Electronic Supplementary Material (ESI) for Sensors & Diagnostics.

Supplementary Information

Magneto-plasmonic bionanocomposites for on site SERS detection of water contaminants

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A. Calibration curves

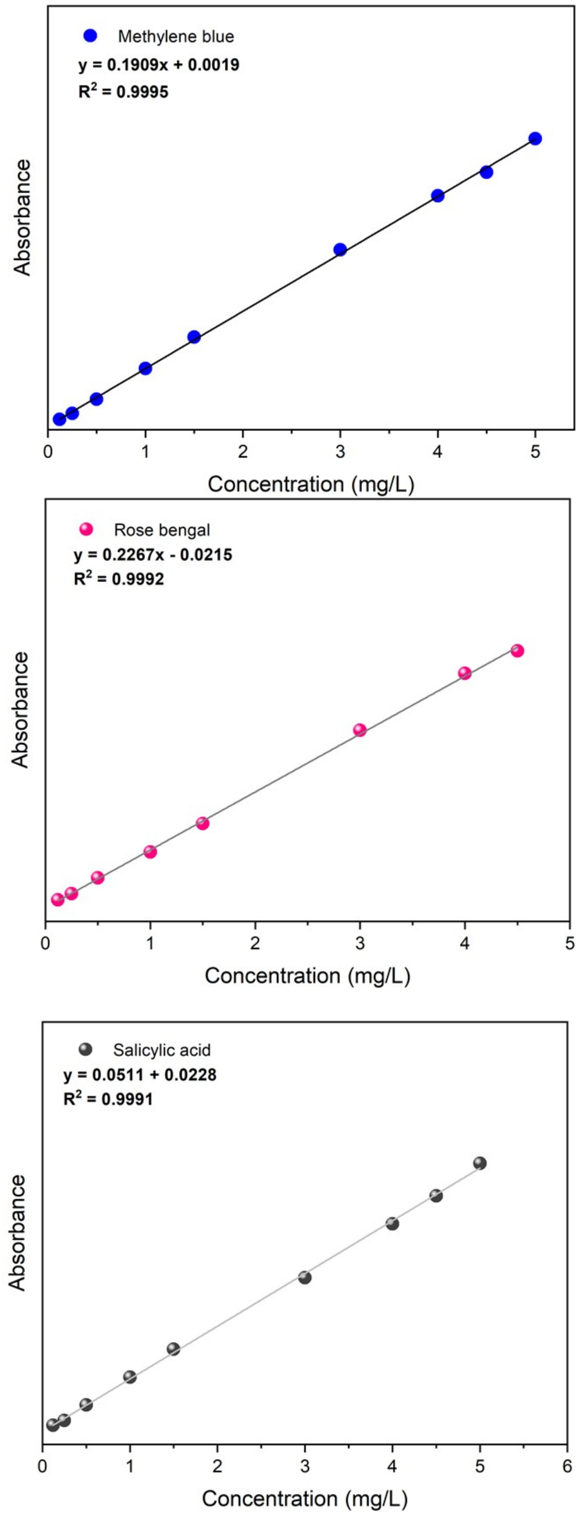

Fig. S1. Calibration

curves for methylene blue, rose bengal and salicylic acid in ultra-pure water, obtained by UV-VIS spectroscopy.

B. Materials characterization

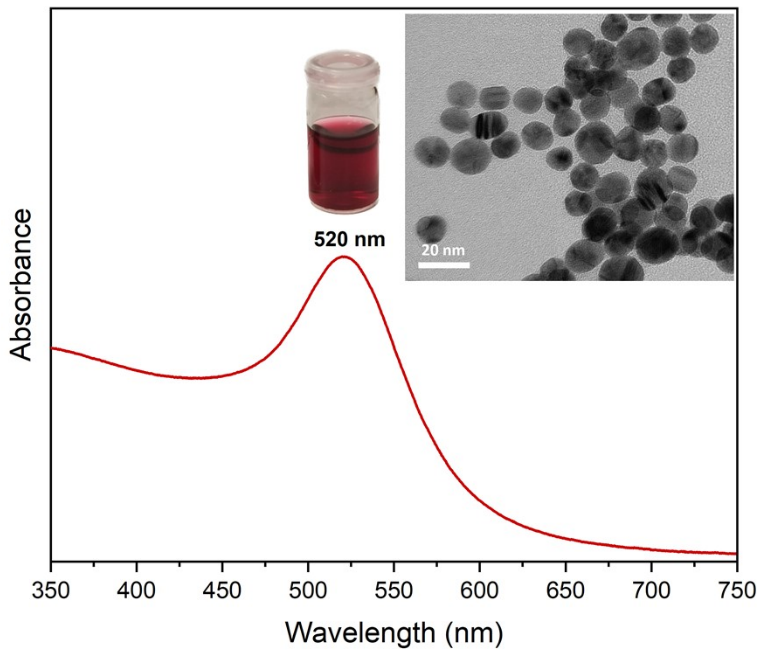

Fig. S2. UV-VIS absorption spectrum of colloidal Au nanoparticles. Inset: photograph of the Au colloid and TEM image of gold nanoparticles.

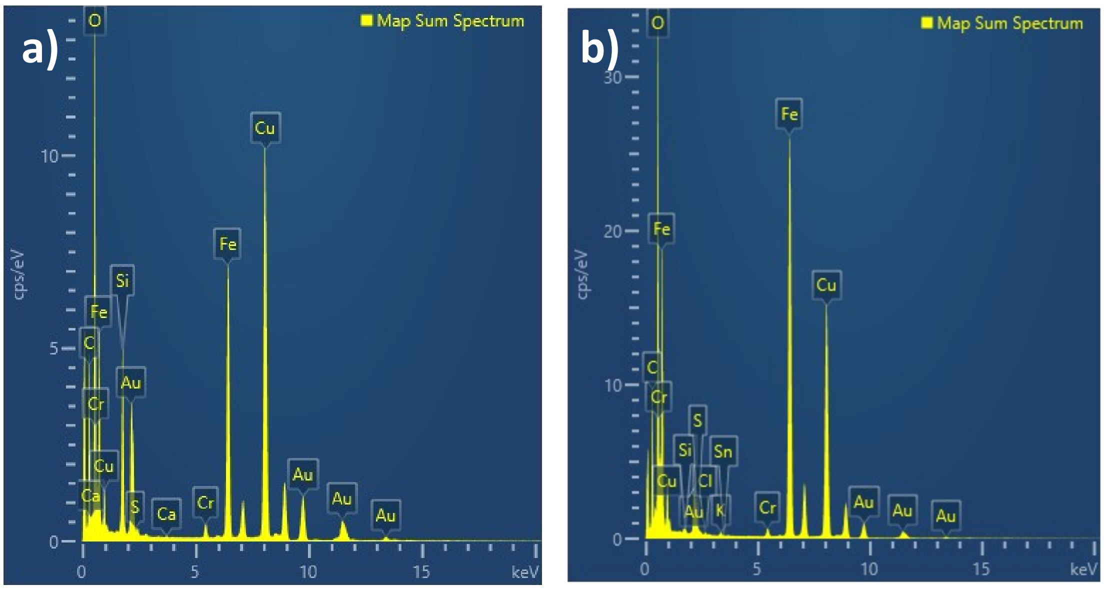

Fig. S3. EDS spectra of a) $Fe_3O_4@SiO_2$/SiTMC/$Au_{ex\ situ}$ and b) $Fe_3O_4@SiO_2$/SiTMC/$Au_{in\ situ}$ nanocomposites.

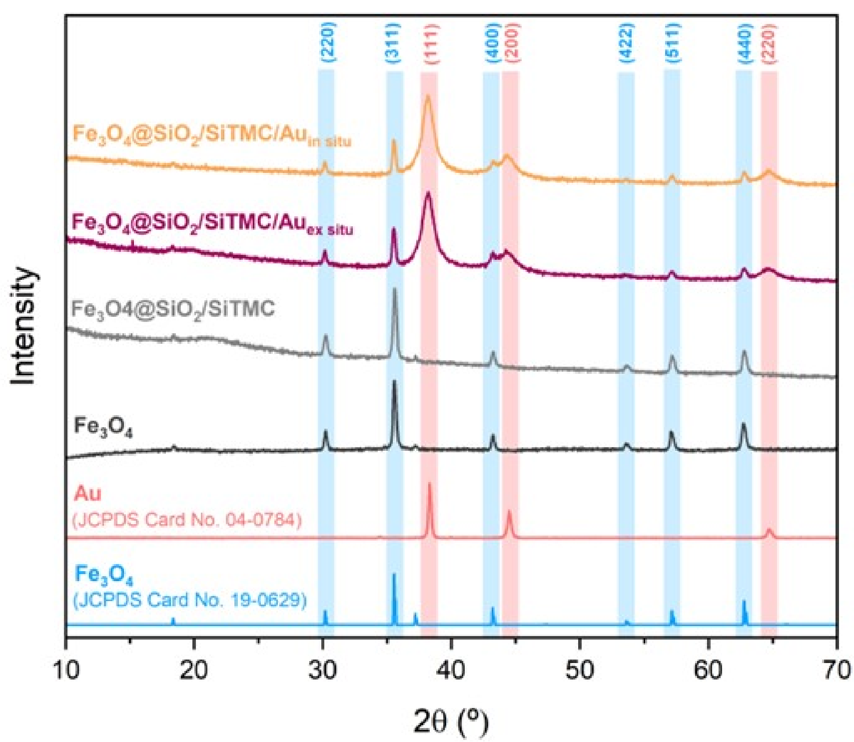

Fig. S4. XRD diffraction patterns of the synthesized materials: Fe_3O_4, Fe_3O_4@SiO_2/SiTMC, Fe_3O_4@SiO_2/SiTMC/$Au_{ex\ situ}$ and Fe_3O_4@SiO_2/SiTMC/$Au_{in\ situ}$ nanocomposites. For comparison purposes, reported diffractograms for crystalline gold with face centered structure (JCPDS Card No. 04-0784) and Fe_3O_4 (JCPDS Card No. 19-0629) were also included.

C. Dyes adsorption

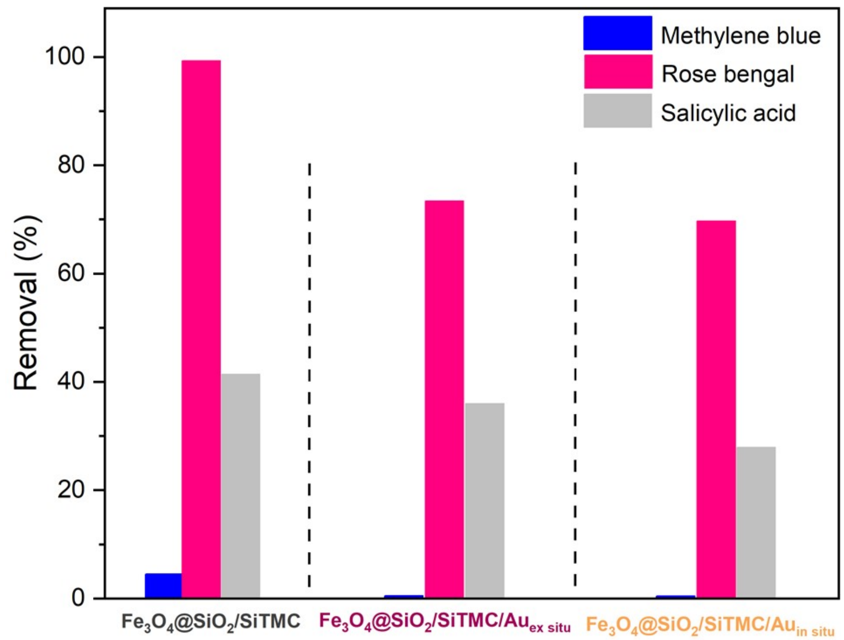

Fig. S5. Removal percentage of methylene blue, rose bengal and salicylic acid using Fe_3O_4@SiO_2/SiTMC, Fe_3O_4@SiO_2/SiTMC/$Au_{ex\ situ}$ and Fe_3O_4@SiO_2/SiTMC/$Au_{in\ situ}$ particles (Conditions: adsorbent dose of 0.5 mg/mL, 4 h of contact time, initial concentration of $1x10^{-5}$ M, $5x10^{-5}$ M and $1x10^{-3}$ M for methylene blue, rose bengal and salicylic acid respectively).

D. SERS

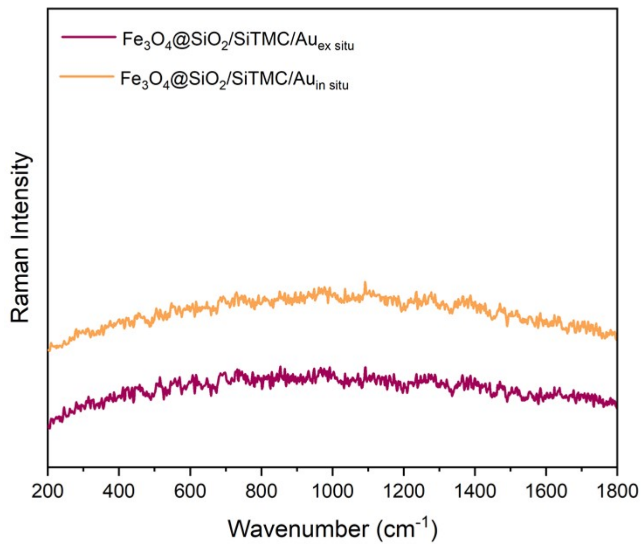

Fig. S6. Conventional Raman spectra of Fe_3O_4@SiO_2/SiTMC/$Au_{ex\ situ}$ and Fe_3O_4@SiO_2/SiTMC/$Au_{in\ situ}$ nanocomposites, under 633 nm laser excitation.

Table S1: Experimental Raman band positions (wavenumber, cm^{-1}) for methylene blue (MB) [1,2], rose bengal (RB) [3,4] and salicylic acid (SA) [5,6]with the corresponding vibrational mode assignments.

Wavenumber (cm^{-1})	Vibrational modes
MB	
1621	ν(CC) + $\delta_{in-plane}$(CH) (ring), ν(CN) + ν(CC)
1430	$\delta_{out-plane}$(CH), δ(CH_3), ν(CC), ν_{sym}(CN)
1396	ν_{sym}(CN) (lateral and centre) + $\delta_{in-plane}$(CH) (ring) + $\delta_{out-plane}$ (CH), δ(CH_3), ν(CN) + ν(CC), ν_{asym}(CN)
1181	$\delta_{in-plane}$(CH) (ring) + $\delta_{out-plane}$(CH), δ(CH_3), $\delta_{in-plane}$(CH)
480	$\delta_{in-plane}$thiazine (ring)
448	Skeletal deformation (CN, CS and CH_3), CN skeletal deformation
RB	
1619	ν_{sym}(C=C) (ring)
1488	ν_{asym}(C=C) (ring)
1297	δ(CCC) (ring) +δ(C−H)
614	ν(C−I) +δ(CCO)
SA	
1625	ν(C=O)
1583	ν_{asym}(OCO)

1390	$\nu_{sym}(OCO)$
1353	$\delta(C_{ring}\text{-}OH)$
1255	$\nu(C_{ring}\text{-}OH)$

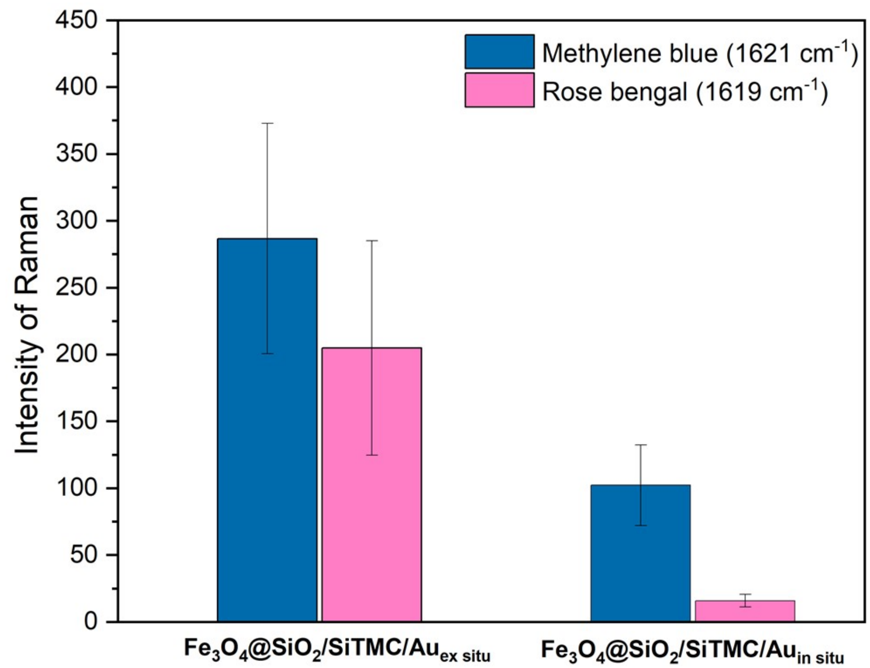

Fig. S7. Plot of the Raman intensities of selected vibrational bands of MB and RB, for comparing the SERS performance of the Fe_3O_4@SiO_2/SiTMC/$_{Auex\ situ}$ and Fe_3O_4@SiO_2/SiTMC/$Au_{in\ situ}$ bionanocomposites (data from 5 random Raman spectra).

References

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