



# Metal ions-modulated near-infrared electrochemiluminescence from Au nanoclusters enhanced by 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid at physiological pH

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## ABSTRACT

The enhancement of near IR ECL from Au nanoclusters by the commonly used good's buffer 4-(2-Hydroxyethyl)-1-Piperazineethanesulfonic Acid (HEPES) as coreactants is presented. Lipoic acid (LA) stabilized Au<sub>22</sub> nanocluster is used based on its high quantum efficiency of near IR photoluminescence, also in reference to the EDTA enhancement and metal ion responses previously reported. Metal ions are demonstrated to be effective in modulating ECL signal. Specifically, zinc ion is found to drastically enhance the AuNC-HEPES ECL while magnesium and calcium ions lower the ECL intensity. Differentiation of different metal ions or sensing specificity can be better achieved by both intensity and kinetics analysis. The enhancement in ECL by zinc ions is attributed to the direct coordinate interactions with ligand monolayer in the presence of HEPES and confirmed by similar enhancement in the near IR photoluminescence. The ECL profiles are sensitive to pH and display optimal responses at physiological pH which makes HEPES better suited over EDTA for the corresponding applications. The design is translational to other ions and other amine-based good's buffers.

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## 1. Introduction

Electrochemiluminescence or electrogenerated chemiluminescence (ECL) is a photoemission process resulted from the reactions between electrochemically produced, highly reactive radical species [1]. As a subcategory of chemiluminescence, ECL has found wide applications such as immunoassays and sensing owing to its relative simple and low cost detection platform [2–6]. Because of the relatively low efficiency of ECL limited by the intrinsic signal generation mechanism, the merit of less interference in near infrared (near IR) spectrum window is significant to achieve high contrast or signal/noise ratio for ECL based analysis. Compared to the near IR photoluminescence that has attracted widespread interest, near IR ECL probes remain to be further developed for better imaging/sensing applications [7].

Nobel-metal nanoclusters, especially gold nanoclusters (AuNCs), possess rich electrochemical and optical properties specifically the

photoluminescence in near infrared spectrum window [8–14], making them promising candidates as near IR ECL luminophores. The AuNCs are often considered nanomolecules with high stability under the protection of thiolate monolayer, which can be characterized at precise atomic compositions Au<sub>x</sub>Ligand<sub>y</sub> and (core) structures [15,16]. Workentin, Ding and coworkers have reported a series of ECL analysis from organic soluble AuNCs by adopting excess coreactants [17–20]. In aqueous system, tertiary amines were covalently attached as part of ligand monolayer of lipoic acids stabilized AuNCs which drastically enhanced the ECL efficiency by simplifying the reaction pathway [21].

Basically, there are two main pathways to generate AuNCs ECL in the vicinity of a working electrode: 1. Self-annihilation of ECL reagents and 2. ECL reagents with extra coreactants. Ion annihilation presents major challenges including short lifetime and instability of the radical species, correspondingly sacrificial side reactions that quench the reactive intermediates, which limit ECL efficiency. For better ECL detection, a reducing or oxidizing intermediate electrogenerated from a coreactant is normally employed in high excess to react with the ECL reagents to produce the radiative excited state species [1]. One of the mostly used coreactants is tri-*n*-propylamine

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(TPrA). The tertiary amine of TPrA can be oxidized electrochemically, subsequently become strong reductive radicals after a deprotonation from the alpha carbon [22]. The pKa of the amine groups and solution pH, therefore, play significant role in this oxidative-reduction ECL generation pathway [23,24]. Despite its popularity, the toxicity, moderate solubility in water and pH response range impose practical limitations for applications in physiological systems and alternatives are highly desirable.

Our group recently reported the adoption of the widely used chelating agent, EDTA, as effective ECL coreactant for the enhancement of near IR ECL from AuNCs in aqueous system at physiological pH [25]. Complexation with magnesium ions was demonstrated to be effective in modulating ECL signals as the nitrogen atom/s coordination will be affected and thus ECL pathway. HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), representative good's buffer, possess similar tertiary amine structure that is considered effective in ECL generation in prototype ECL reagent tris(2,2'-bipyridyl)ruthenium (II) ( $\text{Ru}(\text{bpy})_3^{2+}$ ) [26]. The two pKas of the amine groups are 7.5 and around 10 respectively. At a physiological pH of 7.4, one of the nitrogen is fully protonated while about half of the other nitrogen is not protonated. Hence, HEPES could be very good ECL coreactant because of its known limited toxicity and moderate oxidation potential for physiological sample analysis. Moreover, affinity to metal ions is still expected, as the lone electron pair on N atom could serve as monodentate ligand similar as ammonia or other amines, though weaker than multidentate ligands or EDTA type chelators. Such weak interactions could still be employed to modulate the ECL responses.

Herein HEPES enhancement of near IR ECL from AuNCs is presented. Lipoic acid (LA) stabilized  $\text{Au}_{22}$ NCs were used due to the high quantum efficiency of the near IR photoluminescence [27]. Representative metal ions are selected to demonstrate the effective modulation of ECL profiles at different pHs for sensing applications.

## 2. Experimental

### 2.1. Materials

Tetrachloroauric acid trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , >99.99%), lipoic acid (LA,  $\geq 99\%$ ), sodium borohydride ( $\text{NaBH}_4$ ,  $\geq 99\%$ ), sodium hydroxide ( $\text{NaOH}$ ,  $\geq 97\%$ ), 4-(2-Hydroxyethyl)piperazine-1-ethanesulfonic acid or N-(2-Hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid) (HEPES,  $\geq 99.5\%$ ), zinc chloride ( $\text{ZnCl}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ), calcium chloride ( $\text{CaCl}_2$ ), sodium perchlorate hydrate ( $\text{NaClO}_4 \cdot x\text{H}_2\text{O}$ ,  $\geq 99.99\%$ ), sodium phosphate monobasic ( $\text{NaH}_2\text{PO}_4$ ,  $\geq 99.5\%$ ) and sodium phosphate dibasic ( $\text{Na}_2\text{HPO}_4$ ,  $\geq 99\%$ ) were purchased from Sigma-Aldrich and used as received. In all solution preparations, nanopure water ( $>18 \text{ M}\Omega \text{ cm}$ ) from a Barnstead system was used.

### 2.2. Synthesis of aqueous Au nanoclusters stabilized by lipoic acid (LA)

The synthesis followed reported procedure with some modifications [27–29]. In a typical reaction,  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (0.006 M) and Lipoic acid (0.035 M) were separately dissolved in nanopure water. The pH of the lipoic acid solution was adjusted with  $\text{NaOH}$  to basic to ensure solubility prior to mixing. Under vigorous stirring, the  $\text{HAuCl}_4$  and lipoic acid solutions were mixed to reach a final Au:LA mole ratio of 1:3. After ca. 4 h reaction when the color of the mixture solution changed from light yellow to colorless,  $\text{NaBH}_4$  (0.7 equiv.) was added at room temperature. The reaction proceeded for about 17 h periodically checked by near IR photoluminescence until the emission reached maximum (the emission would decrease afterwards). The solvent was then removed by rotovap at  $40^\circ\text{C}$ . The

final AuLA NCs was dialyzed in cellulose dialysis tube (M.W.C.O.  $\sim 3000$ ) in nanopure water over 4 days with periodic water replacements. The final products were collected after the removal of solvent with rotovap at  $40^\circ\text{C}$ .

### 2.3. Electrochemical measurements

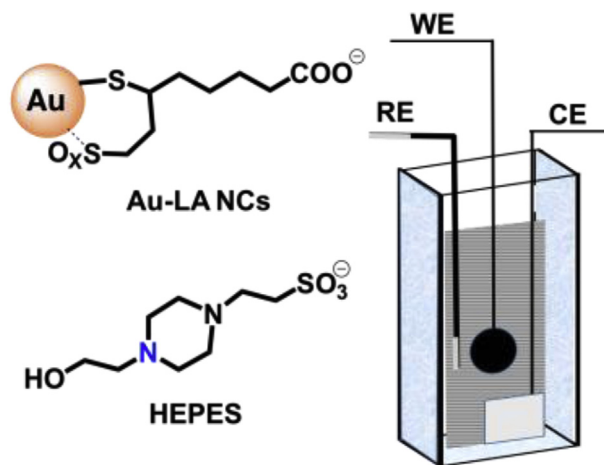
Cyclic voltammograms were collected using a CH Instruments (CHI 750C) with Picoamp booster in Faraday Cage with a Ag/AgCl quasi-reference electrode, a platinum (Pt) foil counter electrode and a 3-mm-diameter Glassy carbon working electrode.

### 2.4. ECL measurement

The ECL was measured in a  $0.5 \times 1 \text{ cm}$  quartz cuvette (Scheme 1). A standard spectrometer cuvette holder was used to hold the cuvette in front of the camera window at a fixed position. A printed 3-electrode with carbon strip as working (DRP-110 from Drop-senes) was inserted in the light path at a fix position benefiting from the tight fit that ensures consistent electrode-camera alignment. The supporting electrolyte was 0.2 M  $\text{NaClO}_4$ . All measurements were under ambient conditions without degassing so that the results are directly relevant to real life broader application settings. Unless defined otherwise, the electrode potential was held for 2 s at 0.0 V and then stepped to 1 V for 6 s. No potential was applied after 8 s. The emission intensity was recorded with an Andor iDUS CCD camera (Model DU401A-BR-DD) under ambient conditions without purging. To synchronize the camera and electrical potential, the camera is externally triggered by the potentiostat (Gamry Reference 600) at time zero when the potential is applied. The ECL intensity is the sum of photon counts from all pixels. Data collection rate is 13.3 ms unless otherwise noted. The standard deviation of the noise level is about 40 counts under regular measurement conditions.

### 2.5. ECL spectrum collection

The spectrometer (Isoplane 160, Princeton Instrument) with 300 g/mm and 500 nm blaze grating coupled with a PIXIS 100 camera was used for ECL spectrum collection. The electrode test strip was fixed on the stage with working electrode facing the objective (Olympus LUMPlanFL N 40X) in close proximity. The sampling area for photon collection is estimated to be  $1.88 \text{ mm}^2$  with the depth of field about  $1 \mu\text{m}$ . The ECL spectrum wavelength is



**Scheme 1.** Left: Molecular structures of  $\text{Au}_{22}$ -LA<sub>12</sub> NCs and HEPES. Right: A printed 3-electrode strip in quartz cuvette for ECL measurements.

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