## Polymer induced one-step interfacial self-assembly method for the fabrication of flexible, robust and free-standing SERS substrates for rapid on-site detection of pesticide residues

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## **EF** calculation

Enhanced factor was calculated by the equation as below:

$$EF = \frac{I_{SER} / N_{SER}}{I_{NRS} / N_{NRS}} \approx \frac{cN_A \sigma h I_{SER}}{RI_{NRS}}$$

where *c* is the concentration of 4-ATP in ethanol,  $N_A$  is the Avogadro constant,  $\sigma$  is the surface area occupied by an adsorbed 4-ATP molecule, and *R* is the roughness factor of the AuNPs/PVC film, h is the effective waist. In this work, *c* is 0.01 mol·L<sup>-1</sup>,  $N_A$  is 6.02×10<sup>23</sup> mol<sup>-1</sup>,  $\sigma$  is 0.2 nm<sup>2</sup>, *h* is 60 µm, *R* is 2, the calculated result was 3.7×10<sup>6</sup>.



Fig. S1 Raman spectra of AuNPs/PVC films labelled by 4-ATP probe molecules under 785, 633, 532 nm laser radiation as the excitation sources. (a) The AuNPs<sub>20</sub>/PVC film and (b) the AuNPs<sub>50</sub>/PVC film. The intensity has been normalized due to different laser power.



**Fig. S2** SEM images of the section of AuNPs/PVC films with different PVC content. (a) 1.2 mg/cm<sup>2</sup>, (b) 3.1 mg/cm<sup>2</sup>, (c) 6.2 mg/cm<sup>2</sup>, (d) 12.4 mg/cm<sup>2</sup>.



**Fig. S3** a) Raman spectra of 4-ATP detected by AuNPs/PVC film in the front and back side. Front side was full of assembled AuNPs, back side was the PVC template. b) UV-vis spectrum of 6.2 mg/cm<sup>2</sup> PVC film. c) Raman spectrum of PVC template. d) Raman spectrum of the AuNPs/PVC film. Laser wavelength =785 nm; laser power = 0.27 mW; integration time = 5 s.



**Fig. S4** FDTD simulated intensity distribution of electrical field for the AuNPs/PVC film irradiated by 785 nm laser light.



**Fig. S5** SERS signals of the AuNPs/PVC film after different time plasma treatment. Experimental conditions: Laser wavelength = 785 nm; laser power = 0.27 mW; integration time = 5 s.



**Fig. S6** SERS spectra of 4-ATP collected from the freshly prepared AuNPs/PVC film (black) and the same substrate after 3 months storage (red, dashed). Experimental conditions: Laser wavelength = nm; laser power = 0.27 mW; integration time = 5 s.