

Supporting information

Improved Catalytic Activity and Surface Electro-kinetics of Bimetallic Au-Ag Core-Shell Nanocomposites

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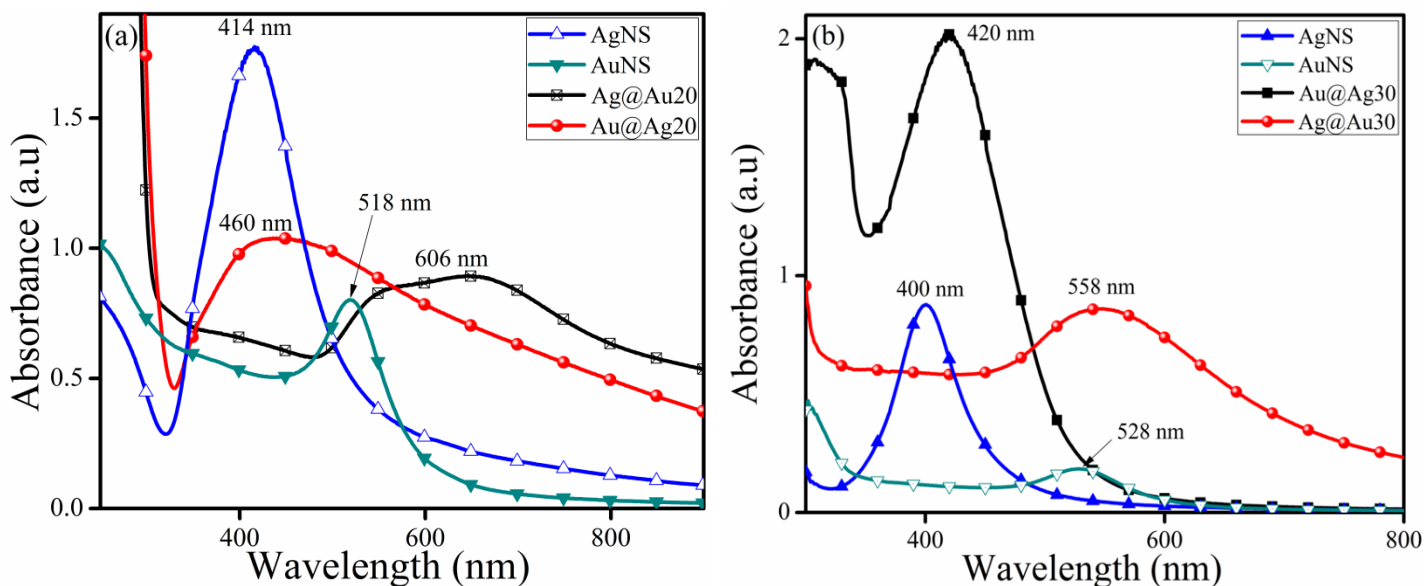


Fig S1. Surface plasmon band changes during the addition of 0.01 M AgNO_3 and AuCl_4^- ((a) 20 μl , and (b) 30 μl) to Au nanospheres and Ag nanospheres.

Table S1. Calculation for the amount of Au and Ag atoms in Au@Ag core-shell NCs.

| Elements | Amount of element (mg) | No. of atoms (atoms) | Atomic ratio (Au:Ag) |
|--|------------------------|----------------------|----------------------|
| AuNS (800 μl) | 0.077 | 2.3×10^{17} | 1:0 |
| Ag⁺ (10 μl) | 0.0107 | 0.6×10^{17} | 1:0.2 |
| Ag⁺ (20 μl) | 0.0213 | 1.2×10^{17} | 1:0.5 |
| Ag⁺ (30 μl) | 0.032 | 1.8×10^{17} | 1:0.7 |

Table S3. Calculation for the amount of Ag and Au atoms in Ag@Au core-shell NCs.

| Elements | Amount of element (mg) | No. of atoms (atoms) | Atomic ratio (Ag:Au) |
|---|------------------------|-----------------------|----------------------|
| AgNS (800 μl) | 0.043 | 2.4×10^{17} | 1:0 |
| Au⁺³ (10 μl) | 0.019 | 0.58×10^{17} | 1:0.2 |
| Au⁺³ (20 μl) | 0.039 | 1.2×10^{17} | 1:0.5 |
| Au⁺³ (30 μl) | 0.059 | 1.8×10^{17} | 1:0.7 |

The zeta potential for bimetallic Au@Ag and Ag@Au NCs was measured in their aqueous medium having core: shell atomic ratio = 1:0.2, 1:0.5, and 1:0.7 as calculated in *Table S2 and S3*. The various core-shell NCs were dispersed in 4 ml aqueous solution and 1.5 ml, of which was taken in a cuvette consisting of the palladium electrode mounted on a machined support for the zeta potential measurement using the Brookhaven zeta plus.

S4. Dynamic light scattering (DLS) study

The measurement of hydrodynamic size distribution of different bimetallic NCs dispersed in water was carried out by Brookhaven 90 plus Particle Size Analyzer at 25 °C. The samples were lighted with 635 nm solid state laser whose power ranged between 15 to 150 mW. The scattered light was detected at an angle of 90° with an avalanche photodiode detector. The random motion (Brownian motion) of small particles in a liquid gives rise to fluctuations in the time intensity of the scattered light. The fluctuating signal is processed by forming the autocorrelation function, $C(\tau)$, τ being the time delay. As depicted in Figure S5 and S6, the $C(\tau)$ decays more rapidly for small particles than for the larger particles. This is because the larger size of the diffusing particle corresponds to slower diffusion and hence by the larger width in autocorrelation function.¹⁻³ We observe that the $C(\tau)$ broadens (Figure S5 and S6) with the increase in the Ag/Au shell thickness with respect to bare monometallic Au/AgNS corresponding to an increase in the hydrodynamic size (25 to 62 nm in case of Au@Ag NCs and 21 to 58 nm in case of Ag@Au NCs, Figure 4).

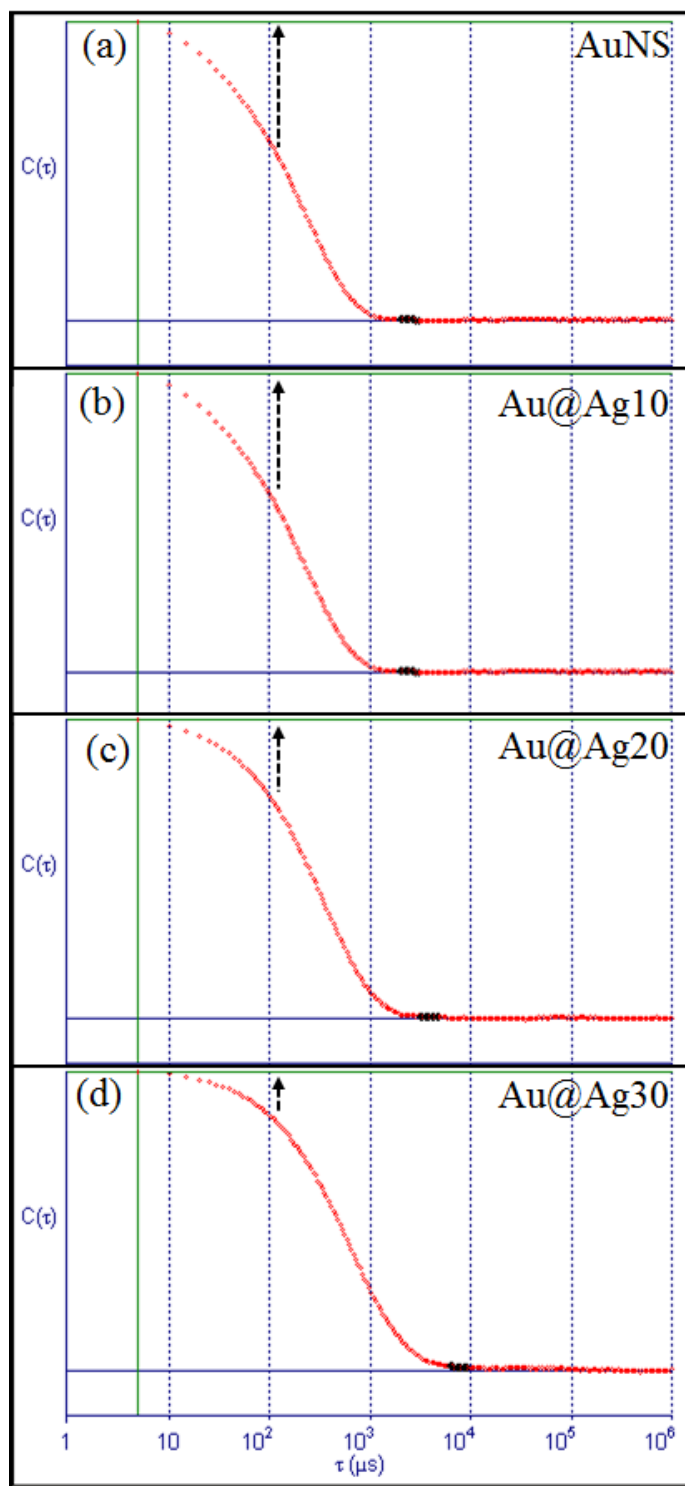


Fig S5. Autocorrelation functions, $C(\tau)$ of (a) bare Au nanospheres, and (b-d) Au@Ag core-shell nanocomposites.

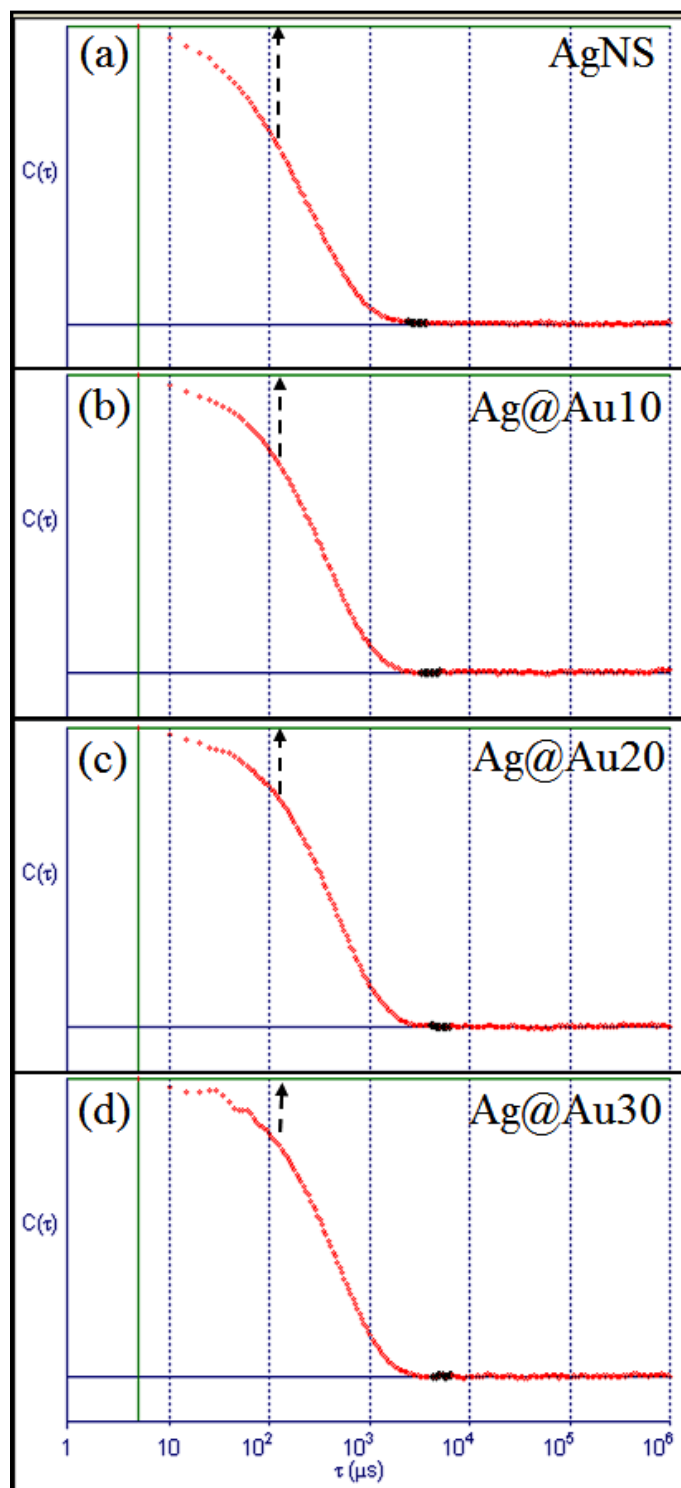


Fig S6. Autocorrelation functions, $C(\tau)$ of (a) bare Ag nanospheres, and (b-d) Ag@Au core-shell nanocomposites.

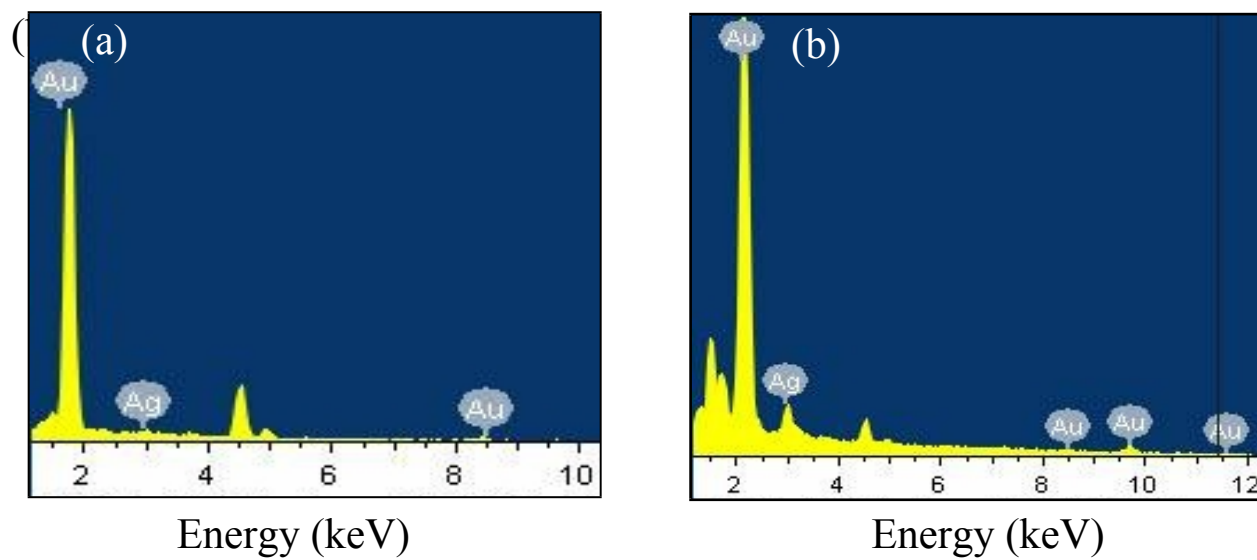


Fig S7. EDS pattern of (a) Au@Ag, and (b) Ag@Au core-shell nanocomposites.

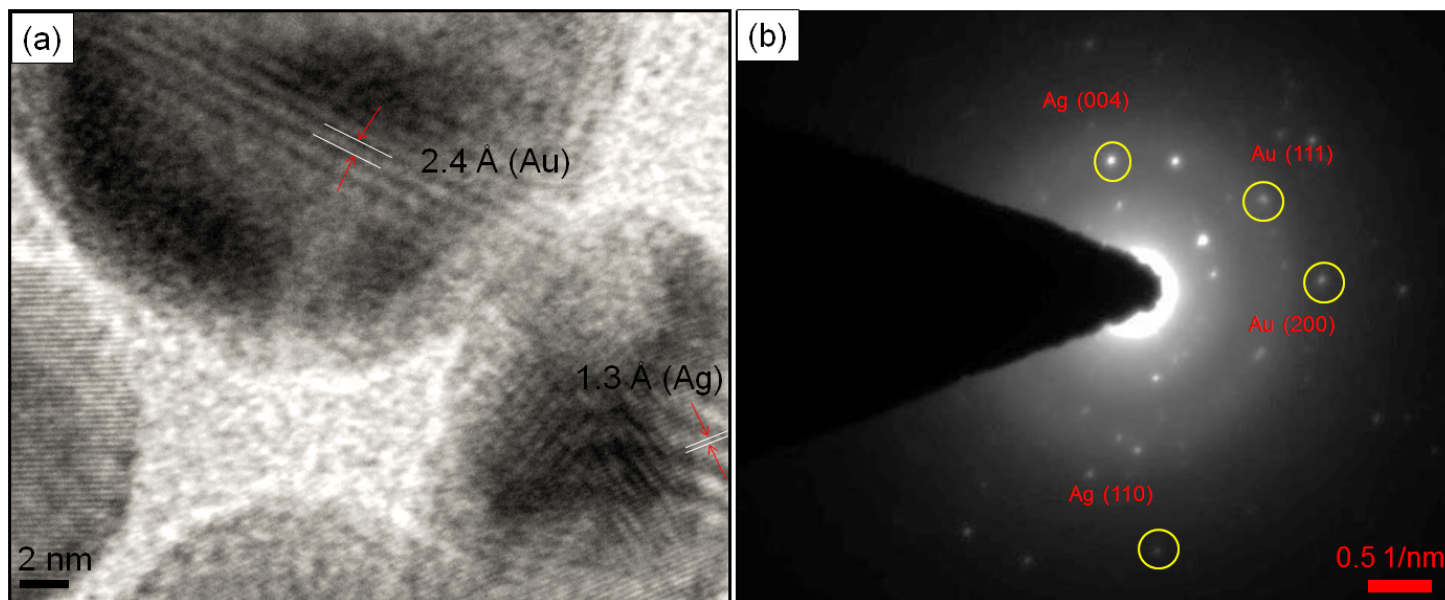


Fig. S8. HRTEM image and SAED pattern of Au@Ag core-shell nanocomposites.

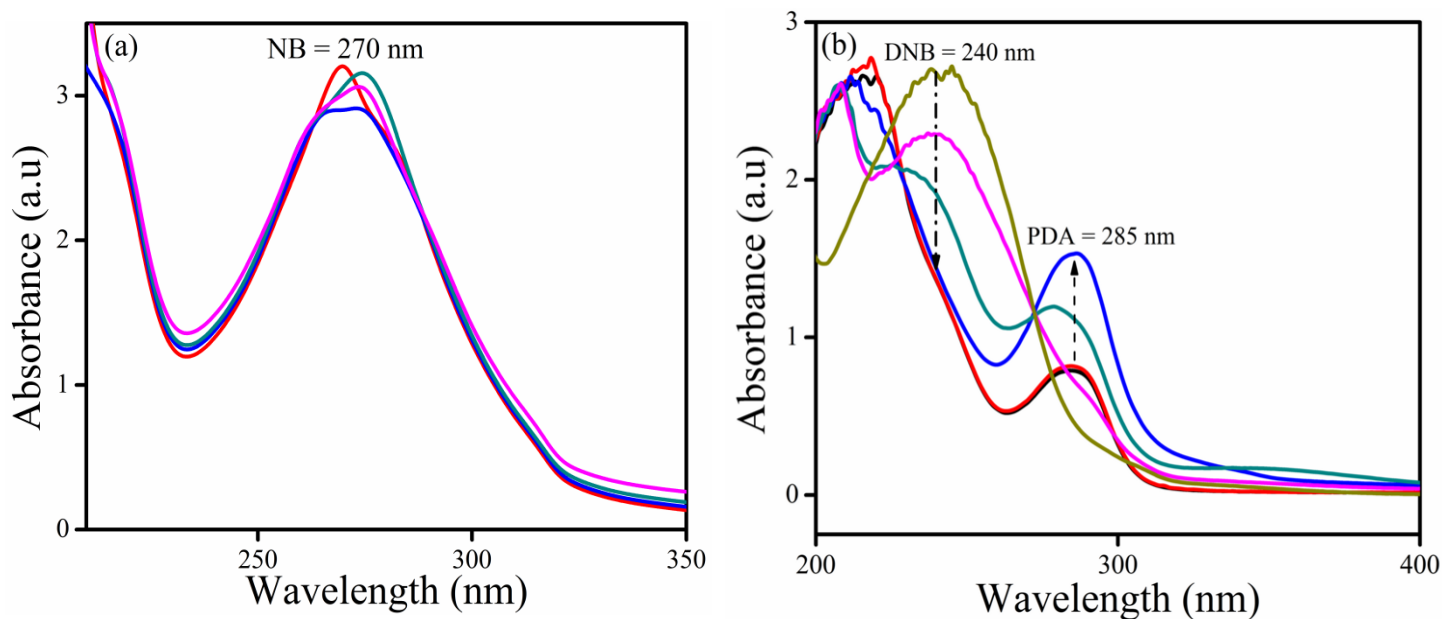


Fig S9. Changes in absorption spectra of (a) nitrobenzene reduction by NaBH_4 in the absence of nanoparticles, and (b) 1,3-dinitrobenzene reduction by NaBH_4 in the presence of various Au-Ag bimetallic nanostructures.

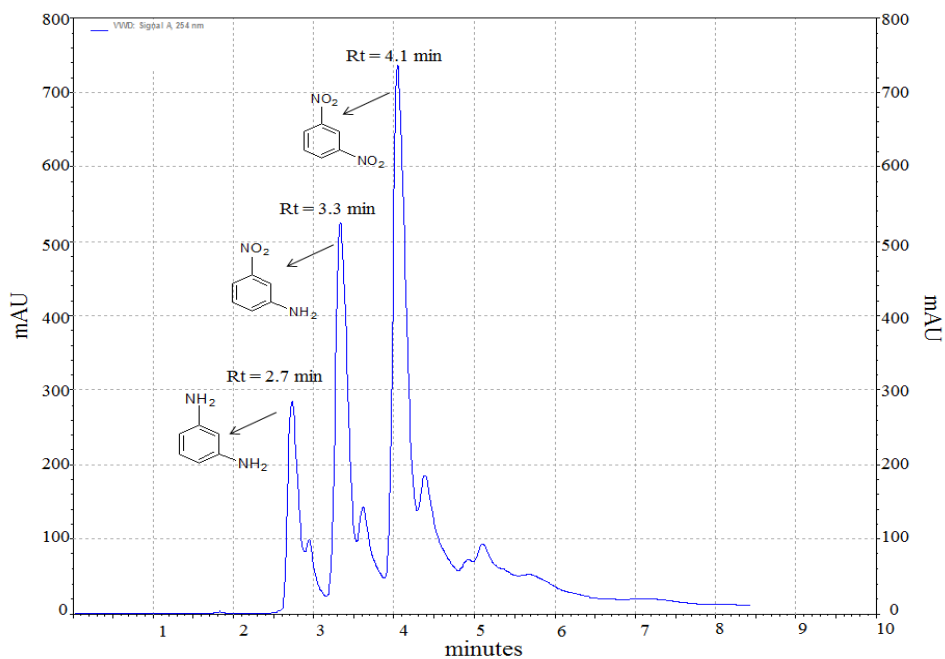


Fig S10. HPLC chromatogram of mixture of authentic 1mM 1,3-dinitrobenzene, 3-nitroaniline and phenylenediamine.

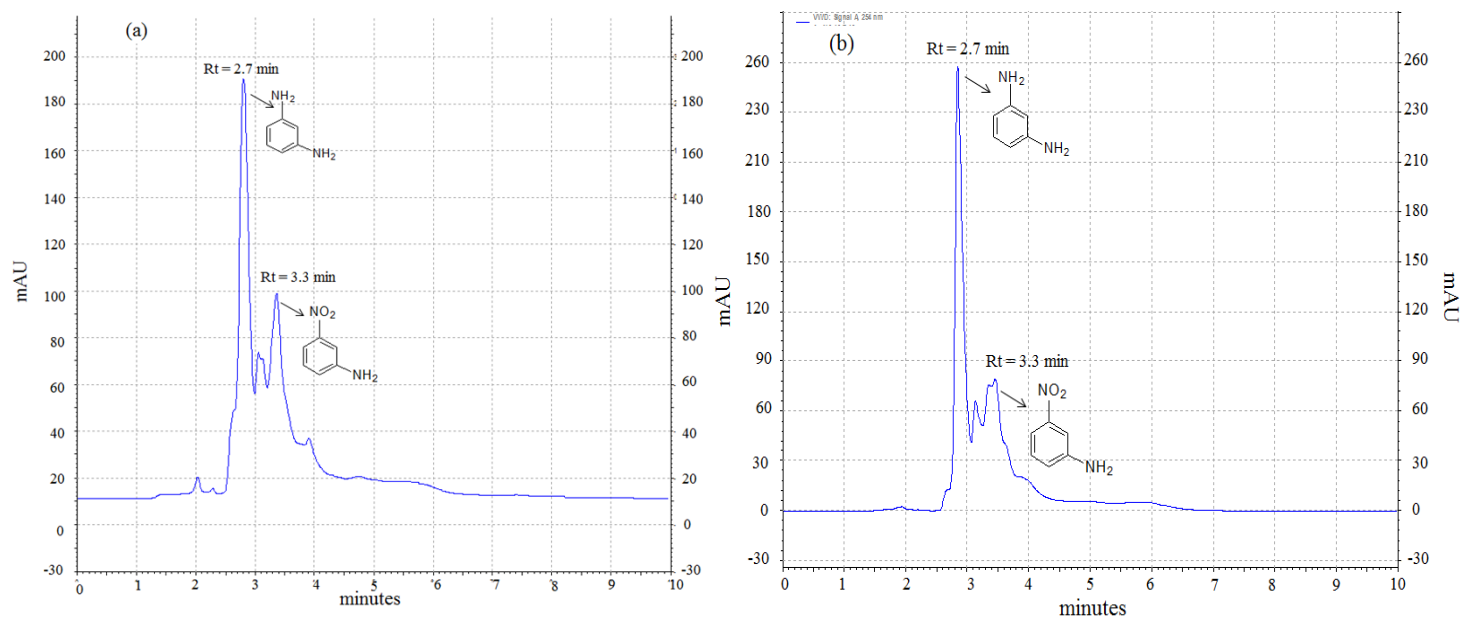


Fig S11. HPLC chromatogram of reaction product obtained after 10-18 min of reduction of 1,3-dinitrobenzene (1mM) by (a) Au@Ag10 core-shell nanocomposites, and (b) hollow Ag-Au alloys.

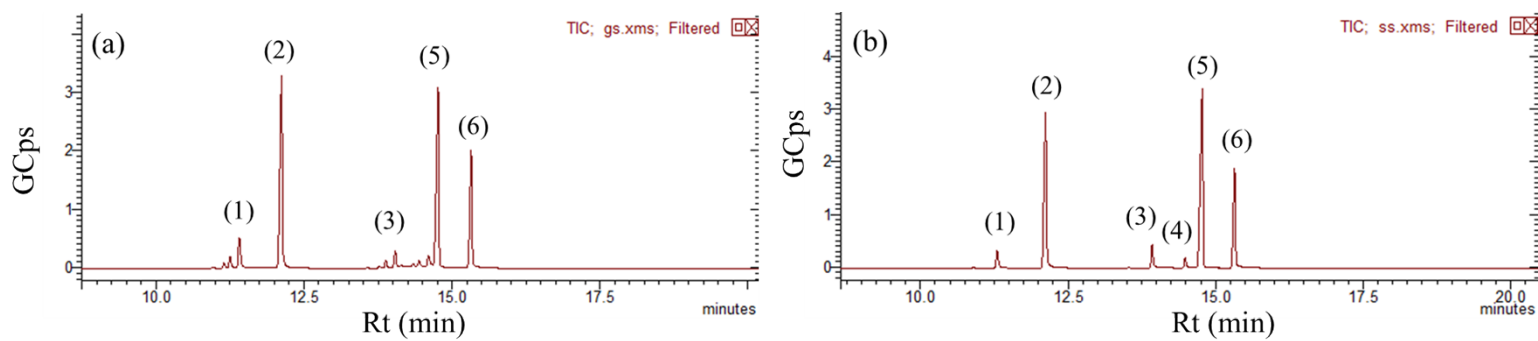


Fig S12. Gas chromatograph (GC) of (a) reaction product obtained after 28-32 min reduction of 1,3-dinitrobenzene by (a) Au nanospheres, and (b) Ag nanospheres.

References

1. J. Lim, S. Pin Yeap, H. X. Che and S. C. Low, *Nanoscale Res. Lett.*, 2013, **8**, 1-14.
2. D. Ray and V. K. Aswal, *Nanosci. Nanotechnol. Lett.*, 2011, **3**, 603-611.
3. P. Pallavicini, G. Chirico, M. Collini, G. Dacarro, A. Dona, L. D. Alfonso, A. Falqui, Y. Diaz-Fernandez, S. Freddi, B. Garofalo, A. Genovese, L. Sironib and A. Taglietta, *Chem. Commun.*, 2011, **47**, 1315-1317.