Supporting Information

Highly Uniform and Optical Visualization SERS Substrate for Pesticide Analysis Based on Au Nanoparticles Grafted on Dendritic α-Fe_2O_3

Xianghu Tang,[a,b] Wenya Cai,[a,c] Liangbao Yang [a *] and Jinhuai Liu [a *]

1 Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei 230031, China

2 Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China

3 School of Chemistry and Chemical Engineering, Anhui University, Hefei, 230039, China

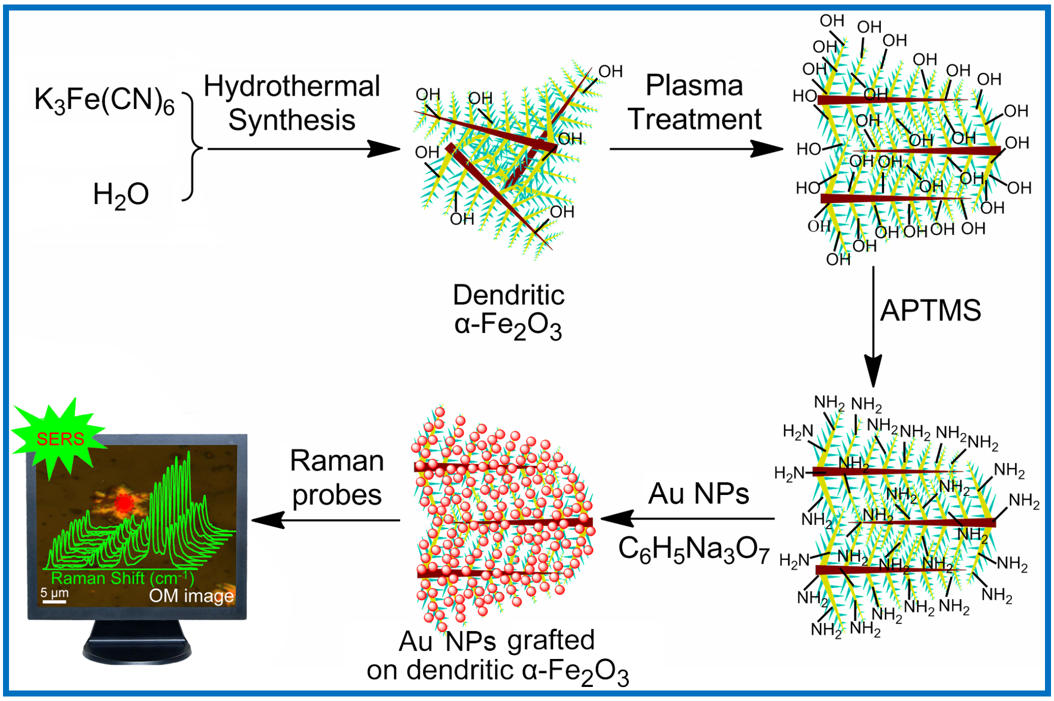

Fig.S1 Schematic diagram of the preparation process of Au Nanoparticles (NPs) grafted on dendritic α-Fe_2O_3 as SERS substrate. The dendritic α-Fe_2O_3 has been synthesized by hydrothermal method and significantly functionalized by plasma treatment. After APTMS has been added, the amine groups were introduced through reaction of APTMS with surface hydroxyls on the surface of dendritic α-Fe_2O_3 and then Au NPs were grafted on it. After that, the products were redispersed in 10 mL water with ultrasonication prior to further use for SERS substrates.

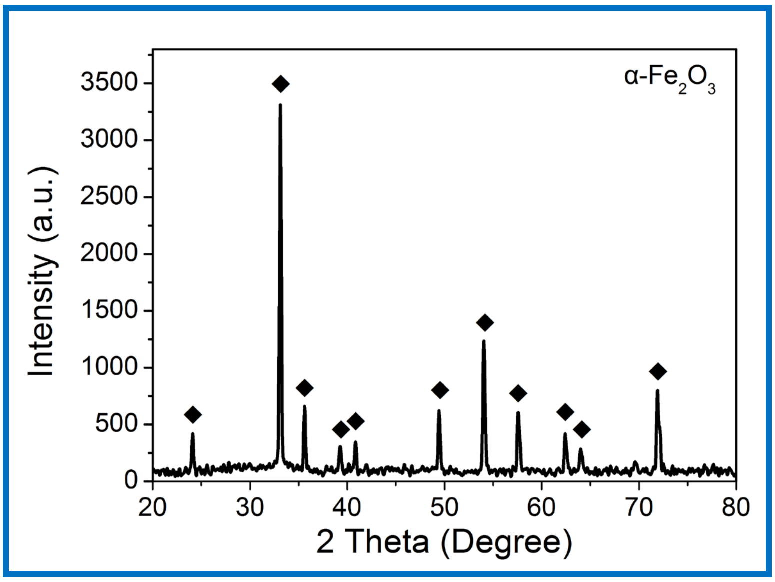

Fig.S2 XRD patterns of as-prepared dendritic α-Fe_2O_3. All of the diffraction peaks can be attributed to the α-Fe_2O_3 phase (JCPDS 33-0664) and the narrow sharp peaks suggest that the products are highly crystalline.

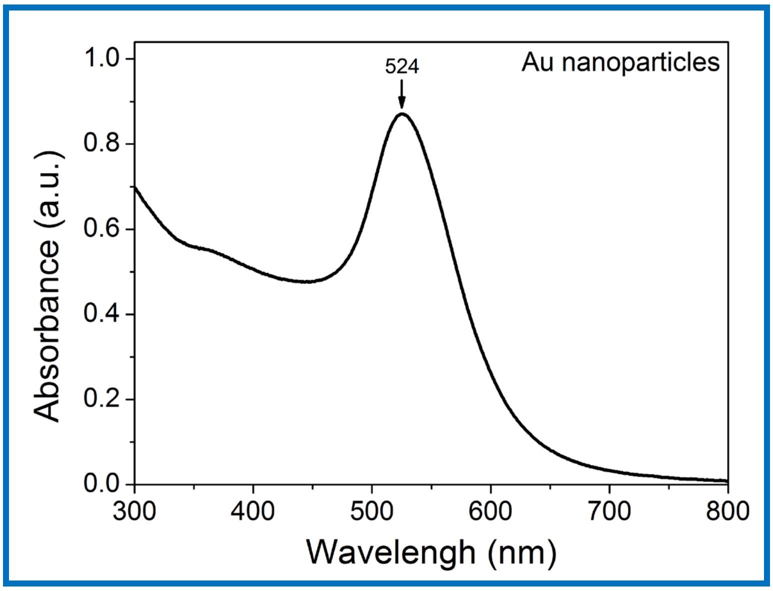

Fig.S3 UV–vis absorption spectra of Au Nanoparticles (NPs). An obvious surface plasmonic absorption band is found around 524 nm. This symmetrical absorption band signifies the narrow size distribution of Au NPs.

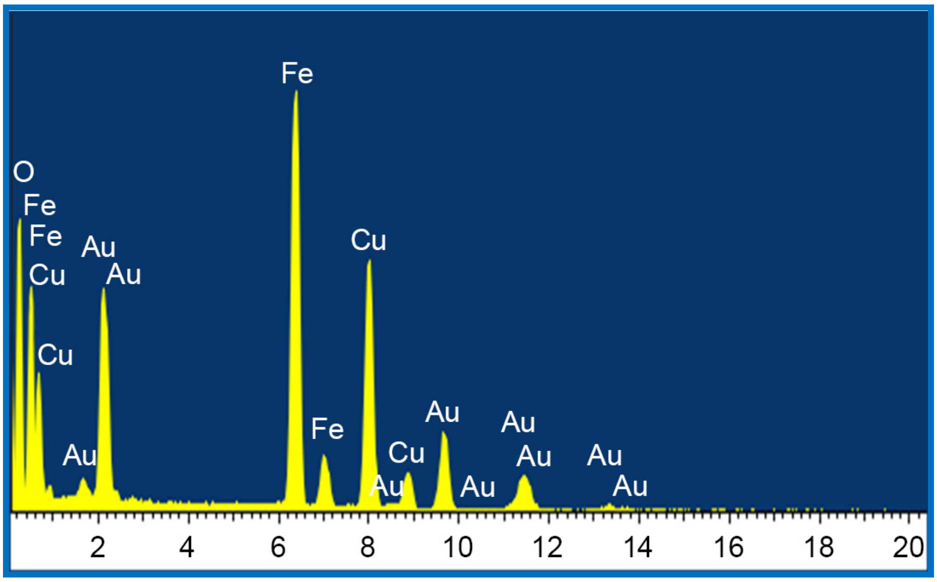

Fig.S4 EDS spectrum of NPGDF. It is indicated that as-prepared product consists of Fe, O and Au. As a note, the Cu element was detected in the sample originate from copper grids.

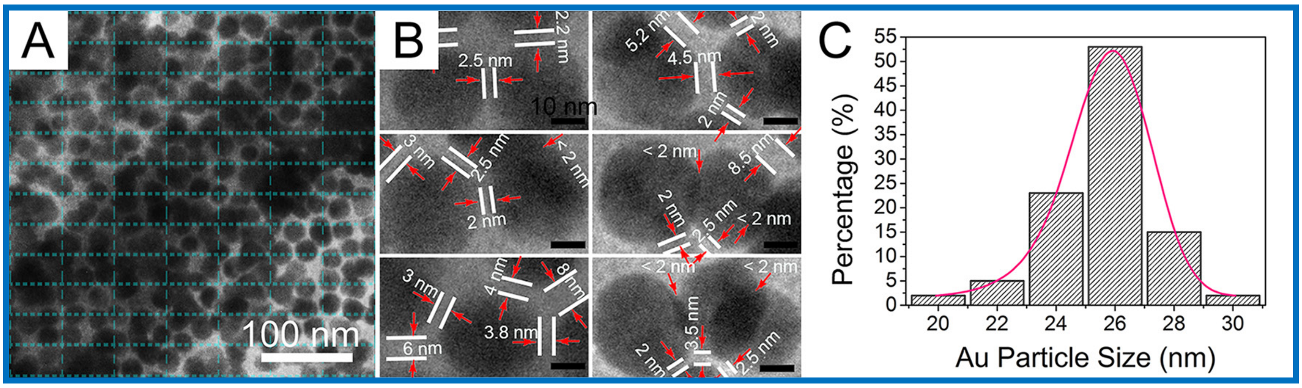

Fig.S5 (A) Typical TEM image of NPGDF. (B) Typical higher-magnification TEM images and the specific measurements of Au NPs size and gap distance distribution of interparticle separations. (C) Au NPs size distribution. Most NPs size were about 24~28 nm with narrow size distribution.

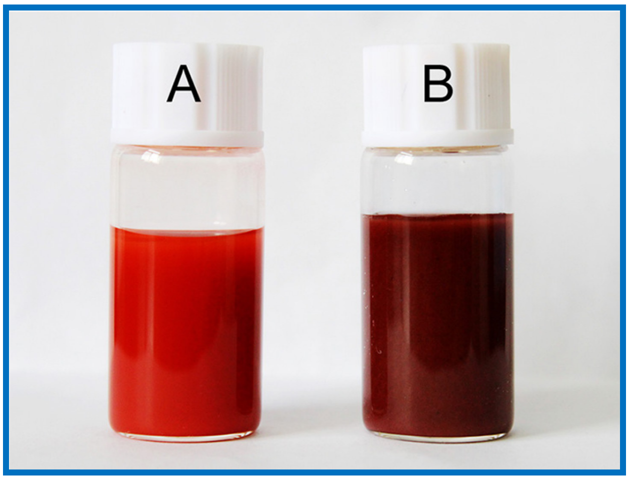

Fig.S6 Digital photos of suspension of (A) pure dendritic α-Fe_2O_3 and (B) Au NPs grafted on dendritic α-Fe_2O_3. It is indicated that, pure dendriticα-Fe_2O_3 is ferric oxide red while NPGDF is dark red.

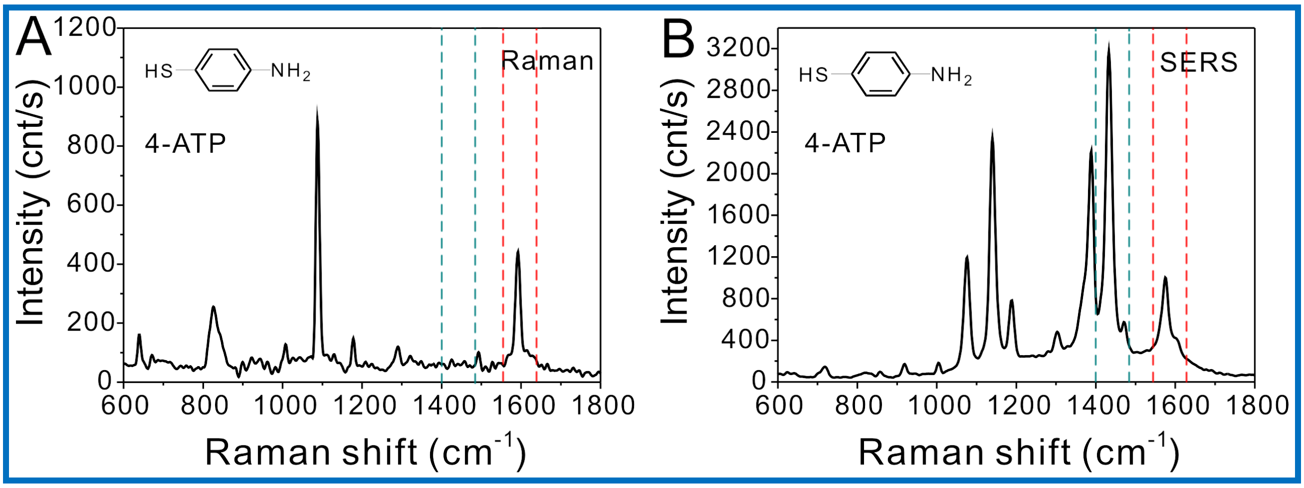

Fig.S7 (A) Raman spectrum of 4-ATP in the solid state. (B) SERS spectrum of 4-ATP obtained on NPGDF surface. SERS spectrum was carried out according to the literatures.[1, 2] For preparation of SERS samples, the 4-ATP molecules were assembled onto the surface of NPGDF by immersing the NPGDF into given concentration of 4-ATP solution for overnight to ensure the saturated coverage. Then the NPGDF was rinsed and centrifuged with ethanol to remove the physically adsorbed 4-ATP molecules. And finally, the Raman spectra were carried out. The laser beam was focused on the sample in a size of about 1.5 μm using a ×50 LMPLFLN microscope objective. The calculated value of N_{bulk} equals to 2.01×10^{11}, and N_{SERS} equals to 1.53×10^{7}. Based on the Raman intensity of the a1 vibration modes at 1576 cm^{-1} and b2 vibration modes at 1435 cm^{-1}, the EF for a1 and b2 vibration modes were calculated to be 3.1×10^{4} and 5.5×10^{5}, respectively.

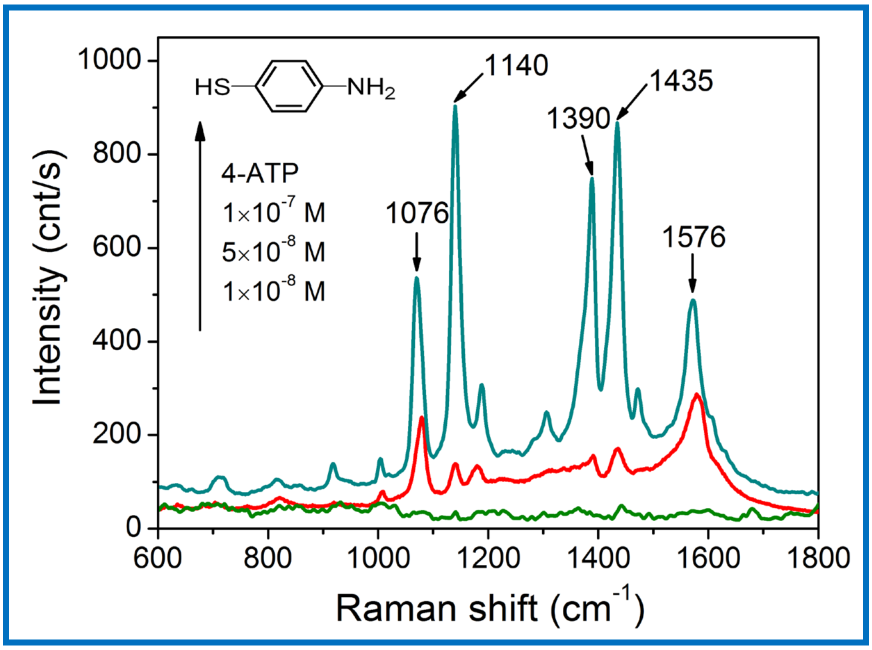

Fig.S8 Series of SERS spectra of 4-ATP with NPGDF as SERS substrates after storing at room temperature for three months.

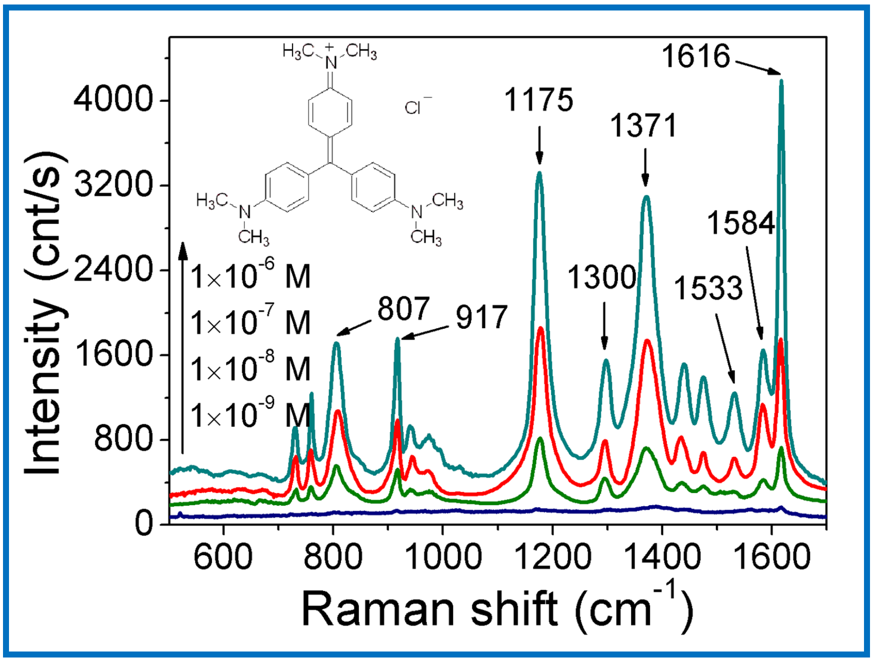

Fig.S9 Series of SERS spectra of CV at different concentrations with NPGDF as SERS substrates. The primary vibrations of CV are confirmed according to the literatures.[3, 4] The results clearly show that the determination capability of CV was below 1×10^{-8} M. That is, it verified further the high sensitivity of the NPGDF as substrate.

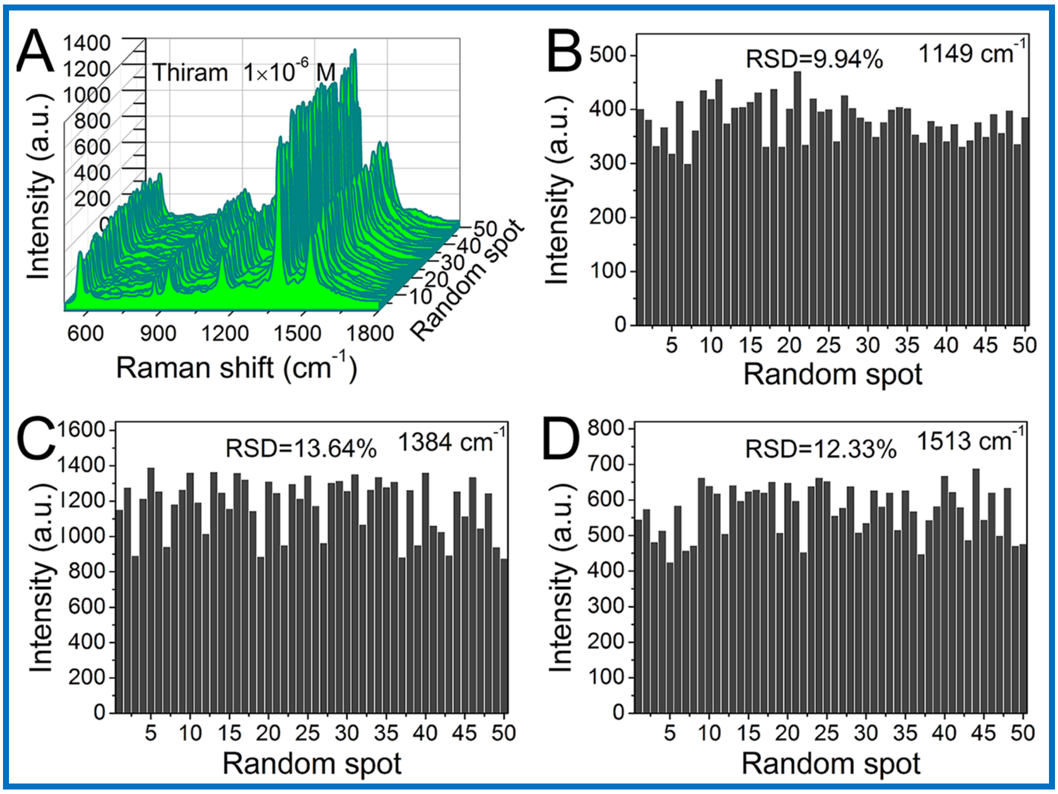

Fig.S10 (A) Series of SERS spectra of 10^{-6} M thiram collected on randomly from 50 spots of the NPGDF. (B), (C) and (D) are the intensities of the main vibrations of 10^{-6} M thiram for the 1149, 1384 and 1513 cm^{-1} corresponding to (A) respectively.

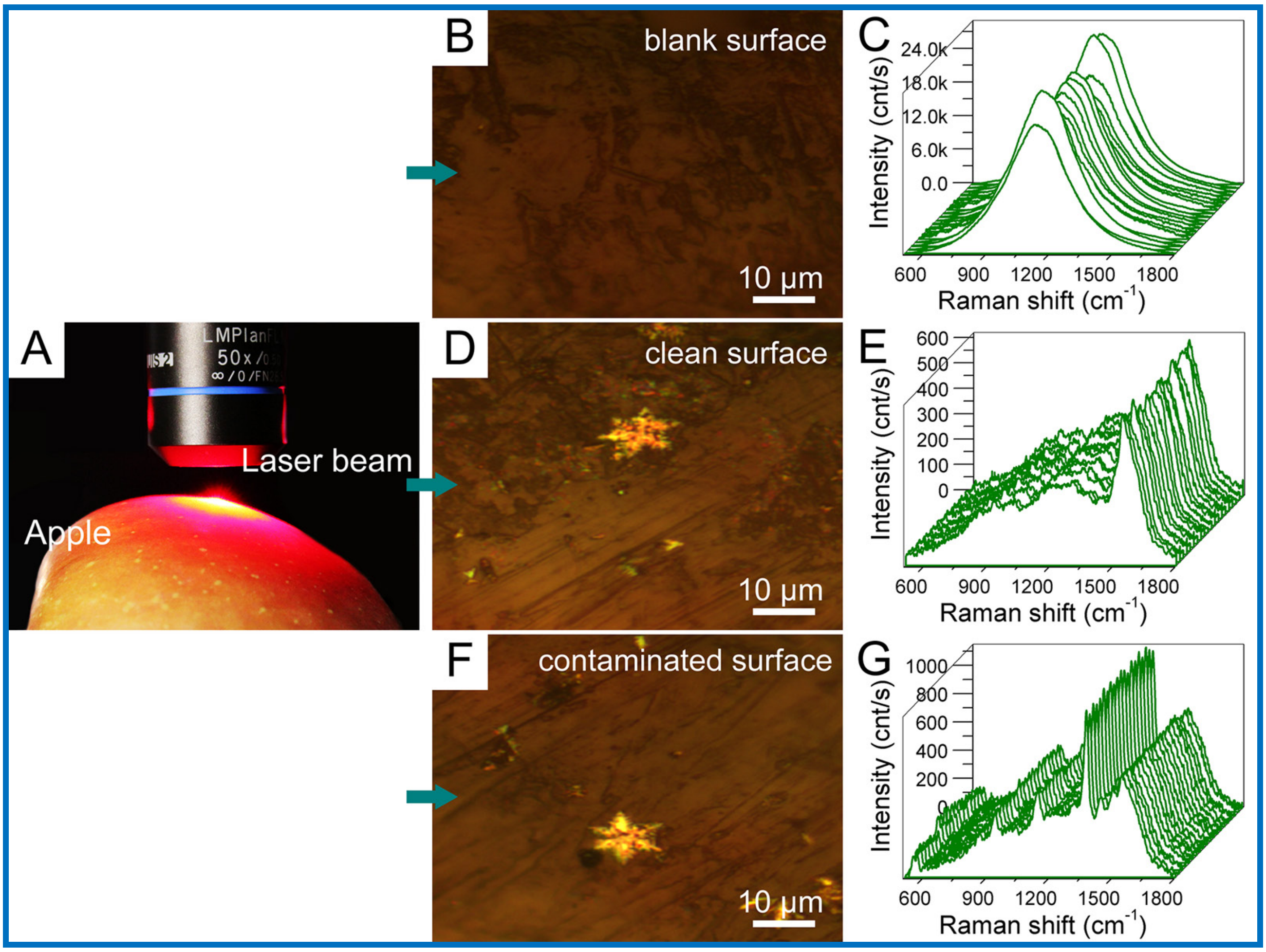

Fig.S11 In situ detection of thiram residues on apple peel. (A) OM platform of Raman spectroscope and sample of apple. (B) and (C) OM image and Raman spectra of blank surface of apple. In the absence of NPGDF, Raman spectra could not be obtained due to the very strong fluorescence of the apple peel. (D) and (E) OM image and Raman spectra of uncontaminated apple peel. SERS spectra and fluorescence of clean apple peel can be found. (F) and (G) OM image and Raman spectra of contaminated apple peel. It is also indicated that strong SERS spectra of thiram on contaminated apple peel were obtained reproducibility.

1. G. Hong, C. Li and L. Qi, *Adv. Funct. Mater.*, 2010, **20**, 3774-3783.
2. S. Tian, Q. Zhou, Z. Gu, X. Gu and J. Zheng, *Analyst*, 2013, **138**, 2604-2612.
3. S. L. Kleinman, E. Ringe, N. Valley, K. L. Wustholz, E. Phillips, K. A. Scheidt, G. C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, 2011, **133**, 4115-4122.
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