Supporting Information

Furthering the Chemosensing of Silver Nanoclusters for Ions Detection

Weihua Ding, a,b Saipeng Huang, a,b Lingmei Guan, a,b Xianhu Liu, a,b Zhixun Luo* a

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 MΩ) 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).](image-url)
Fig. S2. TEM images of (a/b) Ag@SG NCs (2.5 μg/mL), (c/d) Ag@SG NCs with 1.5 mM Mn$^{2+}$, (e/f) Ag@SG NCs with 0.3 mM of I$^{−}$ 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 Kα radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10$^{-10}$ 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.
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. S5 presents the absorbance spectra of HSG with Mn$^{2+}$ and I$^{-}$ ions, where rare changes exist upon the addition of Mn$^{2+}$ (red curve) and I$^{-}$ (blue curve) ions in comparison with the UV-Vis of only HSG (black line).
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 uncertained fragment peaks within several times of repeated mass spectrometry experiments, a fact is that there are always Ag\textsubscript{n}I\textsubscript{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 I\textsuperscript{−}, where the mass spectrum displays one peak at m/z =1117.689 and another at m/z =1175.768, corresponding to the ionic Ag\textsubscript{8}I\textsubscript{2} and Ag\textsubscript{5}I\textsubscript{5} respectively. These observed Ag\textsubscript{n}I\textsubscript{x} fragment peaks probably results of Ag\textsubscript{8}I\textsubscript{2}(SG)\textsubscript{x}(HSG)\textsubscript{y} as proposed in the main text, evidencing that I\textsuperscript{−} ions interacted strongly with the silver core.

**Fig S6.** An ESI-MS spectrum of the as-prepared Ag@SG NCs (2.5 µg/mL) after adding I\textsuperscript{−} ions (~2.5 mM). As an example, the inset images display the HOMO orbitals of two Ag\textsubscript{8}I\textsubscript{2} isomers.