Plasmonic AgNPs decorated heterostructure substrate for synergetic

surface-enhanced Raman scattering identification and quantification of

pesticide residues on real samples

Xueting Li, ^a Chenyue Xu, ^a Lan Yan, ^a Yating Feng, ^a Haoyue Li, ^a Cheng Ye, ^a Maofeng Zhang, ^{*a} Youju Huang, ^{*c} Changlong Jiang, ^{*d} Jianhua Li, ^e Yucheng Wu ^{b*}

^a School of Chemistry and Chemical Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China

^b School of Materials Science and Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China

^c College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 311121, China

^d Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, Anhui, 230031, China

^e Anhui Topway Testing Services Co. Ltd., 18 Rixin Road, Xuancheng Economic and Technological Development Zone, 242000, China

*Corresponding Authors E-mail: mfzhang@hfut.edu.cn , yjhuang@hznu.edu.cn, cljiang@iim.ac.cn

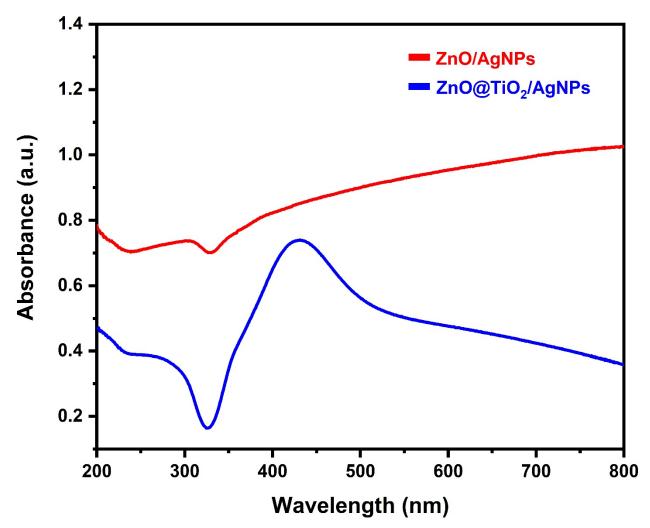
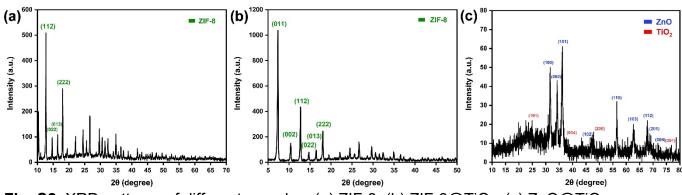
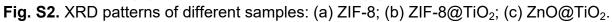


Fig. S1. Ultraviolet absorption spectra of ZnO/AgNPs and ZnO@TiO₂/AgNPs.





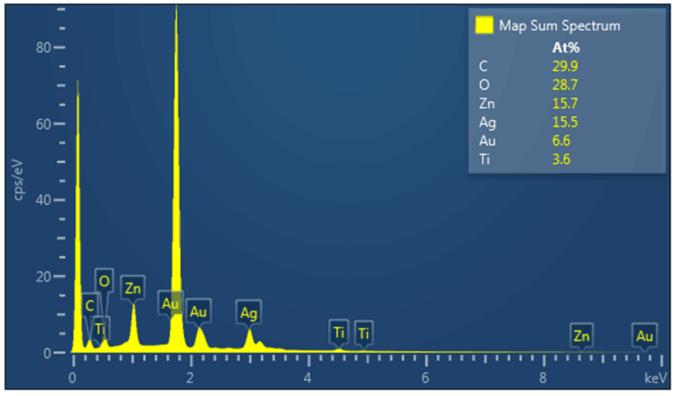


Fig. S3. EDS spectrum of ZnO@TiO₂/AgNPs sample.

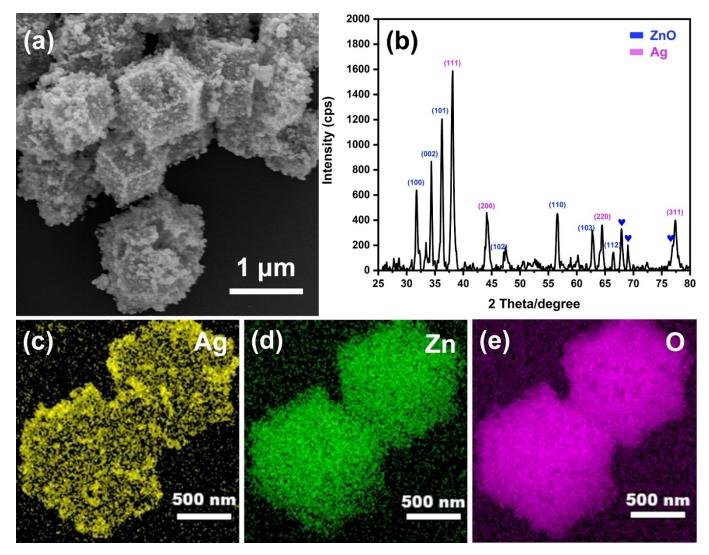


Fig. S4. (a) SEM images of ZnO/AgNPs, (b) XRD patterns of ZnO/AgNPs, (c-e) element mapping

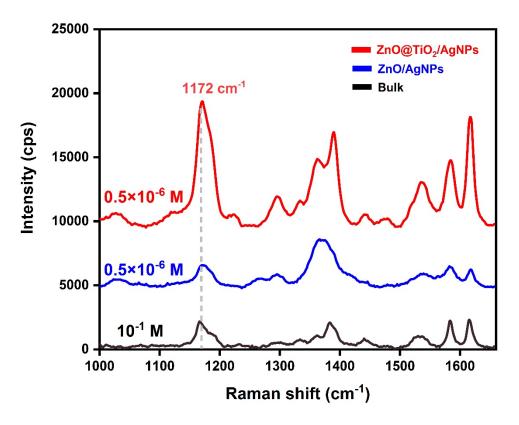


Fig. S5. SERS spectra obtained from bulk CV (10⁻¹ M), ZnO/Ag substrate with CV (0.5 \times 10⁻⁶ M)

and ZnO@TiO₂/AgNPs substrate with CV (0.5 \times 10⁻⁶ M)

Calculation of SERS enhancement factor (EF)

To quantify the enhancement contribution from ZnO/AgNPs and $ZnO@TiO_2/AgNPs$ 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/AgNPs substrate is calculated to be 0.86×10^5 . The EF is calculated to be 7.68×10^5 for the ZnO@TiO₂/AgNPs substrate.

```
\begin{split} &\mathsf{N}_{\mathsf{BULK}} = (\mathsf{Laser spot area/Diffusion area})^* (\mathsf{N}_\mathsf{A} * \mathsf{Volume}_{\mathsf{BULK}} * \mathsf{Concentration}_{\mathsf{BULK}}) \\ &\mathsf{N}_{\mathsf{SERS}} = (\mathsf{Laser spot area/Substrate area})^* (\mathsf{N}_\mathsf{A} * \mathsf{Volume}_{\mathsf{SERS}} * \mathsf{Concentration}_{\mathsf{SERS}}) \\ &\mathsf{Diffusion area} = \pi (d/2)^2 = 0.5027 \mathrm{cm}^{-2} \\ &\mathsf{Substrate area} = 0.25 \mathrm{cm}^{-2} \\ &\mathsf{Volume}_{\mathsf{BULK}} = \mathsf{Volume}_{\mathsf{SERS}} \\ &\mathsf{Concentration}_{\mathsf{BULK}} = \mathsf{10^5} * \mathsf{Concentration}_{\mathsf{SERS}} \\ &\mathsf{N}_{\mathsf{BULK}} / \mathsf{N}_{\mathsf{SERS}} = (0.25/0.5027) \times 10^5 = 4.97 \times 10^4 \\ &\mathsf{I} = \mathsf{intensity of the } 1172 \mathrm{ cm}^{-1} \mathrm{peak} \\ &\mathsf{I}_{\mathsf{BULK}} = 21196.96 \mathrm{a.u.} \\ &\mathsf{I}_{\mathsf{SERS}, \mathsf{ZnO/AgNPs}} = 36739.28 \mathrm{a.u.} \\ &\mathsf{I}_{\mathsf{SERS}, \mathsf{ZnO/AgNPs}} / \mathsf{I}_{\mathsf{BULK}} = 1.73 \\ &\mathsf{EF} = (\mathsf{I}_{\mathsf{SERS}} / \mathsf{I}_{\mathsf{BULK}}) \times (\mathsf{N}_{\mathsf{BULK}} / \mathsf{N}_{\mathsf{SERS}}) = 0.86 \times 10^5 \\ &\mathsf{I}_{\mathsf{SERS}, \mathsf{ZnO}@\mathsf{TIO2/AgNPs}} = 327581.56 \mathrm{a.u.} \end{split}
```

$$\begin{split} &I_{\text{SERS, ZnO}@\text{TiO}_{2/\text{AgNPs}}} / I_{\text{BULK}} = 15.45 \\ &\text{EF} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 7.68 \times 10^{5}. \end{split}$$