Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Highly sensitive and label-free determination of thiram residue using surface-enhanced Raman spectroscopy (SERS) coupled with paper-based microfluidics

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1. Synthesis of Au@Ag NPs

According to previous report,[1] first, 0.25 ml of 0.1 M HAuCl4 was added into 100ml of ultrapure water and then heated to boiling under magnetic stirring. After quickly injecting 1.5 ml of 1% sodium citrate, the mixed solution was refluxed for ~30 min until it became wine red. After gradually cooling to room temperature under stirring, the resulting solution was filtered through 0.22 μm Millipore membrane, and the Au NPs colloid with the size of 30 nm was stored in a refrigerator at 4 ºC for further use. Second, 10 ml of above Au NPs colloid and 1.5 ml of 0.1 M ascorbic acid were mixed in a round flask under magnetic stirring. Then 3.5 ml of 1mM AgNO3 was dropwise added into the above mixture at a rate of one drop per 30 s. Silver nitrate was reduced by ascorbic acid and the resultant silver continuously grew at the surface of Au seeds. After the wine red of solution changed into orange yellow, the solution was stirred for 30 min and the Au@Ag NPs were obtained.

2. Reproducibility and stability evaluation of Au@Ag NPs

The SERS enhancement factor depends on size, shape, aggregation and spatial distribution of the metallic nanoparticles. In order to demonstrate the reproducibility and stability of Au@Ag NPs, we have synthesized another batch Au@Ag NPs according to the same method. The characterizations of Au@Ag NPs is shown in Fig.S1.The SEM observation was performed (Fig.S1A) to show the highly uniform nanoparticles, the core-shell structure of Au@Ag NPs with 30 nm Au core and 7nm Ag shell is clearly shown by the TEM image in Fig. S1B, and the extinction-visible spectrum of Au@Ag NPs is shown in Fig. S1C.

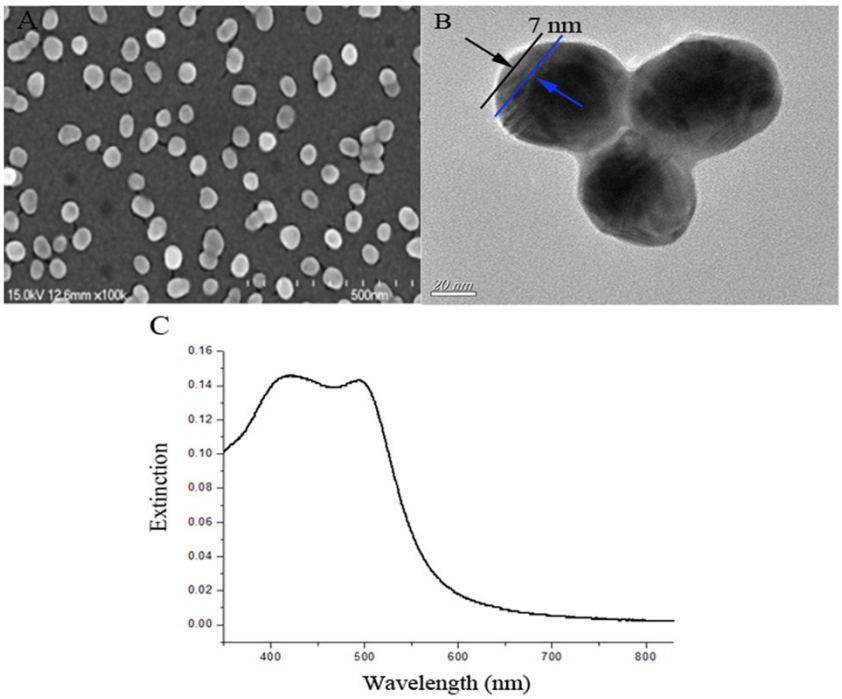

Fig. S1 (A) SEM image of Au@Ag NPs. (B) The TEM image of Au@Ag NPs with 30 nm Au core and 7 nm Ag shell. (C) Extinction visible spectrum of Au@Ag NPs.

Fig. S2 shows the representative SERS spectra of thiram solution at various concentrations from 1.0×10^{-4} to 5.0×10^{-10}mol /L which were measured under the optimal conditions. Each spectrum represents the average of measurements at random 4 spots. The LOD was found to be 1.0×10^{-9} mol/L. Fig.S3 shows the SERS spectra of thiram at the concentration of 1.0×10^{-5} mol/L from 5 different spots. The relative standard deviation (RSD) results of Raman peaks at 564, 1143 and 1379 cm^{-1} are 8.9%, 6.7% and 8.4%. Fig.S4 shows the SERS spectra of thiram at the concentration of 1.0×10^{-6} mol/L from 5 different spots. The relative standard deviation (RSD) results of Raman peaks at 564, 1143 and 1379 cm^{-1} are 3.9%, 3.1% and 3.9%. These results demonstrated Au@Ag NPs has highly reproducibility and stability.

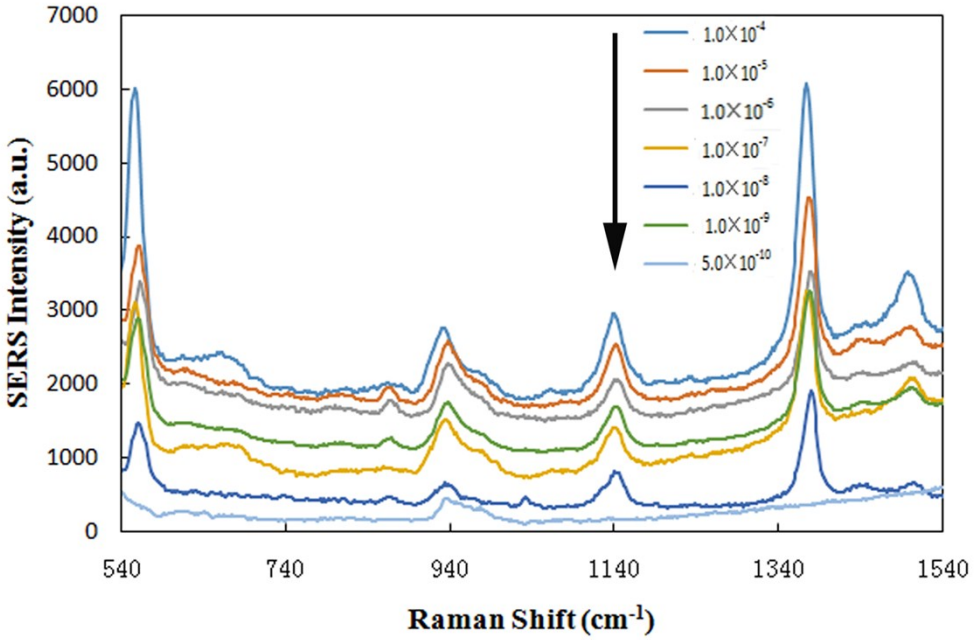

Fig. S2 The SERS spectra of thiram solution with the concentration decreased from 1.0×10^{-4} mol/L to 5.0×10^{-10} mol/L.

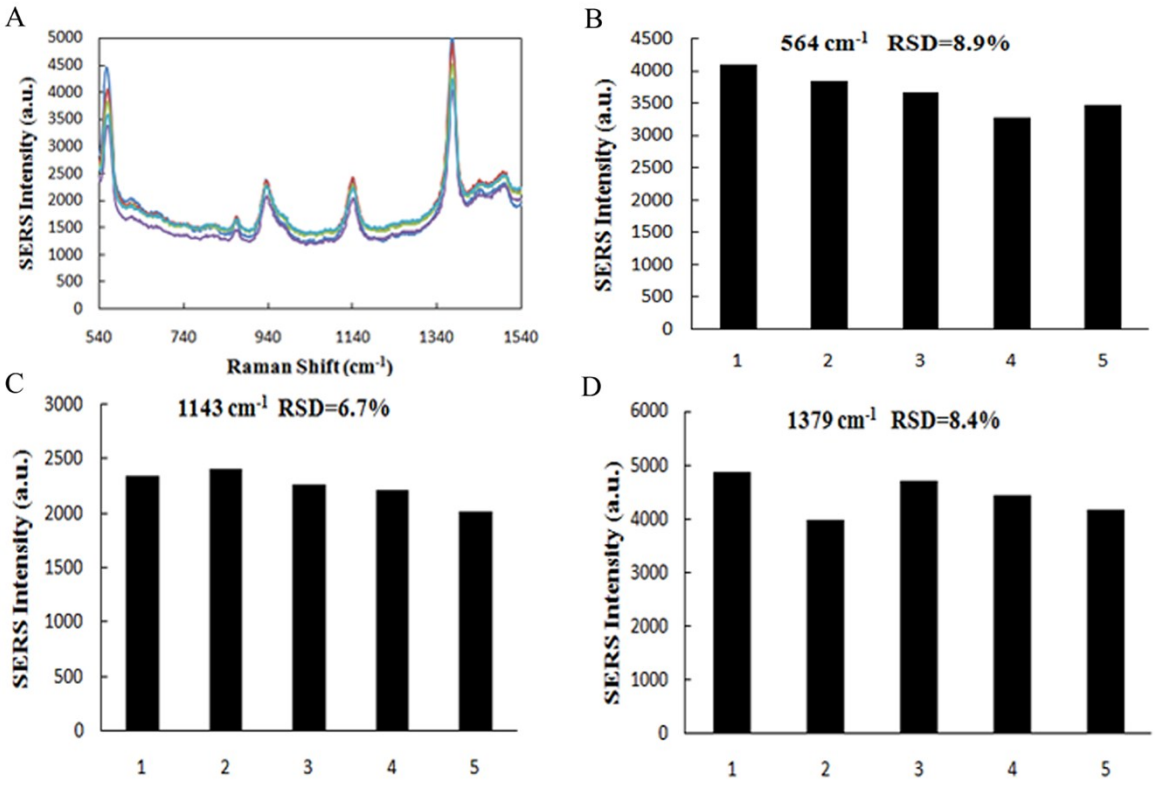

Fig.S3 (A) The SERS spectra of thiram solution (1.0×10^{-5} mol/L) at 5 different spots. The peak intensities and RSD results at (B) 564cm^{-1}. (C) 1143cm^{-1}. (D) 1379cm^{-1}.

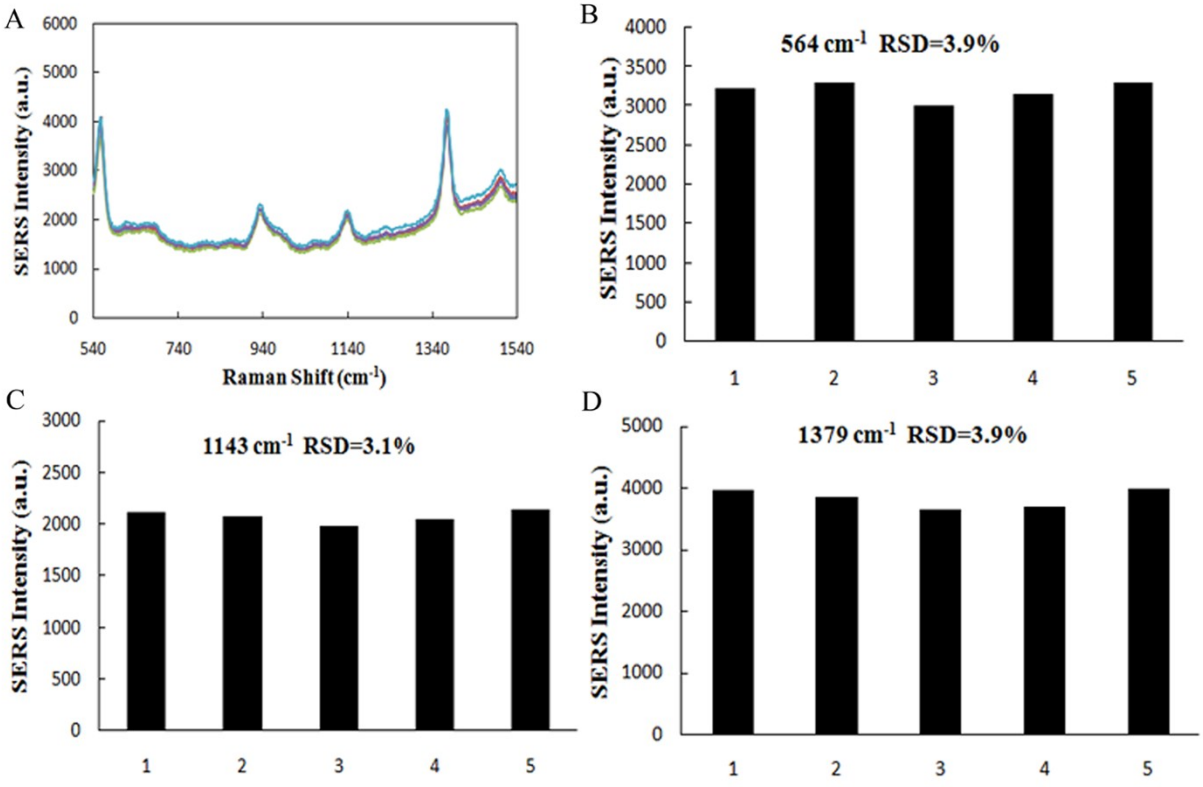

Fig.S4 (A) The SERS spectra of thiram solution (1.0×10^{-6} mol/L) at 5 different spots. The peak intensities and RSD results at (B) 564cm^{-1}. (C) 1143cm^{-1}. (D) 1379cm^{-1}.

3. Real sample pretreatment

Pretreatment of tea according to previous reports.[2] In this work, tea samples were purchased from local market and dried in a vacuum oven at 35 °C until constant weight. First, samples of green tea (5 g) were mixed with 30 mL acetonitrile (C_2H_3N) in a 50 mL centrifuge tube and sonically extracted for 5 min, then centrifugation for 5 min at 4500 rpm. The extraction procedure was repeated for three times and the extract were combined. Subsequently, filter column for the removal of pigment was prepared, 0.8 gram Fe_3O_4 nanoparticles (100 nm in diameter) mixed uniformly with 0.3 gram graphitized carbon in a 10 mL centrifuge tube. Then, various concentrations of thiram were added in to the extract after which was filtered by filter column.

Finally, we obtained gradient concentration solution (1.0×10^{-4} mol/L, 1.0×10^{-5} mol/L, 1.0×10^{-6} mol/L, 1.0×10^{-7} mol/L, 1.0×10^{-8} mol/L, 1.0×10^{-9} mol/L) for measurement. Fig.S5 shows the spectra of the tea, with and without thiram.

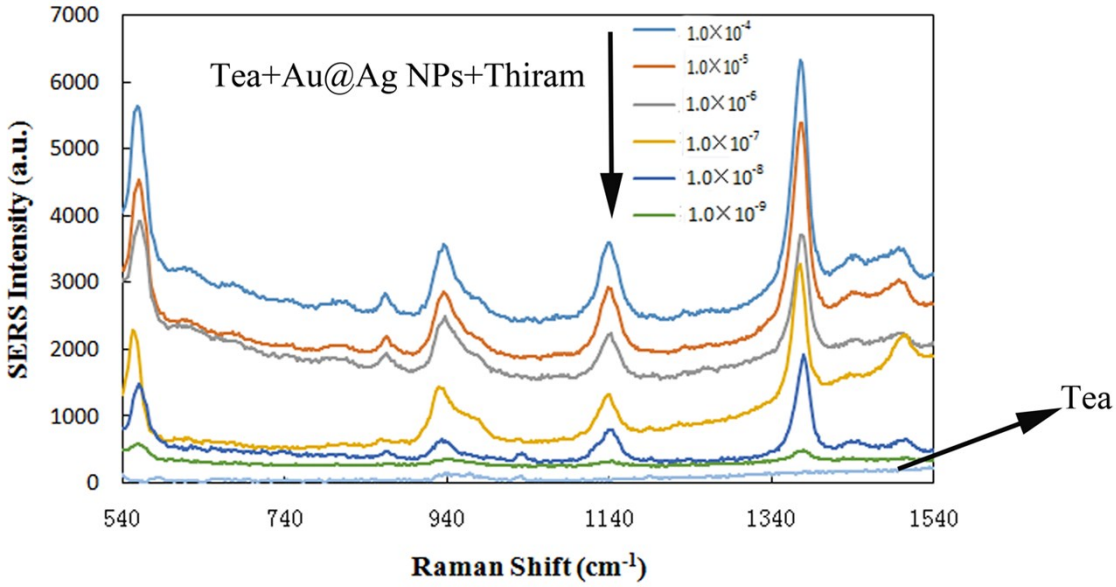

Fig. S5 The spectra of the tea, with and without thiram.

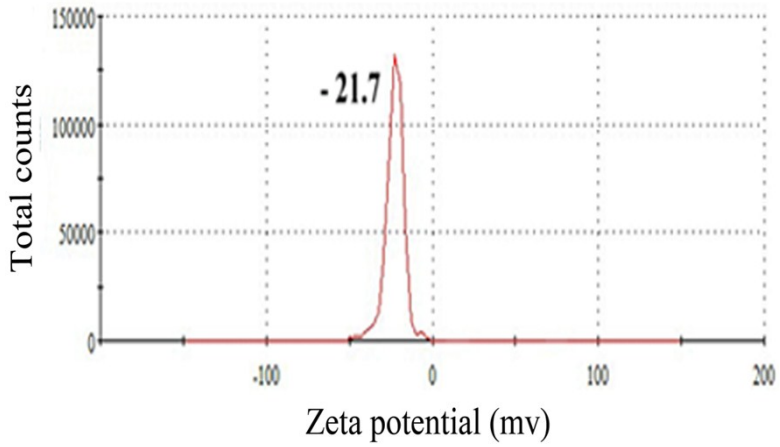

Fig. S6 The zeta potential value of Au@Ag NPs.

References

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2 Ruyan H., Weiting J., Xiaosan Q., Xiaohui W., Yu X., Xiaochun W., J. Agric & Food. Chem. 2013, 61(51), 12565–12571.