Supporting Information

Sea-Urchin-Like Fe_3O_4@C@Ag Particles: An Efficient SERS Substrate for Detection of Organic Pollutants†

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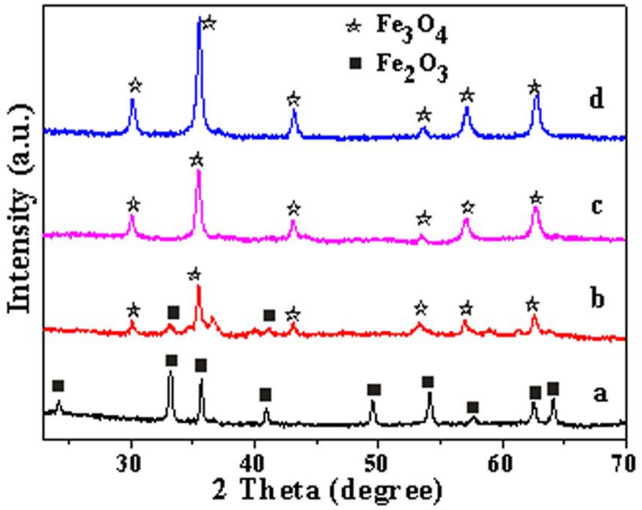

Fig. S1. XRD patterns of the products obtained with the addition of different amount of glucose: (a) 0 g, (b) 0.1 g, (c) 0.2 g, (d) 0.4 g. The patterns can be easily indexed to Fe_3O_4 (JCPDS 89-2355), Fe_2O_3 (JCPDS 01-1053).

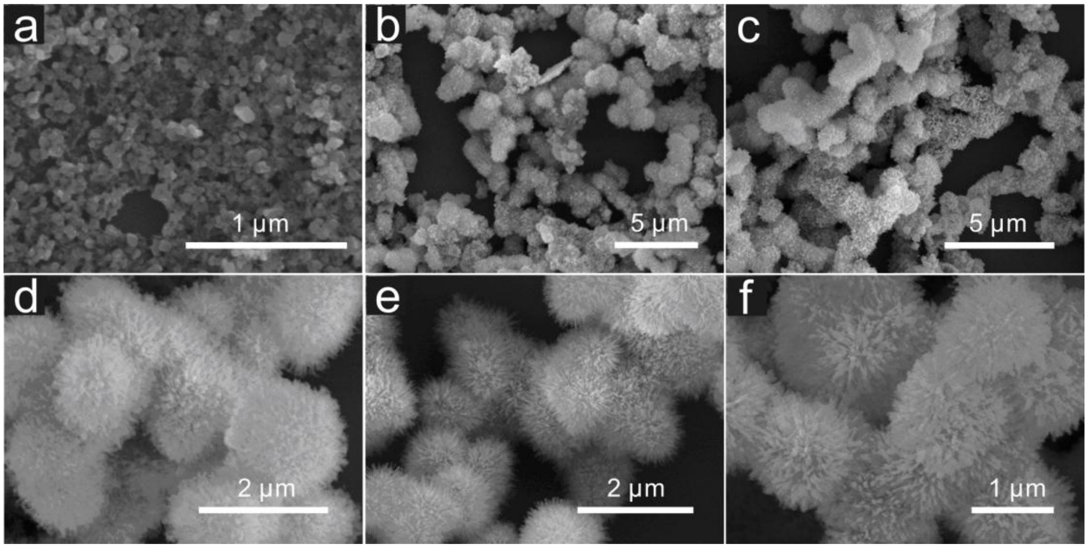

Fig. S2. SEM images of the products obtained with the addition of different amount of glucose: (a) 0 g, (b) 0.05 g, (c) 0.1 g, (d) 0.2 g (e) 0.4 g, (f) 0.8 g.

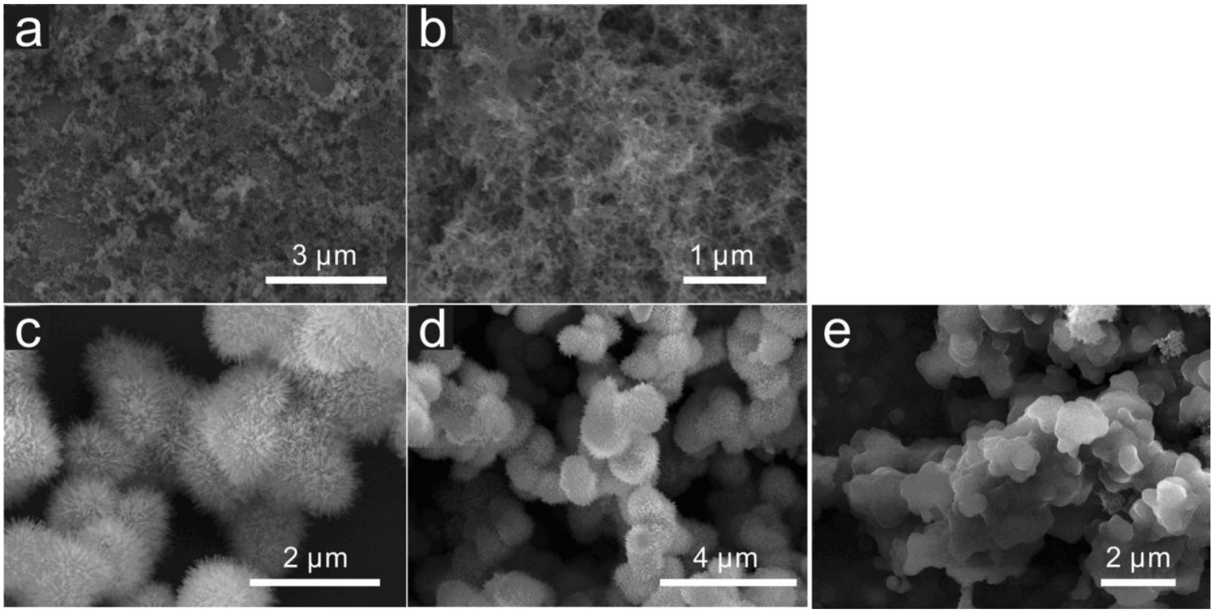

Fig. S3 SEM images of the products obtained with the addition of different amount of PAM: (a) 0 g, (b) 0.05 g, (c) 0.1 g, (d) 0.2 g, (e) 0.5 g.

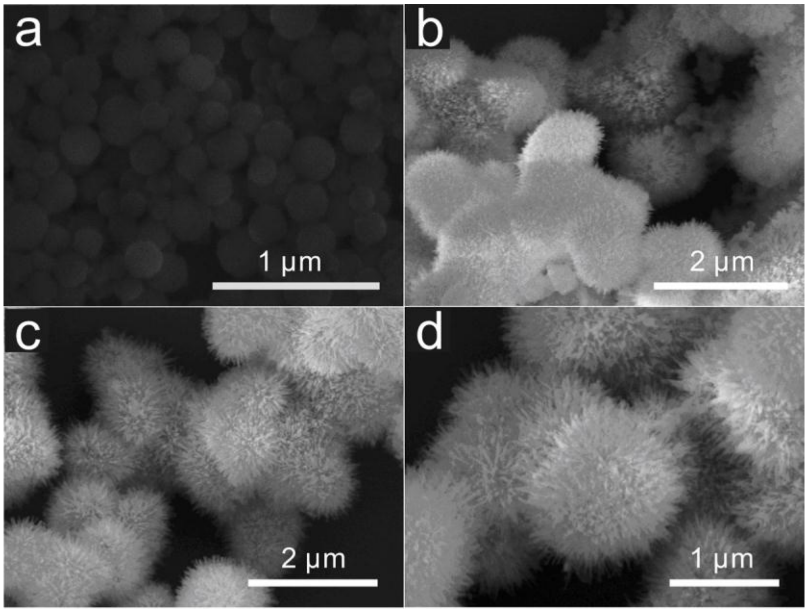

Fig. S4 SEM images of the products obtained with the addition of different amount of urea: (a) 0 g, (b) 0.12 g, (c) 0.24 g, (d) 0.48 g.

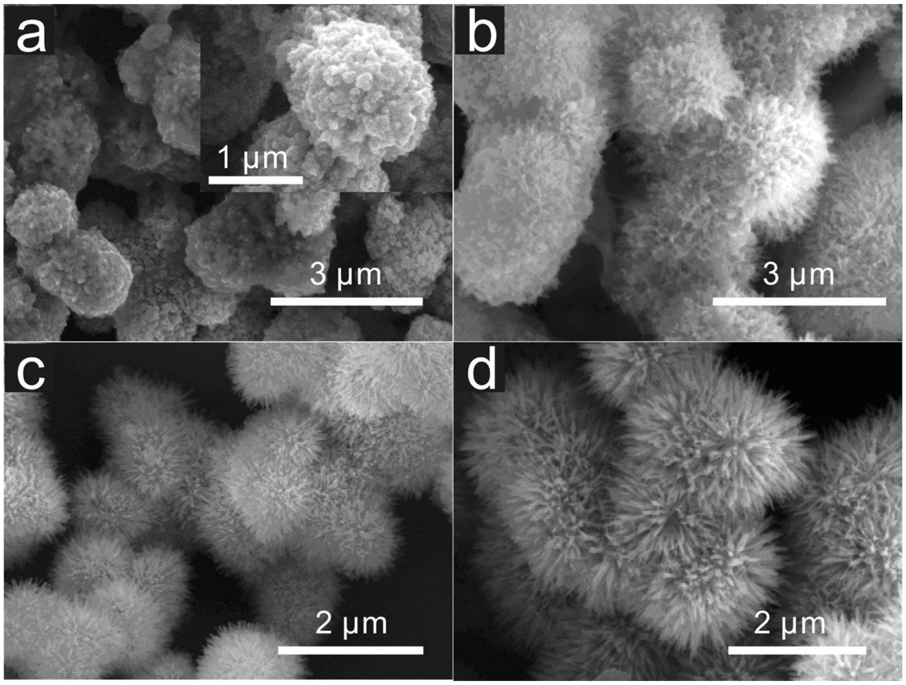

Fig. S5 SEM images showing the morphological evolution of the particles with increasing reaction time from (a) 4, (b) 8, (c) 12 to (d) 16 h. inset: the magnified observation of the particles.

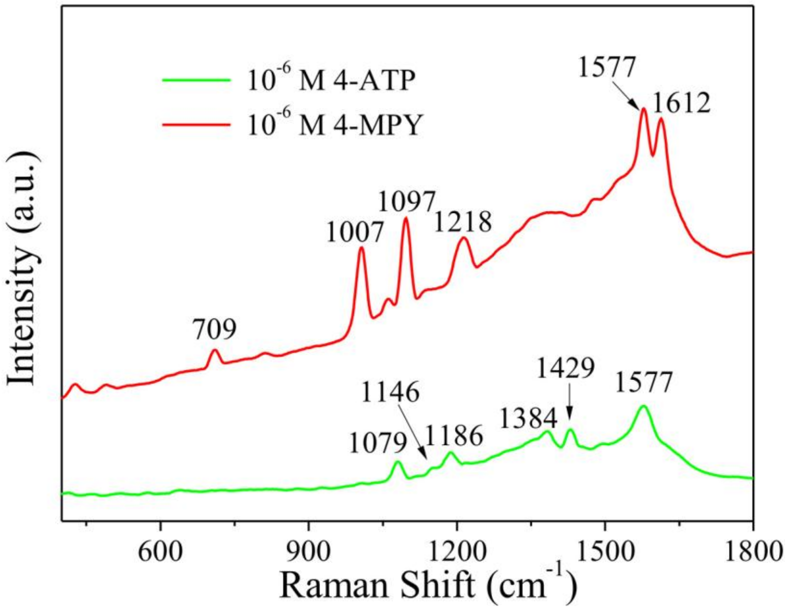

Fig. S6. Raman spectra of 4-ATP and 4-MPY using Fe_3O_4@C@Ag particles as the active substrates.

The UV-Vis absorption before and after enrichment was done. 10 mg Fe_3O_4@C@Ag particles were added to 20 mL of 10 μM of each of dyes R6G and CV solutions. The mixed solution was then shaken at room temperature for 10, 20, and 30 min, respectively. Subsequently, the Fe_3O_4@C@Ag particles with adsorbed dyes were separated from the mixture via a permanent magnet within 30 s. And UV-visible absorption spectra were recorded to monitor changes in the residual amounts of dyes in the solution with a Shimadzu UV-2550 spectrophotometer. As shown in Fig. S7, the absorbance of dyes solutions are found to be decreased monotonically by increasing contact time. This phenomenon is attributed to an efficient adsorption of dyes by the Fe_3O_4@C@Ag particles.

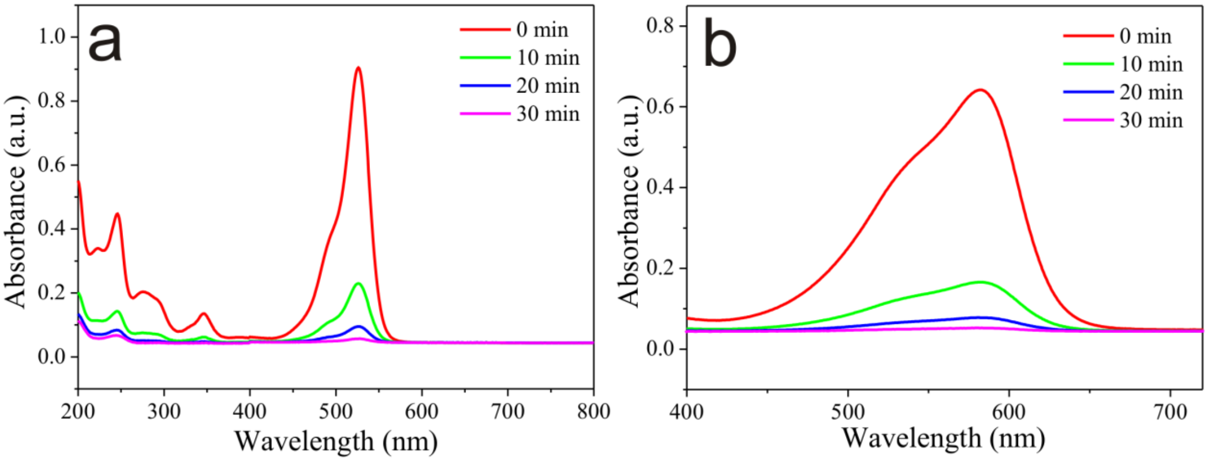

Fig. S7. The absorbance of a series of (a) R6G and (b) CV solutions indicates the effect of contact time on the adsorption of dyes on Fe_3O_4@C@Ag particles. From the topmost curve to the undermost one the contact time are 0, 10, 20, and 30 min respectively.

5 mg Fe_3O_4@C@Ag particles were added to 10 mL ultrapure water. A dark solution was obtained after ultrasonic dispersion for 1h. As shown in Fig. S8a and b, The TEM and SEM images of Fe_3O_4@C@Ag particles after ultrasonic dispersion for 1 h show that the Fe_3O_4@C@Ag particles still have core/shell structure and the Ag nanoparticles remain highly dispersed in the carbon layer. No detachment or aggregation of Ag nanoparticles during the catalytic reaction is observed, indicating that the special substrate-supported structures protect the Ag nanoparticles from being lost. The Fe_3O_4@C@Ag particles before and after ultrasonication were used for SERS studies, and we found that the SERS intensity were almost the same (Fig. S8c). Fig. 8 also shows that the Fe_3O_4@C@Ag particles can be recycled after cleaning using water and ethanol with no obvious decrease of the SERS intensity. So we considered that ultrasonication or cleaning could not do damage to Fe_3O_4@C@Ag particles.

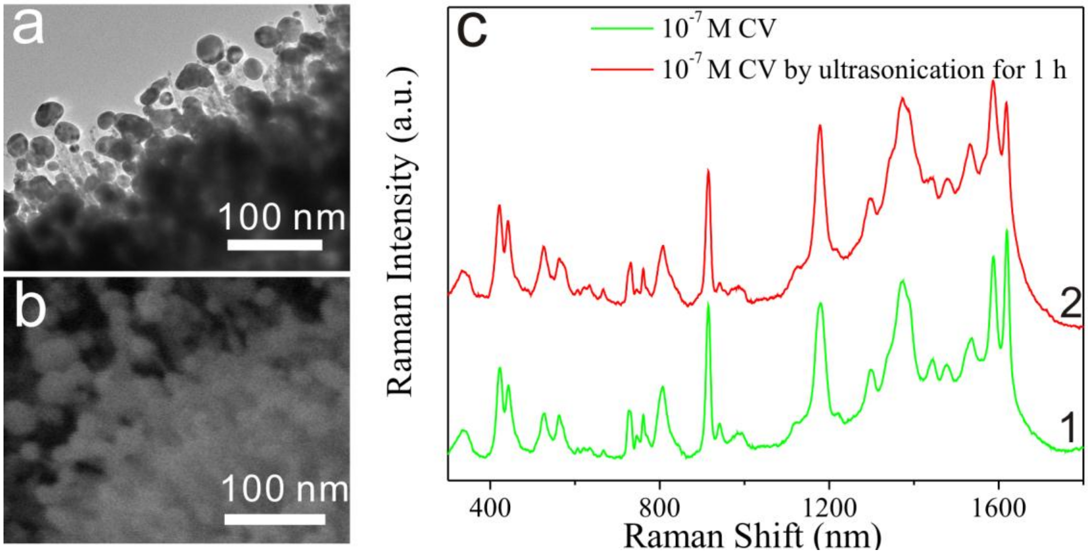

Fig. S8. (a-b) The TEM and SEM images of Fe_3O_4@C@Ag particles by ultrasonication for 1h. (c) curve 1: The SERS signal of 10^{-7} M CV using Fe_3O_4@C@Ag particles as substate; curve 2: the SERS signal of 10^{-7} M CV using Fe_3O_4@C@Ag particles by ultrasonication for 1h as substate.

Magnetic properties of the Fe_3O_4@C particles and Fe_3O_4@C@Ag particles were investigated at 300 K between -5000 and 5000 Oe. They exhibit typical ferromagnetic behavior, and their M_s values are 50.2 and 43.1 emu g^{-1}, respectively. The M_s value of the Fe_3O_4@C particles is smaller than the corresponding single-crystal Fe_3O_4 microspheres (81.9 emu g^{-1}),[1] which could be due to the amorphous carbon shell at the interface providing a smaller magnetic moment per unit mass as opposed to that of the ferromagnetic cores. The further decrease in M_s of the Fe_3O_4@C@Ag particles can be explained by taking into account the diamagnetic contribution of the Ag nanoparticles surrounding the magnetic cores. The magnetization of the hybrid Fe_3O_4@C@Ag particles were also revealed by the fact that they were easily attracted by an external magnetic field within 30 s (inset in Fig. S7). This will provide an easy and efficient way to separate and recycle Fe_3O_4@C@Ag particles from a suspension system under an external magnetic field.

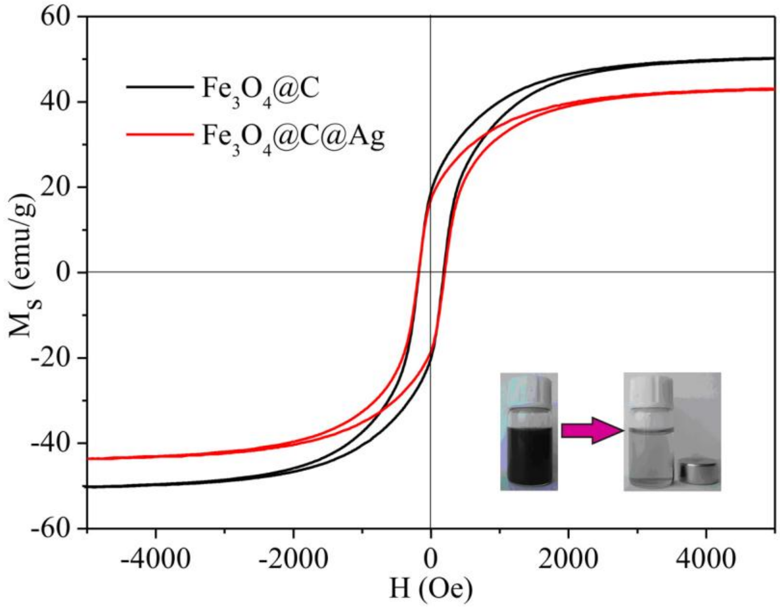

Fig. S9 Magnetic behaviors of Fe_3O_4@C and Fe_3O_4@C@Ag particles at 300 K. Inset: separation of the obtained Fe_3O_4@C@Ag particles from the aqueous solution under external magnetic field.

References

1. Deng, H.; Li, X. L.; Peng, Q.; Wang, X.; Chen, J. P.; Li, Y. D., Monodisperse magnetic single-crystal ferrite microspheres. *Angew Chem Int Edit* 2005, 44, 2782-2785.