

**Synergistic action of star-shaped Au/Ag nanoparticles decorated on AgFeO<sub>2</sub> for ultrasensitive SERS detection of chemical warfare agent on real samples**

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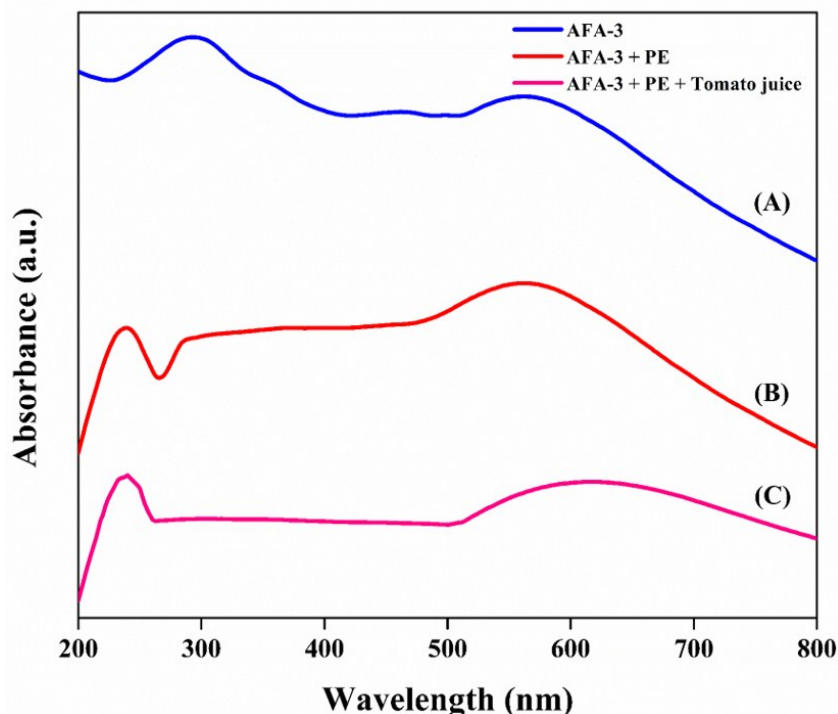
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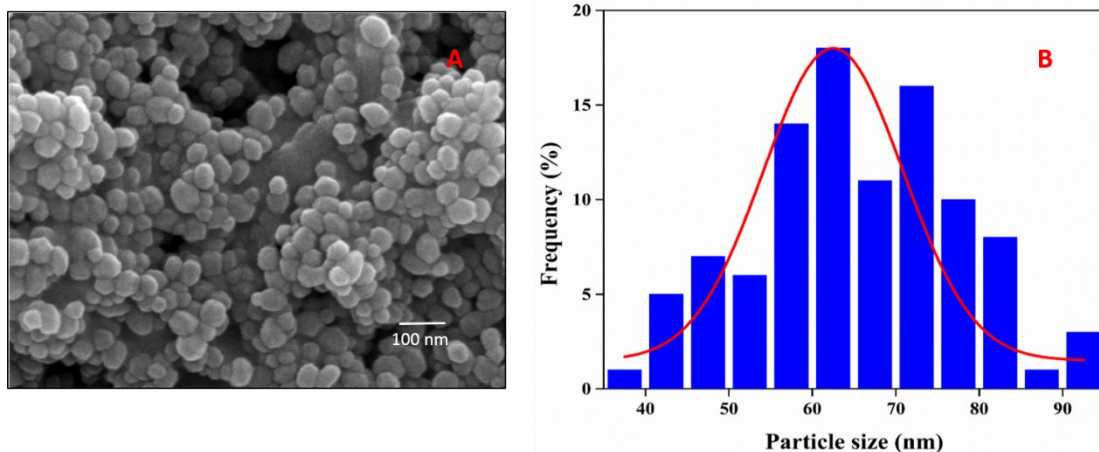
## UV-Visible spectroscopy



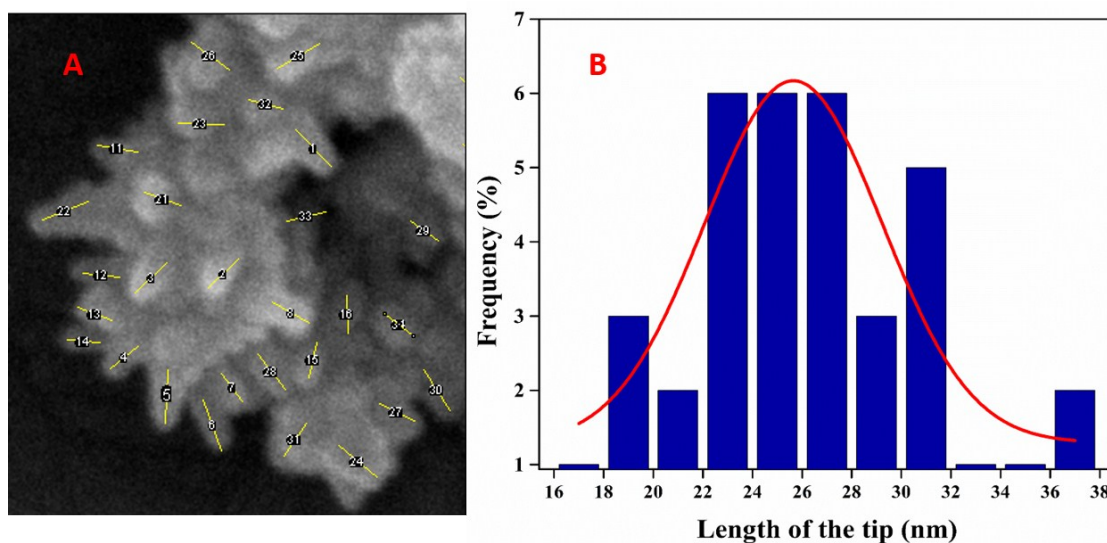
**Figure S1.** UV-Vis absorbance spectra of (A) AFA-3 (B) AFA-3 + PE (C) (AFA-3) + (tomato juice) + PE.

The degree of aggregation for the PE addition and the PE/tomato addition was analyzed using UV-vis absorbance spectroscopy, as shown in Fig. S1. The size, shape and nature of aggregation can be estimated from the surface plasmon resonance bands. Addition of PE in the mixture of  $\text{AgFeO}_2@Au/Ag$  NPs (AFA-3) induces an increase in dielectric constant around the nanoparticles, which shifts the absorbance peak to the longer wavelength. The aggregation will lead to the broadening and the reduction of peak absorbance. The red shift of broad band absorbance peak from 587 nm to 597 nm has been observed. It indicates the typical aggregation behavior of PE with AFA-3, where the PE molecules attach to the AFA-3 nanoparticles to form aggregates. The broad band absorbance around 297 nm has also diminished. The rise in the absorbance peak around 245 nm is due to the PE molecules. The addition of tomato juice with PE to the AFA-3 substrate still shows greater aggregation, which is revealed by the red shift of absorbance peak from 597 nm to 620 nm and a decrease in the absorbance peak around 297 nm.

## Particle size analysis

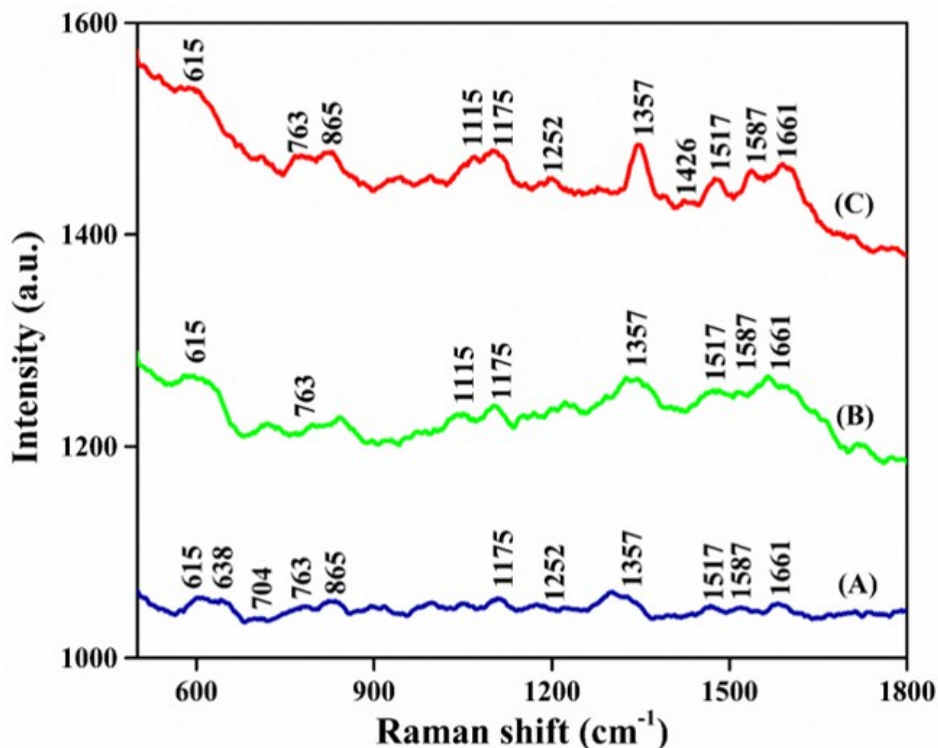


**Figure S2.** (A) FE-SEM image of AgFeO<sub>2</sub> (B) particle size distribution of AgFeO<sub>2</sub>.



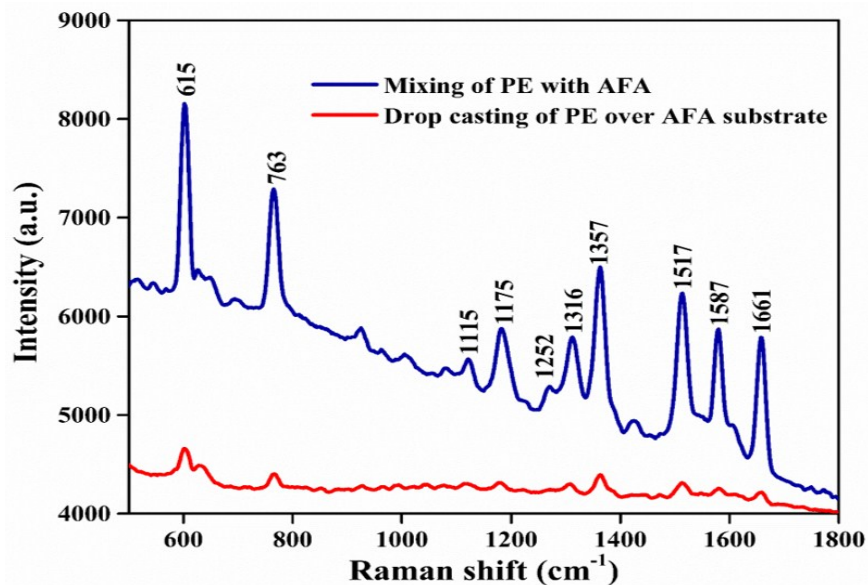
**Figure S3.** (A) FE-SEM image of Au/Ag NPs and (B) particle size distribution of Au/Ag NPs.

The analysis of particle size distribution displays that the mean sizes of AgFeO<sub>2</sub> and Au/Ag NPs were  $62.5 \pm 9.85$  nm and  $25.6 \pm 3.57$  nm, respectively.

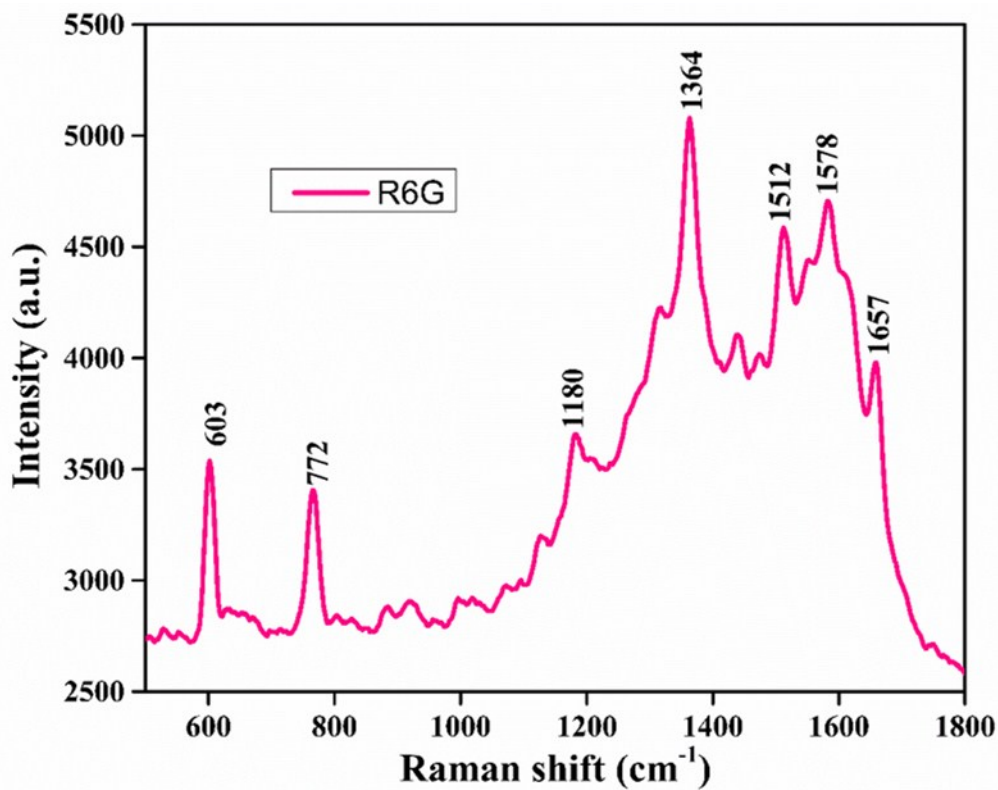


**Figure S4.** SERS spectra of PE ( $10^{-5}$  M) adsorbed on (A) AgFeO<sub>2</sub>, (B) Au/Ag NPs, and (C) AgFeO<sub>2</sub>@Au/Ag NPs (AFA-1).

The intensities of characteristic Raman peaks are compared at 1175, 1357, 1517, 1587 and 1661 cm<sup>-1</sup>. The Au/Ag NPs show relatively higher performance compared with the pure AgFeO<sub>2</sub>, but lower SERS intensity compared with the AgFeO<sub>2</sub>@Au/Ag NPs. For the AFA-1 substrate, the intensities of Raman band centered at 615, 763, 1175, 1357, 1517, 1587 and 1661 cm<sup>-1</sup> have been boosted with the addition of Au/Ag NPs.

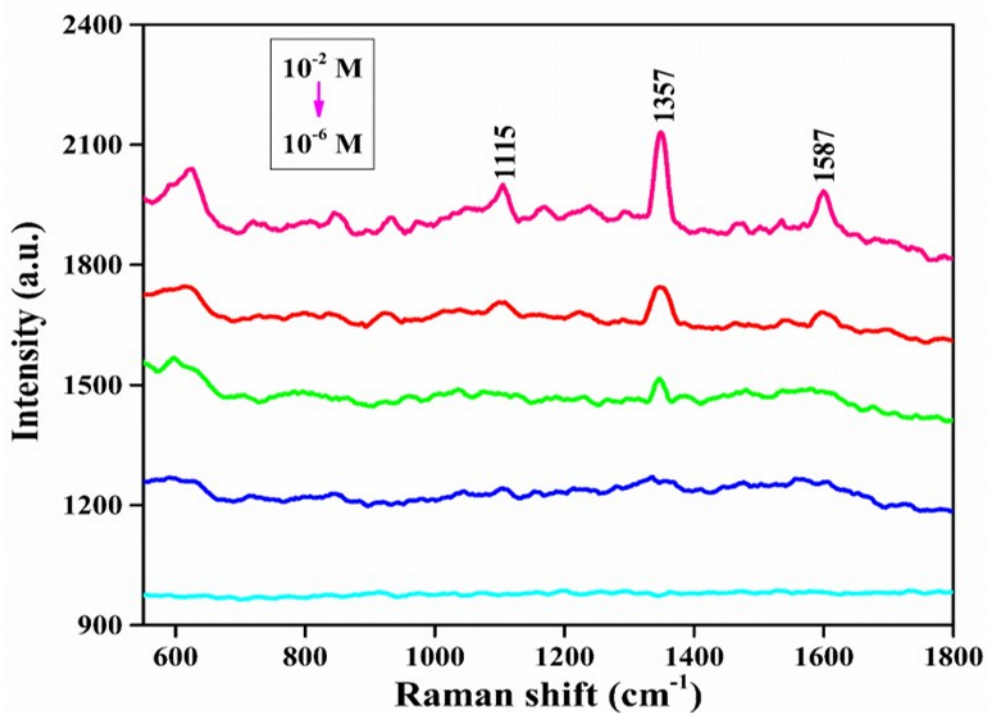


**Figure S5.** Comparison of SERS spectra of PE ( $10^{-2}$  M) by the methods of the PE/AFA pre-mixing and the PE post-dropping on the AFA substrate.

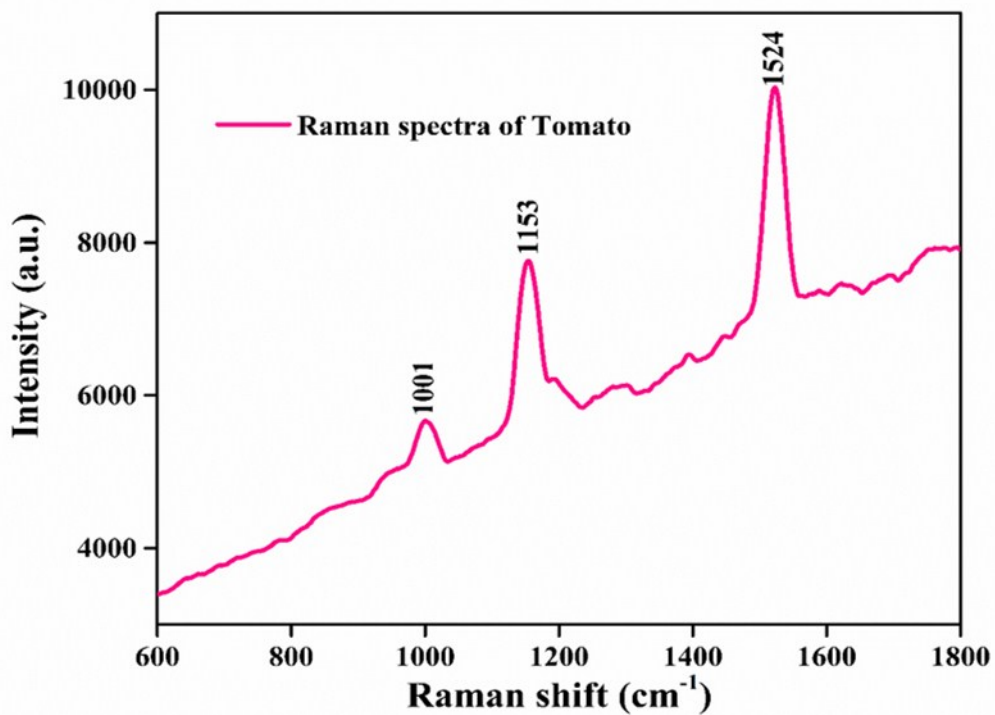


**Figure S6.** SERS spectra of R6G ( $10^{-2}$  M) using the AFA-3 substrate.

The Raman bands at 603, 772, and 1180  $\text{cm}^{-1}$  are associated with the C-C-C in-plane vibration, the out of plane C-H bending vibration and the C-C stretching mode, respectively. The intense peaks of R6G at 1364, 1512, 1578, and 1657  $\text{cm}^{-1}$  are associated with the C-C ring stretching vibration and the phenyl ring vibration. The Raman peak at 1431  $\text{cm}^{-1}$  is associated with the C-H bending mode. These results confirm the ability of AFA-3 substrate to enhance the intensity of Raman signal of PE as well as R6G.



**Figure S7.** SERS spectra of PE with different concentrations from  $10^{-2}$  M to  $10^{-6}$  M adsorbed on Au/Ag NPs.



**Figure S8.** SERS spectra of tomato juice.

The Raman peaks centered at 1001, 1153 and 1524 cm<sup>-1</sup> are mainly associated with the in-plane rocking mode of CH<sub>3</sub> group in polyene chain and coupled with C-C band, stretching vibration of C=C band, stretching vibration of C-C band in  $\beta$  carotene or lycopene in tomato.