# Supporting Information

## SERS detection of thiram by a 3D sea cucumber-like composite flexible porous substrate

*Yimeng Shi* [a, b] *Yan Zhu* [b, c] *Jiaojiao Sun* [b] *Huancai Yin* [a, b*] *Jian Yin* [a, b*]

[a] School of Biomedical Engineering (Suzhou), Division of Life Sciences and Medicine, University of Science and Technology of China, Suzhou, Jiangsu 215163, PR China

[b] CAS Key Lab of Bio-Medical Diagnostics, Suzhou Institute of Biomedical Engineering and Technology, Chinese Academy of Sciences, Suzhou, Jiangsu 215163, PR China

[c] Key Laboratory of Integrated Regulation and Resource Development on Shallow Lake of Ministry of Education, College of Environment, Hohai University, Nanjing, Jiangsu 210098, PR China

**CORRESPONDING AUTHOR**

*E-mail: yinj@sibet.ac.cn (for J. Yin).

*E-mail: yinhc@sibet.ac.cn (for H. Yin).

**Table of Content**

## 1. Calculation Method for Thiram Recovery Rate

Based on the current results, the recovery efficiency is difficult to calculate as the liquid volume on the substrate/apple peels is difficult to monitor. Therefore, we used a different method to conduct the semi-quantitative analysis. Solutions of thiram at various concentrations were sprayed onto apple peels and allowed to air dry. A 1 $cm^2$ section of the treated apple peel was then cut into small pieces, placed into a 2 mL EP tube, and immersed in 1 mL of ethanol to dissolve the thiram. The Ag/Au/ZnO/P substrate was subsequently soaked in the tube for 10 minutes, after which Raman analysis was performed. The mass of the thiram was calculated using calibration curves and 1 mL as the total volume. The recovery rate was determined by the ratio of values obtained with Raman detection and the sprayed doses. As a result, the recovery rate for a concentration of 4.8 $mg/cm^2$ was approximately 88%.

## 2. The average Raman spectra of 4-MBA on Au/Ag/ZnO/P substrate under the excitation of three wavelengths

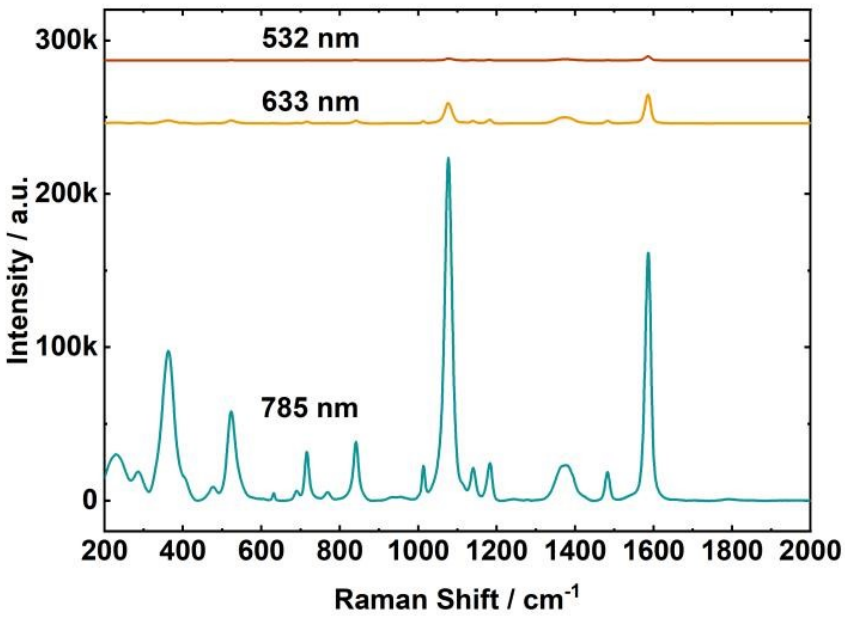


Figure S1 The average Raman spectra of 4-MBA on the Au/Ag/ZnO/P substrate under the excitation of

three wavelengths.

**3. Comparison of the Enhancement Effects of ZnO/P, Au/ZnO/P and Ag/Au/ZnO/P Substrates**

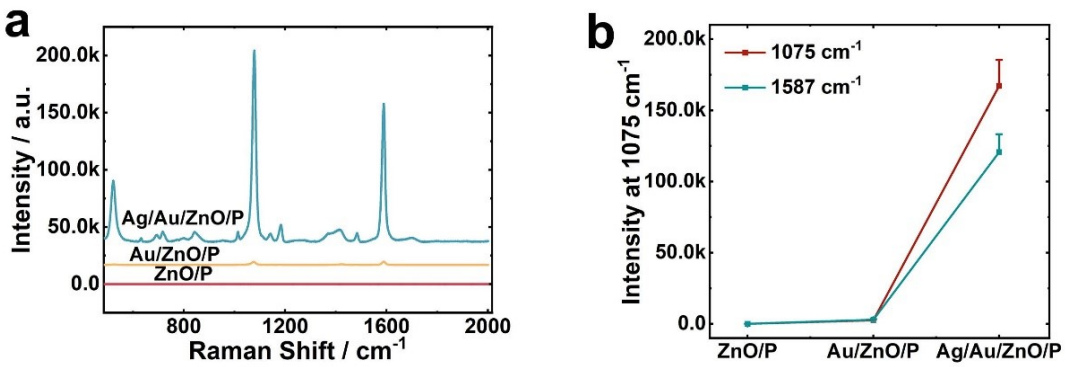


Figure S2 (a) SERS spectra of 4-MBA ($10^{-3}$ M) on ZnO/P, Au/ZnO/P, and Ag/Au/ZnO/P substrates; (b) Band intensities at 1075 $cm^{-1}$ and 1587 $cm^{-1}$ (laser power: 0.0001%).

**4. EDS spectrum and elemental mapping of Ag/Au/ZnO/P substrate**

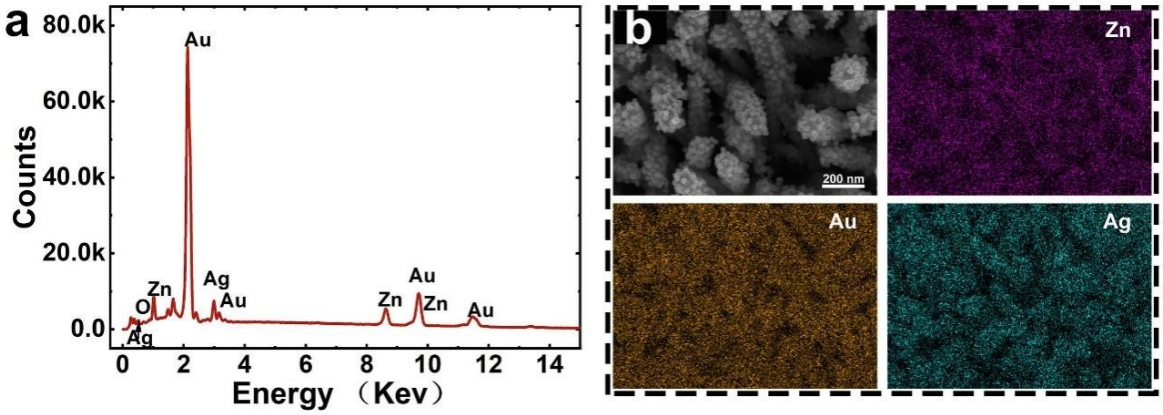


Figure S3 EDS spectrum (a) and elemental mapping (b) of Ag/Au/ZnO/P substrate.

**5. XPS survey spectrum of the Ag/Au/ZnO/P substrate and high-resolution XPS spectra of Zn 2p, Au 4f and Ag 3d**

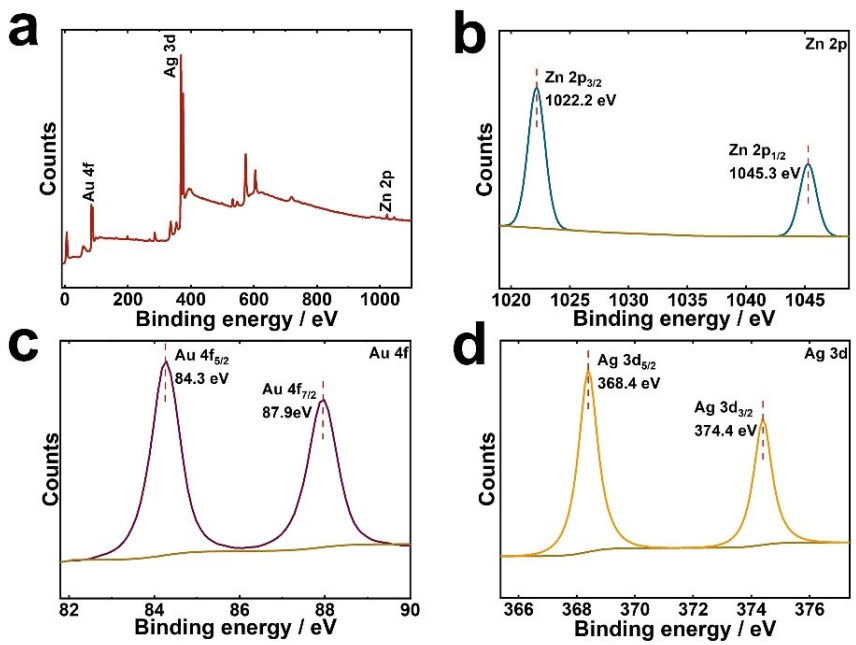


Figure S4 XPS survey spectrum of the Ag/Au/ZnO/P substrate (a) and high-resolution XPS spectra of (b) Zn 2p, (c) Au 4f, and (d) Ag 3d.

**6. XRD analysis of the Ag/Au/ZnO/P substrate**

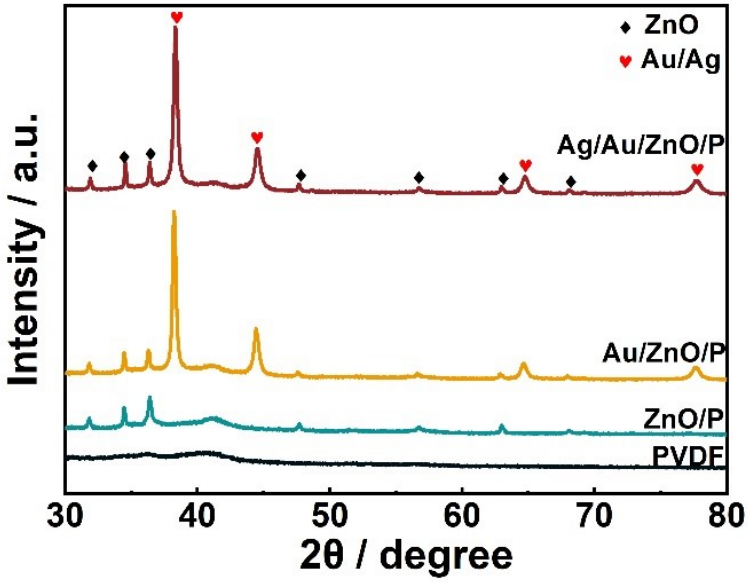


Figure S5 XRD analysis of the Ag/Au/ZnO/P substrate.

**7. Comparison of the Enhancement Effects of Au/Au/ZnO/P and Au/Ag/ZnO/P Substrates**

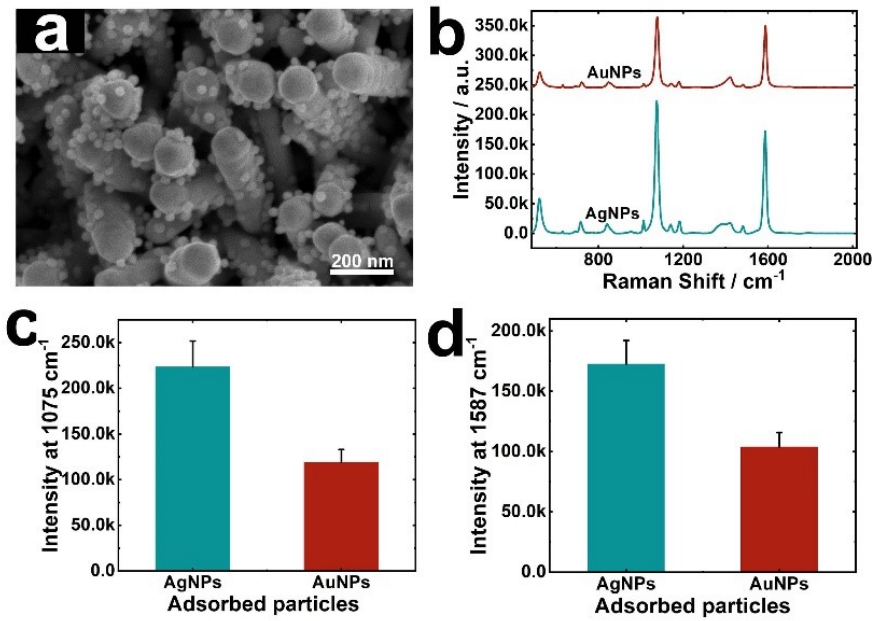


Figure S6 SEM images of (a) AuNPs adsorbed on Au/ZnO/P substrate; (b) The average Raman spectra of 4-MBA on Au/Au/ZnO/P substrate and Au/Ag/ZnO/P; (c) 1075 $cm^{-1}$ and (d) 1587 $cm^{-1}$ peaks of $10^{-3}$ M 4-MBA on Ag/Au/ZnO/P and Au/Au/ZnO/P.

**8. Stability Evaluation of the Ag/Au/ZnO/P Substrate**

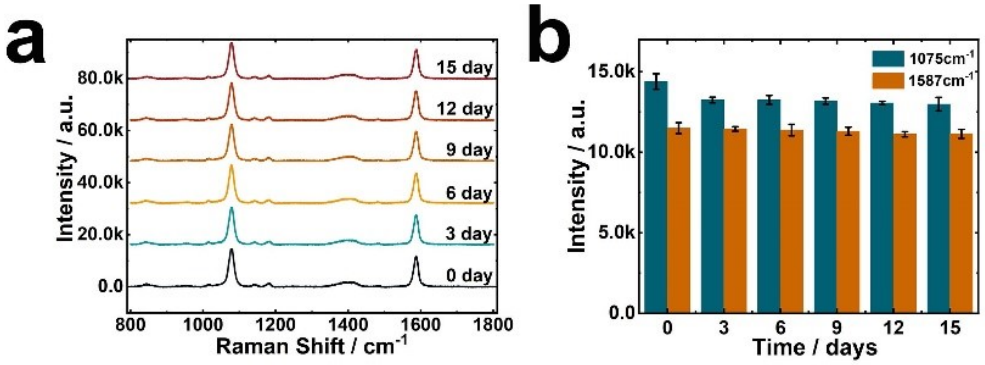


Figure S7 (a) Raman spectra of $1\times10^{-6}$ M 4-MBA using the Ag/Au/ZnO/P substrate stored over different time (laser power: 0.0001%). (b) Intensity variation histogram of 1075 $cm^{-1}$ and 1587 $cm^{-1}$ peaks.

**9. The average Raman spectra of thiram on apple peels**

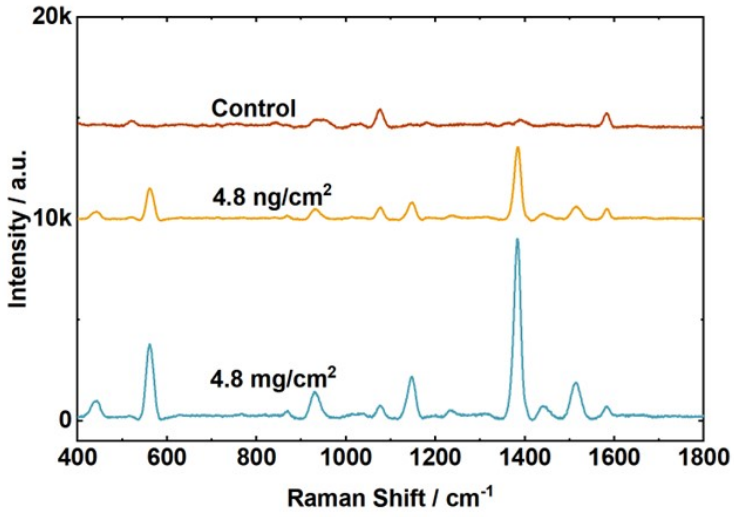


Figure S8 The average Raman spectra of thiram on apple peels. Thiram were sprayed on the peels at 4.8 mg/cm$^2$ and 4.8 ng/cm$^2$. After that, their residue amounts on the peels were detected as described in Method 1.

**10. Electron microscopy images of PVDF membrane and seed layer**

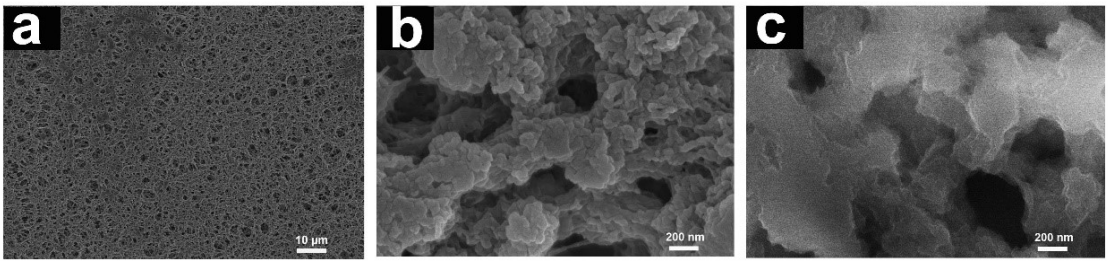


Figure S9 Electron microscopy images of PVDF membrane at magnifications of 1× (a) and 50× (b), respectively. (c) Seed layer electron microscope picture of zinc oxide growth, it is not visible under the electron microscope.