Supporting Information

Supramolecular Assembly-induced Electrochemiluminescence Enhancement of Gold Nanoclusters for Hemoglobin Detection

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Materials and reagents

Hemoglobin (Hb), potassium chloride (KCl) and fructose were obtained from Aladdin Chemical Co., Ltd. (Shanghai, China). 4-hydroxy-2-mercapto-6-methylpyrimidine (MTU), L-arginine (Arg), and guanidine (Gua), ferroheme (heme), uric acid (UA), alanine and glutamic acid were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH), ascorbic acid (AA) and isopropyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) and triethylamine (TEA) were purchased from Sigma-Aldrich (USA). Phosphate-buffered saline (PBS), sodium chloride (NaCl) and glucose were purchased from Sangon Biotech (Shanghai, China). Ultrapure water was obtained from a Millipore water purification system (18.2 MΩ·cm). All reagents were of analytical grade and not further purified.

Apparatus

Transmission electron microscopy (TEM) were performed on Talos F200X G2, (FEI, USA). The X-ray photoelectron spectrometer (XPS) were recorded through an ESCALAB 250XI (Thermo, USA). Electrochemiluminescence (ECL) spectra were measured with a Fluoromax-4 fluorescence spectrometer (Horiba, Japan). UV-vis absorption spectra were recorded on Cary 100 UV-vis spectrophotometer (Agilent, USA). The cyclic voltammogram (CV) curves were recorded on a CHI660E electrochemistry workstation (CHI China). ECL measurements were performed through MPI-EII ECL analyzer system (Xi'an Remex, China). All the electrochemical experiments were performed with conventional three-electrode system, where the glassy carbon electrode (GCE, d = 3 mm) was used as working electrode, Pt electrode was used as the counter electrode and Ag/AgCl electrode was used as the reference electrode.

The calculation of the ECL efficiency

The ECL efficiency (Φ_{ECL}) was measured according to the reported method, and $Ru(bpy)_3^{2+}$ was used as the reference. [1, 2] The equation was calculated as follows, where

x represented the Au NCs and st represented $Ru(bpy)_3^{2+}$. The Φ_{ECL} of MTU-Au NCs and Arg/ MTU-Au NCs were measured in 0.01M PBS (pH 7.4) containing 200 mM TEA with 0.03 mg mL^{-1} MTU-Au NCs and 0.03 mg mL^{-1} Arg/MTU-Au NCs, respectively. Φ_{ECL} of $Ru(bpy)_3^{2+}$ were measured in 0.01M PBS (pH 7.4) containing 200 mM TEA and 10 μM $Ru(bpy)_3^{2+}$.

$$\emptyset_{ECL} = \frac{\left(\frac{\int ECL\, dt}{\int current\, dt}\right)_x}{\left(\frac{\int ECL\, dt}{\int current\, dt}\right)_{st}} \times 100\%$$

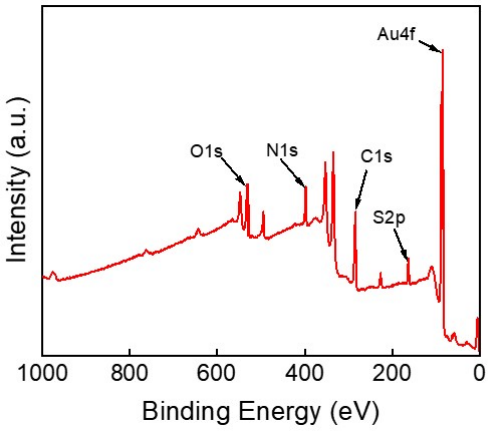

Figure S1. XPS survey spectrum of Arg/MTU-Au NCs.

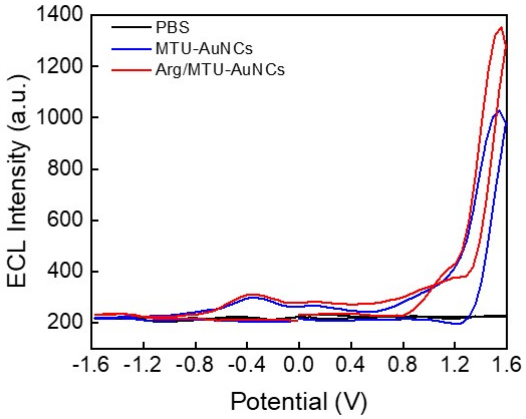

Figure S2. ECL-potential profiles of bare GCE in 0.01 M PBS (pH 7.4), and 0.01 M PBS (pH 7.4) containing MTU-Au NCs, and Arg/MTU-Au NCs. Scan rate: 0.5 V/s. The photomultiplier tube (PMT) was biased at 750 V.

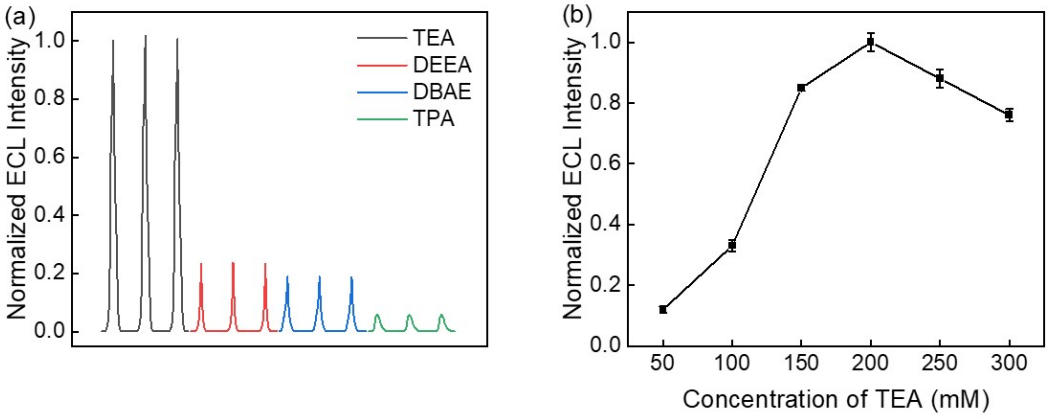

Figure S3. (a) Normalized ECL intensity of Arg/MTU-Au NCs with different coreactants. (b) Normalized ECL intensity of Arg/MTU-Au NCs with different concentrations of TEA as coreactant.

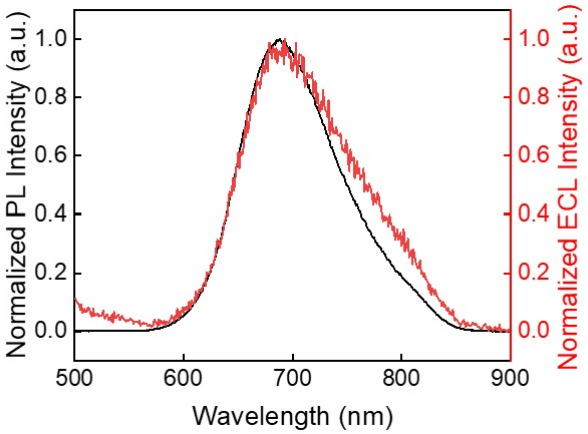

Figure S4. Normalized PL (blank) and ECL (red) emission spectra.

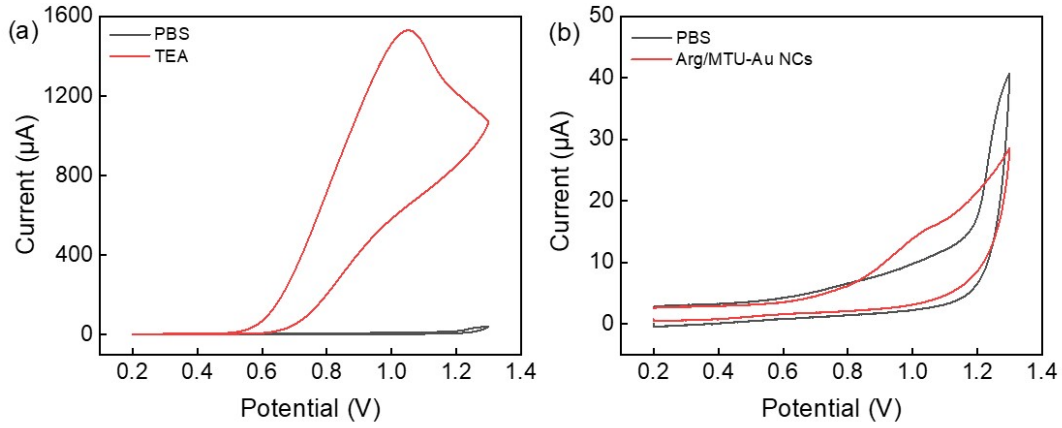

Figure S5. (a) CV curves of GCE in 0.01 M PBS (pH 7.4) and 0.01 M PBS (pH 7.4) containing TEA. (b) CV curves of GCE in 0.01 M PBS (pH 7.4) and 0.01 M PBS (pH 7.4) containing Arg/MTU-Au NCs.

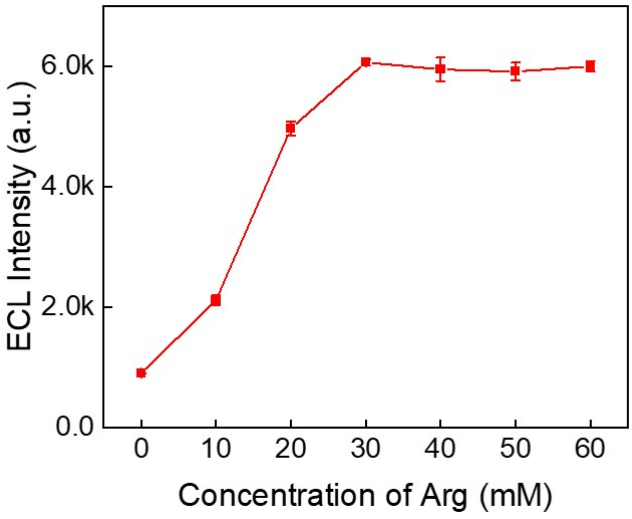

Figure S6. The ECL intensity of Arg/MTU-Au NCs by using different concentrations of Arg for the preparation of Arg/MTU-Au NCs.

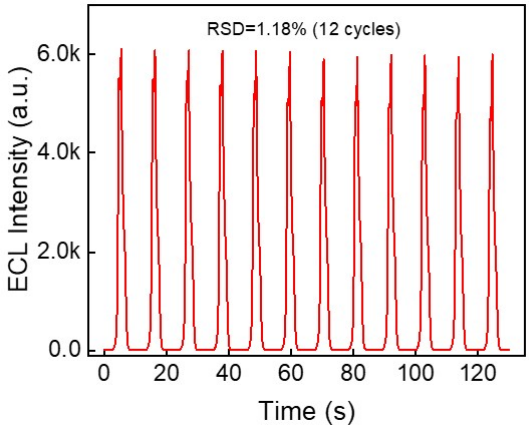

Figure S7. ECL signals of Arg/MTU-Au NCs upon successive scanning for12 cycles.

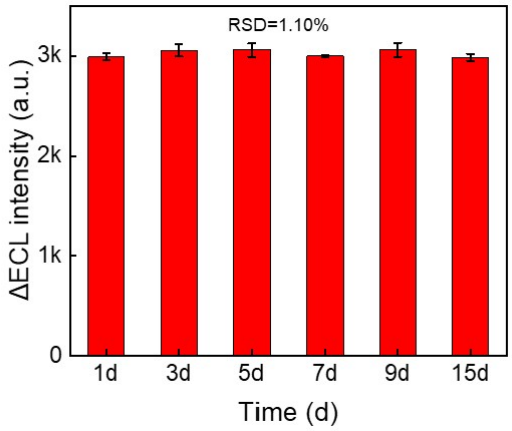

Figure S8. The signal stability of the biosensing platform for the detection of Hb after a storage of 1, 3, 5,7, 9 and 15 days.

References

1. D. Pan, Z. Fang, E. Yang, Z. Ning, Q. Zhou, K. Chen, Y. Zheng, Y. Zhang and Y. Shen, *Angew. Chem. Int. Ed.*, 2020, **59**, 16747-16754.
2. M. Sun, J. Liu, Y. Zhou, J. Zhang, Y. Chai, Z. Li and R. Yuan, *Anal. Chem.*, 2020, **92**, 14723-14729.