

Electronic supplementary information

for

Electrogenerated chemiluminescence from Au nanoclusters

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1. Synthesis of Au₂₅ nanocluster.

The synthesis of Au₂₅ is the same as the previous work.^{S1} In brief, 250 mg BSA was dissolved in 9mL water and mixed with 1mL HAuCl₄ solution (the concentration of Au, 0.02 g/mL), reacting at 37°C for half an hour, then 0.5 mL 1 M NaOH was added in the solution and stirred for 12 hours. The Au₂₅ nanoclusters solution is purified via dialysis using 5000 Da MWCO dialysis bag. The concentration of Au₂₅ clusters solution is estimated to be ca. 4×10⁻⁴ M according to the previous work.^{S2} The pH value of Au₂₅ clusters solution is ca 8.

2. Instruments and chemicals

Cyclic voltammogram (CV) was recorded with a CHI 604B Electrochemical Analyzer (ChenHua Instrument, Shanghai, China) by a conventional three-electrode configuration. Pt electrode (3 mm in diameter) was used as a working electrode, an Ag/AgCl (3 mol/L KCl) reference electrode and a Pt foil were used as reference and auxiliary electrodes, respectively. ECL signals were recorded by ECL Instrument with a PMT (MP 963, PerkinElmer Optoelectronics, Germany. 185 nm ~ 850 nm) controlled by a personal computer. The PMT was set at 800 V in the process of luminescence detection. ECL spectrum was obtained by a series of optical filters (see supporting information). All the other chemicals were of analytical grade. Deionized water (Millipore, Bedford, MA, USA) was used throughout.

3. ECL curves in the presence of BSA

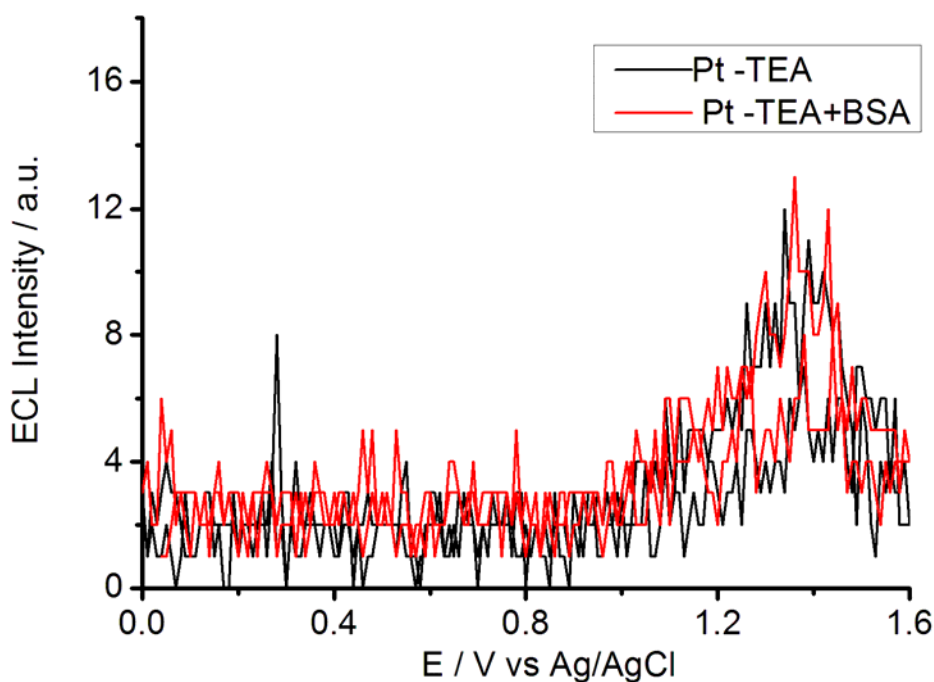


Figure S1. ECL curves in the presence and absence of 0.25 mg/mL BSA in 70 mM TEA + 0.1 M NaClO₄ solution at Pt electrode. scanning rate: 100mV/s.

ECL curves at the Pt electrode in the presence and the absence of BSA using TEA as coreactant are indicated in the Figure S1. There is no obvious difference in the presence and the absence of BSA, which suggesting the BSA is not a luminescent species for ECL. (The concentration of BSA is the same as that in Figure 1 in the main text where a strong ECL is observed, other experimental conditions are also the same)

4. Experimental details for measure of ECL spectrum.

The ECL spectrum of Au₂₅ cluster can be measured by fluorometer directly as it is strong, as shown in Figure S2. However, for the ECL spectrum from bare Pt electrode using TEA as coreactant, it is too weak to measure by fluorometer. Therefore, to solve this problem, and for the aim of comparison, ECL spectra are all measured by a series of optical filters(400, 425, 460, 490, 535, 555, 575, 620, 640, 680, 705, 745 nm). Before the measure of ECL spectrum, the ECL Instrument and the optical filter are rectified to the fluorometer using a tungsten lamp. Specifically, the spectrum of tungsten lamp is measured by the fluorometer, and then by the optical filters with the ECL instrument. The rectificatory factors are calculated by the difference between these two ECL spectrums. For the ECL spectrum of Pt electrode, the high voltage of PMT is set to 1200V and the concentration of TEA is 0.7 M, while for Au₂₅ clusters, the high voltage is set to 800 V, TEA concentration is 0.14 M. The agreement of ECL spectrum of Au₂₅ clusters measured by fluorometer and optical filters, both at ca 680 nm, implies the validity of spectrum measured by optical filters.

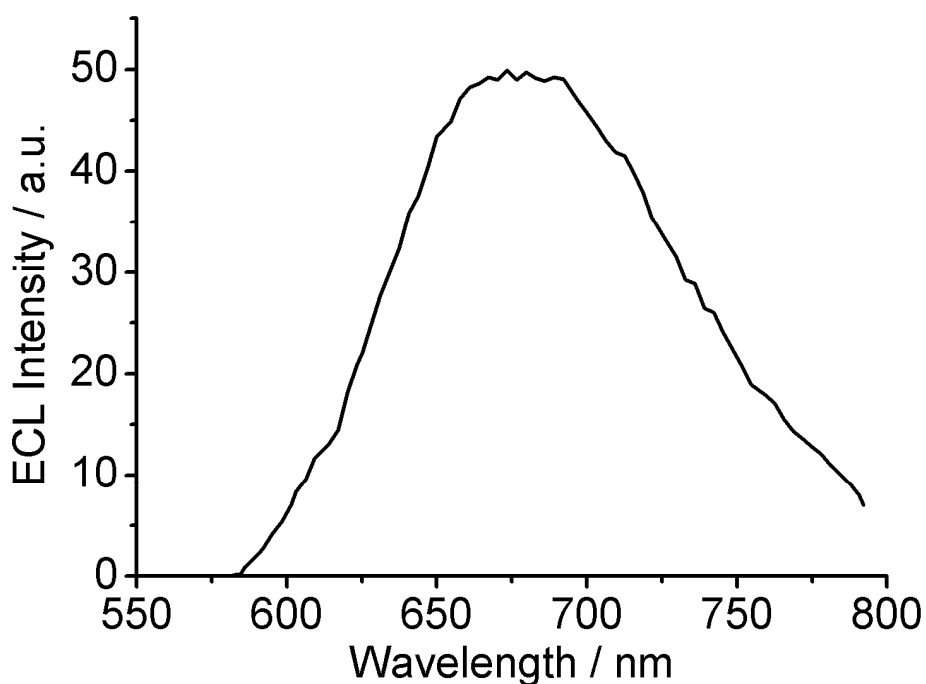


Figure S2. ECL spectrum of Au₂₅ clusters measured by fluorometer.

5. Influences of heavy metal ions.

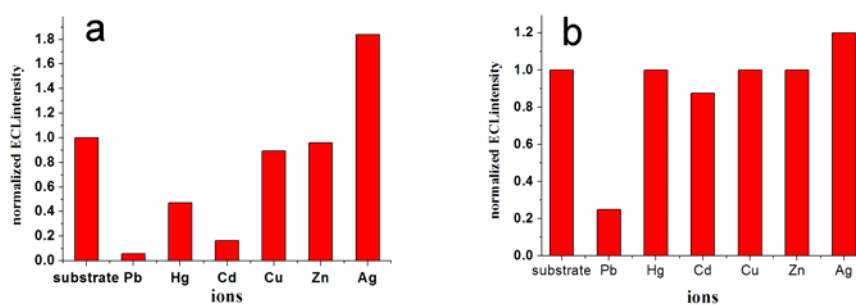


Figure S3. Influence of 1×10^{-5} M heavy metal ions on the ECL of Au clusters before (a) and after (b) the addition of 7.5×10^{-4} M L-cysteine. Solution: 0.1 M NaClO₄, 140 mM TEA, and 8.0×10^{-7} M Au₂₅ clusters solution.

Table S1. Solubility product K_{sp} of heavy metal ions sulfide and stability constant ($\lg\beta$) with ligands

M	K_{sp} of Sulfide	$\lg\beta$ of ML	$\lg\beta$ of MX ₂
Ag	6.3×10^{-50}	3.03	12.07
Cd	8.0×10^{-27}	4.12	10.82
Hg	4.0×10^{-53}	9.6	19.65

Cu	6.3×10^{-36}	8.0	16.0
Zn	1.6×10^{-24}	5.3	12.35
Pb	1.0×10^{-28}	2.9	7.5

L = 2, 2'-bipyridyl;

X = 1, 10-phenanthroline

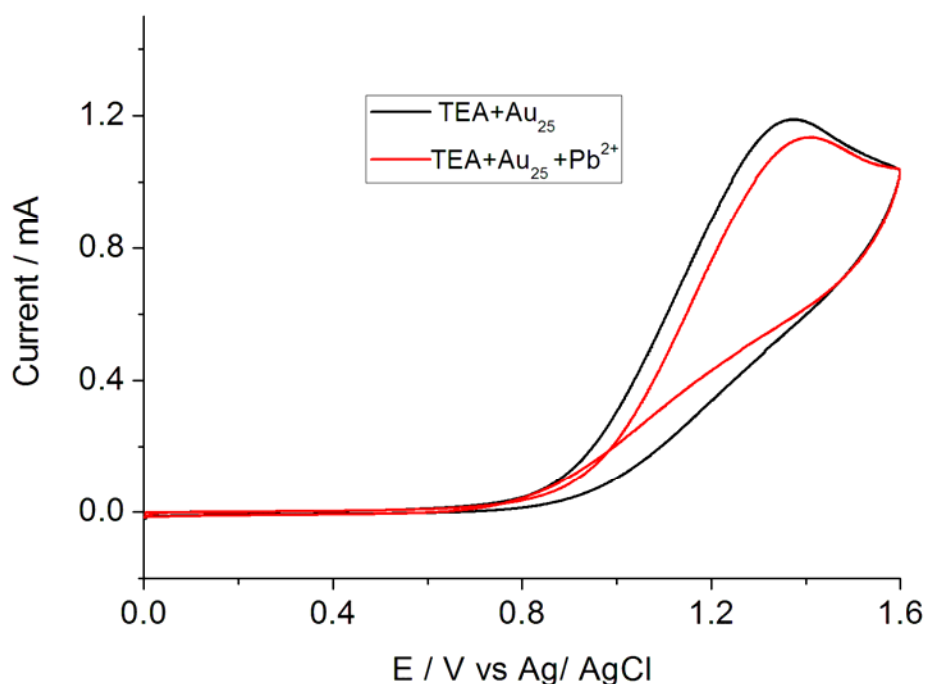


Figure S4. CV curves in the presence (red line) and absence (black line) of 1×10^{-5} M Pb^{2+} at Pt electrode in 0.1 M NaClO_4 , 140 mM TEA, 8.0×10^{-7} M Au_{25} clusters solution.

As can be seen from Figure S3 (a), we found that the influence of ECL intensities doesn't follow the order of $\text{Hg} > \text{Ag} > \text{Cu} > \text{Pb} > \text{Cd} > \text{Zn}$, which suggested by the K_{sp} value of sulfide. The discrepancy can be attributed to the competing coordination between Sulfide and Nitride from the coreactant TEA. For example, although Hg ion can be strongly bond to sulfide, it has a competing coordination effect from TEA (Hg-N is stronger than other heavy metal ions according to the stability constant in Table S1), which can be very strong when the TEA concentration is ca 5-6 order higher than sulfide from the BSA. For Pb ion, as it has much weaker interaction with N, therefore, the inhibition is strong.

The reason why Ag^+ has an enhancing effect on the ECL is not clear, and will be investigated in our later work.

The CVs in the presence and the absence of Pb^{2+} are also indicated in Figure S4, with the addition of Pb^{2+} , the oxidation current is slightly inhibited, while the ECL can be strongly inhibited as shown in Figure S3 a. It is estimated that the metal ions complex the amine, thus changing the amount of $\text{TEA} \cdot ^+$ generated. However, since the concentration of amine is several order higher than metal ions, therefore, the inhibition from complexing of TEA is minor, as indicated from CVs, while the ECL can still be strongly inhibited as they can react with the capping agent S of Au_{25}

clusters.

6. CV curves in the presence of Au₂₅ clusters

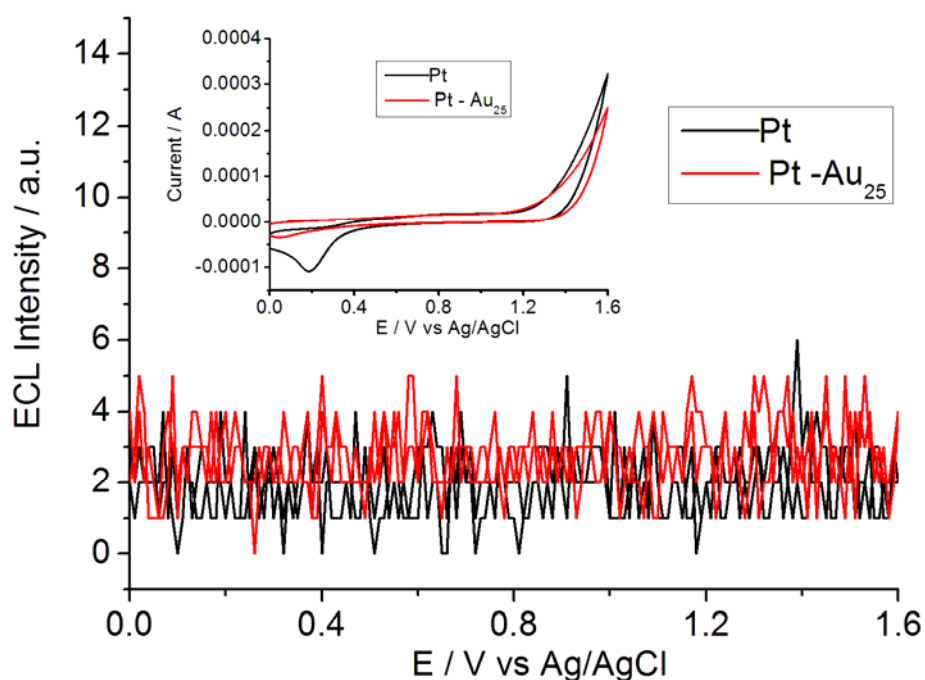


Figure S5 ECL and their corresponding CV(Inset) curves in the presence and absence of 1×10^{-4} M Au₂₅ cluster in 0.1 M NaClO₄ solution at Pt electrode. scanning rate: 100mV/s.

In the presence of higher concentration of Au₂₅ cluster, as shown in the insert of Figure S5, there is no oxidation peak observed, implying that the BSA protected Au₂₅ cluster can not be electrochemically oxidized directly at this scanning range.

7. Influence of Amines

Although amines like tris-n-propylamine (TPrA) can be much soluble in acidic media, the protonation of amines retards their oxidation, making the ECL of Au₂₅ very weak. Therefore, we didn't use buffer solution in this work. The pH value of the solution (70 mM TEA) in this work is ca 11.5. Without using buffer solution, TEA is much more soluble than TPrA, therefore, the ECL of Au₂₅ is very much stronger. The pH value for TPrA is 10.9, and the solubility is poor. However, for other amines, like 2-(Diethylamine)ethanol, with better solubility, it also generates strong ECL compared to TEA.

^{S1} Xie, J.; Zheng, Y.; Ying, J. Y. *J. Am. Chem. Soc.* **2009**, *131*, 888.

^{S2} Xie, J.; Zheng, Y.; Ying, J. Y. *Chem. Commun.* **2010**, *46*, 961.