

## Supporting Information

### Furthering the Chemosensing of Silver Nanoclusters for Ions Detection

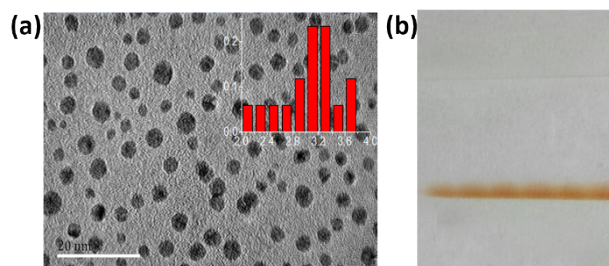
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#### S1. Chemicals

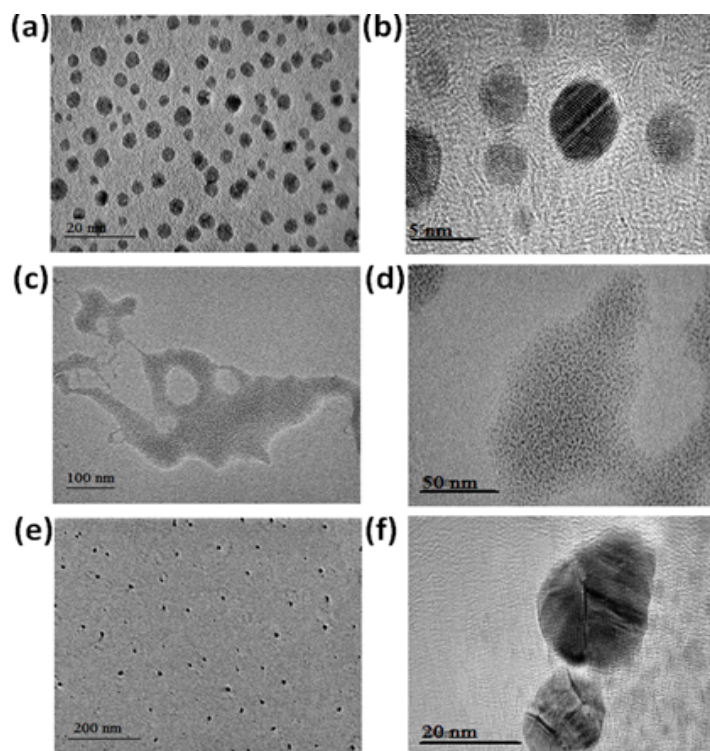
Silver nitrate (99.9995% metals basis) was purchased from Alfa Aesar. L-glutathione (reduced, 99%) and sodium borohydride (99%) were obtained from J&K Scientific Ltd. (Beijing, China). Methanol was purchased from Sinopharm Chemical Reagent Co., Ltd. (HPLC, Beijing, China). Ultrapure water (18.2 M $\Omega$ ) was used in all experiments.

#### S2. TEM Characterizations and PAGE analysis

**Fig. S1** presents a TEM image and related PAGE analysis of the as-prepared silver nanocluster sample.



**Fig. S1.** A typical TEM image (a) of the as-prepared silver nanoclusters, and related polyacrylamide gel electrophoresis (PAGE) analysis (b).

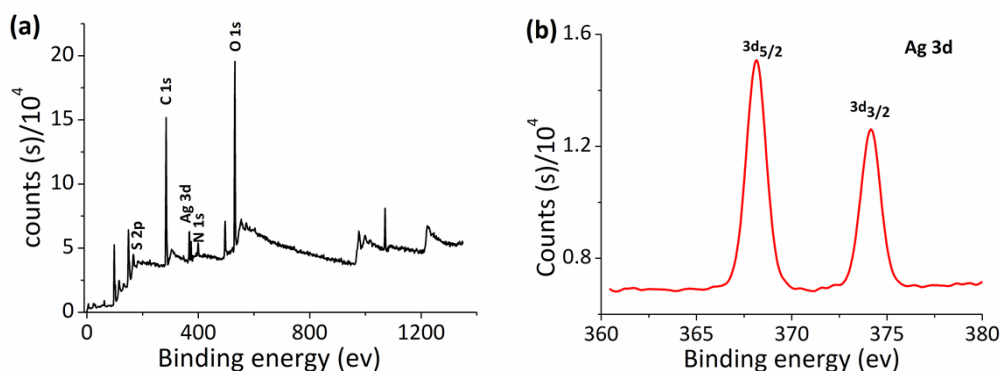


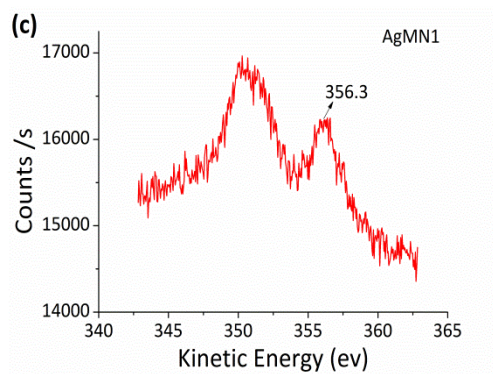
**Fig. S2.** TEM images of (a/b) Ag@SG NCs (2.5 µg/mL), (c/d) Ag@SG NCs with 1.5 mM Mn<sup>2+</sup>, (e/f) Ag@SG NCs with 0.3 mM of I<sup>-</sup> ions.

### S3. XPS analysis

**Fig. S3** shows the XPS patterns of Ag@SG NCS, respectively. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al K $\alpha$  radiation. The 500 µm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about  $3 \times 10^{-10}$  mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

The auger peak of silver is provided (**Fig S3c**), where the auger parameter is: 368.2 (Binding Energy) + 356.3 (Kinetic Energy) = 724.5 ev, suggesting the presence of Ag(I) state.

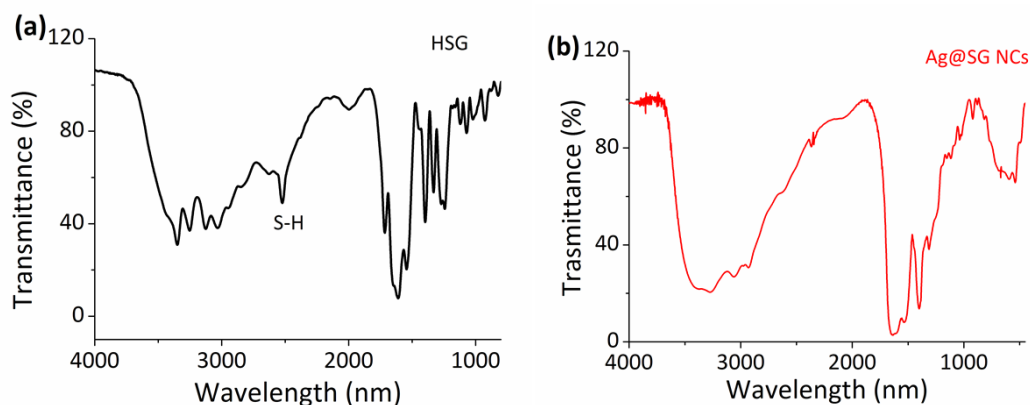




**Fig. S3.** A XPS survey spectrum of Ag@SG NCs (a), the expanded Ag 3d region (b), and the auger peak of silver.

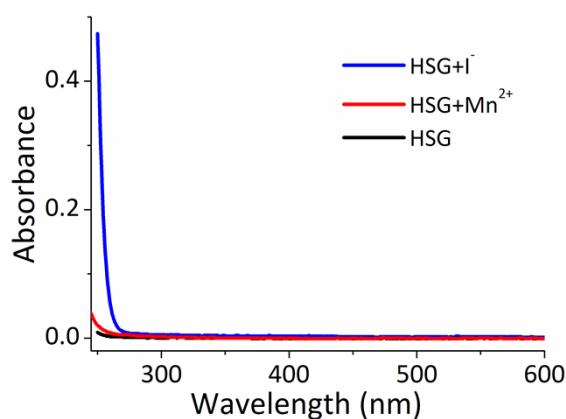
## S4. Spectral Analysis

**Fig. S4** shows the IR spectrum of the Ag@SG NCS, comparing with the IR of respectively and IR spectra of HSG. It is notable that the obvious peak assigned to S-H group disappeared for the Ag@SG NCs.



**Fig. S4.** IR spectrum of HSG (a) and the as-prepared Ag@SG NCS (b).

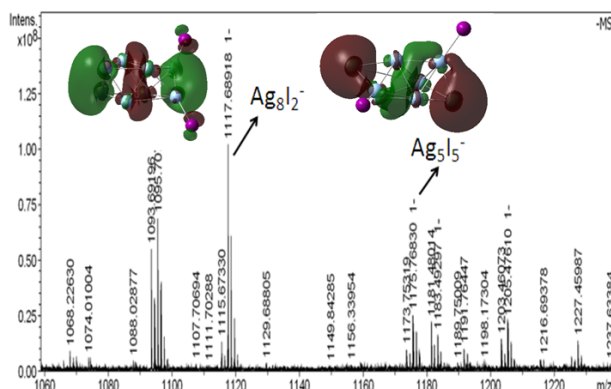
**Fig. S5** presents the absorbance spectra of HSG with  $\text{Mn}^{2+}$  and  $\text{I}^-$  ions, where rare changes exist upon the addition of  $\text{Mn}^{2+}$  (red curve) and  $\text{I}^-$  (blue curve) ions in comparison with the UV-Vis of only HSG (black line).



**Fig. S5.** UV-Vis spectra of HSG, HSG plus  $\text{Mn}^{2+}$  and HSG plus  $\text{I}^-$ .

## S5. Regarding to the sensing mechanism

While we cautiously did not provide a reliable mass spectrum of as-prepared Ag@SG NCs due to the uncertain fragment peaks within several times of repeated mass spectrometry experiments, a fact is that there are always  $\text{Ag}_n\text{I}_x^-$  peaks being observed for the Ag@SG NCs after adding iodine ions. **Fig. S6** presents an ESI-MS spectrum of Ag@SG NCs upon the addition of  $\text{I}^-$ , where the mass spectrum displays one peak at  $m/z = 1117.689$  and another at  $m/z = 1175.768$ , corresponding to the ionic  $\text{Ag}_8\text{I}_2^-$  and  $\text{Ag}_5\text{I}_5^-$  respectively. These observed  $\text{Ag}_n\text{I}_x^-$  fragment peaks probably results of  $\text{Ag}_x\text{I}_y(\text{SG})_z(\text{HSG})_r^-$  as proposed in the main text, evidencing that  $\text{I}^-$  ions interacted strongly with the silver core.



**Fig S6.** An ESI-MS spectrum of the as-prepared Ag@SG NCs (2.5  $\mu\text{g/mL}$ ) after adding  $\text{I}^-$  ions ( $\sim 2.5$  mM). As an example, the inset images display the HOMO orbitals of two  $\text{Ag}_8\text{I}_2^-$  isomers.