Facile Solvothermal Synthesis of Ag/Fe_3O_4 Nanocomposites and Their SERS Applications in On-line Monitoring of Pesticide Contaminated Water

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Fig. S1 The magnified low field magnetic hysteresis loops of the composites of Ag and Fe_3O_4 with different Ag/Fe molar ratios.



Fig. S2. (a) Schematic illustration for the qualitative alteration of the magnetic field intensity by adjusting the distance (*d*) between the sample and magnet. (b) The SERS spectra collected on sample of Ag/Fe=5 with different d value to the magnet. The spectrum collected on the sample in the absence of an applied magnet is also given for reference.



Fig. S3 (a) TEM image of Ag NPs wrapped by glue-like Fe_3O_4 , bringing about large amount of "hot-spots". (b) Schematic diagram showing the function of glue-like Fe_3O_4 NPs towards the increased SERS activity.



Fig. S4 (a) Raman spectra of solid R6G and R6G (10^{-6} M) in the presence of sample of Ag/Fe = 5. (b) Raman spectra of solid MB and MB (10^{-6} M) in the presence of

sample of Ag/Fe = 5.



Scheme S1. The diagrams of the composite SERS substrates of Ag/Fe = 5 and Ag/Fe = 2 under a laser beam irradiation.



Scheme S2. The molecular structure of atrazine.

Table S1. Peak positions, FWHM, and area of the XPS Fe 2p peaks for Fe³⁺ and Fe²⁺ of Fe₃O₄ compounded with Ag in sample of Ag/Fe = 5. ($\chi^2 = 1.58$)

	Valence	Position	FWHM	Area
$2p_{3/2}$	Fe ²⁺	710.5	1.9	13925.2
	Fe ³⁺	712.2	3.5	28860.8
Satellite		718.8	7.0	22709.8
$2p_{1/2}$	Fe ²⁺	723.9	2.0	4497.0
	Fe ³⁺	725.5	3.3	9321.4

Enhancement factor (EF) calculation

Here solid R6G and MB powder are used for EF calculation.^{1, 2} Given that the volume

of laser spot for SERS substrate (Ag/Fe = 5) and solid dye are identical, then the EF formula can be written as:

$$\text{EF} = \left(\frac{I_{\text{SERS}}}{I_{\text{Raman}}}\right) \left(\frac{C_{\text{dye}}}{C_{\text{solution}}}\right)$$

where C_{dye} is the molar density (mol/L) of solid R6G and MB, and $C_{solution}$ is the dye concentration detected by composite SERS substrate. The molar density is calculated from the common density (g/cm³), which are 0.79 g/cm³ for R6G and 1.757 g/cm³ for MB. I_{SERS}/I_{Raman} are evaluated to be considering the integrated intensity of R6G band at 1650 cm⁻¹ and MB band at 915 cm⁻¹ from surface enhanced and Raman spectrum.

Reference

- 1. Y. Peng, L. Qiu, C. Pan, C. Wang, S. Shang and F. Yan, *Electrochim. Acta*, 2012, **75**, 399-405.
- 2. D. Jana, A. Mandal and G. De, Acs Appl. Mater. Inter., 2012, 4, 3330-3334.