Electronic Supplementary Material (ESI) for Analyst.

Combination use of graphene SERS substrate and magnetic solid phase micro-extraction for rapid detection of trace illegal additives

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(Supporting Information)

1. Characterization of Fe_3O_4@GO@Ag and GO.

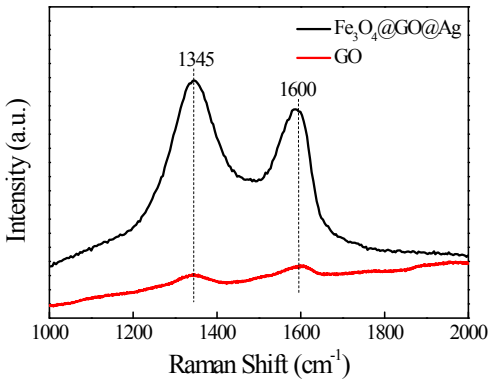

Fig. S1. Raman spectra of Fe_3O_4@GO@Ag and GO, the peak intensities of D and G bands were enhanced greatly in Fe_3O_4@GO@Ag due to the loading of silver nanoparticles at surface.

2. Sensitivity of Dis-MSPME-SERS to CAP

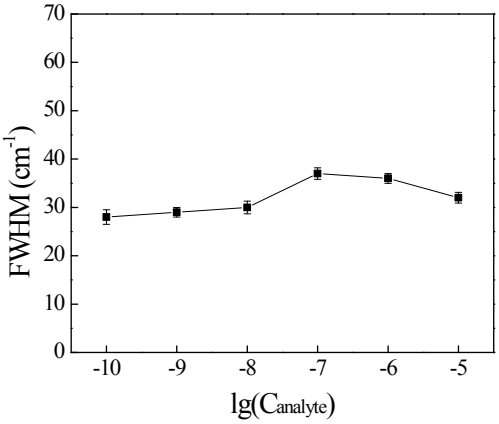

Fig. S2. The FWHM of the bands at 1345 cm^{-1} changes with CAP concentration.

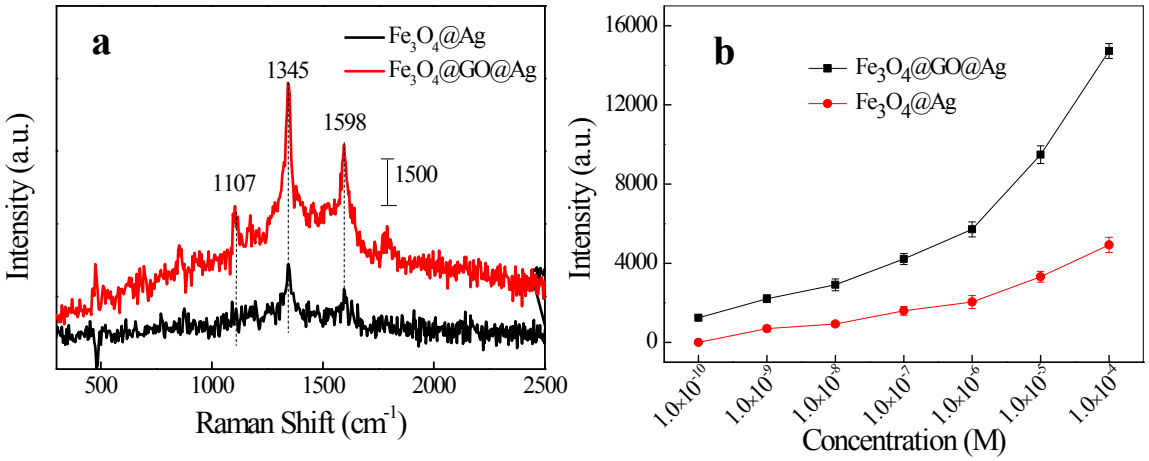

Fig. S3. (a) SERS spectrum of CAP (1.0×10^{-9} M) on the Fe_3O_4@GO@Ag and Fe_3O_4@Ag particles, respectively; (b) The corresponding Raman intensity variations at 1345 cm^{-1} with different concentrations of CAP on two substrate, respectively.

3. Adsorption experiment

The adsorption of CAP on graphene was performed. The experimental steps were depicted as follows: 30 mg Fe_3O_4@GO@Ag or Fe_3O_4@Ag was added into the solution of CAP (50 mL × 50 μg/mL) at room temperature by stirring. Then, then the adsorbent was separated by using an external magnetic field. The adsorption concentration of CAP was finally detected by HPLC (Fig. S4). The adsorption capacity Q (mg/g) of the analyte was defined as:

$$Q = \frac{(C_0 - C_t) * V}{m}$$

where C_0 (μg/mL) is the initial concentration of analyte, while C_t (μg/mL) is the concentration of it left in supernatant solution after t min, V (mL) is the volume of the initial solution and m (g) is the mass of the adsorbent.

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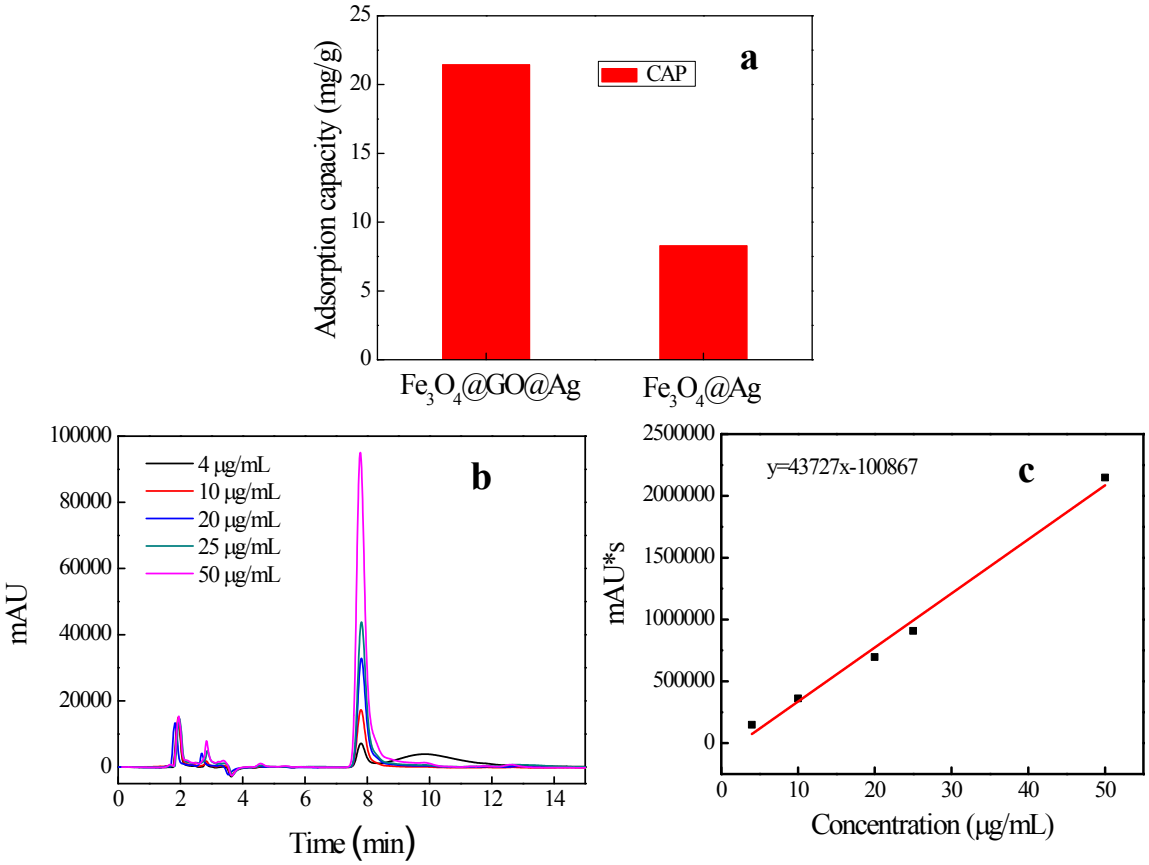

Fig. S4. (a) The comparison of the adsorption capacities of CAP on the surface of Fe_3O_4@GO@Ag and Fe_3O_4@Ag, respectively, after mixing of them in 20 min; (b) Chromatograms of CAP at different concentrations; (c) Standard curves of CAP from the data of (b).

4. Stability of the magnetic particles

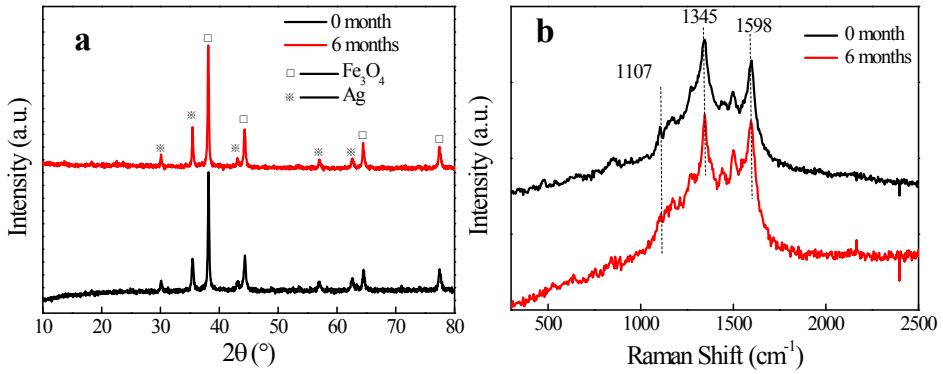

Fig. S5. (a) XRD pattern of Fe_3O_4@GO@Ag and (b) SERS spectra of CAP (1.0×10^{-9} M) on Fe_3O_4@GO@Ag after 0 and 6 months storage in water, respectively.

Table S1. 2θ value of Fe_3O_4@GO@Ag, Ag, Ag_2O.

Nano particle	2θ/(º)			
Fe_3O_4@GO@Ag	38.0	44.1	64.4	77.2
Ag	38.2	44.2	64.4	77.4
Ag_2O	26.6	32.8	38.3	54.9