

# Low-Potential Electrochemiluminescent Sensing Based on Surface Unpassivation of CdTe Quantum Dots and Competition of Analyte Cation to Stabilizer

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A novel electrochemiluminescent (ECL) sensing system was constructed for low-potential detection of metal ion by immobilizing surface-unpassivated CdTe quantum dots (QDs) on a glassy carbon electrode. The surface-unpassivated CdTe QDs were prepared using meso-2,3-dimercaptosuccinic acid (DMSA) as a stabilizer to cap CdTe QDs and characterized with scanning electron micrograph and X-ray photoelectron spectroscopy. The immobilized QDs showed a strong cathodic ECL emission peak at  $-0.87$  V with an onset potential at  $-0.64$  V (vs Ag/AgCl/saturated KCl) in air-saturated, pH 9.0 HCl–Tris buffer. On the basis of the competition of metal ion to the stabilizer, the quenching effect of metal ion on ECL emission was observed, which led to a sensitive chemical sensing application. Using cupric cation as a model analyte, the sensor showed a linear range from  $5.0$  nM to  $7.0$   $\mu$ M with a detection limit of  $3.0$  nM and had been successfully applied in the detection of copper in human hair. It could be extended to detect other metal ions with stronger metal–S interaction than with the Cd–S bond. As an example, the sensor could be used to detect  $Hg^{2+}$  down to  $1.4$  nM. The bidentate chelate QD-based sensor exhibited a promising platform for rapid detection of cations with strong metal–S interaction and could be further applied for development of other low-potential electrochemical sensing systems.

Quantum dots (QDs) have attracted more and more attention during the past two decades owing to the unique optical and electronic properties.<sup>1–4</sup> They have been extensively used as photoluminescence (PL) labels for fluorescent detection and cellular imaging in bioanalysis.<sup>5–7</sup> Since the electrochemiluminescent (ECL) behavior of semiconductor Si in organic solvent

was reported,<sup>8</sup> the QD-based ECL analytical technique has been quickly developed in many fields because of its superiorities such as low cost, high sensitivity and stability, simple instrumentation, and wide range of analytes.<sup>9,10</sup> The first water-phase QD-based ECL sensor was fabricated by coating CdSe QDs on a paraffin-impregnated graphite electrode, which showed a response to  $H_2O_2$  at the applied potential of  $-1.2$  V.<sup>11</sup> Subsequently, the ECL biosensors based on CdS,<sup>12,13</sup> CdSe,<sup>14–16</sup> ZnS,<sup>17</sup> and ZnO<sup>18</sup> QDs were gradually reported. Their ECL emission peaks occurred at the potentials more negative than  $-1.0$  V. The high applied potential limits the application of QD-based ECL sensors.

Although the ECL emission of water-soluble CdTe QDs have been used for analytical purposes due to the excellent ECL behavior,<sup>19–21</sup> the cathodic ECL peak potential is rather negative,  $-2.0$  V at a glassy carbon electrode (GCE).<sup>20</sup> Furthermore, the high solubility of these used monothiol compound-capped QDs makes them hardly able to be immobilized on the electrode surface for sensor preparation. Thus, decreasing the solubility of CdTe QDs and lowering the applied potential for ECL emission are urgently needed for extending the sensing application of CdTe QDs. The solubility can be conveniently adjusted by changing the stabilizer. This work used meso-2,3-dimercaptosuccinic acid (DMSA) as a stabilizer, which has lower solubility than the generally used monothiol stabilizer for preparation of water-soluble

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QDs, to synthesize a kind of bidentate chelate CdTe QD by combining the reduction of Te electrode to produce the Te precursor. The resulting QDs could be easily immobilized on an electrode surface with a drop-coating method due to the relatively low solubility in aqueous solution. Interestingly, the rigid structure and steric hindrance of the short chain bithiol compound<sup>22,23</sup> resulted in an unpassivated surface of CdTe QDs, which produced low surface energy level and narrow band gap, thus providing an avenue for obtaining low-potential ECL emission.<sup>24</sup> The QD modified electrode showed stable ECL emission at low applied potential by the surface electron transfer and using hydrogen peroxide, produced from the electrochemical reduction of dissolved oxygen, as a coreactant. Furthermore, considering DMSA as an antidote of heavy metals,<sup>25</sup> the competition interaction of metal ion to the dithiol stabilizer could lead to a quenching effect on the ECL emission; thus, a sensor for detection of metal ion was proposed.

Cu<sup>2+</sup> is of significant importance in several physiological processes. Many enzymes need the participation and activation of Cu<sup>2+</sup>, and lack of Cu<sup>2+</sup> may cause hypomnesia, vitiligo, and degradation of cardiovascular function.<sup>26</sup> Several methods, such as UV-vis absorption and PL spectroscopy,<sup>27-31</sup> atomic absorption spectrometry,<sup>32</sup> ion-selective electrode,<sup>33</sup> and anodic stripping voltammetry,<sup>34</sup> have been developed for Cu<sup>2+</sup> detection. Recently, a method for Cu<sup>2+</sup> detection based on its quenching effect on the anodic ECL of mercaptosuccinic acid protected CdTe QD solution at the indium tin oxide electrode has been developed,<sup>35</sup> which is also based on the competitive binding of Cu<sup>2+</sup> to the stabilizer. Here, using Cu<sup>2+</sup> as a model competitive cation, the QD modified electrode showed a sensitive quenching effect of Cu<sup>2+</sup> on the ECL emission. The proposed sensor showed good stability, excellent selectivity, and acceptable reproducibility. The quenching and sensing mechanism was further demonstrated through the response of the sensor to Hg<sup>2+</sup>. To the best of our knowledge, this was the first QD-based ECL sensor for metal ions, which provided a novel sensing approach for rapid detection of cations with stronger metal-S interaction than the Cd-S bond. Compared to the PL detection,<sup>29</sup> this

method did not need any light source and introduced cation exchange onto the GCE surface, which greatly enhanced the sensitivity. The bidentate chelate QDs open a new opportunity for development of other low-potential electrochemical sensing systems.

## EXPERIMENTAL SECTION

**Materials and Reagents.** DMSA and cadmium chloride (CdCl<sub>2</sub>·2.5H<sub>2</sub>O) were purchased from Alfa Aesar China Ltd. (China). Tris(hydroxymethyl)-aminomethane hydrochloride and tris(hydroxymethyl)-aminomethane (Tris, reagent grade) were purchased from Sigma Chemical Co. (MO, U.S.A.). Isopropyl alcohol (A.R.) was purchased from Nanjing chemical reagent Co., Ltd. Tellurium rod (4 mm in diameter) was purchased from Leshan Kayada Photoelectricity Co. (China). All other chemicals were of analytical grade and without further purification. HCl-Tris solution (0.1 M, pH 9.0) containing 0.1 M KNO<sub>3</sub> was used throughout the ECL detection. Ultrapure water obtained from a Millipore water purification system (≥ 18 MΩ, Milli-Q, Millipore) was used in the entire work. Human hair sample was digested with the mixture of 1 M HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub>, which was then adjusted to neutral with NaOH. The resulting sample solution was diluted prior to detection.

**Equipment.** The synthesis of DMSA-CdTe QDs was carried out using Te rod as working electrode at a CHI 660B. Cyclic voltammetric (CV) and ECL behaviors were studied on an MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature with a configuration consisting of a glassy carbon working electrode, a Ag/AgCl (saturated KCl) reference electrode, and a platinum counter electrode. All potentials were quoted in this manuscript against this reference electrode. The ECL cell was self-made with three side necks and one middle neck. The reference and counter electrodes were put in two side necks, while the GCE was put in the middle neck with its surface downward approximating the optical window for recording the ECL signal. Another side neck was used for injecting samples and bubbling nitrogen. The emission window was placed in front of the photomultiplier tube (detection range from 300 to 650 nm) biased at -600 V. UV-vis absorption spectra were recorded with UV-3600 UV-vis-near infrared (NIR) photospectrometer (Shimadzu Co., Japan). The ECL spectrum was obtained by collecting the ECL data at -0.90 V during a cyclic potential sweep with 7 pieces of filters at 650, 630, 600, 580, 550, 535, and 510 nm. Their thickness and transparent efficiency were 2 mm and 88%, respectively. The PL spectrum was recorded with RF-5301 PC fluorometer (Shimadzu). X-ray photoelectron spectra (XPS) were obtained on a K-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific Co., USA). Scanning electron microscopic (SEM) images were obtained using a Hitachi S-4800 scanning electron microscope (Japan). Inductively coupled plasma (ICP) spectroscopic detection of copper in the hair sample was carried out on a J-A1100 inductively coupled plasma spectrometer (Jarrell-Ash Co. U.S.A.).

**Synthesis of DMSA-CdTe QDs.** The DMSA-CdTe QDs were synthesized according to our electrolysis method.<sup>36</sup> First,

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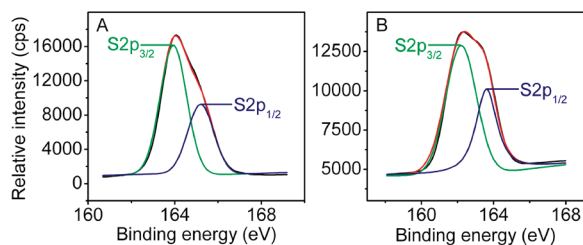
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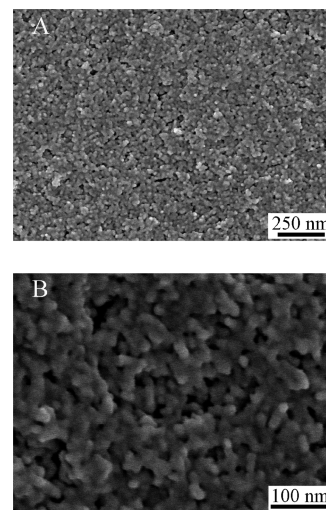
**Figure 1.** S2p XPS spectra of (A) DMSA and (B) DMSA–CdTe QDs.

20 mL of 0.01 M NaOH was mixed with 12  $\mu\text{mol}$  of  $\text{CdCl}_2$  and 32.9  $\mu\text{mol}$  of DMSA to obtain a homogeneous solution. After being bubbled with highly pure  $\text{N}_2$  for 20 min, this solution was used as electrolyte by applying a constant potential of  $-1.0$  V on the Te electrode until an electricity quantity of 0.5 C was reached. During the electrolysis process, the solution was continuously bubbled with highly pure  $\text{N}_2$ . The resulting solution was refluxed at  $80^\circ\text{C}$  for 20 h in the presence of highly pure  $\text{N}_2$  to obtain the DMSA–CdTe QDs and stored at  $4^\circ\text{C}$  prior to use. The as-prepared QDs were quite stable. After storage for 1 month, the QD solution was clear and transparent, and the ECL intensity and peak potential of the GCE modified with the stored QD solution did not show an obvious change.

**Preparation of QD Modified GCE.** First, 300  $\mu\text{L}$  of as-prepared QD solution was mixed with 300  $\mu\text{L}$  of isopropyl alcohol and centrifuged at  $8000\text{ rpm min}^{-1}$  for 5 min. The precipitation was twice washed with a 1:1 mixture of isopropyl alcohol and water and then dissolved in 20  $\mu\text{L}$  of water and dropped onto GCE. After being dried in air at room temperature, the QD modified electrode was obtained. The formed QD film was very stable due to the low solubility and strong physical absorption of QDs on the surface of GCE.

## RESULTS AND DISCUSSION

**Characterization of DMSA–CdTe QDs.** The precursor for preparation of QDs was obtained by electrolysis using Te electrode in water phase. After reflux for 20 h, the resulting QDs showed an absorption peak at 463 nm. According to the Peng's empirical equation,<sup>37</sup> the diameter of QDs was estimated to be 0.93 nm, which could be attributed to the steric hindrance and electrostatic repulsion caused by the rigid structure of the short chain bidentate DMSA. Further, the XPS spectra of S2p were recorded to characterize the formation of bidentate chelate QDs. The typical S2p spectrum of DMSA showed a doublet structure due to the spin–orbit splitting (Figure 1A), which was assigned to the  $2p_{1/2}$  and  $2p_{3/2}$  with a separation of binding energy around 1.2 eV.<sup>38</sup> In comparison with the S2p of DMSA, the binding energy for  $2p_{1/2}$  and  $2p_{3/2}$  spin orbit of DMSA–CdTe QDs shifted to lower energy from 165.2 and 163.9 to 163.4 eV and 162.2 eV, respectively (Figure 1B), which were consistent with those for Cd–SR bond,<sup>38–40</sup> confirming the existence of chemical bonds



**Figure 2.** SEM images of DMSA–CdTe QD film on GCE at different amplifications.

between thiols of DMSA and  $\text{Cd}^{2+}$  on the surface of CdTe QDs. Moreover, the molar ratios of Cd, Te, and S atoms at the QD surface were detected as 31.57:0.27:23.07, suggesting most Cd atoms at the QD surface were stabilized by thiol ligands instead of Te atoms. This core–shell like structure obviously prevented the oxidation of Te, leading to a stable structure of the QDs.<sup>39</sup> From the molar ratios of the three atoms, the sum amount of S and Te atoms was less than the amount of Cd atom, suggesting the unpassivated QD surface with many surface traps, which could decrease the surface band gap of QDs<sup>41</sup> and, thus, lead to a low ECL emission potential.<sup>24</sup>

**Effect of Reflux Time on ECL Properties of QDs.** After 14.1 nmol of as-prepared QDs was coated on GCE surface, the SEM morphologies of the formed QD film exhibited a uniform layer with the homogeneous aggregate size less than 20 nm (Figure 2). This size range was much smaller than those of 860 nm for unmodified CdTe QDs,<sup>42</sup> probably due to the electrostatic repulsion among these negatively charged caps ( $\text{DMSA}^{2-}$ ) around CdTe cores. The decline in aggregation and the homogeneous surface structure were favorable for improving the ECL efficiency.

The ECL properties of QDs greatly depended on the reflux time. As seen from Table 1, the UV–vis absorption wavelength moved from 439.4 to 465.0 nm with the increasing reflux time, which referred to the increment of diameter of CdTe QDs. Thus, the change in ECL properties of QDs mainly resulted from the different sizes of CdTe QDs obtained at various reflux times. With the increasing reflux time or size, the ECL peak potential of CdTe QD films shifted positively from  $-1.45$  to  $-0.91$  V, indicating the decreasing band gap of the QDs and the easier injection of electrons to the surface states of QD particles.<sup>43</sup> Moreover, the ECL peak intensity increased with the decreasing band gap, i.e., the increasing reflux time for preparation of QDs. However, when the reflux time was longer than 13 h, the ECL intensity decreased due to the relatively small surface-to-volume ratio of QDs, which decreased the contact area of QDs with electrode and the efficient

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**Table 1. Effect of Reflux Time on QD Properties**

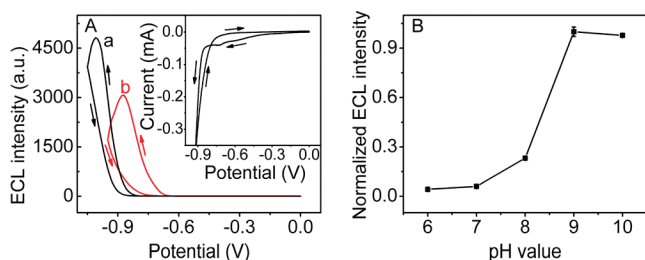
reflux time (h)	3	7	10	13	17	20	23
absorption wavelength (nm)	439.4	450.2	453.2	456.4	460.0	463.6	465.0
ECL peak potential (V)	-1.45	-1.07	-0.99	-0.96	-0.93	-0.91	-0.91
normalized ECL peak intensity	0.139	0.936	0.932	1.000	0.780	0.748	0.556

electron transfer.<sup>43</sup> Since the QDs obtained with a reflux time of 20 h gave a sufficient, sensitive response and the acceptable ECL peak potential, this reflux time was selected for preparing the ECL emitter.

**Optimization of Buffer.** The cathodic ECL intensity of DMSA–CdTe depended on the components and pH of electrolyte. As shown in Figure 3A, although the ECL intensity of the resulting DMSA–CdTe modified electrode in pH 9.0 PBS was higher than that in HCl–Tris buffer at the same pH, the peak potential in pH 9.0 PBS was about 100 mV more negative than that in HCl–Tris buffer. Thus, 0.1 M, pH 9.0 HCl–Tris buffer was used throughout the following experiments. The ECL intensity increased with the increasing pH value from 6.0 to 9.0 and reached a platform at pH 9.0 (Figure 3B). Considering that pH 10.0 was unfavorable for further application, pH 9.0 buffer solution was selected for ECL measurement.

#### Electrochemical and ECL Behaviors of QD Modified GCE.

The as-prepared DMSA–CdTe QDs exhibited outstanding ECL properties. As shown in Figure 3A, even when the photomultiplier tube was biased at -600 V, the DMSA capped CdTe QDs showed an intensive ECL emission peak around -0.87 V, with an onset potential of -0.64 V in air-saturated, pH 9.0 HCl–Tris buffer solution in the absence of any other coreactant (curve b), suggesting high ECL efficiency of the DMSA–CdTe QDs. Moreover, the ECL emission was quite stable in the next hundreds of CV scanning. In addition, the CV curve of the CdTe QD modified GCE showed two reduction peaks at -0.78 and -0.64 V (inset, Figure 3), which could be attributed to the reduction of DMSA–CdTe QDs and oxygen, respectively.<sup>44</sup> This ECL emission mechanism should be similar to other CdSe QD modified electrode.<sup>43</sup> Briefly, during the cathodic scanning in air-saturated, pH 9.0 HCl–Tris buffer solution, O<sub>2</sub> could be reduced at -0.64 V to produce H<sub>2</sub>O<sub>2</sub>, which then reacted with electron-injected DMSA–CdTe QDs generated at -0.78 V to produce excited-state QDs. The excited QDs then gave out ECL emission. This ECL emitter could be demonstrated by the ECL spectrum of CdTe QD modified GCE, which showed an ECL emission wavelength of 628 nm, consistent with the PL emission peak



**Figure 3.** (A) Cyclic ECL curves of QD modified GCE in air-saturated, 0.1 M, pH 9.0 (a) phosphate and (b) HCl–Tris buffer, and (B) effect of pH on ECL intensity collected at -0.90 V in air-saturated, 0.1 M HCl–Tris buffer ( $n = 3$ ). Inset: CV curve of the modified GCE in air-saturated, pH 9.0 HCl–Tris buffer. Scan rate: 100 mV s<sup>-1</sup>.

at 622 nm.<sup>45</sup> Therefore, H<sub>2</sub>O<sub>2</sub>, formed from the reduction of dissolved oxygen, acted as a coreactant, leading to a very mild ECL system for bioanalysis.

**Quenching Effect and Detection of Cu<sup>2+</sup>.** After adding trace Cu<sup>2+</sup> into the detection solution and waiting for several minutes, the cathodic ECL emission intensity decreased, accompanied with a tiny shoulder peak around -0.93 V from QD assemblies (Figure 4A).<sup>11</sup> Upon addition of Cu<sup>2+</sup> into the detection solution, the ECL intensity quickly decreased and became stable after 8 min (Figure 4B). Thus, the waiting time of 8 min was used to achieve the cation exchange equilibrium. On the basis of the quenching effect on the cathodic ECL emission of DMSA–CdTe QDs, a simple analytical method for Cu<sup>2+</sup> detection could be developed, which followed the treatment of the fluorescence quenching principle described by the Stern–Volmer equation,

$$I_0/I = 1 + K_{sv} \times [Q] \quad (1)$$

Here,  $I_0$  is the initial ECL intensity,  $I$  is the ECL intensity at a given concentration of quencher  $[Q]$ , and  $K_{sv}$  is the quenching constant. The constructing sensor showed a linear relationship in the Cu<sup>2+</sup> concentration range from 5.0 nM to 7.0 μM ( $R = 0.997$ ) with a detection limit of 3.0 nM at signal-to-noise of 3 (inset in Figure 4A). The quenching constant was  $4.6 \times 10^5 \text{ M}^{-1}$ , which is obviously larger than  $5.4 \times 10^3 \text{ M}^{-1}$  in CdTe QD solution by glutathione<sup>21</sup> and  $1.5 \times 10^4 \text{ M}^{-1}$  in CdSe QD solution by dopamine,<sup>46</sup> indicating the more sensitive response of DMSA–CdTe QD modified electrode to the analyte.

**Quenching Mechanism.** After the detection procedure, the ECL emission of QD modified GCE could not be recovered to the original intensity prior to the quenching of Cu<sup>2+</sup>, indicating a structure destruction of the QDs by Cu<sup>2+</sup>. This could be demonstrated from the changes of UV–vis absorption and XPS spectra of CdTe QDs upon addition of Cu<sup>2+</sup>. After addition of trace Cu<sup>2+</sup> into the QD solution, the UV–vis absorption peak of CdTe QDs at 465 nm decreased and then disappeared at high Cu<sup>2+</sup> concentration (Figure 5A). In the presence of sufficient Cu<sup>2+</sup>, the color of QD solution changed from light yellow to brown, and the brown precipitation could finally be generated, which led to a colorless and transparent upper phase. The Cu2p of XPS spectrum of the precipitation showed two spin–orbit components of Cu2p<sub>3/2</sub> and Cu2p<sub>1/2</sub> at 933.4 and 953.3 eV, respectively (inset in Figure 5A), which were consistent with those of Cu–S.<sup>47,48</sup> In comparison with the CdTe QDs, the component of Cd element in the precipitation decreased

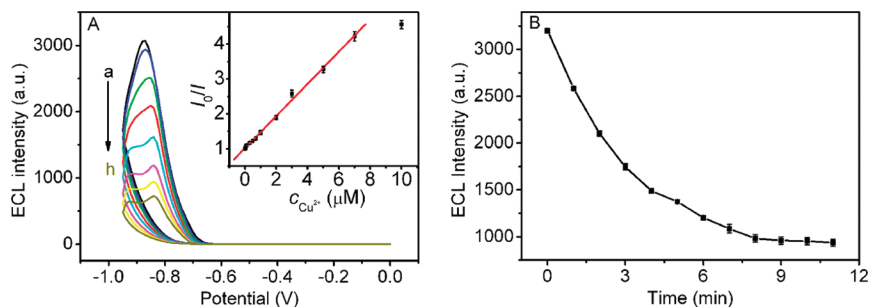
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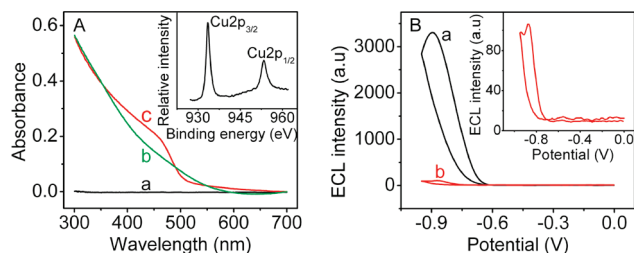
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**Figure 4.** (A) Cyclic ECL curves of QD modified GCE in air-saturated, 0.1 M, pH 9.0 HCl-Tris buffer in the presence of (a–h) 0, 0.06, 0.5, 1.0, 2.0, 3.0, 5.0, and 7.0  $\mu\text{M}$   $\text{Cu}^{2+}$  with a waiting time of 8 min and (B) plot of ECL intensity vs waiting time after addition of 5.0  $\mu\text{M}$   $\text{Cu}^{2+}$  into air-saturated, 0.1 M, pH 9.0 HCl-Tris buffer ( $n = 3$ ). Inset in (A): linear calibration plot for  $\text{Cu}^{2+}$  detection.



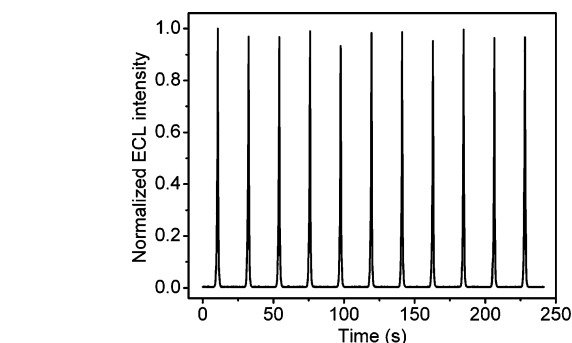
**Figure 5.** (A) UV-vis spectra of (a) 5  $\mu\text{M}$   $\text{Cu}^{2+}$  and (b) 5  $\mu\text{M}$   $\text{Cu}^{2+}$  + 19.9  $\mu\text{M}$  QDs with a waiting time of 8 min and (c) 19.9  $\mu\text{M}$  QD solution and (B) cyclic ECL curves of (a) DMSA-CdTe QDs and (b) Cu doped DMSA-CdTe QD modified GCEs in air-saturated, 0.1 M, pH 9.0 HCl-Tris buffer. Insets in (A) Cu2p XPS spectrum of DMSA-CdTe QDs after reaction with  $\text{Cu}^{2+}$  and (B) amplification of ECL curve (b). Scan rate: 100  $\text{mV s}^{-1}$ .

from 31.6% to 18.0%. Thus, after addition of  $\text{Cu}^{2+}$ , cupric ion was captured on the surface of CdTe QDs.

Furthermore, the  $\text{Cu}^{2+}$  doped DMSA-CdTe QDs were synthesized, and the cathodic ECL behavior was investigated. Compared with the ECL curve of DMSA-CdTe QD modified electrode, the ECL peak of  $\text{Cu}^{2+}$  doped DMSA-CdTe QD modified electrode moved to more positive potential with the appearance of a shoulder peak (Figure 5B), which was consistent with the phenomenon of DMSA-CdTe modified electrode during the detection of  $\text{Cu}^{2+}$  (Figure 4A), indicating the adulteration of  $\text{Cu}^{2+}$  to the QD structure.

The  $K_{\text{sp}}$  of CuS is  $6 \times 10^{-36}$ , which is much lower than  $8 \times 10^{-27}$  of CdS.<sup>49</sup> The adulteration of  $\text{Cu}^{2+}$  to the DMSA-CdTe QD structure was thermodynamically reasonable. According to the above results, the possible quenching mechanism of the ECL emission of DMSA-CdTe QDs by  $\text{Cu}^{2+}$  was proved to be that  $\text{Cu}^{2+}$  was doped on the DMSA-CdTe QD surface due to the thermodynamic tendency and then decreased the ECL signal.

Following the same mechanism, the DMSA-CdTe QD modified electrode could be used to detect other metal ions with stronger metal-S interaction than the Cd-S bond. For example, the  $K_{\text{sp}}$  of HgS is  $4.0 \times 10^{-53}$ ,<sup>49</sup> upon addition of  $\text{Hg}^{2+}$  into the electrolyte, a quenching effect was also observed, suggesting the cation exchange between  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$ .<sup>50</sup> With the waiting time of 7 min, at which the cation exchange reached equilib-



**Figure 6.** Successively cyclic ECL curves of QD modified GCE in air-saturated, 0.1 M, pH 9.0 HCl-Tris buffer. Scan rate: 100  $\text{mV s}^{-1}$ .

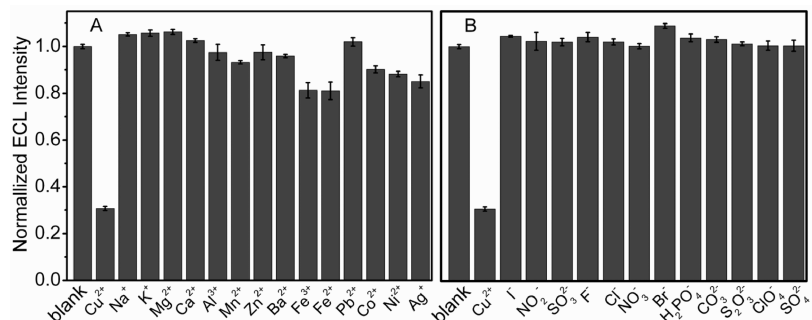
rium and the ECL emission become stable, the constructed modified electrode showed a linear relationship in the  $\text{Hg}^{2+}$  concentration range from 70.0 nM to 35.0  $\mu\text{M}$  ( $R = 0.996$ ) and a detection limit of 1.4 nM at signal-to-noise of 3, indicating a sensitive  $\text{Hg}^{2+}$  detection. The lower  $K_{\text{sp}}$  value produced a higher sensitivity than  $\text{Cu}^{2+}$  detection. Although the modified electrode showed a sensitive response to  $\text{Hg}^{2+}$ , it would not impact  $\text{Cu}^{2+}$  detection in real biological samples, since the concentration of  $\text{Hg}^{2+}$  in the organism was much lower than  $\text{Cu}^{2+}$ .

**Stability of QD Modified GCE.** Ten ECL measurements of the QD modified GCE upon continuous cyclic scans in air-saturated, pH 9.0 HCl-Tris buffer showed constant signals with relative standard deviation (RSD) of 1.8% (Figure 6), indicating the excellent stability of the modified electrode. The intraassay RSDs for five parallel measurements at 1.0 and 5.0  $\mu\text{M}$   $\text{Cu}^{2+}$  with the QD modified electrodes prepared with the same GCE was 6.4% and 3.7%, respectively, indicating a good precision. The ECL intensity of the QD modified electrodes prepared with four GCEs independently in air-saturated, pH 9.0 HCl-Tris buffer in the absence and presence of 1.0  $\mu\text{M}$   $\text{Cu}^{2+}$  showed the interassay RSDs of 7.8% and 6.0%, giving acceptable fabrication reproducibility. When the sensor was not in use, it was stored in air condition at room temperature and measured in pH 9.0 HCl-Tris buffer every few days. No obvious change in the ECL intensity was observed after storage for 4 weeks.

**Interference.** To evaluate the selectivity of the present sensing system, the effects of 14 cations and 12 anions on the ECL intensity of the modified electrode were examined. As shown in Figure 7, the cations with strong metal-S interaction such as  $\text{Ag}^+$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  showed weak quenching to the cathodic ECL emission; other ions had no obvious effect on ECL emission.

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**Figure 7.** Normalized ECL intensities of QD modified GCE in air-saturated, 0.1 M, pH 9.0 HCl–Tris buffer in the presence of (A) 5  $\mu$ M individual cation and (B) 10  $\mu$ M individual anion with a waiting time of 8 min ( $n = 3$ ).

However, the interference of these cations could be prevented by the coordination agents such as Br<sup>-</sup> or F<sup>-</sup>.<sup>49</sup> In addition, Pb<sup>2+</sup> did not affect the detection of Cu<sup>2+</sup> due to the formation of Pb(OH)<sub>2</sub> precipitation at pH 9.0. Thus, the as-prepared Cu<sup>2+</sup> sensor had acceptable selectivity.

**Analysis of Human Hair Samples.** To evaluate the analytical reliability and application potential of the proposed method, the DMSA–CdTe QD modified electrode was employed to detect copper in a human hair sample. The result showed a copper content of  $9.19 \pm 0.61 \mu\text{g g}^{-1}$  ( $n = 3$ ), which was close to the value of  $8.38 \mu\text{g g}^{-1}$  obtained from ICP measurement. Further, when 0.1  $\mu$ M standard Cu<sup>2+</sup> solution was spiked into the detection solution containing human hair sample, the obtained recovery was  $101.9 \pm 5.6\%$  ( $n = 3$ ), indicating acceptable practicability of the method.

## CONCLUSIONS

In this work, a low-potential ECL sensor for metal ion was constructed using bidentate chelate CdTe QDs. Due to the steric hindrance caused by the rigid structure of the short chain DMSA as the stabilizer, the DMSA–CdTe QDs showed unpassivated surface with narrow band gap, which led to a low ECL potential. Under the optimal conditions, the DMSA–CdTe QD modified GCE showed a strong ECL emission at relatively low potential

with a coreactant of H<sub>2</sub>O<sub>2</sub> produced from the reduction of dissolved oxygen. The competitive binding of Cu<sup>2+</sup>, with stronger metal–S interaction than the Cd–S bond, to the stabilizer led to a quenching effect on ECL emission, which was proved to be due to the thermodynamic tendency for formation of Cu–S on the DMSA–CdTe QD surface. Thus, a method for low-potential ECL detection of Cu<sup>2+</sup> and other metal ions was suggested. This method showed a good performance with high sensitivity, good stability, and acceptable selectivity. The bidentate chelate QD-based sensor exhibited a promising platform for rapid detection of cations with strong metal–S interaction and could be further applied to develop other low-potential ECL sensing systems.

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