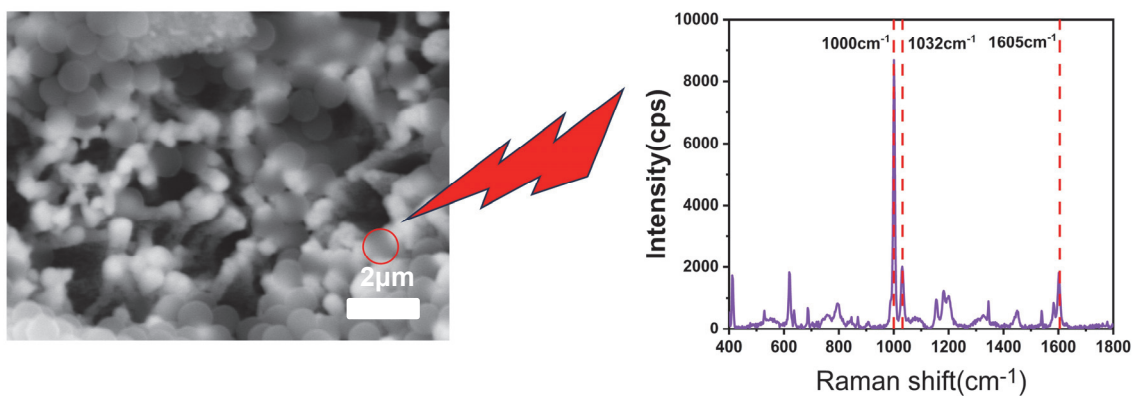


Figure S7. SEM image and SERS spectrum of 1 μm , 2.5 mg/mL PS on the substrate.

Calculation of SERS enhancement factor (EF)

To quantify the enhancement contribution from $\text{Co}_3\text{O}_4/\text{AgNPs}$ and $\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}$ substrates, we calculated their enhancement factor (EF) based on the following formula:

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

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 4-ATP molecules effectively excited by a laser beam. According to the above formula, the EF for the $\text{Co}_3\text{O}_4/\text{AgNPs}$ substrate is calculated to be 9.29×10^6 . The EF is calculated to be 3.77×10^7 for the $\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}$ substrate. As a result, the EF for the $\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}$ substrate shows a 4.06-fold enhancement compared to the $\text{Co}_3\text{O}_4/\text{AgNPs}$ substrate.

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

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

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

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

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

$$\text{Concentration}_{\text{BULK}} = 10^5 \times \text{Concentration}_{\text{SERS}}$$

$$N_{\text{BULK}} / N_{\text{SERS}} = (0.25 / 0.5027) \times 10^5 = 5 \times 10^4$$

$$I = \text{intensity of the } 1075 \text{ cm}^{-1} \text{ peak}$$

$$I_{\text{BULK}} = 1107.33$$

$$I_{\text{SERS, Co}_3\text{O}_4/\text{AgNPs}} = 205835.09$$

$$I_{\text{SERS, Co}_3\text{O}_4/\text{AgNPs}} / I_{\text{BULK}} = 185.88$$

$$\text{EF}_{\text{Co}_3\text{O}_4/\text{AgNPs}} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 9.29 \times 10^6$$

$$I_{\text{SERS, Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}} = 834196.49$$

$$I_{\text{SERS, Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}} / I_{\text{BULK}} = 753.34$$

$$\text{EF}_{\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 3.77 \times 10^7$$

$$\text{EF}_{\text{Co}_3\text{O}_4/\text{Co}_3\text{S}_4/\text{AgNPs}} / \text{EF}_{\text{Co}_3\text{O}_4/\text{AgNPs}} = 3.77 \times 10^7 / 9.29 \times 10^6 = 4.06$$