Electronic Supplementary Material (ESI) for Analytical Methods

Supporting Information

Tunable Plasmon Properties of Fe_2O_3@Ag Substrate for Surface-enhanced Raman Scattering

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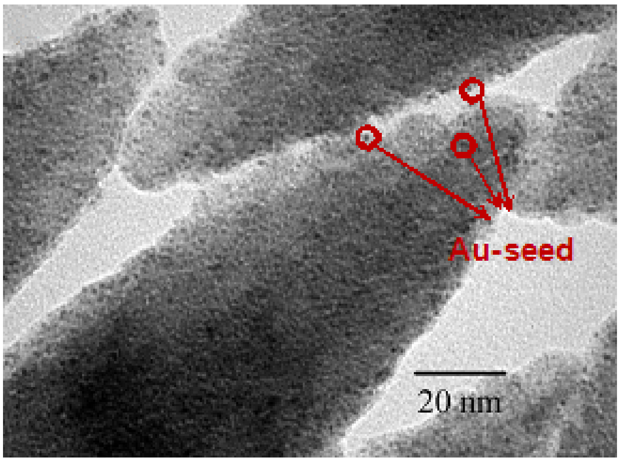
SERS enhancement factors (EF) of Fe_2O_3@Ag substrate. SERS enhancement factor values were calculated by comparing the intensity of benzenethiol (TP) bands measured in the SERS experiment to the corresponding bands measured from neat TP.

SERS EF is defined as: $EF = (I_{SERS}/I_{NR})(N_{NR}/N_{SERS})$, where, N_{NR} and N_{SERS} are the number of molecules probed in the liquid sample and on the SERS substrates, respectively, while I_{NR} and I_{SERS} are the corresponding normal Raman and SERS intensities.

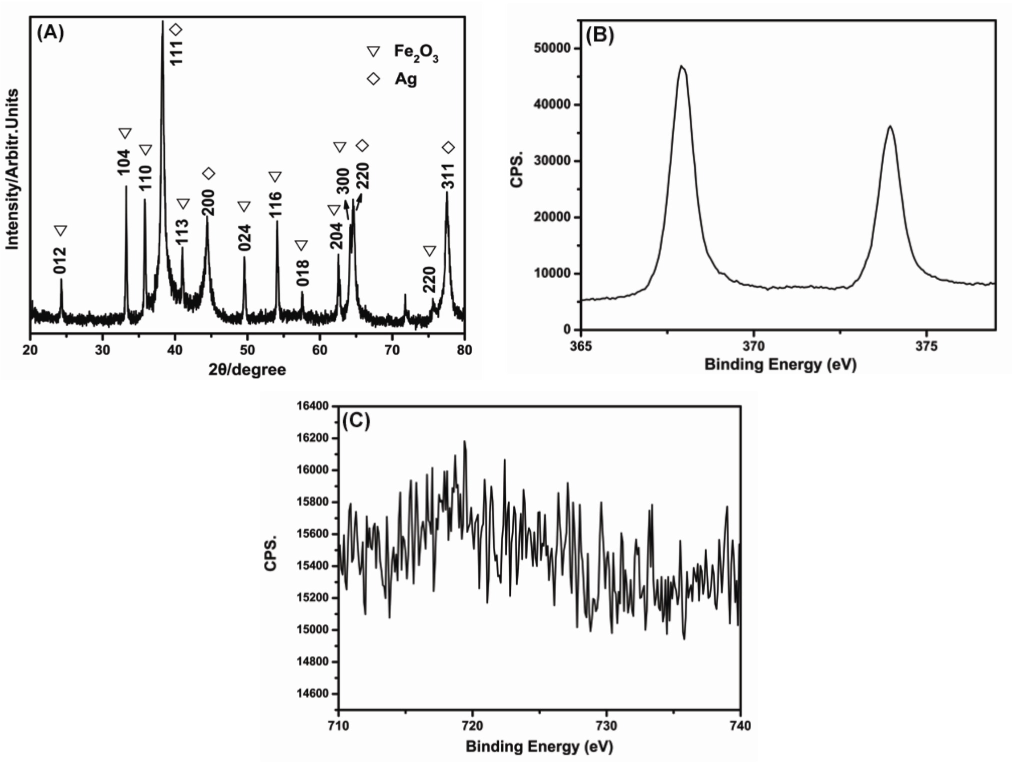
N_{NR} is defined as: $N_{NR} = N_A A h\rho/m$, where, A is the area of the focal spot of the laser, h, ρ, and m are the penetration depth, the density, and the molecular weight of TP, respectively. N_{SERS} is defined as: $N_{SERS} = N_d A_{laser} A_N/\sigma$,[1] where N_d is the density of nanoparticals, A_{laser} is the area of the focal spot of the laser, A_N is the nanoparticle's footprint area, and σ is the surface area occupied by an adsorbed molecule. N_d and A_N can be generally obtained from the SEM images. A_{laser} can be obtained from the diameter of the laser spot (1 μm), σ can be adopted as 0.147 nm^2/ molecule.[2] In case of full coverage limit of TP molecules on Fe_2O_3@Ag substrate, the SERS EF at the Fe_2O_3@Ag substrate can be estimated (the calculated EF of different assignments were given in Table 1).

The absorption intensity in Figure 2 increases continuously in NIR area which is because of the silver nanoparticle grown bigger and aggregated with silver deposition time increasing. The SERS contribution is mainly from the aggregation process for formation of large clusters of nanoparticles which can provide more hot-spots. Upon increasing the time of silver deposition the silver nanoparticles on the Fe_2O_3 tend to coalesce and form a continuous films, resulting in a decrease in the number of hot-spots, which depresses the SERS enhancement. The SERS intensity will thus change as the deposition time increase.

In Figure 4, the SERS spectra of TP show four pronounced bands at 1575, 1072, 1022 and 999 cm^{-1}. These bands are assigned to modes C-C stretching, C-C stretching and in plan ring deformation, in plan ring deformation and S-H bending and in plan ring deformation, respectively. We observed that the intensity of a band at 1575 cm^{-1} compared with other band is changed with different excitation wavelengths. This change may be due to the chemical mechanism through the Herzberg-Teller contribution. When the molecule absorbed on the silver surface, there is involving a charge transfer (CT) between the molecule and metal. On the basis of professor Lombardi's theory,[3] two terms that A term and B or C term are relevant. The so-called A term is operative only in case of resonance of the excitation wavelength with the CT transition. For the non-totally symmetry mode, this term vanishes. The B or C term represent Herzberg-Teller contributions and result in the selected enhanced the 1575 cm^{-1} (b_2 mode) band. With the excitation wavelength decreasing (energy increasing), the CT degree is increasing, consequently the comparable intensity are increased.



SI_Figure 1. A TEM of Fe_2O_3@Au-seed (the surface decorated with 2-3 nm gold nanoparticles).



SI_Figure 2. (A) XRD patterns of Fe_2O_3@Ag particles; XPS data of the obtained Fe_2O_3@Ag particles (B) Ag 3d, (C) Fe 2p.

From SI_Figure 2(A), we conclude that the four diffraction peaks can be indexed to the (111), (200), (220) and (311) planes of the fcc structure of silver.[4] This result indicates that Ag nanoparticles have been coated on the surface of Fe_2O_3 nanoparticles. The XPS analysis gives some insight into the chemical of the Fe_2O_3@Ag nanoparticles. SI_Figure 2(B) shows the silver 3d spectral region of the obtained

Fe_2O_3@Ag nanoparticles. The Ag $3d_{5/2}$ peak appears at a binding energy of 367.9 eV, and the splitting of the 3d doublet is 6.1 eV. These data prove the formation of metallic silver, indicating the formation of Ag nanoparticles on the surface of Fe_2O_3 nanoparticles.[5] Moreover, the weak peak with a binding energy of 715 eV corresponding to Fe 2p is also observed (SI_Figure 2(C)),[6] indicating the existence of Fe_2O_3 nanoparticles in the core of Fe_2O_3@Ag nanoparticles.

References

(1) C. J. Orendorff, A. Gole, T. K. Sau, C. J. Murphy, *Anal. Chem.*, 2005, **77**, 3261-3266.

(2) A. D. McFarland, M. A. Young, J. A. Dieringer, R. P. Van Duyne, *J. Phys. Chem. B*, 2005, **109**, 11279-11285.

(3) J. R. Lombardi, R. L. Birke, *J. Phys. Chem. C*, 2008, **112**, 5605-5617.

(4) W. Song, Y. F. Wang, H. L. Hu, B. Zhao, *J. Raman Spectrosc.*, 2007, **38**, 1320-1325.

(5) D. Briggs, Practical Surface Analysis. Wiley: New York, 1983.

(6) X. Xu, M. B. Cortie, *J. Phys. Chem. C*, 2007, **111**, 18135-18142.