Supporting Information

Polyethylenimine-interlayered core-shell-satellite 3D magnetic microspheres as versatile SERS substrate

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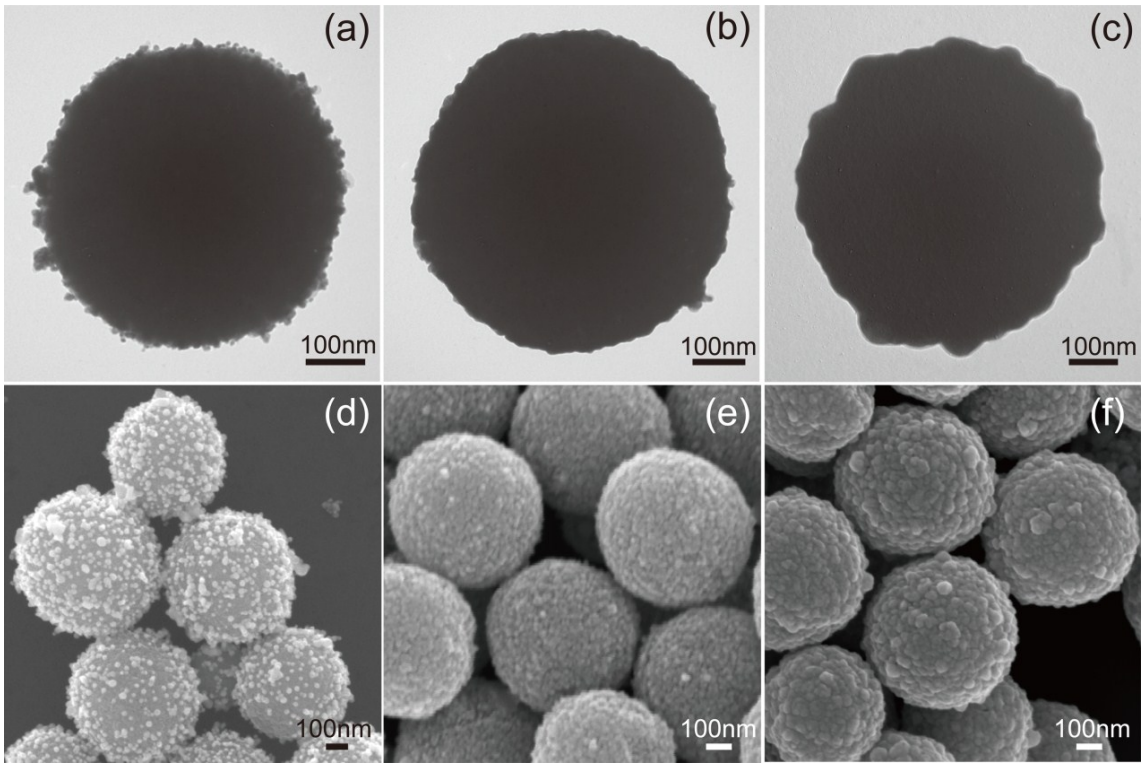

Figure S1. TEM images of Fe_3O_4@Ag microspheres synthesized with different concentration of $AgNO_3$: (a) 0.05 mM, (b) 0.1 mM, (c) 0.2 mM and their corresponding SEM images (d), (e), and (f), respectively.

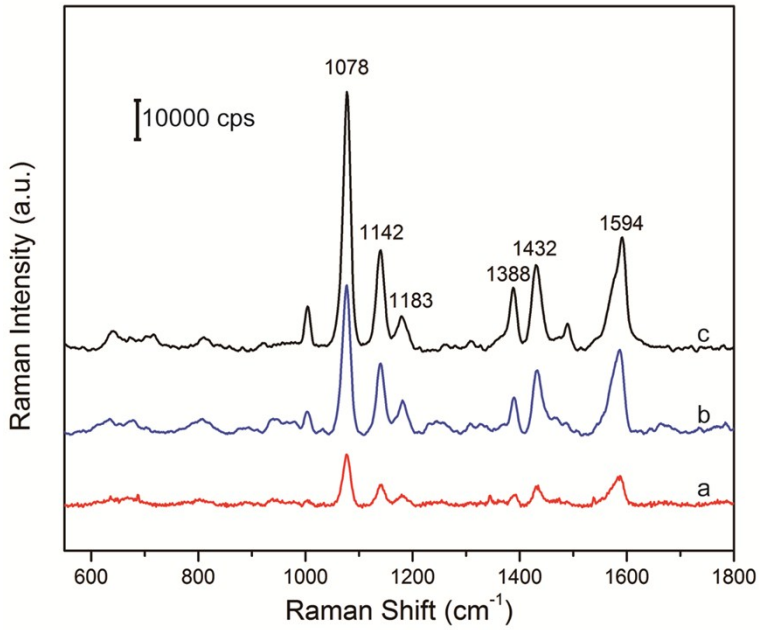

Figure S2. SERS spectra of 10^{-5} M PATP absorbed on Fe_3O_4@Ag microspheres prepared at following concentrations of $AgNO_3$: a- 0.05 mM, b- 0.1 mM, and c- 0.2 mM.

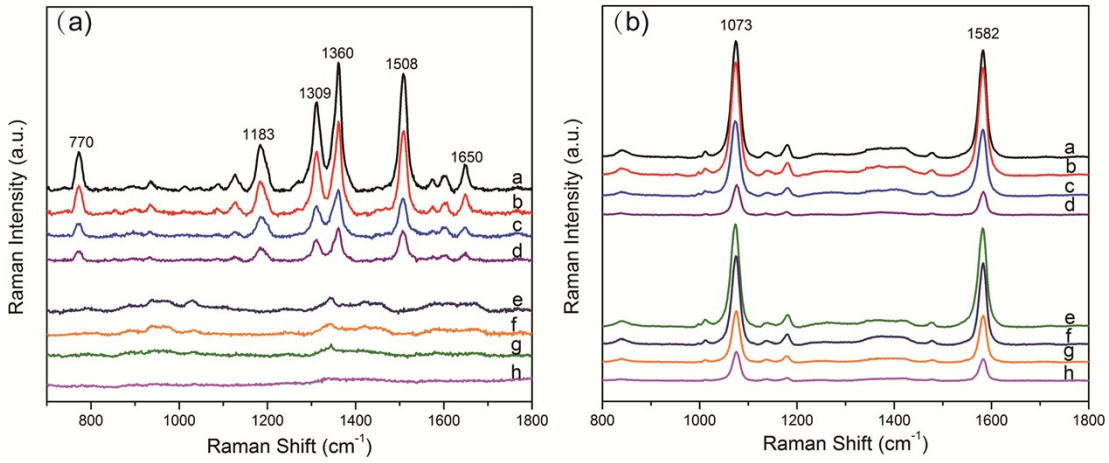

Figure S3(a) Comparison of the SERS spectra of the R6G solution (10^{-5} M) from the Fe3O4@Ag microspheres with different thinkness PEI interlayer: a- 0 nm, b-1.5 nm, c- 8 nm, d- 18nm, and their corresponding SERS spectra (e-h) with ethanol wash three times. **S3(b)** Comparison of the SERS spectra of the 4-MBA solution (10^{-5} M) from the Fe3O4@Ag microspheres with different thinkness PEI interlayer: a- 0 nm, b-1.5 nm, c- 8 nm, d- 18nm, and their corresponding SERS spectra (e-h) with ethanol wash three times. The spectra were recorded in the same way, and have been offset vertically for visualization

Normal Raman	SERS Signal In 785 nm	assignments
391	--	$\delta CS,(a_1)$
463	--	$\gamma CCC,7a(a_1)$
634	--	$\gamma CCC,12(a_1)$
1004	1005	$\delta CC+\gamma CCC,18a(a_1)$
1076	1076	$\upsilon CS,7a(a_1)$
1140	1142	$\delta CH,9b(b_2)$
1172	1172	$\delta CH,9a(a_1)$
	1392	$\upsilon CS_+\delta CH,14b(b_2)$
	1439	$\upsilon CS_+\delta CH,(3b_2)$
1482	1475	$\upsilon CS_+\delta CH,19a(a_1)$
1586	1578	$\upsilon CC,8a(a_1)$

Table. S1 Raman peaks of PATP and according assignments.

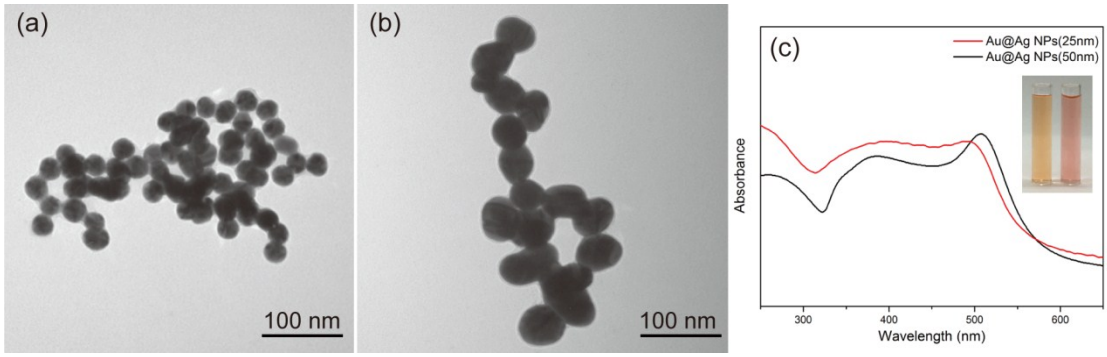

Figure S4. Characterization of the synthesized Au@Ag NPs. (a) TEM images of 25nm Au@Ag NPs, (b) TEM images of 50 nm Au@Ag NPs and (c) UV-visible spectra of the two Au@Ag NRs. The inset shows the photograph of 25nm Au@Ag NRs (right) and 50 nm Au@Ag NRs (left).

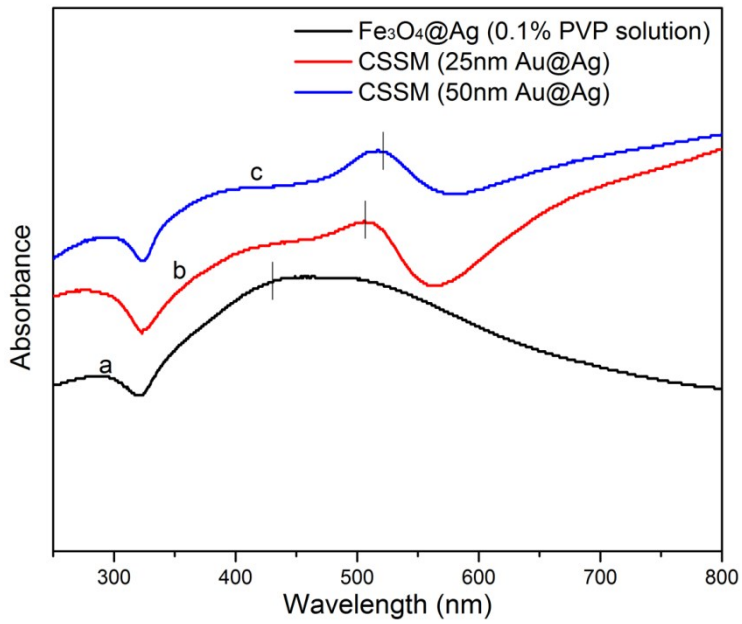

Figure S5. UV-vis spectra of a- Fe3O4@Ag microspheres in 0.1% PVP water solution, b- CSSM (25nm Au@Ag) and c- CSSM (50nm Au@Ag) in water solution.

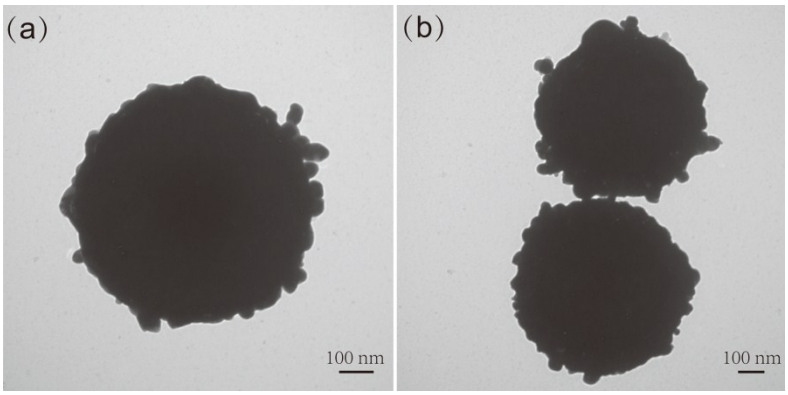

Figure S6. TEM images of (a) Fe_3O_4@Ag-PEI-60nm Au@Ag CSSM, (b) 70nm Au@Ag CSSM. Sparse satellites were observed on the surface of Fe_3O_4@Ag microspheres, suggesting the Au@Ag NPs larger than 55 nm could not assemble uniformly.

S7 EF calculation:

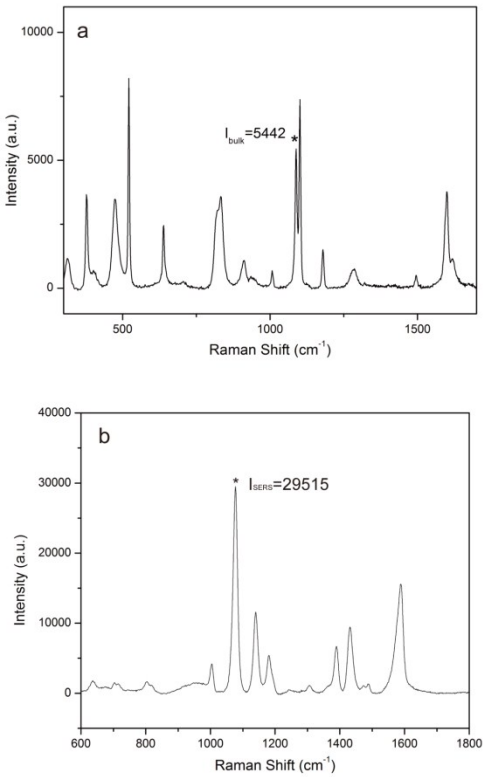

Figure S7 (a) Raman spectrum of pure PATP. (b) SERS spectrum of PATP with a concentration of 10^{-9}M.

The SERS enhancement factor (EF) was defined as $EF=(I_{SERS}/I_{bulk})(N_{bulk}/N_{SERS})$, whereas N_{bulk} and N_{SERS} is the number of molecules contributed to the Raman and SERS signal, respectively, and I_{SERS} and I_{bulk} is the respective signal intensity of the related peaks. From the obtained SERS spectra of PATP and Raman spectra of solid PATP on Si substrate, the I_{SERS}/I_{bulk} is 5.42. The number of PATP molecules in Raman stimulation, $N_{bulk} = \pi(d/2)^2h\rho_0N_A/M_0$. ρ_0 (1.18 g/mL) and M_0 (125.19 g/mol) is the density and molar mass of melted PATP, respectively. Besides, the penetration depth of laser h is measured to be 460 μm. N_{bulk} is calculated equal to 2.26×10^{19}. As for N_{SERS} calculation, the following procedure was used, 0.2 mg Fe_3O_4@Ag-PEI-50nm Au@Ag CSSM were added to 1 mL ethanol solution of the PATP at the concentration of 10^{-9} M, after vigorous sonication for 15 min, the CSSM were separated from the solution by a magnet, and then the precipitate was transferred onto a clean Si wafer, and analyzed with the Raman spectrometer. Therefore, it could be calculated by $N_{SERS}=c \times V \times N_A$, where c and V is the concentration and the volume of the PATP solution respectively. N_{SERS} is calculated equal to 6.02×10^{11}. Therefore, the N_{bulk}/N_{SERS} is calculated equal to 3.75×10^7. Finally, the EF value of peaks at 1078 cm^{-1} is calculated to be about 2.03×10^8.