

Supporting information

Copper foam *in situ* loaded with precious metal nanoparticles as transmission SEIRAS substrate for rapid detection of dithiocarbamate pesticides

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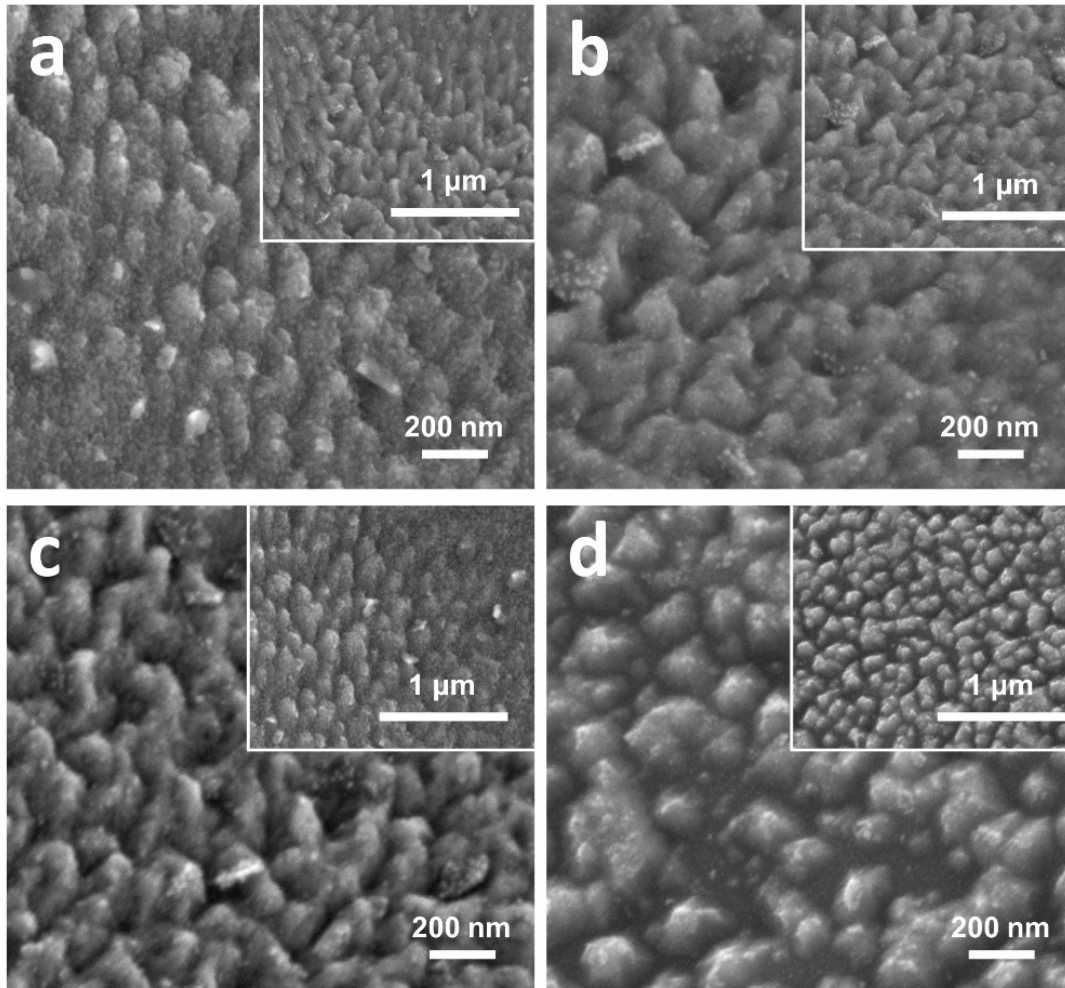


Fig. S1. SEM images of Au NPs-CF transmission SEIRAS substrate that prepared with various amount of H_{AuCl}₄ and PVP. Note that from **a** to **d** represent SEM image of the Au NPs-CF substrate prepared with excessive PVP, excessive H_{AuCl}₄, the median dosage of H_{AuCl}₄ and PVP, and the optimized dosage, respectively. The concentrations of H_{AuCl}₄ solution (10 mL) from **a** to **d** were 0.1, 2.0, 1.0, and 0.2 mM, respectively. The volumes of PVP solution (0.05 g/mL) from **a** to **d** were 5.0, 0.5, 1.0, and 3.0 mL, respectively. The FDTD simulation was conducted to investigate the distribution of electromagnetic field along the x-y plane in these condition (Fig. S2).

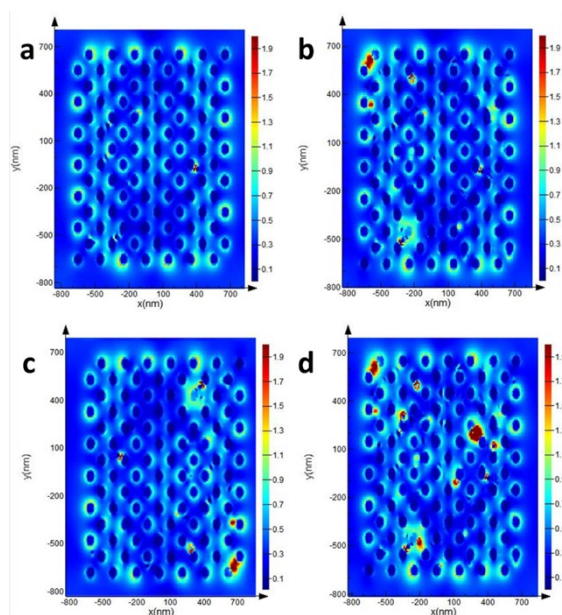


Fig. S2. Electromagnetic field distributions of x-y plane for the Au NPs-CF substrate that prepared with various amount of HAuCl_4 and PVP. From **a** to **d** represent SEM image of the Au NPs-CF substrate prepared with excessive PVP, excessive HAuCl_4 , the median dosage of HAuCl_4 and PVP, and the optimized dosage, receptively. See the method section in support information for details.

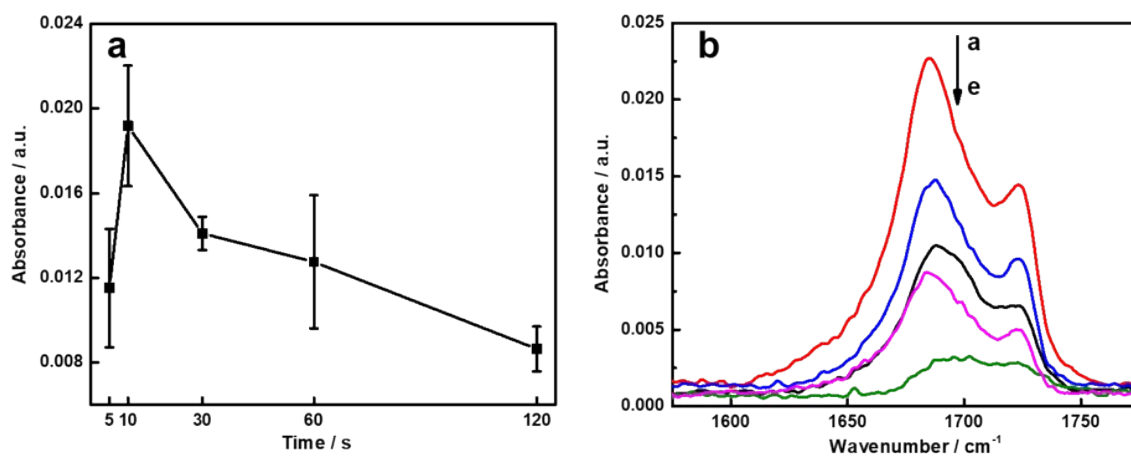


Fig. S3. a SEIRAS performance of Au NPs-CF substrates prepared under different reaction times. Error bars represent the SD of three measurements ($n = 3$). **b** SEIRAS spectra obtained with Au NPs-CF

substrates prepared under different reaction times. From *a* to *e*, the reaction times were 10, 30, 60, 5, and 120 s, respectively. The CF was shaken in the mixture of 10 mL 0.2 mM HAuCl₄ and 3 mL 0.05 g/mL

PVP solution

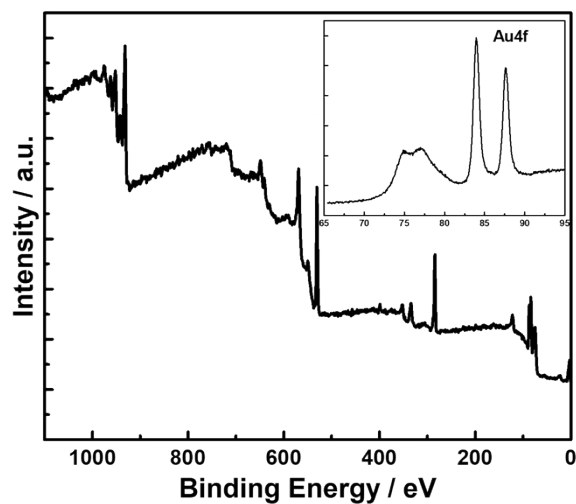


Fig. S4. XPS spectrum of Au NPs-CF transmission SEIRAS substrate and (insets) the narrow spectra of Au4f. The detailed information could be found in Tab. S1.

Tab. S1. Detailed information of the XPS spectrum of Au NPs-CF substrate.

Name	Peak BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N)	Atomic %
C1s	284.78	10726.54	1.23	19075.12	0.24	55.33
Au4f	83.97	9405.16	0.87	16967.38	0.01	2.8
O1s	531.25	12451.11	1.92	27582.74	0.13	28.62
Cu2p	934.29	18870.21	1.32	95291.02	0.06	13.24

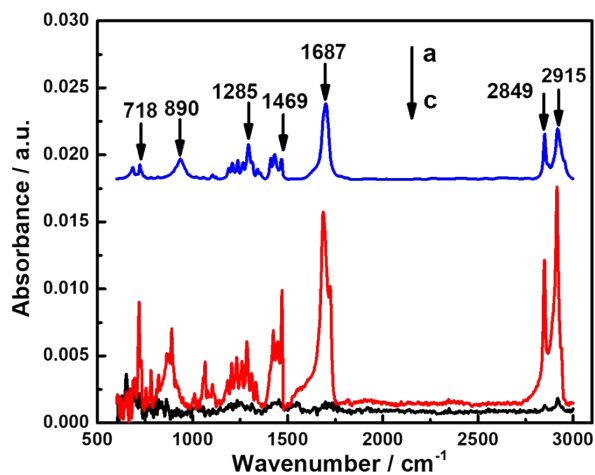


Fig. S5. IR transmission spectra of MUA. The spectra from *a* to *c* were obtained with KBr disk, Au NPs-CF substrate, and CF without Au NPs, respectively.

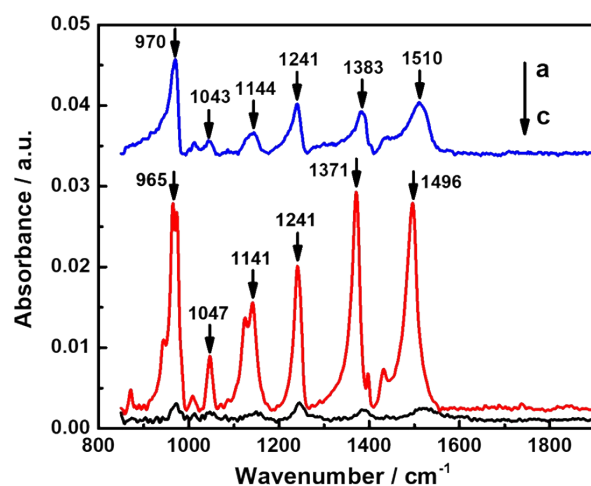


Fig. S6. IR transmission spectra of Ziram. The spectra from *a* to *c* were obtained with CaF₂ disk, Au NPs-CF substrate, and CF without Au NPs, respectively.

Tab. S2 Peak assignment for Ziram ^a.

frequency (cm ⁻¹)	assignment
965	$\nu(\text{C-S})$ motion

1047	$\nu(\text{C}=\text{S})$ motion
1141	$\delta(\text{CNC})$, $\delta(\text{HCN})$, $\nu(\text{C-N})$, and $t(\text{CH}_3)$ vibrations
1241	$\delta(\text{CNC})$, $\delta(\text{HCN})$, $\nu(\text{C-N})$, and $t(\text{CH}_3)$ vibrations
1371	$\nu(\text{C-N})$ motion coupled to $\delta_s(\text{CH}_3)$
1496	$\delta_{\text{as}}(\text{CH}_3)$

^a From ref 20

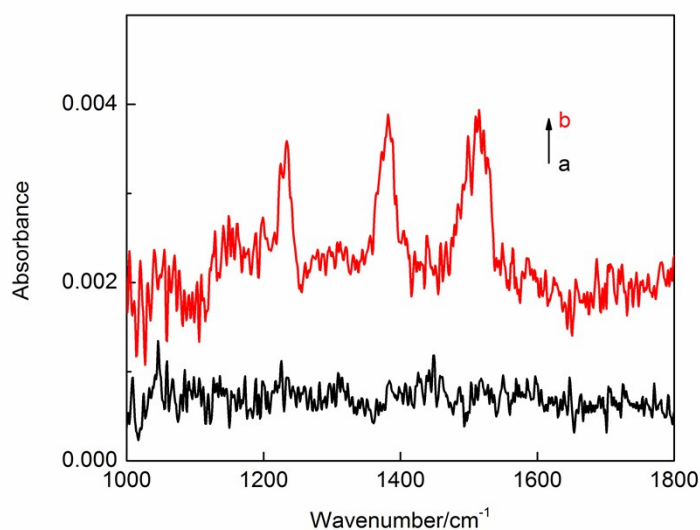


Fig. S7. SEIRAS spectra of Ziram at different concentrations obtained with Au NPs-CF substrate. From *a* to *b* represent 0 mg/mL and 0.018 mg/mL, respectively.

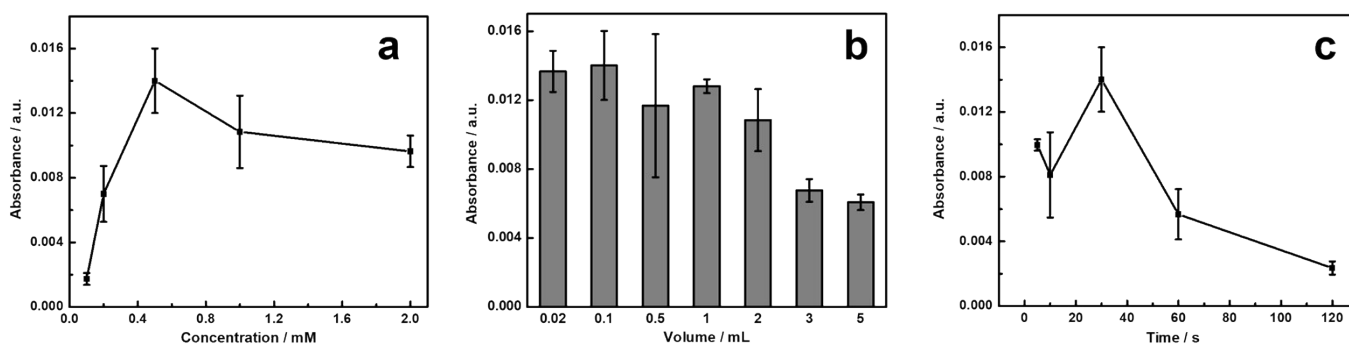


Fig. S8. **a** SEIRAS performance of Pt NPs-CF substrates that prepared with different concentrations of H_2PtCl_6 solution (10 mL). **b** SEIRAS performance of Pt NPs-CF substrates that prepared with different

volumes of PVP solution (0.05 g/mL). **c** SEIRAS performance of Pt NPs-CF substrates prepared under different reaction times. All error bars represent the SD of three measurements ($n = 3$). MUA (1 mM) was served as a probe molecule throughout the evaluation experiment. The characteristic peak at 1687 cm^{-1} was analyzed.

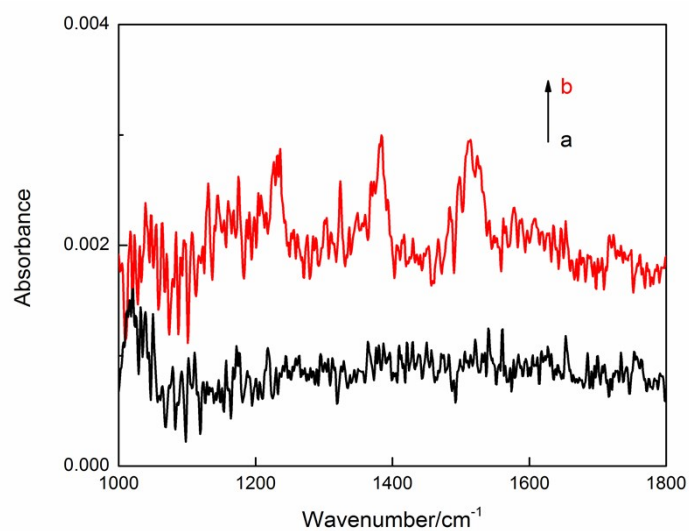


Fig. S9. SEIRAS spectra of Febram at different concentrations obtained with Pt NPs-CF substrate. From *a* to *b* represent 0 mg/mL, and 0.025 mg/mL, respectively.

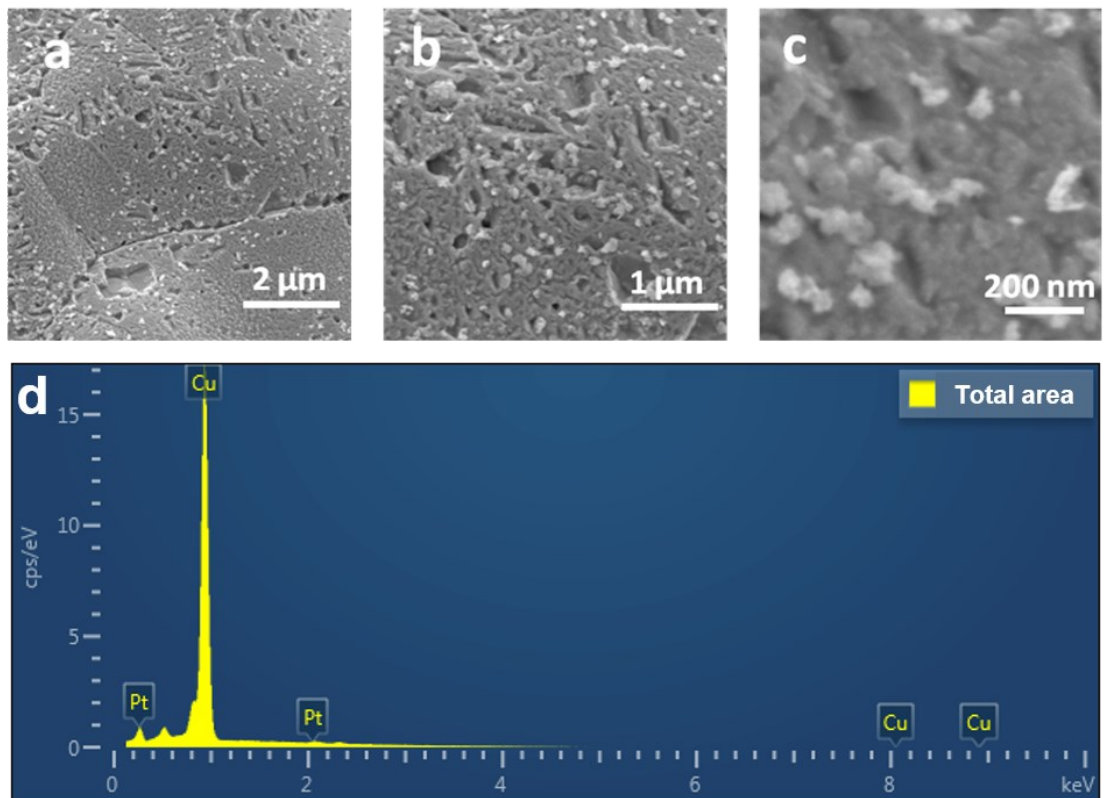


Fig. S10. a-c SEM images of Pt NPs-CF transmission SEIRAS substrate. **d** EDS result of Pt NPs-CF transmission SEIRAS substrate. The atomic percentage (%) of Pt, Cu were 3.33 and 96.67, respectively.

The distribution of Pt and Cu in the characterization area of EDS was shown in Fig. S10.

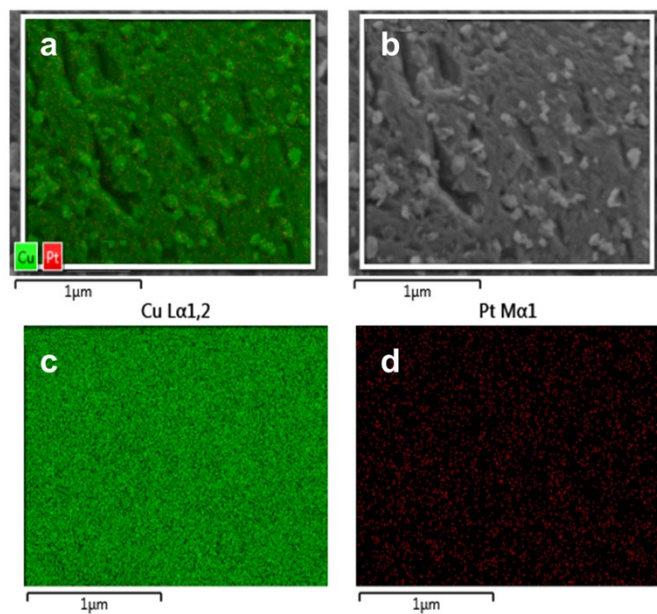


Fig. S11. The distribution of Pt and Cu in the characterization area of EDS. **a** EDS layered image. **b**

Electronic image. **c** Distribution image of Cu. **d** Distribution image of Pt.

Methods

Sample preparation. The prepared MNPs-CF transmission SEIRAS substrates were immersed in analyte (MUA/ Ziram/ Ferbam) solution for 30 mins with gentle shaken (120 r/min). The concentration of MUA was 1 mM. The gradient concentrations of Ziram and Ferbam were prepared (Fig. 4 and Fig. 5). Finally, the MNPs-CF was dried in N₂ flow before measurement. Each sample carried out 3 parallel experiments.

Parameter settings. The MNPs-CF substrates were measured by Fourier Transform Infrared (FT-IR) Spectrometer (Perkin Elmer, Spectrum Two) with transmission mode. The spectral resolution is adjusted to 4 cm⁻¹, the number of scans is 10 times, and the scanning range is 400 - 4000 cm⁻¹.

Numerical Simulations. The electromagnetic distributions (Fig. S2) were calculated by the 3D FDTD numerical method (Lumerical Solutions, Canada). In simulations, a Total-Field Scattered-Field (TFSF) source was used to illuminate at the normal incident angle. The CF was used as a solid support material, and the Au NPs were randomly distributed. The simulation time was set to 1000 fs to guarantee convergence. A nonuniform mesh method was employed to save computation time. The dielectric function of Au was taken from a multi-coefficient fitting model offered by FDTD software.