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Short communication

# Anodic near-infrared electrochemiluminescence from CdTe/CdS $core_{small}/shell_{thick}$ quantum dots and their sensing ability of $Cu^{2+}$

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ABSTRACT

Anodic near-infrared electrochemiluminescence (NECL) from 3-mercaptopropionic acid (MPA)-capped CdTe/CdS $core_{small}/shell_{thick}$ quantum dots (QDs) without any co-reactants were studied in aqueous solution for the first time. A stable and intensive anodic NECL emission at +1.32 V with an onset potential of +0.84 V was observed in pH 7.4 PBS at an indium tin oxide electrode, which results from the annihilation process between the oxidation products of QDs and the produced QDs anions. Various influencing factors, such as pH, electrolyte, scan rates and electrode materials on the NECL were investigated. Based on the selective quenching by $Cu^{2+}$ to the NECL emission from the QDs, a simple and sensitive method for the determination of $Cu^{2+}$ was developed. Moreover, as a practical application, the proposed method was used to monitor $Cu^{2+}$ level in lake water and milk with satisfactory results obtained.



## 1. Introduction

The exploration and advancement concerning near-infrared electrochemiluminescence (NECL) not only open an avenue for the development of low-interference biosensors in actual complex samples but also complement the near-infrared fluorescence sensing strategy and the conventional visible ECL as well [1]. Semiconductor nanocrystals, or quantum dots (QDs) as one kind of the most promising NECL emitters have been extensively studied benefiting from their unique size-tunable optical and electronic properties [2]. In the past several years, many attempts have been made in designing new QD-based NECL systems with higher NECL efficiencies. A number of novel NECL agents were synthesized and their NECL properties have been investigated [3–7]. Among them, the CdTe based NECL emitters are of particular interest to researchers owing to their distinctive merits, such as narrow bandgap, simple aqueous synthetic route, as well as facile adjustment of surface states through stabilizers and shell coating [8]. Our earlier report described the influences of intensity, stability, and potential by shell coating on the cathodic NECL from CdTe/CdS QDs [5] and further developed a NECL immunosensor for the detection of target antigen with dual-signal amplification [9]. However, as practical applications, anodic NECL are highly desired because the overwhelming majority of commercially available tests are based on the anodic ECL of the $Ru(bpy)_3^{2+}$-tripropylamine system. Although the anodic NECL from stabilizers driven CdTe QDs has been well studied, there was no reports regarding the surface passivation from shell coating on anodic NECL from QDs to our knowledge [6,10,11]. Therefore, the investigation of anodic NECL from core/shell QDs with higher intensity and stability is extremely essential. Additionally, much attention has been paid to the development of fluorescent and ECL nanoprobes for trace amounts of $Cu^{2+}$ detection in recent years since $Cu^{2+}$ is a significant pollutant and an essential trace element in biological systems [12–16]. Unfortunately, the current reported sensing systems were mainly located in the visible range. To implement the application of $Cu^{2+}$-selective nanosensors in complex biological systems, the disposable QD-based near-infrared (NIR) sensors should be a more suitable and reliable choice.

In this communication, the anodic NECL property of 3-mercaptopropionic acid (MPA)-capped CdTe/CdS $core_{small}/shell_{thick}$ QDs was studied in aqueous solution, and then it was demonstrated as a sensitive and selective NECL $Cu^{2+}$ probe with low detection limit. Furthermore, the proposed sensing system has been applied for the determination of $Cu^{2+}$

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in lake water and milk samples and the recovery test was satisfactory.

## 2. Experimental

### 2.1. Preparation of CdTe/CdS $core_{small}/shell_{thick}$ QDs

MPA-capped NIR-emitting CdTe/CdS $core_{small}/shell_{thick}$ QDs were directly prepared in aqueous solution using the method described previously [17]. Briefly, $2.5 \times 10^{-4}$ mol of $CdCl_2 \cdot 2.5H_2O$ was dissolved in 50 mL of water, and 37 μL of MPA was added under stirring, followed by adjusting the pH to 12.2 by adding dropwise 1.0 M NaOH. The solution was deaerated by $N_2$ bubbling for 30 min. Under vigorous stirring, the freshly prepared NaHTe solution ($1.0 \times 10^{-5}$ mol) was injected to the above solution. Afterward, the solution was aged at 4 °C overnight and the small CdTe cluster solution was obtained. The NIR-emitting CdTe/CdS $core_{small}/shell_{thick}$ QDs were synthesized by further aging small CdTe cluster solution at 90 °C for 10 h.

### 2.2. NECL detection in aqueous buffer

In a typical NECL assay in aqueous buffer, copper nitrate ($Cu(NO_3)_2$) aqueous solution was used for the determination of $Cu^{2+}$. The purified CdTe/CdS $core_{small}/shell_{thick}$ QDs solution mixed with different concentrations of $Cu^{2+}$ were used in 0.1 M phosphate buffer solution (PBS, pH 7.4), scanning from 0 V to +1.5 V with a scan rate of 200 mV/s. The final concentration of QDs is 0.067 μM. The

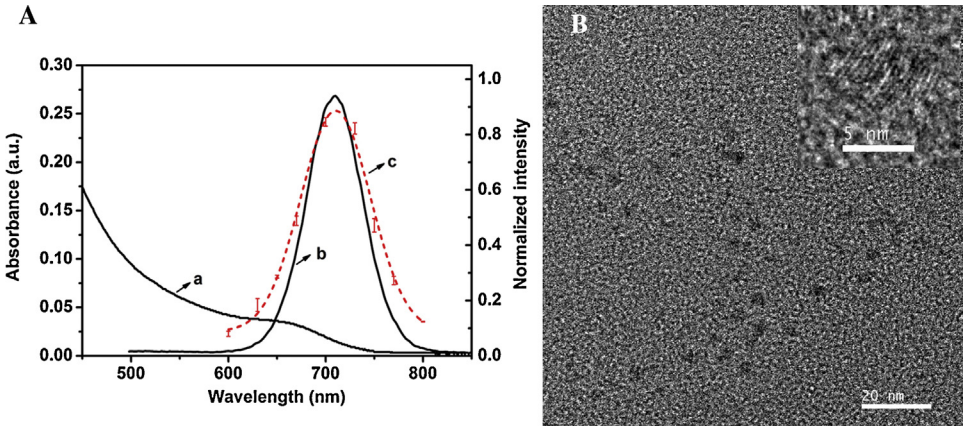


**Fig. 1.** (A) Absorption spectra (a), PL (b), ECL (c) spectra of CdTe/CdS $core_{small}/shell_{thick}$ QDs. (B) TEM and HRTEM images (inset) of CdTe/CdS $core_{small}/shell_{thick}$ QDs.

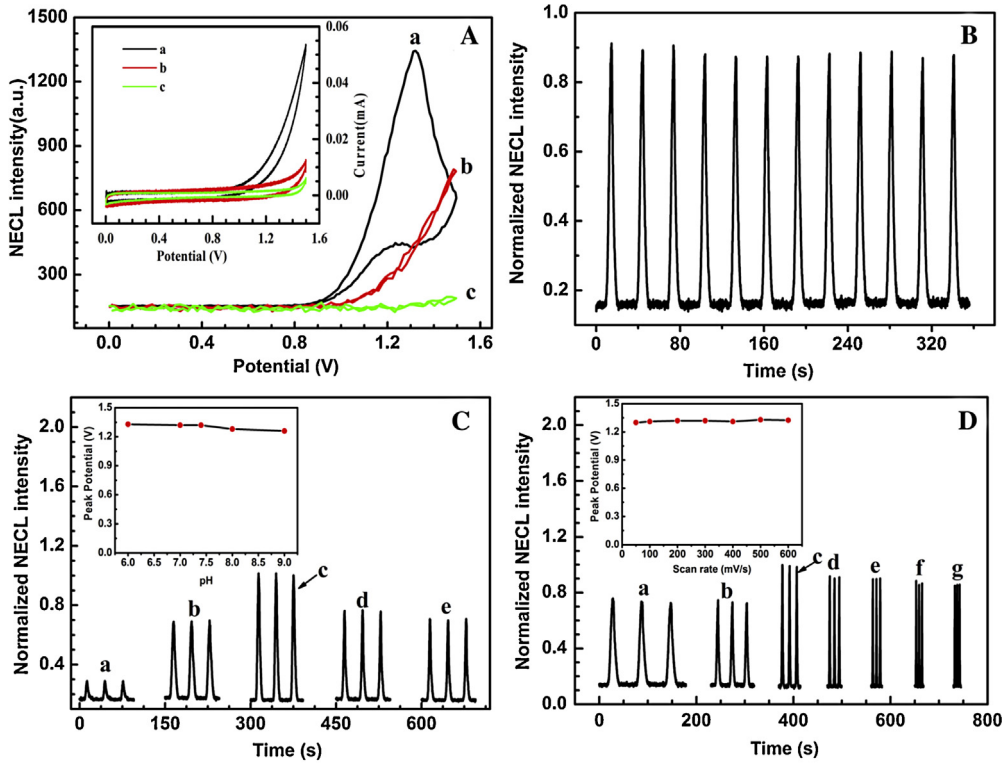


**Fig. 2.** (A) NECL–potential curves and CVs (inset) of (a) CdTe/CdS $core_{small}/shell_{thick}$ QDs, (b) CdTe/CdS $core_{small}/shell_{thick}$ QDs with 2 μM $Cu^{2+}$, (c) PBS blank in 0.1 M PBS (pH 7.4). Scan rate: 200 mV/s. (B) NECL emission from CdTe/CdS $core_{small}/shell_{thick}$ QDs under continuous CVs for 12 cycles. (C) NECL intensity of CdTe/CdS $core_{small}/shell_{thick}$ QDs in pH (a) 6.0, (b) 7.0, (c) 7.4, (d) 8.0 and (e) 9.0 PBS (0.1 M). Inset of C: effects of pH on NECL peak potential. (D) NECL intensity of CdTe/CdS $core_{small}/shell_{thick}$ QDs at a scan rate of (a) 50, (b) 100, (c) 200, (d) 300, (e) 400, (f) 500 and (h) 600 mV/s in 0.1 M PBS (pH 7.4). Inset of (D): effects of scan rate on NECL peak potential.