Electronic Supplementary Information

Experimental Details

Materials

All thiol compounds, i.e., thioglycol (TG), 3-mercaptoproprionic acid (MPA), mercaptosuccinic acid (MSA), dimercaptosuccinic acid (DMSA), glutathione (GSH), cysteamine hydrochloride (CyA), cysteine (Cys), and N-acetylcysteine (NAC), were purchased from Sigma-Aldrich (St. Louis, MO, USA). Chloroaurate acid was purchased from Sinoreagent Co. Ltd. (Shanghai, China). Phosphate buffer (PB) of 0.1 M (pH 7.0) was prepared by mixing stock solution of Na_2HPO_4 and NaH_2PO_4 with a volume ratio of 61:39. Milli-Q water (Millipore, USA) was used throughout.

The GSH capped Au (Au-GSH) NCs were synthesized in our common steps. [S1] To prepare Au NCs with different GSH capping density, the feeding ratios of GSH/$AuCl_4^-$ tune from 0.8:1 to 1.5:1. The increasing GSH capping number will enhance the fluorescence of Au-GSH NCs.

Methods

The fluorescent spectra were obtained on an RFPC 5301 fluorescent spectrometer (Shimadzu Co. Ltd., Japan). The ECL was acquired on an IFFM-E chemiluminescence analyzer (Remax, Xi'an, China) accompanied with an electrochemical workstation (CHI 660C, CH Instrument, TX, USA). The bias potential of chemiluminescence analyzer was set at – 800 V. A three-electrode system was comprised of a glassy carbon electrode (3 mm in diameter) as working electrode, a Pt electrode as counter electrode, and an Ag/AgCl (in saturated KCl) as reference electrode, respectively. Nitrogen (99.9% purity) was bubbling during the experiments to remove oxygen interference and facilitate the diffusion. As comparison, the ITO electrode (Nanbo Display Technology Co. Ltd., Shenzhen, China, 0.5× 0.5 cm^2, < 10 Ω cm^{-1}) and Pt disk electrode (3 mm in diameter) was used.

The ECL spectra were measured by using a series of light filters with the cut-off wavelengths of 450, 470, 490, 510, 535, 550, 565, 580, 600, 630, 650, 670, 720, 750 nm, respectively. The transparency of all filters are 90%, enabling the effective comparison. The calculation methods are same as those we described previously. [S2]

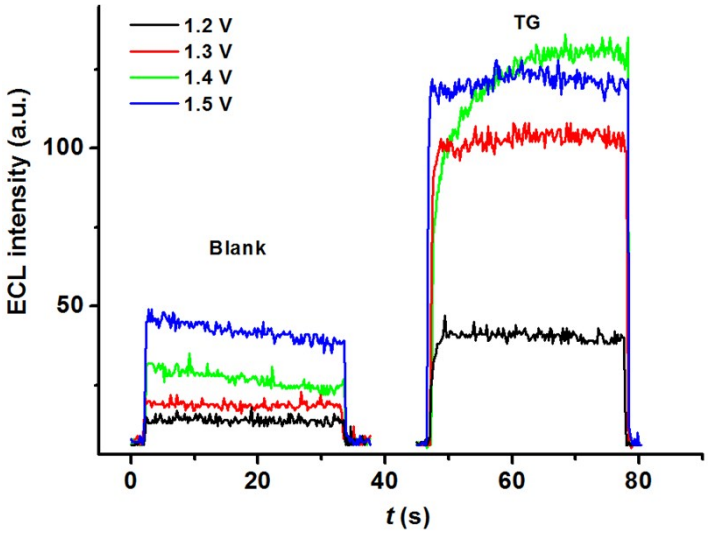

Fig. S1 Potential influences on ECL of low luminescent AuGSH of 0.18 mg/mL before and after addition of TG of 0.1 mM in ECL reaction buffer, i.e., PB (pH 7.0) containing 10 mM TEA.

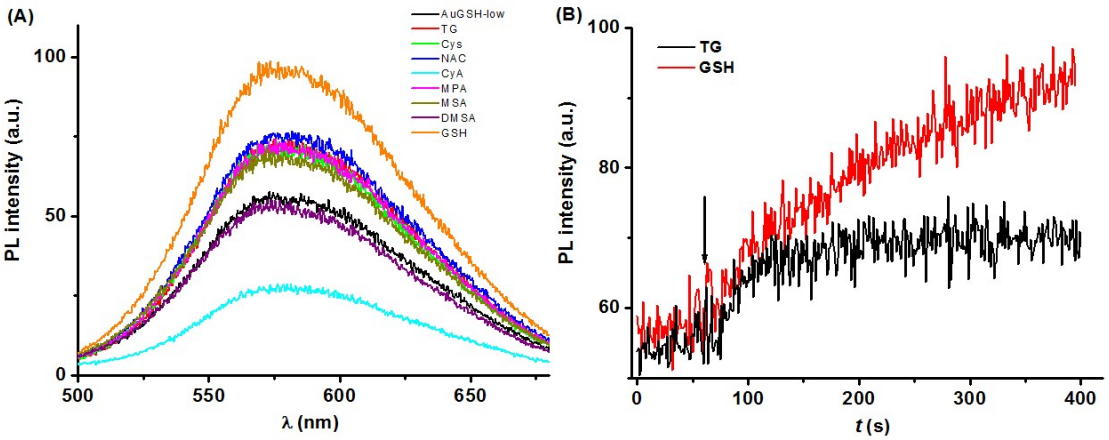

Fig. S2 (A) PL responses of low luminescent AuGSH (1:1) of 0.09 mg/mL to thiols of 0.1 mM in ECL reaction buffer. Excitation wavelength: 390 nm. Note that the fluorescence enhancement by DMSA (purple) was not observed, possibly due to the steric hindrance of the dual thiol and carboxyl groups. CyA (cyan) showed a decreased fluorescence, which might be related to the presence of TEA. (B) PL time course of low luminescent AuGSH after injection of GSH and TG with a final concentration of 0.1 mM (Ex/Em wavelength: 390/570 nm) in ECL reaction buffer.

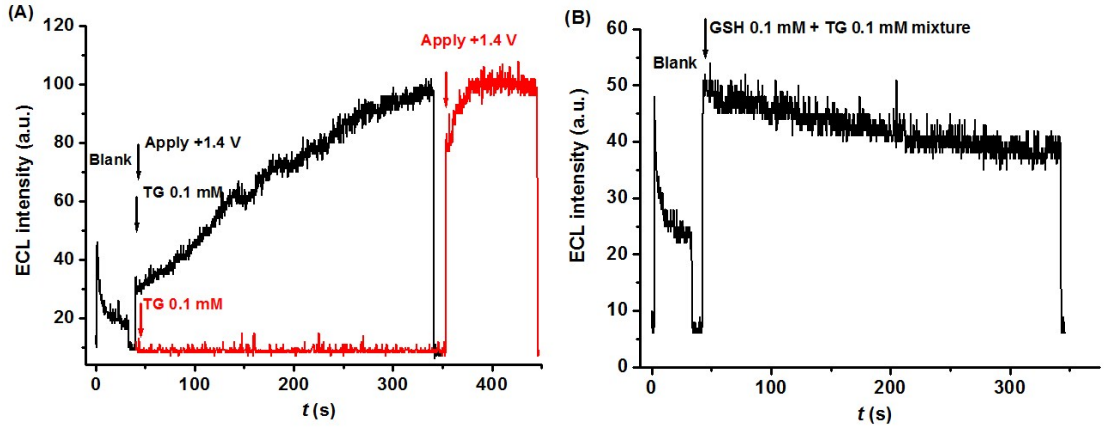

Fig. S3 (A) ECL responses with (black) or without (red) of applying a potential of +1.4 V during 5-min incubation. (B) ECL changes in the presence of TG and GSH mixture. Concentration: 0.09 mg/mL.

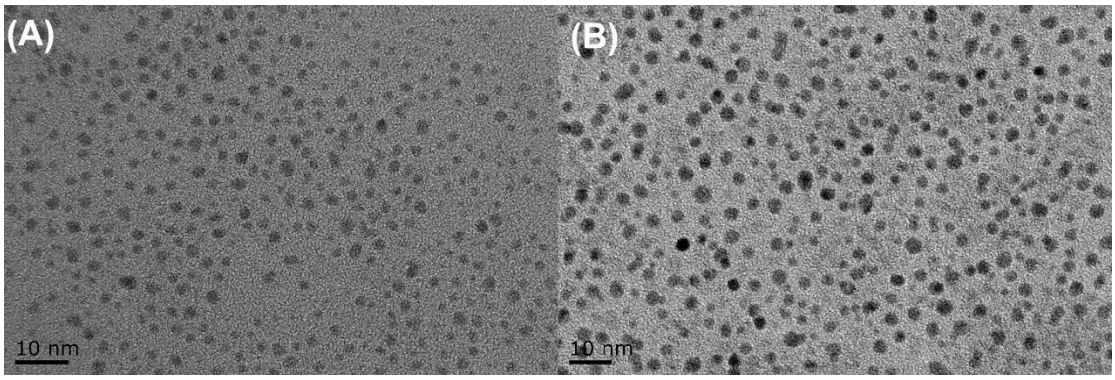

Fig. S4 TEM of low luminescent AuGSH (A) and AuGSH/TG (B) samples.

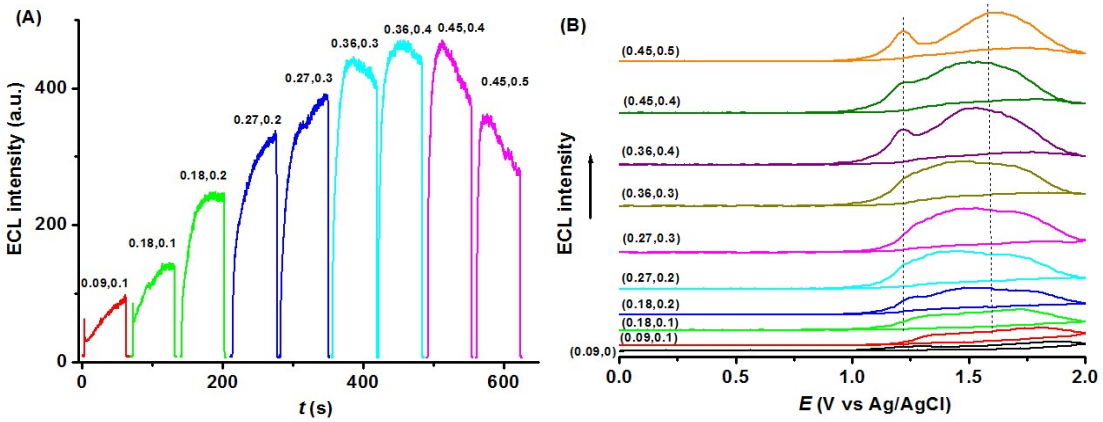

Fig. S5 (A) ECL responses to different concentrations of AuGSH and TG at +1.4 V. The concentrations of AuGSH and TG pairs were denoted as [low luminescent AuGSH (mg/mL), TG (mM)]. (B) ECL of AuGSH/TG by using cyclic voltammetric mode.

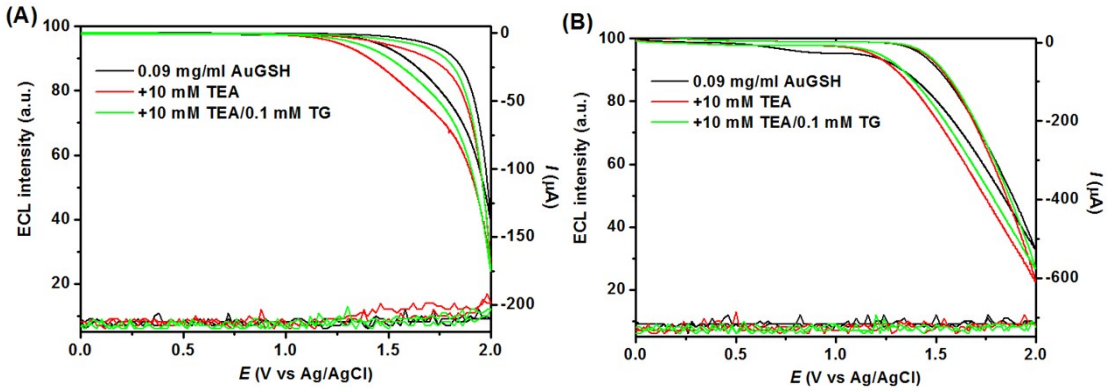

Fig. S6 ECL of AuGSH/TG on (A) ITO and (B) Pt electrode by using cyclic voltammetric mode.

References

[S1] X. Su, H. Jiang and X. M. Wang, *Anal. Chem.*, 2015, **87**, 10230-10236.

[S2] H. Jiang and X. M. Wang, *Electrochem. Commun.*, 2009, **11**, 1207-1210.