Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

A dual-functional PDMS-assisted paper-based SERS platform for reliable detection of thiram residue both on fruit surface and in juice

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EXPERIMENTAL

Materials

Cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC, 97%) and polyvinyl pyrrolidone (PVP) were purchased from Sigma-Aldrich, sodium borohydride ($NaBH_4$) and ascorbic acid (AA) were purchased from Acros Organics, silver nitrate ($AgNO_3$) and chloroauric acid ($HAuCl_4$) were purchased from Sinopharm Chemical Reagent Co. Ltd., dichloromethane (CH_2Cl_2) was purchased from Kermel and n-hexane was purchased from Tianjin Bodi Chemical Co., Ltd., crystal violet (CV) was purchased from Adamas Reagent Co., Ltd., filter papers were purchased from Whatman International Ltd Maidstone England, Polydimethylsiloxane (PDMS) was purchased from Dow Corning Co., Ltd., polymethyl methacrylate (PMMA), orange juice and orange were purchased from the local supermarket. Ultrapure water was obtained from a Milli-Q system in all experiments.

Synthesis of Au NBPs

Au NBP sample was prepared using the seed-mediated growth method, as described in previous works.[34] Twinned gold seeds were prepared via a thermal treatment procedure. Briefly, CTAC solution (5 mL 100 mM), $HAuCl_4$ solution (5 mL, 0.5 mM) and citric acid (0.5mL 100 mM) were added in a scintillation vial. Then, freshly prepared $NaBH_4$ (0.25 mL, 25 mM) was injected into the mixture under vigorous stirring at room temperature. After 2 minutes, the scintillation vial was closed and the seed solution was heated in an oil bath at 80 ℃ for 6 hours under gentle stirring. Finally, the thermally treated seed solution was removed from the bath and stored at room temperature. A growth solution was made by mixing together CTAB solution (100 mL, 100 mM), $HAuCl_4$ (2 mL, 25 mM), $AgNO_3$ (1 mL, 10 mM), HCl (2 mL, 1 M), and AA (0.8 mL, 100 mM). The twinned seed solution (1.25 mL) was injected into the growth solution under vigorous stirring. The reaction solution was left undisturbed for 2 hours at room temperature. The longitudinal plasmon wavelength of the obtained Au NBP sample was ~805 nm. The Au NBPs (~107 mL) were centrifuged at 9000 rpm for 15 min. The precipitate was redispersed in water (10 mL).

Synthesis of Au@Ag NRs

Au NBP solutions (1 mL) were added into CTAC solution (20 mL, 20 mM) at 65 °C under magnetic stirring, followed by subsequent addition and mixing of $AgNO_3$ (100 mM, 150 μL) and AA (100 mM, 1.5 mL). The mixture solution was kept for 4.5 h at 65 °C, during which Ag was overgrown on the Au NBPs to form Au@Ag NRs. The resultant samples were centrifuged for 15 min. The precipitate was redispersed in CTAC solution (20 mL, 1 mM) for further use.

Self-assembly of Au@Ag NRs monolayer film

The self-assembled process of monolayer film could refer to our previous works. Typically, the nanoparticles were centrifuged twice and re-dispersed into ethanol solution. Then a certain amount of water and CH_2Cl_2 were added to form a water-oil interface. Subsequently, Au@Ag NRs concentrated by 10 times dispersed in ethanol of 100 μL were added. After vigorous shocking, a small amount of n-hexane was added and a dense monolayer was slowly formed on the interface. Finally, the redundant n-hexane was removed slowly and gently by a pipette and then deposited on the filter paper.

Preparation of thiram spiked orange juice samples and thiram spiked orange surface

To prepare thiram standard solution, 0.024 g thiram powder was weighed and then dissolved it into 10 mL dimethylformamide. Aqueous solutions of thiram were prepared by diluting thiram standard solution with different proportions. To prepare spiked orange juice samples, the orange juice with pulp obtained from local market. Then 1 mL thiram aqueous solution with different concentrations was added to the 9 mL orange juice sample. Thus thiram spiked orange juice samples were obtained. The oranges were soaking for two hours in different concentrations of thiram solution, and then dried in an oven. Spraying a certain amount of ethanol on the orange surface is required before SERS detection, and then the sample was extracted by SERS platform.

Characterization and SERS measurement

UV-Vis spectroscopy was measured by a spectrophotometer (Model Lambdfca 750, Perkin Elmer, USA) and the spectra were detected between 300 nm and 1600 nm. Scanning electron microscopy (SEM) images were obtained by a microscopy (model S-4800, Hitachi, Japan) with an acceleration voltage of 5.0 kV. The Transmission electron microscope (TEM) images of the particles were taken by a JEM-2100 TEM instrument (JEOL, Japan). Raman spectra were collected using a portable compact laser Raman Spectrometer (BWS415-785H B&W Tek, Inc.). The excitation wavelength of the laser is 785 nm. The spot size of focus laser beam is 10 μm in diameter. The spectrum range of the spectrometer is 175 to 2700 cm^{-1} with a spectral resolution of better than 3 cm^{-1}. Boxcar averaging was used to smooth the raw spectrum and a baseline correction routine was performed to obtain the final spectrum with the background subtracted.

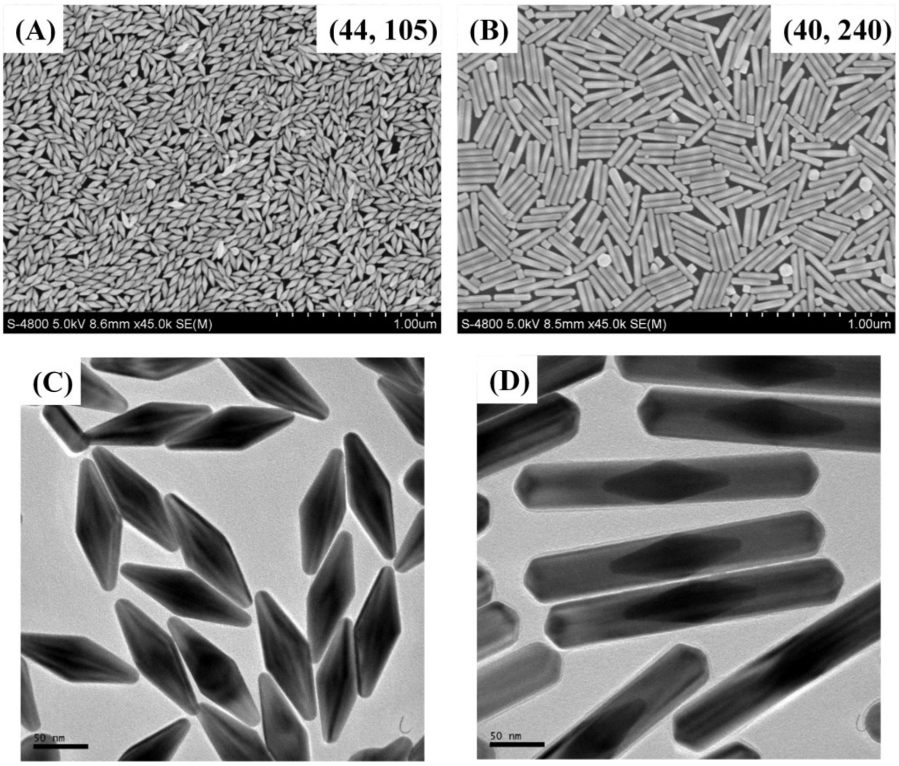

Fig. S1 (A) SEM image of Au NBPs; (B) SEM image of Au@Ag NRs; (C) TEM image of Au NBPs; (D) TEM image of Au@Ag NRs.

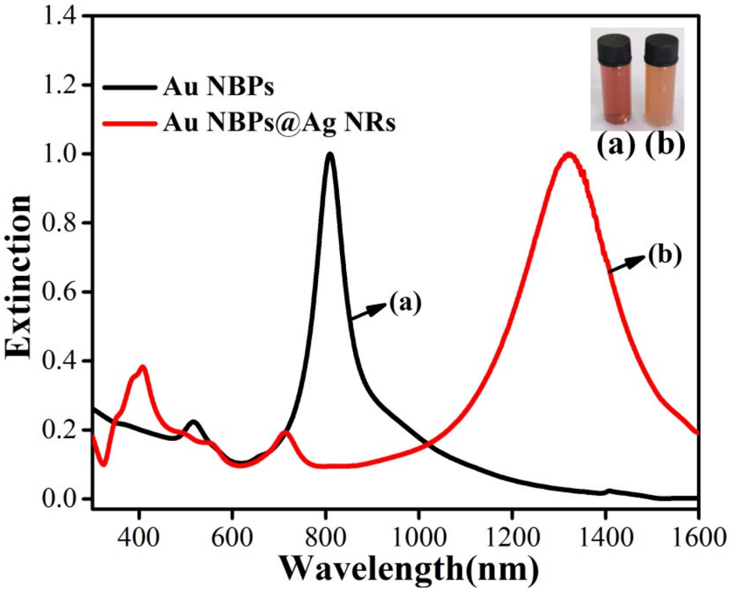

Fig. S2 Extinction spectrum of Au NBPs and Au@Ag NRs, inset: the photograph of Au NBP colloid and Au@Ag NRs colloid.

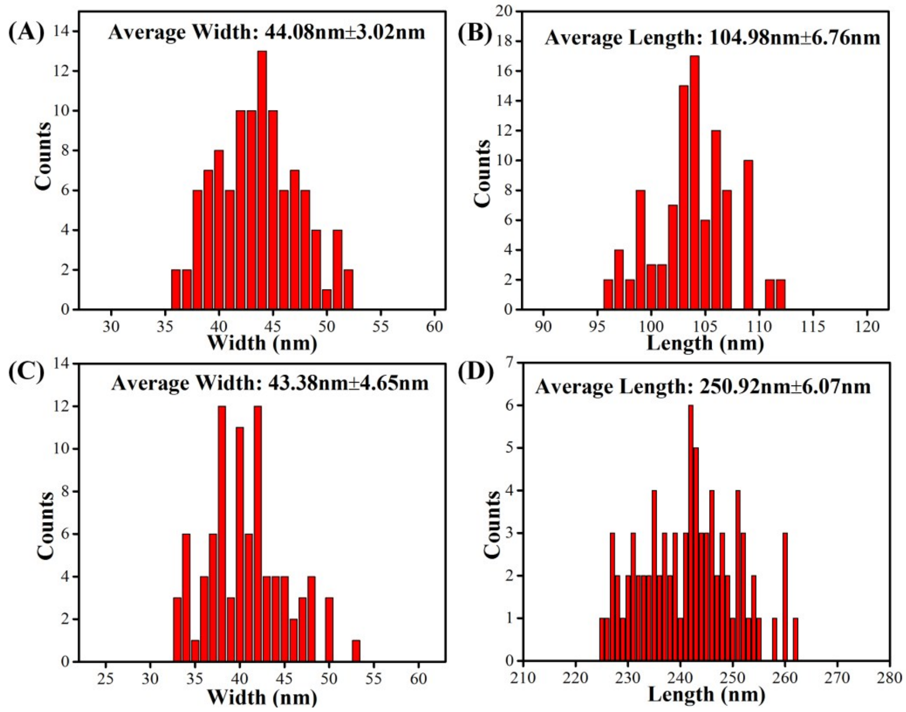

Fig. S3 The particle size distribution statistics results of width and length for core Au NBPs colliod (A) and (B); Au@Ag NRs colloid (C) and (D).

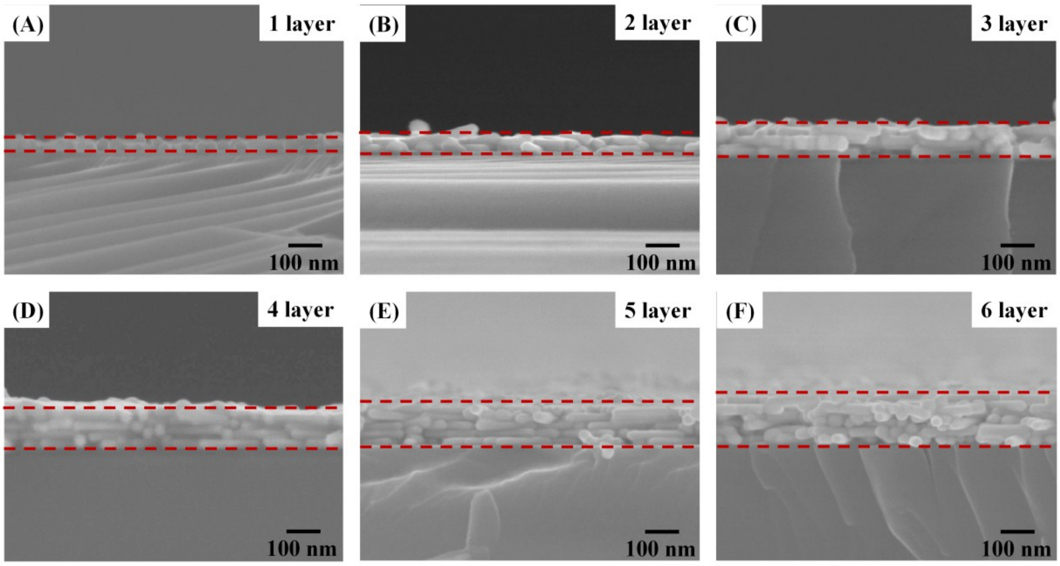

Fig. S4 Cross sectional SEM images of Au@Ag NRs self-assembly monolayer deposited on Si wafer with various layers from 1 to 6 in sectional view (A)~(F).

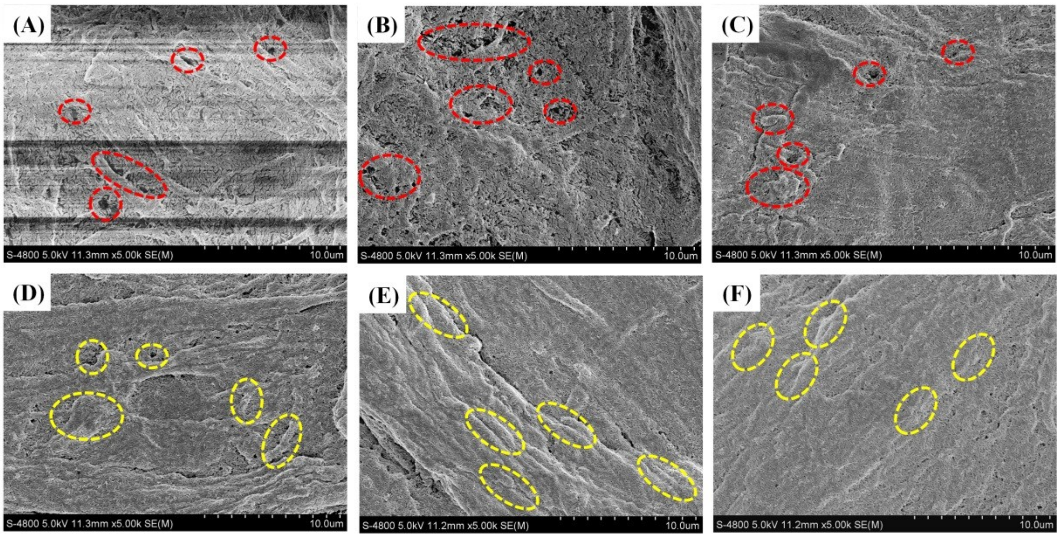

Fig. S5 SEM images of Au@Ag NRs self-assembly monolayer deposited on filter paper with various layers from 1 to 6 at low magnification (A)~(F).

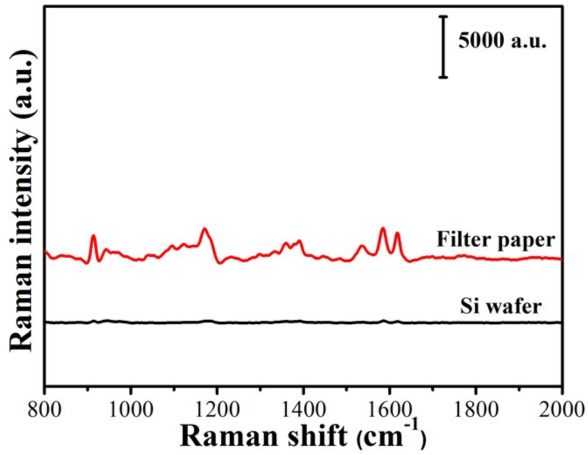

Fig. S6 Normal Raman spectra of CV based on blank Si wafer and filter paper. The laser power is 15% and the integration time is 10 s.

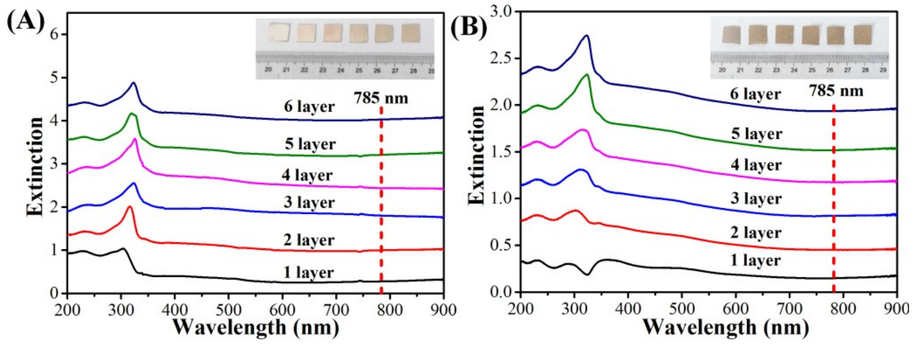

Fig. S7 The extinction spectra of the SERS substrates deposited on Si wafers (A) and filter paper (B) with different layers. Inset: the corresponding photography of Si wafer-based substrate and paper-based substrate with different layers of nanorods.

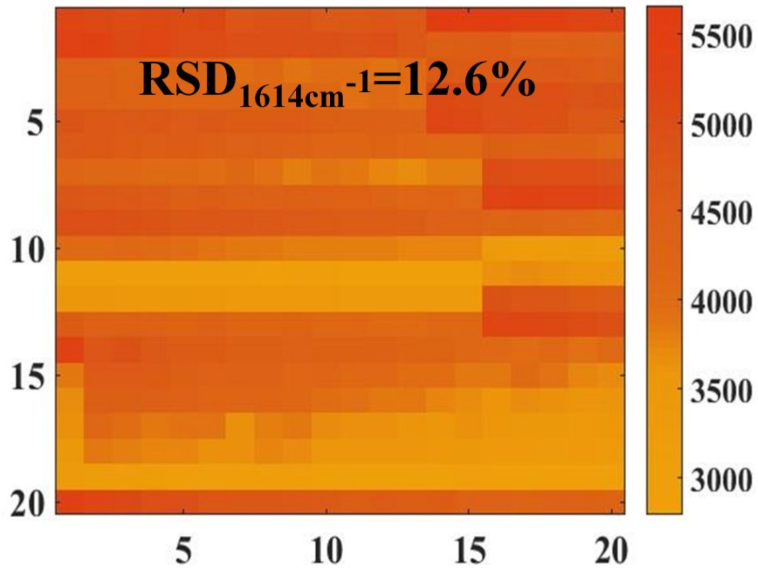

Fig. S8 SERS spectra of CV (10^{-5} M) aqueous solution based on paper-based sensor of 400 different points using the Au@Ag NRs monolayer deposited on filter paper. The laser power is 15% and the integration time is 10 s.

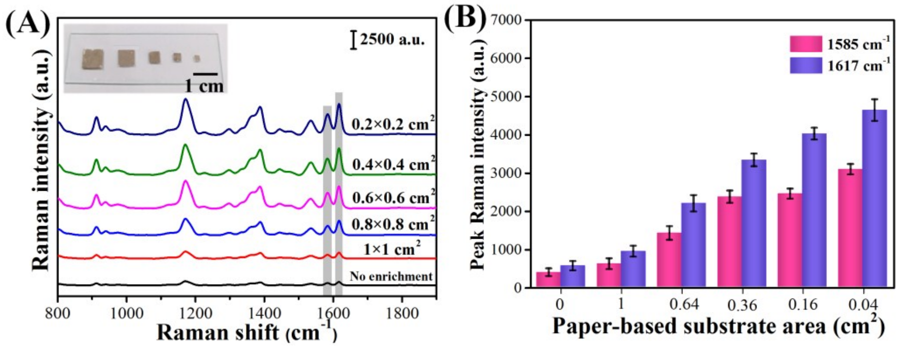

Fig. S9 (A) SERS spectra of CV with concentration of 10^{-5} M based on paper-based PDMS-assisted platform with various areas; (B) The corresponding SERS intensity of CV with concentration of 10^{-5} M based on paper-based PDMS-assisted platform with various areas.