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Anodic Electrochemiluminescence of CdTe Quantum Dots and Its Energy Transfer for Detection of Catechol Derivatives

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This work reported for the first time the anodic electrochemiluminescence (ECL) of CdTe quantum dots (QDs) in aqueous system and its analytical application based on the ECL energy transfer to analytes. The CdTe QDs were modified with mercaptopropionic acid to obtain water-soluble QDs and stable and intensive anodic ECL emission with a peak value at +1.17 V (vs Ag/AgCl) in pH 9.3 PBS at an indium tin oxide (ITO) electrode. The ECL emission was demonstrated to involve the participation of superoxide ion produced at the ITO surface, which could inject an electron into the 1Se quantum-confined orbital of CdTe to form QDs anions. The collision between these anions and the oxidation products of QDs led to the formation of the excited state of QDs and ECL emission. The ECL energy transfer from the excited CdTe QDs to quencher produced a novel methodology for detection of catechol derivatives. Using dopamine and L-adrenalin as model analytes, this ECL method showed wide linear ranges from 50 nM to 5 μM and 80 nM to 30 μM for these species. Both ascorbic acid and uric acid, which are common interferences, did not interfere with the detection of catechol derivatives in practical biological samples.

Semiconductor nanocrystals, or quantum dots (QDs), are bright and photostable materials with broad excitation spectra but narrow Gaussion emission superior to conventional organic fluorescence dyes. Furthermore, their emission positions are tunable in a wide emission range from UV to NIR due to the quantum size effect. Thus, they have been widely used as multicolored photoluminescent probes and biological luminescent labels in bioassays[1−4] and bioimagings,[5,6] especially in enzymatic processes[3] and immunoassays[4] since two breakthrough works were reported in 1998.[7,8] Multifarious water-soluble QDs modified with different compounds have been synthesized to show different optical properties, biocompatibilities, and cellular toxicities,[9−13] which lead to their different applications. One important application is based on the light emission of the excited state of QDs, which can be produced either by absorption of a quantum of light given rise to photoluminescence (PL), by electrical injection of an electron−hole pair (electroluminescence), by electron impact resulting in cathodoluminescence,[14] or by chemical reaction of QDs as chemiluminescent emitters.[15] The fluorescence resonance energy transfer from the excited state of the CdSe/ZnS core/shell[16] or CdTe[17] QDs to acceptors has rapidly been used for monitoring purposes. In recent years, the fluorescence resonance energy transfer from donors to CdSe/ZnS core/shell QDs[4] and the chemiluminescence resonance energy transfer from the excited oxidation product of luminol to CdTe QDs[18] to produce excited QDs have also been suggested. Some methods based on the chemical or physical interaction between analytes and CdS QDs to change their surface charges or components, which can affect the efficiency of the core electron−hole recombination and thus the luminescent emission, have been developed for sensitive detection of metal cation, such as copper cation[19] and cyanide anion.[20] All these transfers and interactions afford new methodolo-

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gies for spectrochemical analysis. This work proposed a new methodology based on the electrogeneration of the excited CdTe QDs and the electrochemiluminescence (ECL) energy transfer from the excited QDs to analytes, producing a new way for analytical application of QDs.

The ECL analytical technique has many advantages over PL techniques, such as low cost, wide range of analytes, and high sensitivity.[21] This technique includes two main systems, i.e., ruthenium complex with amine-containing compounds as coreactants[22−24] and a luminol−H_2O_2 system.[25] The overwhelming majority of commercially available tests are based on the anodic ECL of the $Ru(bpy)_3^{2+}$−tripropylamine system. Recently, aromatic Tb(III) chelate has been used as a cathodic ECL probe for a rapid ECL immunoassay of human C-reactive protein,[26] and the ECL of QDs has also attracted great interest.[27−34] Great efforts to study the ECL of QDs focus on the ECL behaviors and mechanism of QDs dispersed in organic solutions to examine the relevancy between ECL and PL of QDs.[27−29] Although the ECL phenomena of CdS spherical assemblies[30] and Si QDs[31] in aqueous solutions have been observed, the rigorous alkaline media (pH ~13) become a stubborn obstacle when QDs are used for detection of biomolecules. By using peroxide as a coreactant, a cathodic ECL signal of CdSe QDs cast on a paraffin-impregnanted graphite electrode (PIGE)[32] and a carbon nanotubes-enhanced cathodic ECL signal of CdS QDs[33] have been observed at pH 9.3 and 9.0, respectively. The former has been used for preparation of two ECL biosensors for H_2O_2[32] and substrates of oxidase.[34]

This work studied the anodic ECL property of mercapopropionic acid (MPA)-modified CdTe QDs dissolved in aqueous solution. At an indium tin oxide (ITO) electrode, the QDs showed a stable anodic ECL signal. To our best knowledge, this was the first report on the anodic ECL of II−VI QDs in aqueous solution. The ECL energy transfer observed from the excited QDs to quencher resulted in the decrease of anodic ECL emission of QDs; thus, a new method for ECL detection of quencher-related analytes was proposed. With catechol derivatives as model analytes, this method could be used for ECL analysis of dopamine (DA) and L-adrenalin with acceptable reproduction and sensitivity. The anodic ECL response of CdTe QDs would open new avenues in the applications of QDs to construct ECL analytical systems and ECL biosensors.

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EXPERIMENTAL SECTION

Reagents. Cadmium chloride ($CdCl_2{\cdot}2.5H_2O$) was purchased from Alfa Aesar China Ltd.. Mercaptopropionic acid, superoxide dismutase (SOD, EC 1.15.1.1, from bovine erythrocytes, 4200 units mg^{-1} solid), dopamine, and L-adrenalin were purchased from Sigma Chemical Co. Tellurium powder and sodium borohydride were purchased from Sinopharm Chemical Reagent Co. Ltd. Other reagents were of analytical grade and used as received. Doubly distilled water was used throughout. 0.1 M phosphate buffer solution containing 0.1 M KNO_3 (PBS) was used throughout the work, and the pH was adjusted by changing the ratio of Na_2HPO_4 to NaH_2PO_4.

Apparatus. The electrochemical and ECL measurements were carried out on a MPI-A multifunctional electrochemical and chemiluminescent analytical system (Xi'an Remex Analytical Instrument Ltd. Co.) at room temperature with a configuration consisting of an ITO working electrode, a platinum counter electrode, and a Ag/AgCl (saturated KCl solution) reference electrode. The ITO electrodes with a working area of ~1 cm × 1 cm were purchased from Kangdake Photoelectric Technique Ltd. Co. (60 Ω). As control, PIGE, glassy carbon, and Au electrodes were also used as working electrodes, and their areas were 0.283, 0.071, and 0.071 cm^2, respectively. The emission window was placed in front of the photomultiplier tube (detection range from 300 to 650 nm) biased at −1000 V. The ECL spectrum was obtained by collecting the ECL data at +1.17 V during cyclic potential sweep with 10 pieces of filters at 470, 490, 510, 535, 550, 565, 580, 600, 630, and 650 nm. Their thickness was 2 mm, and transparent efficiency was ~88%. Photoluminescence was performed on a Jasco FP 820 fluorometer (Jasco Co.). The UV−visible absorption spectra were obtained on a Shimadzu UV-3600 UV−vis-NIR photospectrometer (Shimadzu Co.). IR spectra were recorded on a Nicolet 400 Fourier transform infrared (FT-IR) spectrometer (Madison, WI).

Preparation of MPA-Modified CdTe QDs. The synthesis of water-soluble CdTe QDs referred to the method reported for thiol-capped CdTe QDs in aqueous phase[35] by changing the tellurium source to simplify the synthesis apparatus. Briefly, 26 μL of MPA (~6 mM) was first added into 50 mL of 2.0 mM $CdCl_2$ solution. After adjusted the pH to 9.0 using 1 M NaOH solution, the resulting clear solution was bubbled with highly pure N_2 for 30 min, and 0.80 mL of 0.0625 M NaHTe solution (produced by reaction of oxygen-free $NaBH_4$ solution with Te powder) was then slowly injected into the vigorously stirred and oxygen-free solution to obtain a yellow brown solution of MPA-modified CdTe QDs. The molar ratios of Cd^{2+}/MPA/HTe^- were 1:3:0.5. The obtained QD solution was refluxed for different times to produce different sizes of QDs. The samples collected in a batch were then dialyzed against doubly distilled water for 5 h to remove excessive MPA. The final QD solutions were rather stable for more than 3 months when kept in a refrigerator at 4 °C.

RESULTS AND DISCUSSION

Characterization of MPA-Modified CdTe QDs. The formation of MPA-modified CdTe QDs was confirmed by FT-IR spectra.

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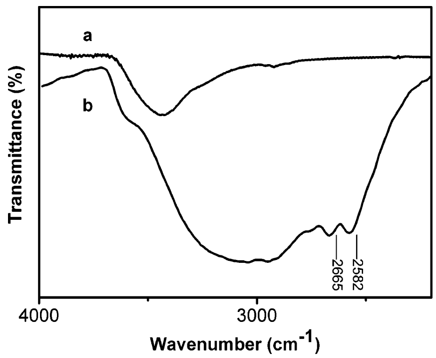

Figure 1. Standard FT-IR spectrum of MPA (a) and FT-IR spectrum of MPA-modified CdTe QDs (b).

Table 1. Effect of QDs Size on ECL Intensity at the Same Concentration

λ (nm)[a]	d (nm)[b]	c (μM)[c]	ECL intensity (normalized)[d]
486	1.90	8.67	0.16
498	2.27	5.79	0.23
517	2.74	3.48	0.28
570	3.43	1.42	1.00
591	3.59	1.36	0.50

[a] The wavelength of UV−vis absorption peaks of five sample solutions. [b] Calculated diameter of QDs particles in solution. [c] Calculated concentration of originally obtained QD solution. [d] ECL intensity was detected at an ITO electrode with the detection solutions containing the same QDs concentration.

The QD powder acquired via centrifugation of the QD solution was used in this experiment. As shown in Figure 1 (curve a), the standard IR spectrum of MPA showed two peaks attributed to the stretch vibration of S−H bond at 2655 and 2582 cm^{-1} and one peak attributed to the asymmetric vibration of carboxyl group at 1708 cm^{-1}. The diminishment of the broad absorption around 2560 cm^{-1} resulting from the S−H bond in MPA molecule indicated the formation of S−Cd bonds between MPA and CdTe core (curve b, Figure 1). The shift of the asymmetric vibration of carboxyl group from 1708 to 1638 cm^{-1} implied that the COOH in MPA turned to its anion in neutral aqueous solution due to the pK_a values of about 4.9[36] and 5.3[37] for MPA.

The sizes of the resulting CdTe QDs and the concentrations of QD solutions were estimated from the first adsorption peaks in UV−visible spectra (not shown) and several empirical equations reported previously.[38] The results were listed in Table 1. The CdTe QDs refluxed with longer time showed a larger wavelength of the adsorption peak, producing the larger size of QDs, combined with the lower concentration of QDs solution.

Anodic ECL Behavior of QDs Dissolved in PBS. The cathodic ECL emission of CdTe nanoparticles in dichloromethane has been observed at a Pt disk electrode.[28] In this system, the anodic ECL emission is very weak and is not often detected even in ECL transients. However, the MPA-modified CdTe QDs in air-saturated pH 9.3 PBS (detection solution) showed an intensive anodic ECL emission at the surface of the ITO electrode, even at

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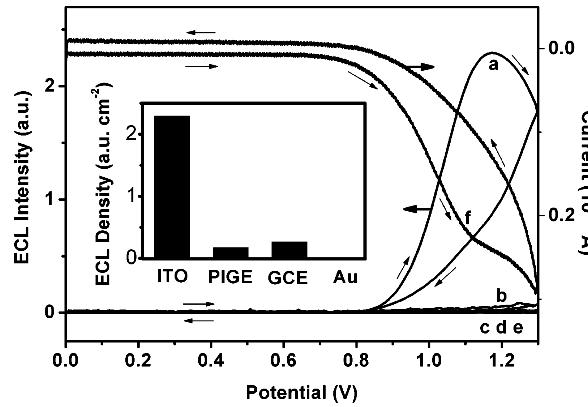


Figure 2. Cyclic ECL (a−d) and voltammetric (f) curves of 0.14 μM QDs dissolved in air-saturated pH 9.3 PBS at ITO (a, f), PIG (b), Au (c), and glassy carbon electrodes (d), and cyclic ECL curve of pH 9.3 PBS at ITO electrode (e). Scan rate, 0.1 V s^{-1}. Inset, ratio of ECL intensity measured at +1.17 V to electrode area at four electrodes.

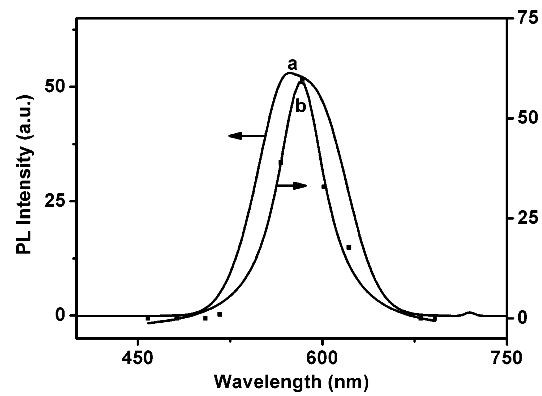


Figure 3. PL (a) and ECL (b) spectra of QDs dissolved in pH 9.3 PBS. The excitation wavelength of PL spectrum is 360 nm, and the ECL data are collected at +1.17 V.

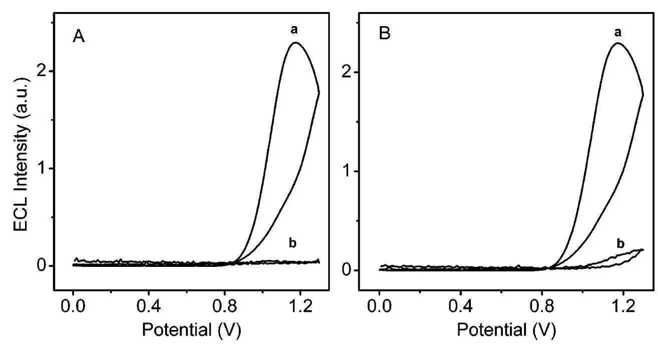
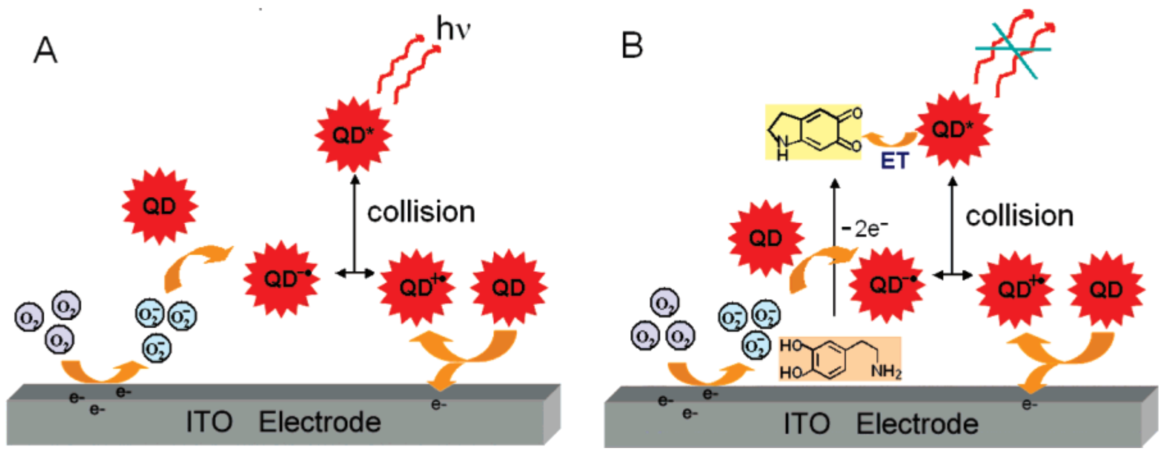


Figure 4. Cyclic ECL curves of QDs in air-saturated (a) and air-free (b) pH 9.3 PBS (A) and air-saturated pH 9.3 PBS containing 0 (a) and 0.2 mg mL^{-1} (b) SOD (B).

a concentration down to 0.14 μM (curve a, Figure 2). The peak value of the ECL emission was at +1.17 V, with an onset potential of +0.75 V. Other electrodes prepared with different materials such as PIGE (curve b), Au (curve c), and glassy carbon (curve d) showed very weak and even negligible ECL emission (inset in Figure 2), though the cyclic voltammograms at these electrodes all exhibited an electrooxidative peak at ~ +0.90 V (not shown). In the air-saturated pH 9.3 PBS, without the presence of QDs no ECL emission was observed (curve e). Thus, the anodic ECL emission resulted from the oxidation of CdTe QDs, which led to

Scheme 1. Anodic ECL Mechanism of QDs (A) and Its Quenching Procedure by Oxidation Product of DA (B)



the formation of an ECL emitter. The cyclic voltammogram showed the electrooxidation peak at $\sim +1.15$ V (curve f, Figure 2), which was more positive than that at other electrodes due to the negative-charged surface of ITO.

ECL Mechanism of QDs. The PL (excited at 360 nm) and anodic ECL spectra of CdTe QDs in air-saturated pH 9.3 PBS showed similar emission peak positions, at 574 and 581 nm, respectively (Figure 3), which indicated that the surface of the QDs was efficiently passivated,[29] and the emitter of the ECL emission was the excited state of QDs (QDs*), the same as the PL procedure. The formation of the QDs* was explained by an electron-transfer reaction between reduced and oxidized QDs (anion radicals $QD^{-\bullet}$ and cation radicals $QD^{+\bullet}$)[28] for direct electron−hole recombination, which resulted from the collision of the anion (e^-) and cation (h^+) radicals at the ITO electrode surface.

As mentioned above, the cation radical $QD^{+\bullet}$ could directly be produced from the electrooxidation of CdTe QDs at +1.15 V by a hole injection. The formation of the anion radicals $QD^{-\bullet}$ was demonstrated to involve the participation of dissolved oxygen and the semiconductor surface. After the detection solution was bubbled with highly pure N_2 for ~30 min, the anodic ECL emission disappeared completely (Figure 4A), which indicated that dissolved oxygen played an important role in the ECL emission procedure. When SOD, an efficient capturer of O_2^-, was added into the air-saturated solution, the ECL response also decreased to a large extent (Figure 4B); furthermore, the decrease of ECL intensity increased with increasing SOD concentration, which confirmed that the ECL emission was related to O_2^- species produced from the dissolved oxygen.

It has been reported that the n-type semiconductor such as TiO_2 can hold an electron on its conduction band[39] with a band gap of 3.4 eV[40] and then transfer the electron to dissolved O_2 rapidly.[39] ITO (SnO_x) has a band gap of 3.5 eV,[41] similar to that of TiO_2 and thus can also hold an electron on its conduction band. In the anodic process, the electrooxidation of CdTe QDs injected electrons into the conduction band of the ITO surface. The electroexcited electrons could hardly return to QDs (h^+) or CdTe QDs because of the repulsion by the negatively charged surface of MPA-modified QDs. But they could transfer to dissolved oxygen molecules in a split second to produce O_2^- species. With the drive of positive potential, the ITO acted as a medium for the electron transfer between QDs and dissolved oxygen. The produced O_2^- then directly injected one electron into the 1Se quantum-confined orbital of CdTe to form reduced QDs (e^-), the anion radicals $QD^{-\bullet}$.[15] Thus, the electrode material was a key in the formation of $QD^{-\bullet}$, which made the anodic ECL emission of CdTe QDs negligible at PIGE, glassy carbon and Au electrodes. The whole process of anodic ECL emission is described in Scheme 1A with the following equations:

$$\mathrm{In/SnO}_x + \mathrm{CdTe/CdSR} \xrightarrow{e-} \mathrm{CdTe\ (h^+)/CdSR} + \mathrm{In/SnO}_x\ (e^-) \quad (1)$$

$$\mathrm{O_2} + \mathrm{In/SnO}_x\ (e^-) \xrightarrow{\text{electron transfer}} \mathrm{O_2}^- + \mathrm{In/SnO}_x \quad (2)$$

$$\mathrm{CdTe/CdSR} + \mathrm{O_2}^- \rightarrow \mathrm{CdTe\ (e^-)/CdSR} + \mathrm{O_2} \quad (3)$$

$$\mathrm{CdTe\ (h^+)/CdSR} + \mathrm{CdTe\ (e^-)/CdSR} \rightarrow \mathrm{CdTe/CdSR^*} \quad (4)$$

$$\mathrm{CdTe/CdSR^*} \rightarrow \mathrm{CdTe/CdSR} + h\nu \quad (5)$$

Size Effect of QDs on Their Anodic ECL Behavior. The size of QDs deeply affected their ECL behavior. The information of the five samples prepared in a batch with the same concentration was shown in Table 1. The ECL intensity increased with the increasing QDs size in the range of 1.90−3.43 nm. Afterward, the ECL intensity decreased. The dependence of ECL intensity on the size of QDs was related to the band gap of QDs, which increased with the decrease of QD size.[38] The decrease of the ECL intensity occurring at QD diameters larger than 3.4 nm was ascribed to the relatively small surface-to-volume ratio. Consider-

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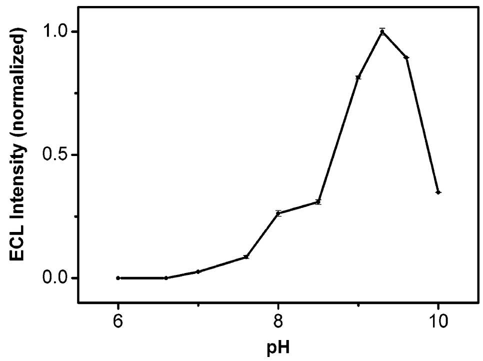

Figure 5. Effect of pH on ECL response of QD solution at ITO electrode. The ECL data are collected at +1.17 V.

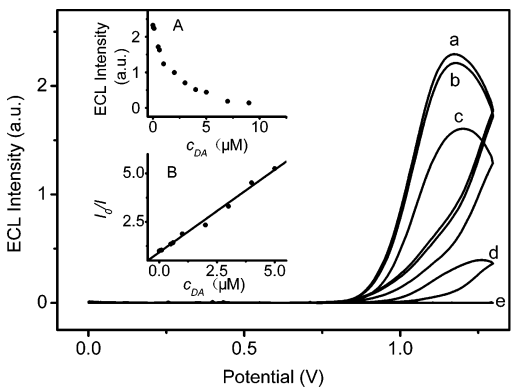

Figure 6. Cyclic ECL curves of QDs dissolved in air-saturated pH 9.3 PBS containing 0 (a), 0.05 (b), 0.5 (c), 5 (d), and 50 (e) μM DA at ITO electrode at 0.1 V s^{-1}. Inset A: relationship between ECL intensity and quencher concentration. Inset B: linear calibration plot for DA.

ing the sensitivity, for detection purpose the CdTe QDs of 3.4 nm with a concentration of 0.14 μM was selected as the ECL emitter.

Effect of pH on ECL Behavior of QDs. The anodic ECL emission of QDs depended on the pH value of the detection solution. When the pH was lower than 6.0, the emission was unobservable. With the increasing pH from 6.0 to 9.3, the ECL intensity increased (Figure 5). Beyond the latter point, the ECL intensity decreased and the onset potential of ECL emission shifted positively. It has been reported that the surface charge of an oxide is related to several factors such as solution pH, the presence or absence of other potential-determining ions, or even trapped species that exist as surface states. Phosphate is known to be absorbed on the surface of oxide, which made the ITO electrode surface more negatively charged.[42] With the increasing pH, the detection solution contained more PO_4^{3-} and HPO_4^{2-} species; thus, the ITO surface was more negatively charged, and the electron transfer from the conduction band of ITO to O_2 was easier. Furthermore, the resulting O_2^- species were more stable at high pH, which was favorable to the ECL emission and led to the increasing ECL intensity. However, when pH was too high, for example, higher than 9.3, too many anions loaded on the surface of the ITO electrode, which extremely suppressed the approach of negatively charged QDs to the ITO electrode, and

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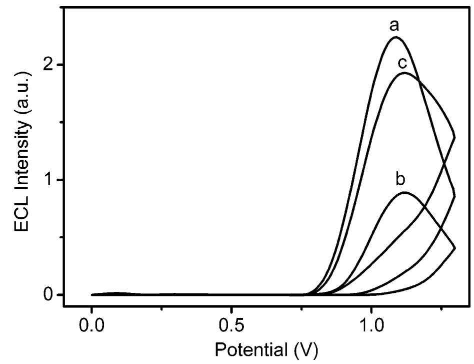

Figure 7. Cyclic ECL curves of QDs dissolved in air-saturated pH 9.3 PBS (a), (a) +2 μM DA (b), and (b) + 100 μM βME (c).

made the ECL intensity decrease quickly. So 0.1 M pH 9.3 PBS was chosen for ECL detection.

Analytical Application of Anodic ECL Emission of QDs. As shown in Figure 6 with DA as a model compound, trace catechol derivatives could quench the anodic ECL emission. Upon successive addition of DA into the detection solution, the ECL intensity at +1.17 V attenuated nonlinearly. The ECL intensity decreased rapidly at low concentrations of DA and trended to complete quenching at 50 μM DA (inset A in Figure 6). The ratio of the initial ECL intensity I_0 to the ECL intensity I at a given concentration of quencher, I_0/I, was proportional to the concentration of DA (inset B in Figure 6). The DA concentration dependence of the anodic ECL intensity of CdTe QDs was coincident to the fluorescence quenching described by a Stern−Volmer equation:

$$I_0/I = 1 + K_{sv}[Q] \tag{6}$$

K_{sv} was found to be 8.5×10^5 M^{-1}. The large value of K_{sv} provided a sensitive ECL detection of DA.

It has been reported that *o*-benzoquinone residues can efficiently quench the PL emission of QDs by energy transfer.[1] The fact that the PL emission of CdTe QD solution decreased upon addition of *o*-benzoquinone, while the addition of DA did not affect the PL emission (not shown), also indicated that the DA itself was not the quencher of PL. In the cyclic sweep process, an anodic peak occurred at $\sim +0.33$ V, which corresponded to the oxidation of DA to produce *o*-benzoquinone species. Thus, the ECL quencher was *o*-benzoquinone species, similar to the quenching process for the ECL of $Ru(bpy)_3^{2+}$ emitter[43] and the PL quenching mechanism. This conclusion was supported by the antioxide experiment (Figure 7). When 100 μM 2-mercapoethanol (βME), an antioxidant for DA,[44] was added into the detection solution containing 2 μM DA, the partially quenched ECL signal of the QD solution (curve b) was recovered to a large extent (curve c). This phenomenon that conformed the ECL quenching mechanism was an energy-transfer process, not a charge-transfer process; otherwise, the ECL quenching would have increased upon addition of βME. The energy transfer resulted from the collision between

(43) McCall, J.; Alexander, C.; Richter, M. M. *Anal. Chem.* **1999**, *71*, 2523−2527.

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the excited state of QDs and the produced *o*-benzoquinone species. Thus, the quenching mechanism could be described in Scheme 1B.

According to eq 6, the quenching process could be developed for detection of both quencher and quencher-related analytes. As shown in inset B in Figure 6, the DA concentration dependence of the anodic ECL intensity of CdTe QDs could be used for DA detection. Under the optimal conditions, the limit of detection of DA was 50 nM, and the linear range was from 50 nM to 5 μM (R = 0.996, n = 10). The relative standard deviation for five measurements at the DA concentration of 0.7 μM was 6.5%, indicating acceptable reproduction.

Other catechol derivatives such as L-adrenalin also showed efficient quenching to the anodic ECL emission of CdTe QDs. The plot of I_0/I versus the concentration of L-adrenalin showed a linear range of 80 nM to 30 μM (R = 0.999, n = 17) (Figure S1 in Supporting Information) with a limit of detection of 20 nM. The K_{sv} value was found to be 6.7×10^5 M^{-1}.

Contrarily, uric acid (UA) and ascorbic acid (AA), which are the common interferences of DA and L-adrenalin, showed very weak quenching to the anodic ECL emission of CdTe QDs, though their molecules also contain conjugated structure. The interference investigation indicated that UA and AA up to the concentrations of 5 and 50 μM did not affect the ECL emission of CdTe QDs (less than 5.3%; see Figures S2 and S3 in Supporting Information). The concentration of AA is generally much higher than that of DA (100−1000 times).[45] Comparing the tolerable concentrations of UA and AA with the limits of detection of catechol derivatives, it was concluded that they did not interfere with the detection of catechol derivatives in practical samples after appropriate dilution. The metal ions showed little effect on the ECL emission of CdTe QDs and thus did not interfere with the detection of catechol derivatives.

(45) Wightman, R. M.; May, L. J.; Michael, A. C. *Anal. Chem.* **1988**, *60*, 769A-779A.

CONCLUSIONS

The MPA-modified CdTe QDs dissolved in aqueous solution show stable and sensitive anodic ECL behavior at an ITO electrode. The maximum ECL emission occurs at +1.17 V. Both dissolved oxygen and the semiconductor surface play important roles in the anodic ECL process, which lead to the formation of electron-injected anion radicals $QD^{-\bullet}$. The direct electron−hole recombination of $QD^{-\bullet}$ with hole-injected cation radicals $QD^{+\bullet}$ that are produced from the oxidation of QDs forms the excited QDs, leading to ECL emission. At pH 9.3, the CdTe QD solution shows the largest ECL intensity. The ECL emission can be quenched by the electrooxidation products of catechol derivatives such as DA and L-adrenalin, which follows the Stern−Volmer equation with relatively large quenching constants, producing a sensitive analytical method for anodic ECL detection of DA and L-adrenalin. The quenching process is demonstrated to be an ECL energy-transfer process from the excited QDs to quencher and could be developed for ECL detection of quenchers and quencher-related analytes. This work proposes a new ECL quenching process of QDs and a new methodology for analytical application of QDs.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Anodic Electrochemiluminescence of CdTe Quantum Dots and Its Energy Transfer for Detection of Catechol Derivatives

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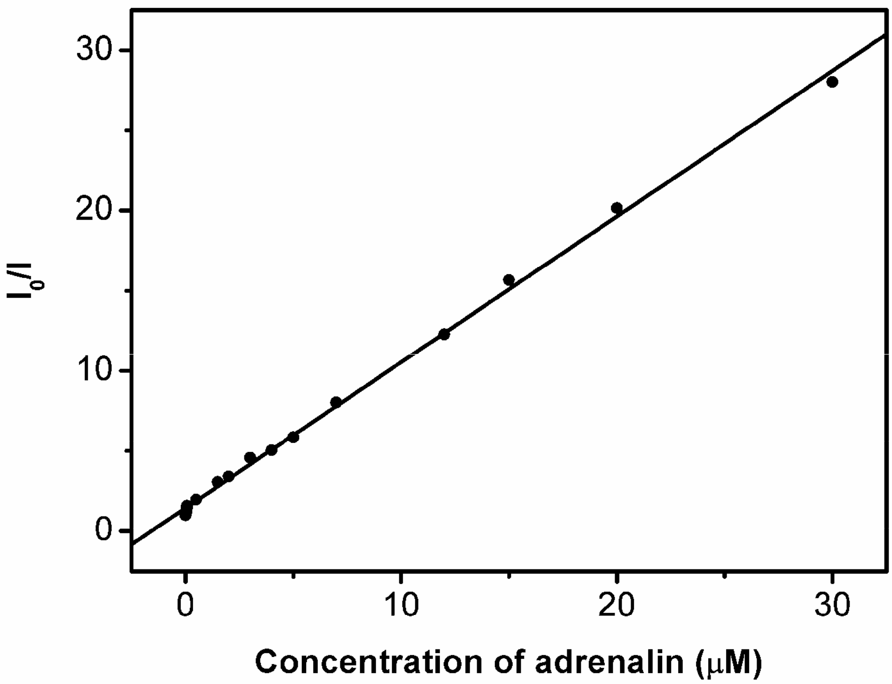

Figure S1. Relationship between ECL intensity and L-adrenalin concentration.

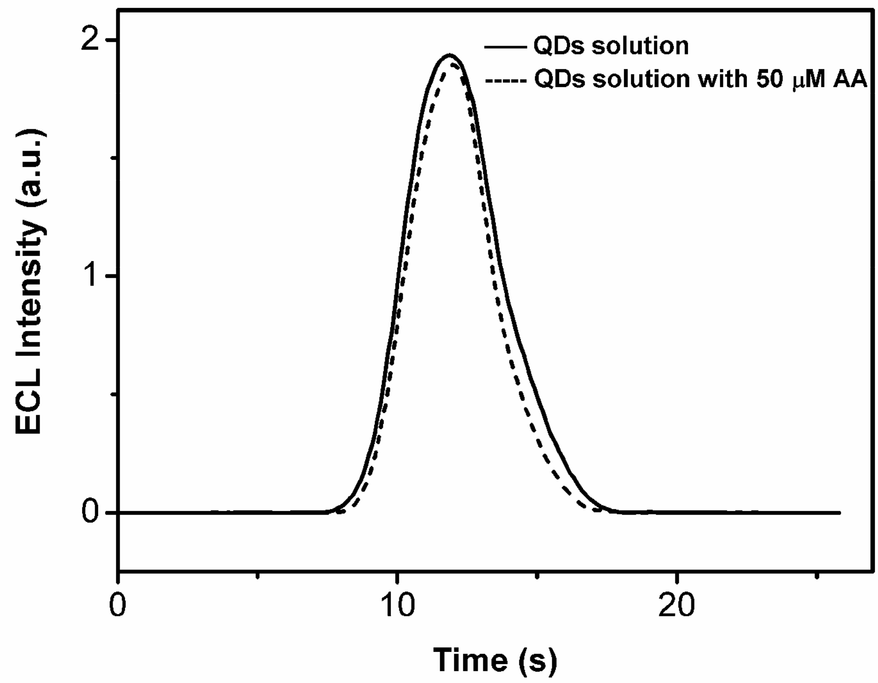

Figure S2. Curve of ECL intensity of detection solution containing 0 (solid line) and 50 μM AA (dash line).

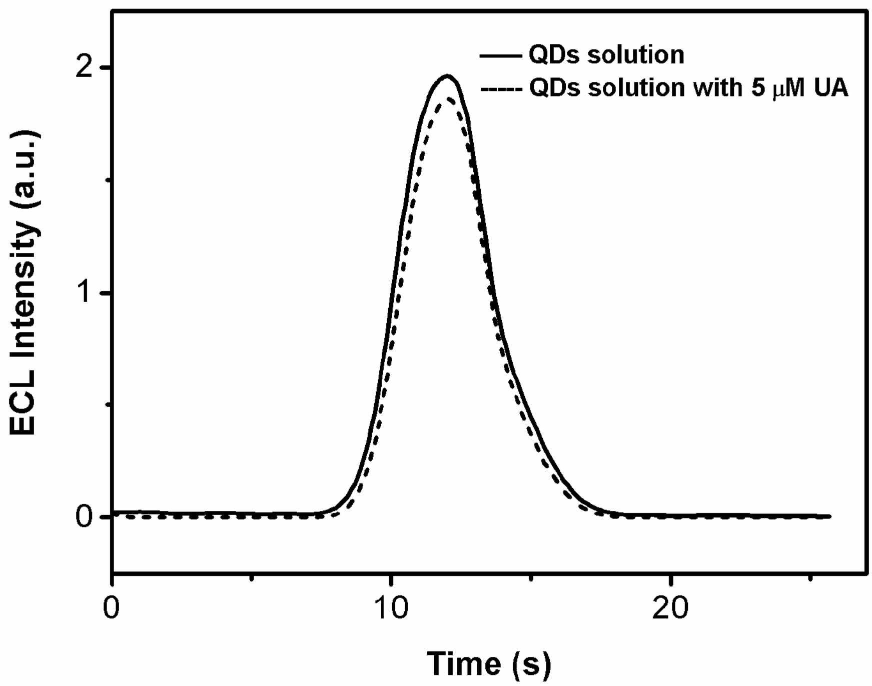

Figure S3. Curve of ECL intensity of detection solution containing 0 (solid line) and 5 μM UA (dash line).