

Electronic Supplementary Information (ESI)

Synthesis of thiolated Ag/Au bimetallic nanoclusters exhibiting anti-galvanic reduction mechanism and composition-dependent fluorescence

Jian Sun,^a Haoxi Wu,^{a,b} and Yongdong Jin^{*a}

^aState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China. ^bUniversity of the Chinese Academy of Sciences, Beijing 100039, China. Phone/fax: +86-431-85262661. E-mail: ydjin@ciac.ac.cn

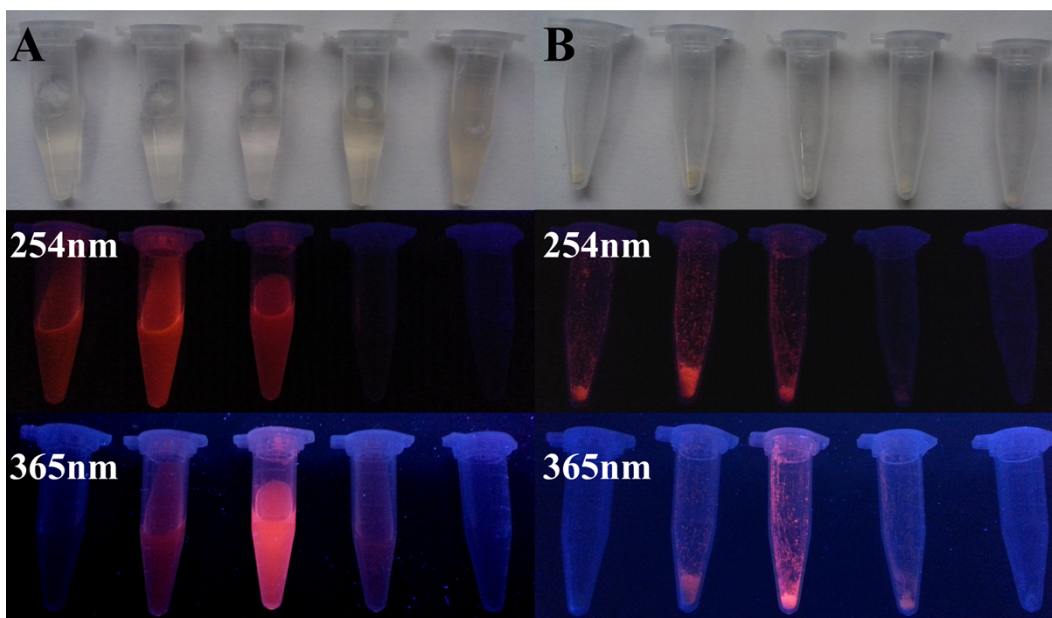


Figure S1. The photographs of the 11-MUA-Ag/Au NCs (Ag-to-Au molar ratios of 0:1, 1:8, 1:2, 1:1 and 1:0 from left to right) in aqueous solution (A) or the freeze-dried powder (B) under irradiation of visible (top), 254 nm (middle) and 365 nm UV light (bottom), respectively.

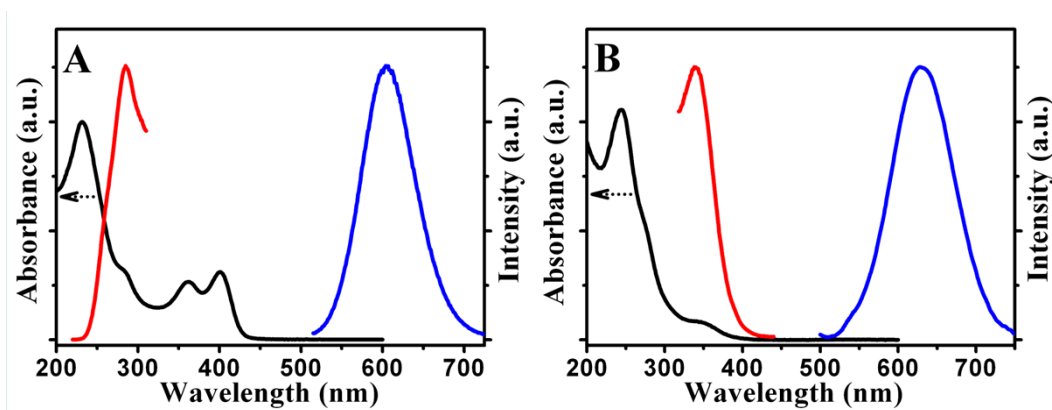


Figure S2. UV-vis absorption (black), fluorescence excitation (red) and emission (blue) spectra of the 11-MUA-AuNCs (A) and 11-MUA-Ag/Au NCs (1:2) (B).

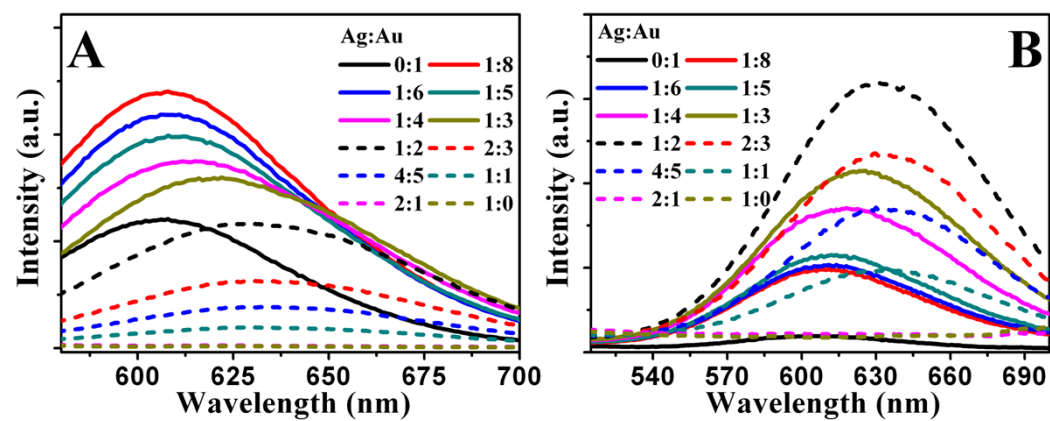


Figure S3. Fluorescence emission spectra of the 11-MUA-Ag/Au NCs at excitation of 280 nm (A) and excitation of 360 nm (B) prepared with different Ag-to-Au molar ratios at a constant total concentration of metal ions (0.75 mM).

Table S1. Fluorescence properties of the 11-MUA-Ag/Au NCs prepared at various concentration ratios of H₂AuCl₄ to AgNO₃

AgNO ₃ : H ₂ AuCl ₄	excitation (nm)	emission (nm)	QYs (%)
0:1	285	605	2.38
1:8	285	607	3.80
1:6	290	608	3.15
1:5	320	610	3.52
1:4	322	612	4.09
1:3	327	620	4.96
1:2	340	630	6.81
2:3	345	632	4.88
4:5	350	635	3.22
1:1	355	635	1.18
2:1	~355	~635	0.04
1:0	—	—	—

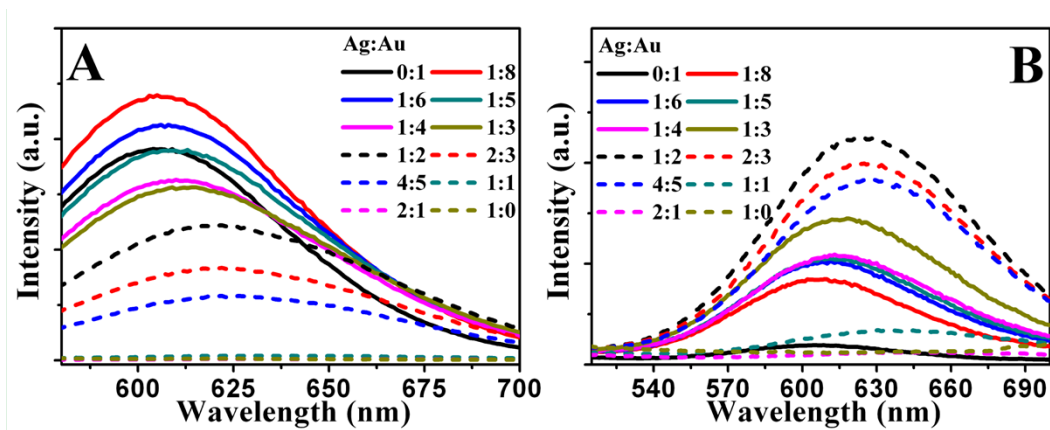


Figure S4. Fluorescence emission spectra at excitation of 280 nm (A) and excitation of 360 nm (B) of the 11-MUA-Ag/Au NCs prepared with constant final HAuCl₄ concentration (0.75 mM) and different Ag-to-Au molar ratios by changing the added volume of AgNO₃ stock solution.

Table S2. ICP-OES data and the Ag-to-Au molar ratios of 11-MUA-Ag/Au NCs calculated from the ICP-OES, EDX and XPS data, respectively.

AgNO ₃ : HAuCl ₄	ICP-OES data			Ag: Au calculated from EDX	Ag: Au calculated from XPS
	Ag (ppm)	Au (ppm)	Ag: Au		
0: 1	—	193600	0: 1	0: 1	0: 1
1: 8	11290	181500	1: 16	1: 30	1: 5.4
1: 2	39660	151400	1: 3.8	1: 2.7	1: 1.2
1: 1	60320	106500	1: 1.8	1: 0.43	1: 0.8
1: 0	18870	—	1: 0	1: 0	1: 0

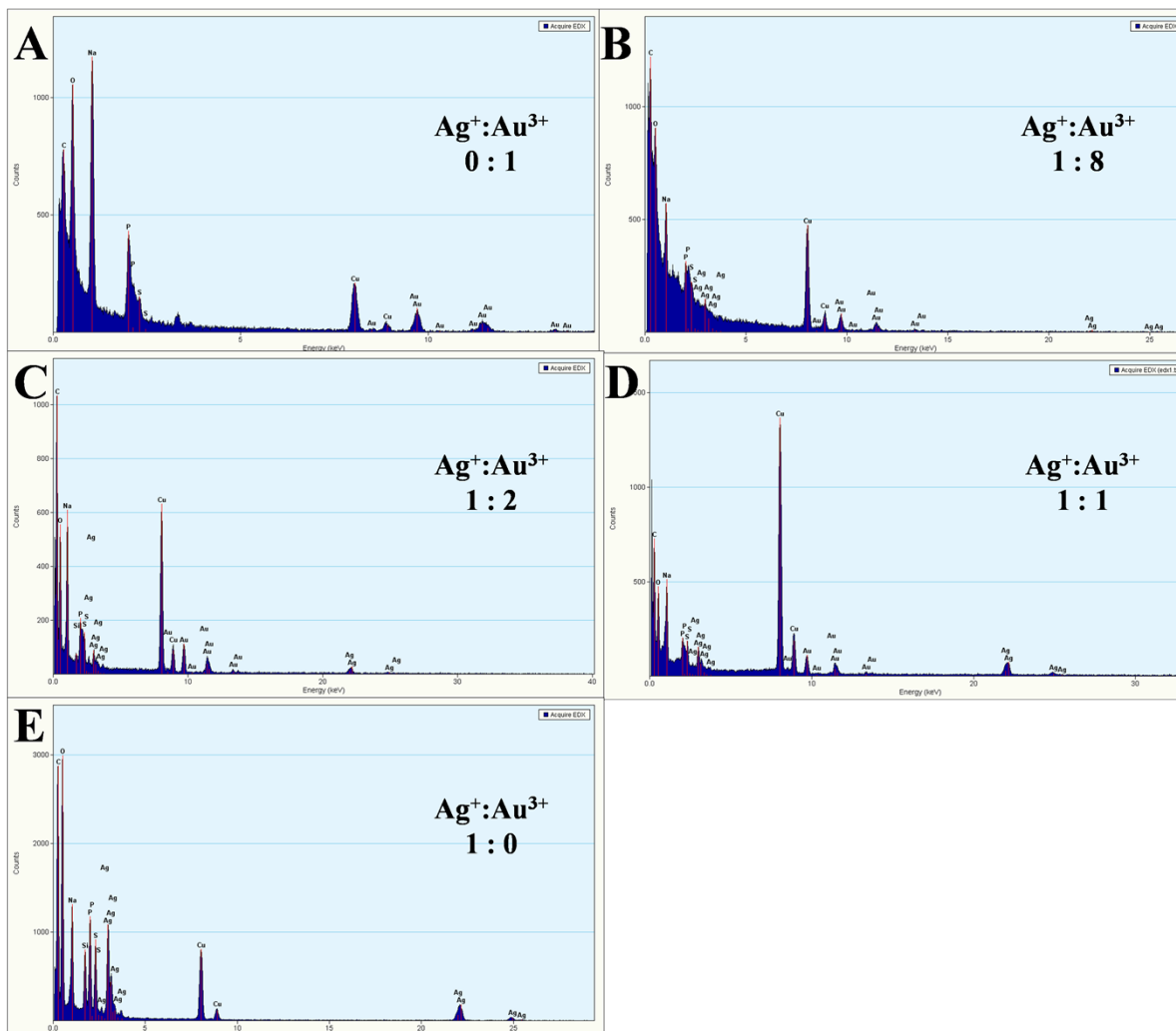


Figure S5. EDX spectra collected for the 11-MUA-Ag/Au NCs prepared at Ag-to-Au molar ratios of (A) 0:1, (B) 1:8, (C) 1:2, (D) 1:1, and (E) 1:0, respectively.

Table S3. The total metal (Ag/Au)-to-S molar ratios of 11-MUA-Ag/Au NCs calculated from the ICP-OES and XPS data, respectively.

AgNO ₃ : HAuCl ₄	Ag/Au: S calculated from ICP-OES	Ag/Au: S calculated from XPS
0: 1	1: 0.17	1: 1.2
1: 8	1: 0.17	1: 0.92
1: 2	1: 0.21	1: 1.3
1: 1	1: 0.26	1: 1.2
1: 0	1: 1.6	1: 1.2

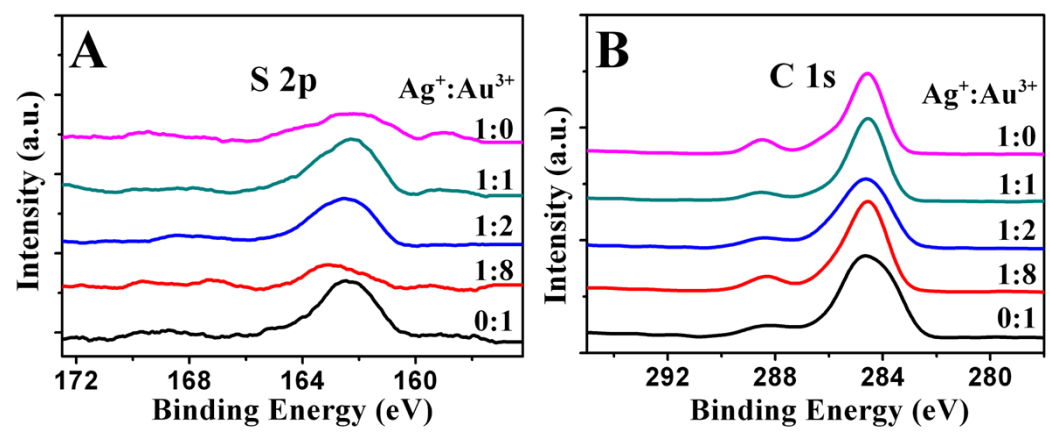


Figure S6. XPS spectra of S 2p (A) and C 1s (B) for the 11-MUA-Ag/Au NCs prepared at Ag-to-Au molar ratios of 0:1, 1:8, 1:2, 1:1, and 1:0, respectively.

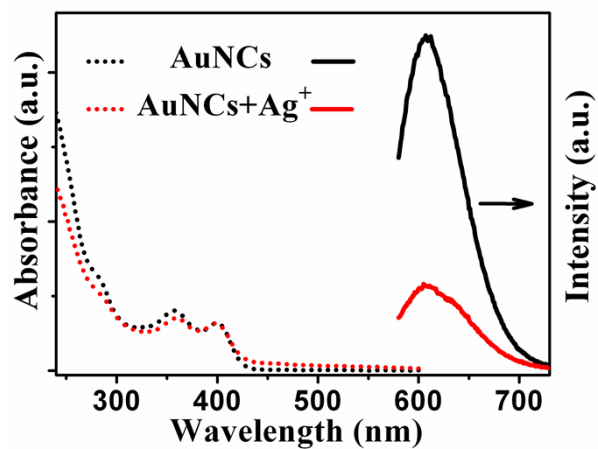


Figure S7. (A) UV-vis absorption (dotted lines) and fluorescence emission (solid lines) spectra of the as-obtained purified 11-MUA-AuNCs before (black) and after (red) adding Ag⁺ ions.

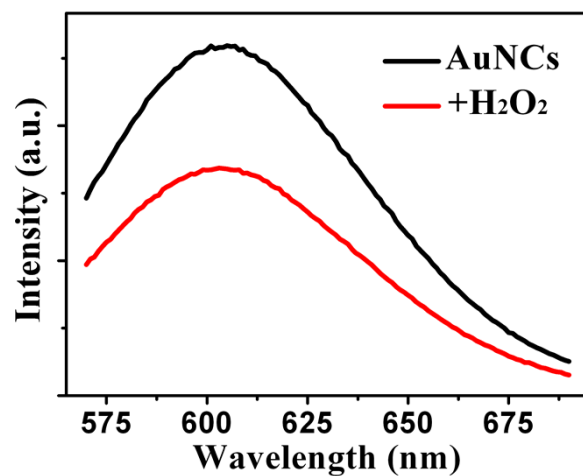


Figure S8. Fluorescence emission spectra (excitation at 280 nm) of the as-obtained purified AuNCs before (black lines) and after (red lines) adding H₂O₂.

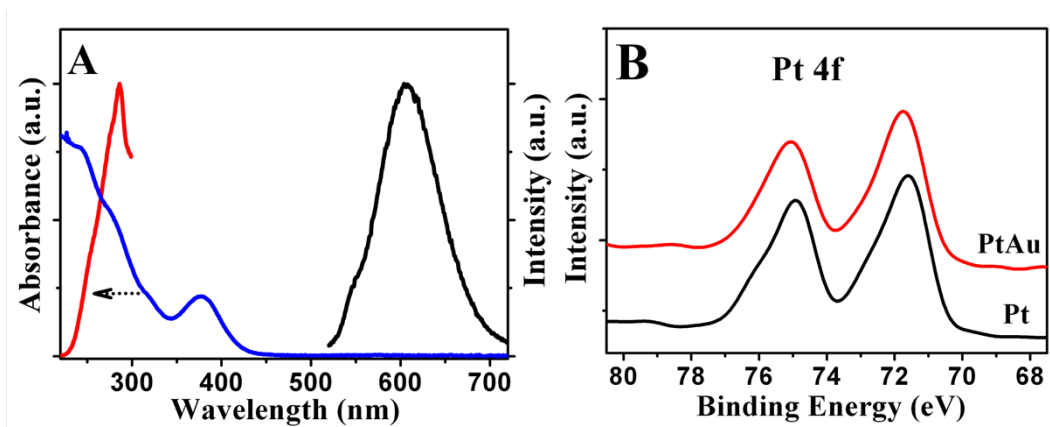


Figure S9. (A) UV-vis absorption (blue), fluorescence excitation (red) and emission (black) spectra of the 11-MUA-Pt/Au NCs prepared at Pt-to-Au molar ratios of 1:2. (B) XPS spectra of Pt 4f for the 11-MUA-Pt (black) and 11-MUA-Pt/Au (1:2) NCs (red).

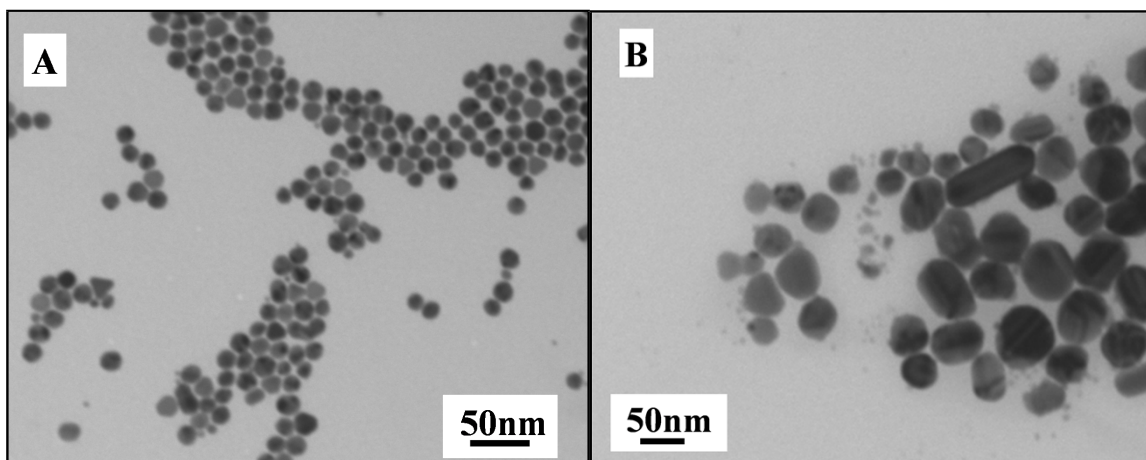


Figure S10. Typical TEM images of the control 11-MUA-AuNPs (A) and 11-MUA-AgNPs (B) prepared through the citrate-mediated reduction and ligand exchange method.

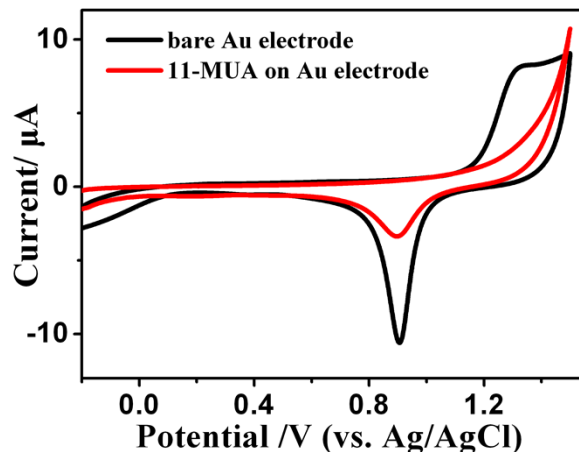


Figure S11. Cyclic voltammograms of the bare bulk Au electrode before (black) and after (red) self-assembling of 11-MUA monolayer, respectively, in 0.5 M H_2SO_4 solution. Note that after surface passivation by 11-MUA monolayer, the oxidation peak around 1.35 V disappeared, but the onset oxidation potential (~ 1.1 V) is quite similar to that of the bare bulk Au electrode.

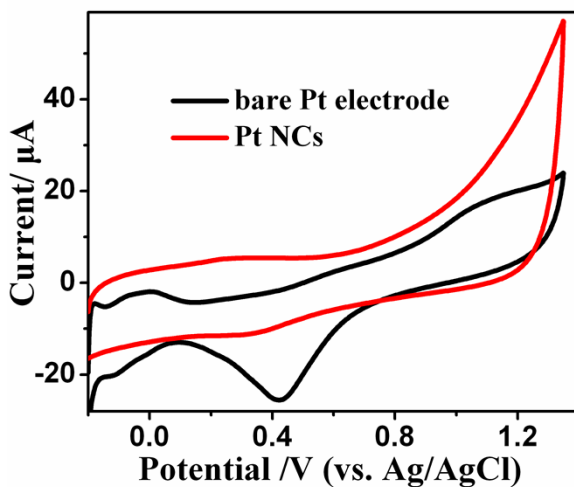


Figure S12. Cyclic voltammograms of the bare bulk Pt electrode (black) and 11-MUA-Pt NCs (red), respectively, in 0.5 M H_2SO_4 solution on the glassy carbon electrode.

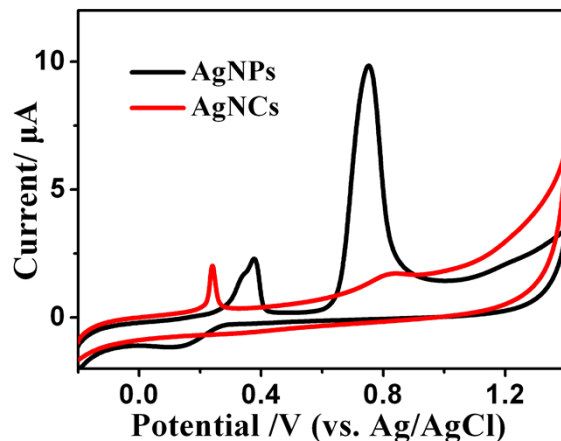


Figure S13. Cyclic voltammograms of the 11-MUA-AgNPs (~ 40–60 nm) and 11-MUA-AgNCs (~ 2.4 nm), respectively, in 0.5 M H₂SO₄ solution on the glassy carbon electrode. Note that the potentials of the oxidation peak of the 11-MUA-AgNPs and 11-MUA-AgNCs increased from ~ 0.75 V to 0.85 V with shrinkage in size.

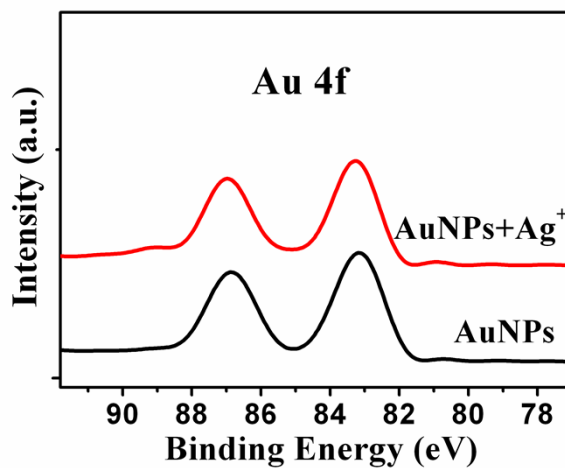


Figure S14. (A) XPS spectra of Au 4f for the as-obtained purified 11-MUA-AuNPs (~15–20 nm in diameter) before (black) and after (red) adding Ag⁺ ions.