

## Supplementary Information

# Ultrasensitive and reusable $\text{Cu}_2\text{O}/\text{Ag}$ composite SERS substrates for trace thiram detection

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## **2. Experimental section**

### **2.1 Chemicals and Materials**

All the chemical reagents are analytical grade reagents and can be used without purification. Fluorine-doped tin oxide (FTO) conductive glasses (1.5 cm \* 2.5 cm) were provided by Luoyang Guluo Glass Co. Copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and anhydrous ethanol purchased from Hangzhou Gaojing Fine Chemical Co. Acetone was purchased from Hangzhou Shuanglin Chemical Reagent Co. Lactic acid was purchased from Shanghai Aladdin Biochemical Technology Co. Sodium hydroxide (NaOH), rhodamine 6G (R6G), 4-Mercaptopyridine (4-Mpy), thiram were purchased from Shanghai McLean Biochemical Technology Co.

### **2.2. Preparation of $\text{Cu}_2\text{O}/\text{Ag}$ Composite Substrates**

The  $\text{Cu}_2\text{O}$  films were electrodeposited at a constant potential on FTO conductive glass substrates. In the three-electrode system, an FTO conductive glass was used as working electrode (WE), Pt electrode as auxiliary electrode (AE), and a saturated calomel electrode (SCE) as reference electrode (RE). Firstly, FTO substrates underwent ultrasonic cleaning with acetone, deionized (DI) water, ethanol, and DI water for 10 min each in sequential order to eliminate surface pollutants. An aqueous solution of 0.4 M copper sulfate and 3 M lactic acid served as the electrolyte. The pH of the electrolyte was adjusted to pH 11 by adding a certain amount of 5 M sodium hydroxide. The reaction took place in a water bath at 60 °C under a constant potential of -0.40 V for a certain duration. Subsequently, the prepared samples were cleaned with ethanol and DI water before being dried in air.

The Ag nanoparticles were subsequently deposited onto the previously synthesized Cu<sub>2</sub>O substrate using magnetron sputtering deposition at room temperature. The base vacuum air pressure was maintained at  $3 \times 10^{-4}$  Pa, while pure argon gas was introduced to maintain a chamber vacuum of  $\sim 8$  Pa. By adjusting the sputtering time, a series of Cu<sub>2</sub>O/Ag composite substrates were obtained, namely Cu<sub>2</sub>O/Ag-60, Cu<sub>2</sub>O/Ag-90, and Cu<sub>2</sub>O/Ag-120 substrates corresponding to deposition times of 60 s, 90 s, and 120 s respectively. Finally, all as-synthesized Cu<sub>2</sub>O/Ag composite substrates were sealed and stored away from light for subsequent experiments.

### **2.3. SERS Measurement**

Rhodamine 6G (R6G) and 4-Mercaptopyridine (4-Mpy) were employed as Raman probe molecules to investigate the SERS performance of the Cu<sub>2</sub>O/Ag composite film. Aqueous solutions containing different concentrations of R6G or 4-Mpy were initially prepared. Subsequently, slices of the Cu<sub>2</sub>O/Ag composite substrate, approximately 1 square centimeter in size, were immersed in the corresponding aqueous solution for 8 hours. Finally, they were rinsed several times with DI water to eliminate excess molecules from the surface and dried in air before SERS analysis.

To investigate the reusability of the as-prepared Cu<sub>2</sub>O/Ag composite substrate, the Cu<sub>2</sub>O/Ag-90 composite substrate adsorbed with R6G ( $10^{-5}$  M) was detected and self-cleaned according to the following procedure. The Cu<sub>2</sub>O/Ag-90 composite substrate was immersed in an R6G solution for 30 minutes, subsequently removed and rinsed with DI water, and finally dried in ambient air. After SERS detection, the Cu<sub>2</sub>O/Ag-90 composite substrate adsorbed with R6G molecules was evenly divided into six pieces

and immersed in R6G solution in a dark environment for 30 minutes, followed by irradiation under a 300 W xenon lamp positioned at a distance of 15 cm from the substrate. Every 20 minutes, one piece was extracted for Raman testing until no Raman signal of R6G molecules could be detected. It was observed that approximately 100 minutes were required for photocatalytic degradation of R6G molecules adsorbed on the Cu<sub>2</sub>O/Ag-90 composite substrate. To assess the reusability of the substrate, three cycles of "detection-cleaning" were repeated.

Thiram, a pesticide, was selected as the SERS-based application. A thiram ethanol solution with concentrations ranging from 10<sup>-5</sup> M to 10<sup>-8</sup> M was prepared and used to immerse Cu<sub>2</sub>O/Ag-90 composite substrates for 6 hours. The prepared substrates were then thoroughly rinsed with ethanol to remove physically adsorbed thiram molecules and dried in air before Raman measurement.

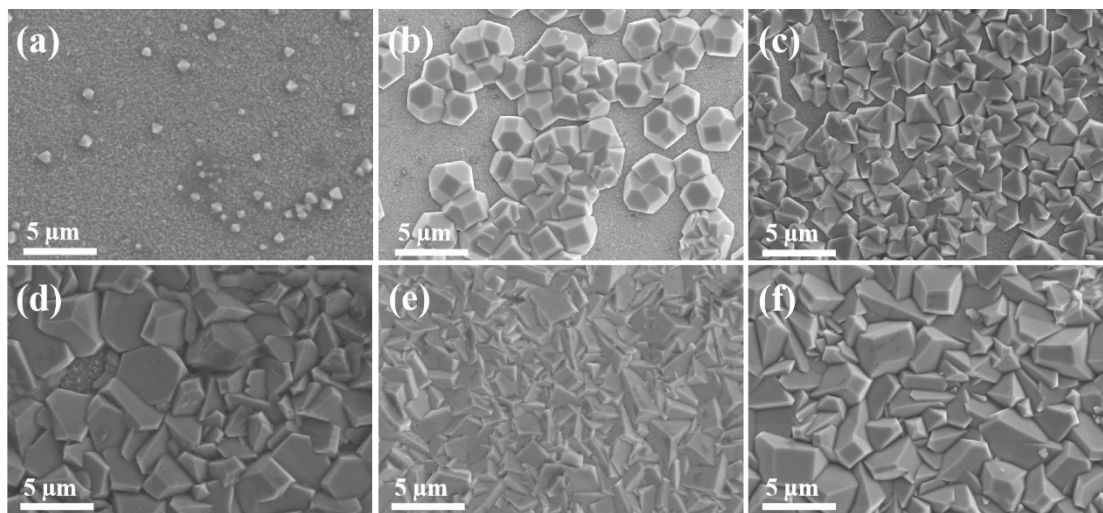
The experimental procedure for thiram detection in soil is as follows. Firstly, the soil from Zhejiang Sci-Tech University was finely ground and annealed at a temperature of 500 °C for 3 hours to eliminate any impurities present in the soil. Subsequently, 1 mg of thiram powder was added to 1 g of the annealed soil, and the mixture was further homogenized and dissolved in 10 mL ethanol. This resulted in obtaining an ethanol solution containing thiram with a concentration of 1000 ppm. Following this step, the solution was successively diluted by ten-fold increments to achieve various desired concentrations. The subsequent procedure remains consistent with that employed during Raman testing on pure ethanol solution containing thiram.

## **2.4. Characterization**

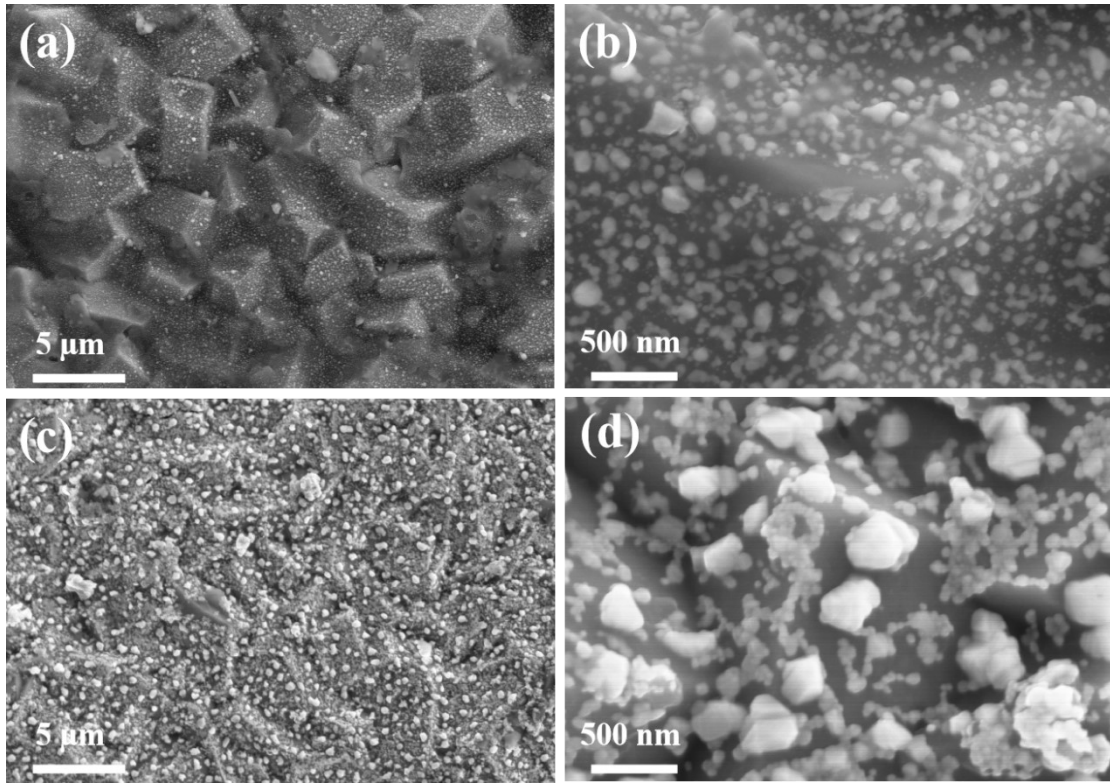
The surface morphology of the as-prepared samples was characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM2010F, Japan). The structure and crystallinity of the samples were analyzed by X-ray diffraction (XRD) pattern, which was acquired using Bruker D8 Discover X-ray diffractometer with a Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation source at 40 kV and 40 mA. The UV–vis absorption spectra were obtained by a spectrophotometer (Hitachi U3900 spectrophotometer). The X-ray photoelectron spectroscopy (XPS) analysis was obtained on the Thermo Scientific K-Alpha X-ray photoelectron spectroscopy equipped with Al-K $\alpha$  X-ray source.

All the SERS measurements were conducted using a Renishaw inVia microscopic confocal Raman spectrometer equipped with a NIR (785 nm) laser and visible (633 and 532 nm) lasers. A 50 $\times$  microscope objective was employed to precisely focus the low power level (<1 mW) of the laser beam onto the surface of the SERS substrates, while collecting corresponding Raman spectra through three scans over a duration of 3 seconds.

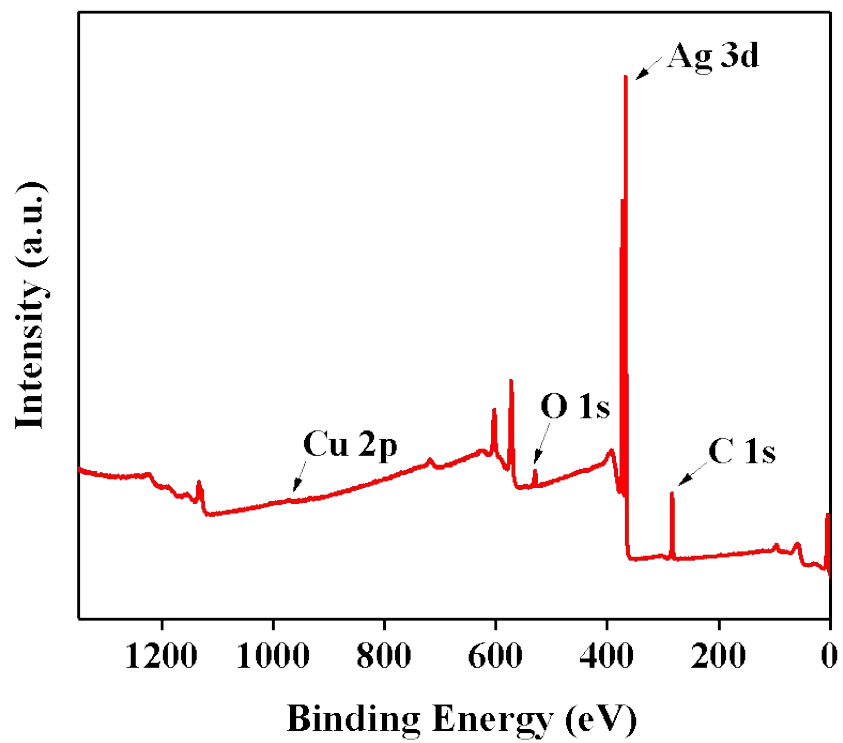
### 3. Results and discussion



**Fig. S1.** SEM images of Cu<sub>2</sub>O films obtained on the FTO conducting glasses after electrodeposition for different times: (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 40 min.

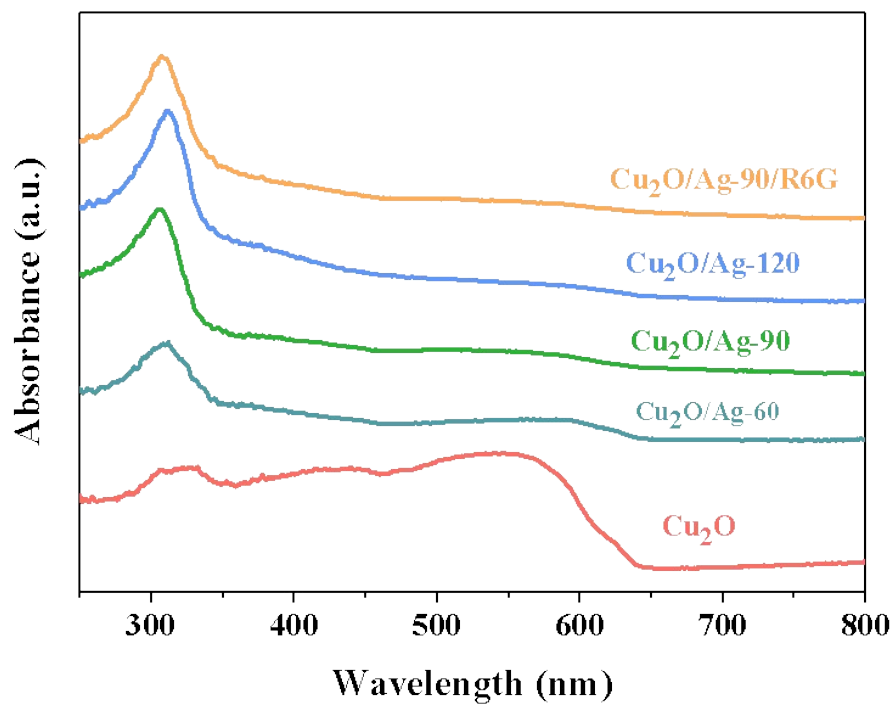


**Fig. S2.** SEM image of  $\text{Cu}_2\text{O}/\text{Ag}$  composite substrates with different magnetron sputtering times of Ag nanoparticles: (a, b) 60 s, (c, d) 120 s.

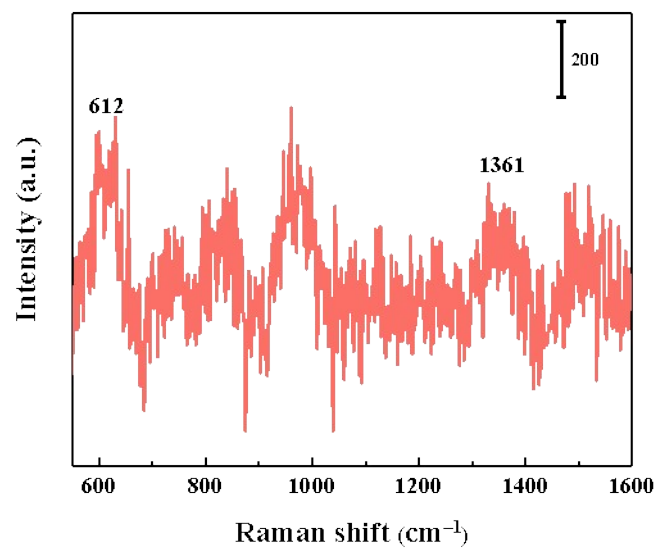


**Fig. S3.** XPS full spectrum of Cu<sub>2</sub>O/Ag-90 composite substrate.

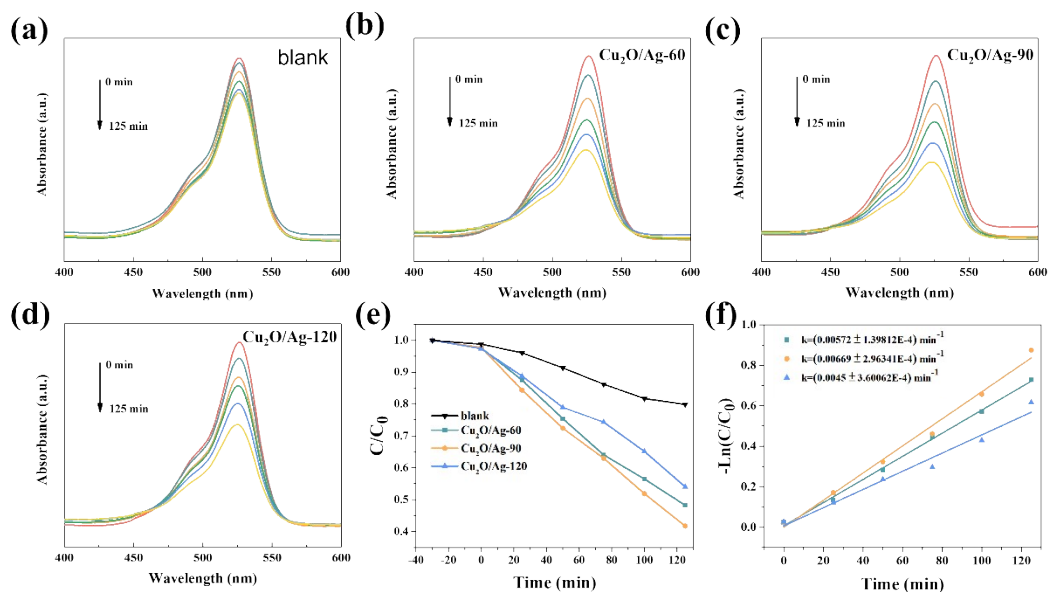




**Fig. S4.** UV-vis absorption spectra of the as-prepared Cu<sub>2</sub>O, Cu<sub>2</sub>O/Ag-60, Cu<sub>2</sub>O/Ag-90, Cu<sub>2</sub>O/Ag-120 composite substrates and Cu<sub>2</sub>O/Ag-90 substrate adsorbed with R6G, respectively.



**Fig. S5.** SERS spectrum of  $10^{-5}$  M concentration of R6G molecules adsorbed on  $\text{Cu}_2\text{O}$  substrate under the 532 nm laser excitation wavelength.



**Fig. S6.** Photocatalytic degradation of R6G molecules ( $10^{-5}$  M) over different substrates under irradiation of xenon lamp. (a) blank, (b) Cu<sub>2</sub>O/Ag-60, (c) Cu<sub>2</sub>O/Ag-90, (d) Cu<sub>2</sub>O/Ag-120. (e) The intensity of R6G absorption peak at 526 nm versus irradiation time in the photocatalytic process. (f) Corresponding kinetics curves.

**Table S1.** Vibrational assignments of the main Raman Characteristic peaks of R6G, 4-Mpy and thiram molecules.

<b>Chemicals</b>	<b>Characteristic peaks and their vibrational modes</b>				<b>Ref.</b>
<b>R6G</b>	613 cm <sup>-1</sup>	774 cm <sup>-1</sup>	1362 cm <sup>-1</sup> , 1509 cm <sup>-1</sup> , 1650 cm <sup>-1</sup>		1-2
	in-plane and out-of-plane vibrations of the C-C-C ring	in-plane bending vibration of the C-H ring	in-plane stretching motions of the aromatic ring		
<b>4-Mpy</b>	1020 cm <sup>-1</sup>	1061 cm <sup>-1</sup>	1217 cm <sup>-1</sup>	1585 cm <sup>-1</sup>	3-4
	stretching vibration of C-S, a <sub>1</sub>	stretching vibration of C-H, b <sub>2</sub>	bending vibration of C-H, a <sub>1</sub>	stretching vibration of C=C in the benzene ring, a <sub>1</sub>	
<b>Thiram</b>	937 cm <sup>-1</sup>	1147 cm <sup>-1</sup>	1381 cm <sup>-1</sup>	1502 cm <sup>-1</sup>	5-6
	C-N and C=S stretching vibrations	C-N stretching mode and the symmetric CH <sub>3</sub> rocking	C-N stretching and CH <sub>3</sub> symmetric deformation mode	C-N stretching vibration and the CH <sub>3</sub> rocking	

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