## **Electronic Supplemental Information**

## In situ SERS study of surface plasmon induced nitration on Ag@Polydopamine@Au structure

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## **ADDITIONAL FIGURES**



Fig. S1. SEM images of the Ag particles after direct reacting with HAuCl<sub>4</sub> for 10 min (up) and 30 min (down).



Fig. S2. SEM image of the Ag@PDA particles after reacting with HAuCl<sub>4</sub>, before washing with ammonia solution.



**Fig. S3.** SEM images of the as-prepared Ag@PDA@Au particles under different magnifications. These particles can be easily dispersed evenly on substrates, making the single particle SERS technique possible.



**Fig. S4.** Extinction spectra of Ag, Ag@PDA, and Ag@PDA@Au particles. The peak located around 510 nm indicates the successful decoration of 10-20 nm Au nanoparticles.



Fig. S5. Extinction spectrum of meatball-like Au particles in cyclohexane.



Fig. S6. XRD pattern of the as-prepared meatball-like Au particles.



Fig. S7. SERS spectrum of 10-8 M benzenethiol (BT) on the as-prpeared Ag@PDA particles.



Fig. S8. SERS spectrum of  $10^{-8}$  M benzenethiol (BT) on the as-prpeared Ag@PDA@Au particles.



**Fig. S9.** SERS spectra of a mixture of benzenethiol (BT) and HNO<sub>3</sub> on the Ag@PDA@Au particles in dark for different time periods. It can be seen that no nitration (-NO<sub>2</sub> peak at 1330 cm<sup>-1</sup>) happened in the dark environment.



**Fig. S10.** SERS spectra obtained by heating a mixture of benzenethiol (BT) and HNO<sub>3</sub> with the presence of Ag@PDA@Au particles at different temperatures for 10 min.



**Fig. S11.** SERS spectra obtained by heating a mixture of benzenethiol (BT) and HNO<sub>3</sub> with the presence of Ag@PDA@Au particles at 65 °C for different time periods.



**Fig. S12.** SERS spectra obtained by heating a mixture of benzenethiol (BT) and HNO<sub>3</sub> without the presence of Ag@PDA@Au particles at 65 °C for different time periods.



Fig. S13. Time-dependent SERS spectra showing the reaction of benzenethiol and nitric acid on a single Au hierarchical particle, with a laser wavelength of 633 nm and power of 54  $\mu$ W. Spectra were recorded every 2 min under continuous laser irradiation.



Fig. S14. Time-dependent SERS spectra showing the reaction of benzenethiol and nitric acid on a single Ag hierarchical particle, with a laser wavelength of 633 nm and power of 54  $\mu$ W. Spectra were recorded every 5 min under continuous laser irradiation.