

# Quantum Dot (QD)-Modified Carbon Tape Electrodes for Reproducible Electrochemiluminescence (ECL) Emission on a Paper-Based Platform

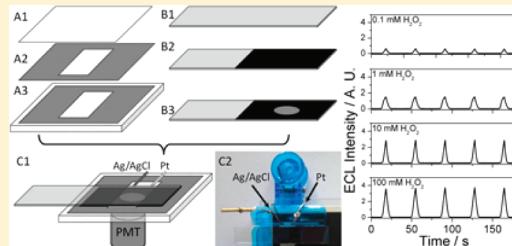
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**ABSTRACT:** Stable and sensitive electrochemiluminescence (ECL) detection relies on successful immobilization of quantum dots (QDs) on working electrodes. Herein, we report a new technique to apply double-sided carbon adhesive tape as the working electrode to improve the stability and reproducibility of QD-based ECL emission. CdS QD-modified electrodes were prepared by dropping and drying CdS QD suspension on the carbon adhesive tape supported by indium tin oxide (ITO) glass. The ECL detection was performed with the prepared electrode on a paper-based platform. We tested our system using H<sub>2</sub>O<sub>2</sub> of various concentrations and demonstrated that consistent ECL emission could be obtained. We attribute stable and reproducible ECL emission to the robust attachment of CdS QDs on the carbon adhesive tape. The proposed method could be used to quantify the concentration of dopamine from 1 μM to 10 mM based on the quenching effect of dopamine on ECL emission of CdS QD system using H<sub>2</sub>O<sub>2</sub> as the coreactant. Our approach addressed the problem in the integration of stable QD-based ECL detection with portable paper-based analytical devices. The similar design offers great potential for low-cost electrochemical and ECL analytical instruments.



Electrochemiluminescence (ECL), or electrogenerated chemiluminescence, is the process in which light is emitted during the high-energy electron-transfer reactions occurring at working electrodes in electrochemical processes.<sup>1</sup> Since ECL detection is performed based on the measurement of light emission from luminophores, it is superior to other luminescent methods, because of its low background and controllable procedure.<sup>2</sup> Three types of luminophores, including Ru(bpy)<sub>3</sub><sup>2+</sup>, luminol, and quantum dots (QDs), have been applied in ECL detection.<sup>1–3</sup> With the additional advantages of low cost and easy preparation, ECL detection with QDs has attracted much attention in bioanalytical and analytical chemistry.<sup>3</sup> ECL based on QDs, such as CdTe,<sup>4–6</sup> CdSe,<sup>7,8</sup> and CdS,<sup>9–11</sup> has been extensively investigated for ECL mechanism study,<sup>3,12</sup> immunoassays,<sup>13</sup> and DNA detection.<sup>11,14,15</sup> One hurdle in these works is that QDs can diffuse into the electrolyte solution during oxidative corrosion at high voltage, which is essentially involved in ECL detection.<sup>16</sup> To address this problem, in recent years, several methods have been demonstrated for stable ECL emission to composite QDs with nanomaterial scaffolds or to develop surface chemistry for QD attachment to the electrode surface.<sup>11,12,17,18</sup>

It is important to note that working electrodes with smooth surfaces (of either carbon or precious metals) were applied for QD ECL detection in almost all previous reports.<sup>10,19–21</sup> These

polished surfaces of working electrodes resulted in the weak QD attachment and low reproducibility of the data for ECL detection. New electrode materials with improved properties for stable QD incorporation are highly desired for ECL detection.

In this report, we tested the use of double-sided carbon adhesive tapes as the working electrodes for QD-based ECL detection. We modified the carbon tape electrodes with QDs and performed ECL detection in portable and inexpensive paper-based analytical devices (PADs).<sup>22</sup> As a benefit from the strong attachment of QDs on the adhesive tape, we were able to obtain highly consistent ECL emission during H<sub>2</sub>O<sub>2</sub> reaction on QD surfaces for 31 cycles of cyclic potential scan that span a period of nearly 20 min. Furthermore, dopamine could be detected based on ECL emission with the integrated system. We expect this simple method to greatly facilitate the use of ECL for analytical purposes.

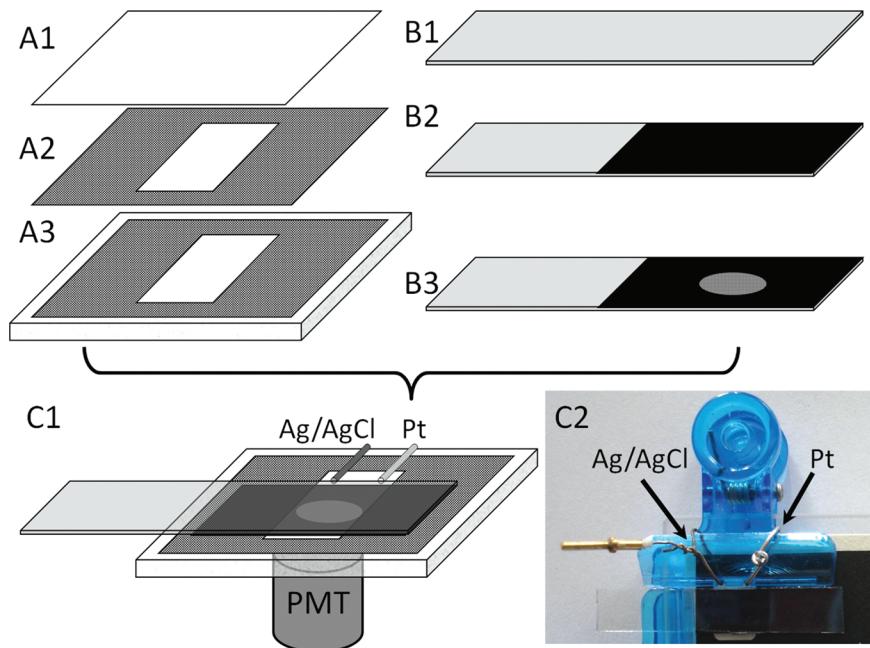
## EXPERIMENTAL SECTION

**Chemicals and Materials.** CdCl<sub>2</sub>, Na<sub>2</sub>S·9H<sub>2</sub>O, thioglycolic acid (TGA), and 30% H<sub>2</sub>O<sub>2</sub> were from Shanghai Chemical

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**Figure 1.** Scheme of the paper-based analytical device for QD ECL detection. Legend: (A1) the filter paper; (A2) the patterned filter paper, which was formed using a common laser printer and was treated at a certain temperature and duration; the shadowing area was printed with toner and the unprinted area ( $11\text{ mm} \times 7.4\text{ mm}$ ) was used as the thin-layer electrochemical cell; (A3) the patterned paper, which was attached on the optical glass; (B1) the ITO glass; (B2) the double-sided carbon adhesive tape, which had an area of  $12\text{ mm} \times 8\text{ mm}$  and was attached on the conductive side of the ITO glass; (B3) the CdS QD solution with a certain volume, deposited dropwise onto the double-sided carbon adhesive tape supported by the ITO glass, so that the CdS QD-modified carbon tape electrode was obtained; (C1) the integrated paper-based analytical device for CdS QD ECL detection; and (C2) an image of the integrated system. The modified surface of the carbon tape electrode was attached on the patterned filter paper and immobilized on the optical glass with a clasp. The CdS QD-modified carbon tape electrode, an Ag/AgCl wire, and a platinum wire were applied with a clasp for three-electrode ECL detection.

Reagent Company (Shanghai, China). Dopamine hydrochloride was from Shanghai Harvest Pharmaceutical Co. Ltd. (Shanghai, China). Indium tin oxide (ITO) glass (electric resistance =  $10\text{ }\Omega$ , membrane thickness = 180 nm) was purchased from Shenzhen Nanbo Display Technology Co. Ltd. (Shenzhen, China). Double-sided carbon adhesive tapes (12 mm wide) were purchased from SPI Supplies (West Chester, PA, USA). The qualitative filter papers (Whatman No. 1) were obtained from Whatman International Co. Ltd. (Maidstone, U.K.). The diluted solution of  $\text{H}_2\text{O}_2$  was freshly prepared. Phosphate buffer solution with the concentration of 0.1 M was prepared by mixing 0.1 M  $\text{K}_2\text{HPO}_4$  and 0.1 M  $\text{NaH}_2\text{PO}_4$ . The pH value of phosphate buffer solution was adjusted to be 10. All chemicals were analytical reagent (AR) grade. Water was purified using a Milli-Q water purification system (Millipore, Billerica, MA, USA).

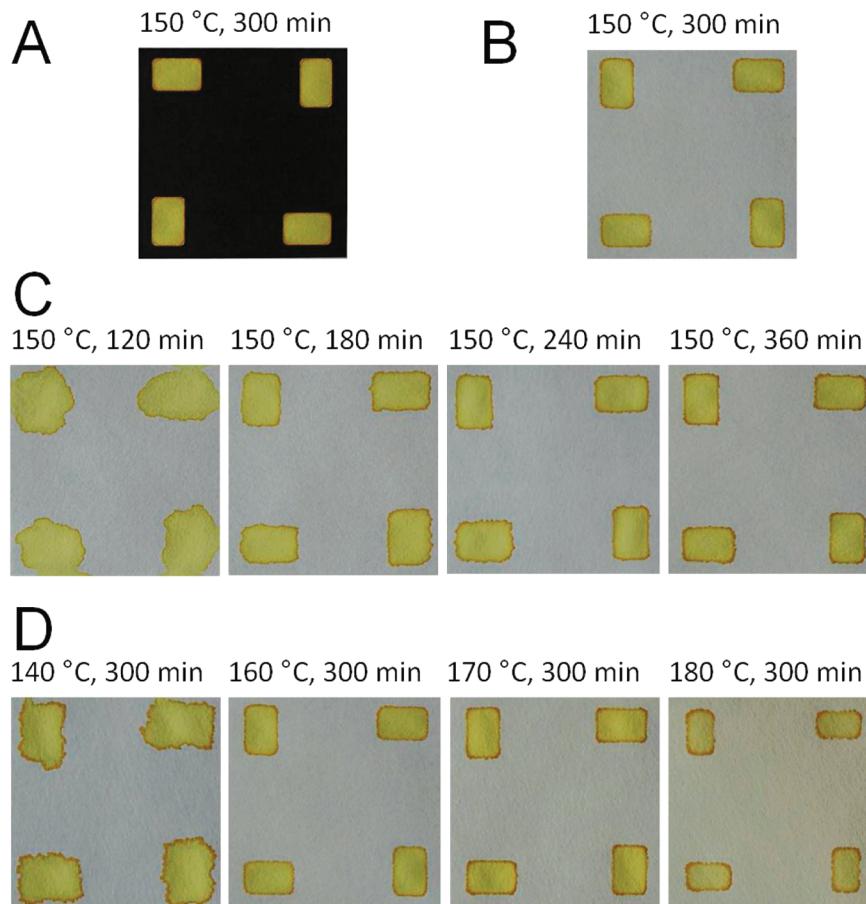
**Synthesis of CdS QDs.** The CdS QDs were synthesized according to previous reports.<sup>10,23</sup> Briefly, 0.093 g of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  was dissolved in 100 mL of water. Then, 0.89 g of TGA was added as a stabilizer to this solution under vigorous stirring. The pH value was adjusted to 10 by dropwise addition of 1 M NaOH solution. Then, 4.06 mL 0.5 M  $\text{Na}_2\text{S}$  solution was introduced into the system under stirring. The reaction mixture was refluxed for 12 h at a temperature of 80 °C. Then anhydrous ethanol was added with extensive stirring for 10 min so that the yellow precipitate could be harvested. The precipitate was then collected by centrifuging and washed for three times with anhydrous ethanol, and being dried in air. The obtained CdS QDs were characterized via transmission electron microscopy (TEM) (Model Tecnai 20, FEI, Hillsboro, OR, USA) and ultraviolet-visible light (UV-vis) spectra. The

diameters of the CdS QDs were measured to be  $\sim 4.0\text{ nm}$ . The stock solution of  $0.1\text{ mg mL}^{-1}$  CdS QDs was prepared via dispersing CdS QDs in water under ultrasonication. This stock solution was optically clear and no precipitate could be observed for 2 months when stored at a temperature of 4 °C.

**Preparation of the Patterned Paper and the Modified Electrode.** The filter paper was patterned with a laser printer and treated by heating (Figure 1A). The patterns were designed and then printed on the filter paper with a printer (Hewlett-Packard, Model HP 1010 LaserJet) with the resolution of 600 dpi. The printed filter paper then was treated at a temperature of 150 °C for 300 min. After heating, the rectangular areas (1.1 cm long and 0.74 cm wide) without the printed toner on the patterned filter paper were used as thin-layer electrochemical cells for ECL detection. The thickness of the filter paper is 11  $\mu\text{m}$ , and the height of the printed toner was  $\sim 10\text{ }\mu\text{m}$ .

The modified electrodes were fabricated by using ITO glass to support the double-sided carbon conductive tape (Figure 1B). ITO glass was thoroughly ultrasonically cleaned for 5 min using acetone, ethanol, and water, successively, and then dried at room temperature. The double-sided carbon adhesive tape with the area of  $12\text{ mm} \times 8\text{ mm}$  was attached on the washed ITO glass. The stock solution of  $0.1\text{ mg mL}^{-1}$  CdS QDs with a volume of  $150\text{ }\mu\text{L}$  was deposited dropwise on the carbon adhesive tape. After the solution was dried at room temperature, a circle area coated with CdS QDs would be formed since the carbon tape is hydrophobic. Thus, the CdS QD-modified carbon tape electrodes were fabricated.

**Integration of PADs.** ECL detection was performed on a MPI-E ECL analyzer system (Xi'an Remax Electronic Science & Technology Co. Ltd., Xi'an, China). The range of the

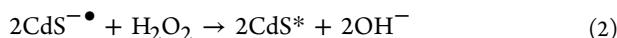


**Figure 2.** Effect of heating on the diffusion of the indicating solution in the filter paper patterned with the laser printer. (A) The printed side of the patterned paper was treated at a temperature of 150 °C for a duration of 300 min; the black area was printed with toner and the yellow part was the diffused area of the marker solution. (B) The back side of the patterned paper, treated at a temperature of 150 °C for a duration of 300 min; the yellow part was the diffused area of the marker solution. (C) The back side of the patterned paper, treated at the temperature of 150 °C for a duration of 120–360 min. (D) The back side of the patterned paper, treated at a temperature of 140–180 °C for a duration of 300 min.

spectral wavelength of the photomultiplier tube (PMT) is from 200 nm to 800 nm. The biased voltage of the PMT was normally set at 800 V during the experiments. As shown in Figure 1, the surface of the modified carbon adhesive tape as the working electrode was attached with the unprinted area of the patterned paper on optical glass. In all experiments, an Ag/AgCl wire and a Pt wire were fixed on the paper with a clasp and used as the reference electrode and the counter electrode, respectively. The overlapped area of the patterned paper and the modified electrode was 8 mm × 7.4 mm. The integrated system (Figure 1C) was placed into the detection area of the ECL analyzer. A phosphate buffer solution (0.1 M, pH 10) containing a certain concentration of H<sub>2</sub>O<sub>2</sub> was added in the unprinted area on the paper for ECL detection.

## RESULTS AND DISCUSSION

In this study, we demonstrate the utility of our electrode system for ECL using a H<sub>2</sub>O<sub>2</sub> reaction with CdS QDs. The following mechanism is widely accepted for CdS QD ECL, using H<sub>2</sub>O<sub>2</sub> as the coreactant:<sup>9</sup>

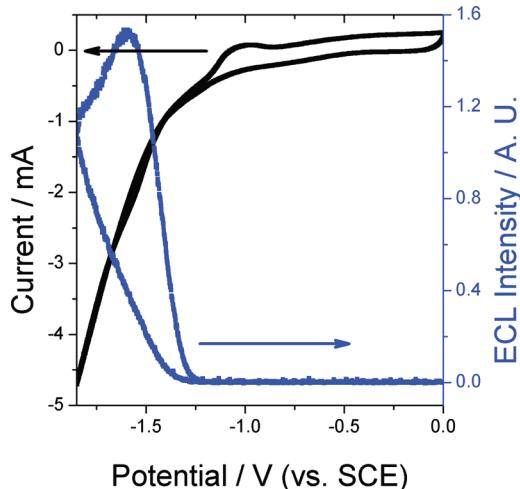


In this mechanism, eq 1 is critical, because it directly determines the intensity of the ECL signal. In order to obtain a stable ECL signal, CdS QDs should closely contact the surface of the working electrode. This requirement conflicts with the fact that CdS QDs could be oxidatively corroded during electrochemical reactions and then diffuse into the electrolyte solution, which could result in the irreversible leakage of QDs.<sup>16</sup> Thus, the attachment of QDs on the working electrodes is essential for the stability of ECL emission. Here, we simply immobilized CdS QDs on the carbon tape electrodes and then integrated the modified carbon tape electrodes with patterned paper to stabilize ECL emission. One side of the double-sided carbon adhesive tape was closely attached on ITO glass for the improvement of conductivity. The other side of the carbon adhesive tape was modified with CdS QDs. The carbon adhesive tape could provide a conductive environment for ECL reactions of CdS QDs. On the other hand, the conductive glue on the tape could also hold fast CdS QDs during ECL detection for stable ECL emission. Moreover, the patterned paper could form a thin-layer electrochemical cell for ECL detection, because the thickness of the patterned paper is at the level of 10 μm.

The process of patterning paper is a critical step for the use of PADs.<sup>22,24,25</sup> Here, we have printed the patterns on filter paper with a common laser printer (HP Laserjet 1010). It has been demonstrated that the printed toner could become soft

during heating.<sup>26–28</sup> We investigated the effect of temperature and duration on the formation of hydrophilic areas on patterned filter papers (Figure 2). It could be observed that the marker solution ( $0.1\text{ M K}_3[\text{Fe}(\text{CN})_6]$  solution) was limited in the unprinted area on the patterned paper treated at the temperature of  $150\text{ }^{\circ}\text{C}$  and the duration of 300 min. At lower temperature or shorter duration, the marker solution could diffuse into the printed area with toner. Such results revealed that, during heating, the printed toner could penetrate the porous paper to form hydrophobic areas while the unprinted areas are still hydrophilic. The regulated hydrophilic areas on the patterned filter paper were used as the thin-layer electrochemical cells for ECL detection in PADs.

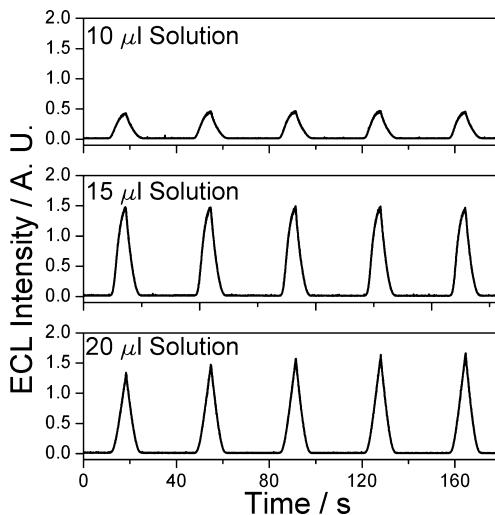
ECL detection was performed by integrating the patterned filter paper with the CdS QD-modified carbon tape electrode, the Ag/AgCl wire, and the Pt wire. As shown in Figure 3, ECL



**Figure 3.** ECL–potential curve and the corresponding cyclic voltammogram using the CdS QD-modified carbon adhesive tape as the working electrode. Experimental parameters: running solution,  $0.1\text{ M}$  phosphate buffer solution ( $\text{pH } 10.0$ ) with  $1\text{ mM H}_2\text{O}_2$  (volume of  $15\text{ }\mu\text{L}$ ); volume of CdS QDs =  $150\text{ }\mu\text{L}$ ; scan rate =  $100\text{ mV s}^{-1}$ ; initial potential =  $0\text{ V}$ ; scan direction, from  $0\text{ V}$  to  $-1.8$  to  $0\text{ V}$ .

emission could be generated when the potential was scanned in the negative direction from  $0$  to  $-1.8\text{ V}$  in  $0.1\text{ M}$  phosphate buffer solution ( $\text{pH } 10.0$ ) containing  $1.0\text{ mM H}_2\text{O}_2$ . In the corresponding cyclic voltammogram, a pair of well-defined reduction and oxidation peaks appeared at ca.  $-1.5\text{ V}$  and  $-1.0\text{ V}$ , respectively. Such results confirmed that electrochemical and ECL reactions occurred using the carbon adhesive tape as the working electrode in the PADs. Since the onset of ECL emission started at the potential of  $-1.25\text{ V}$ , it is also believed that the ECL detection in PADs could be explained with the same mechanism described by eqs 1–3.<sup>9,10</sup>

Figure 4 illustrates that the volume of the electrolyte solution has great influence on ECL emission and its stability. With the volume of the electrolyte solution at  $10\text{ }\mu\text{L}$ , the ECL signal produced had a small relative standard deviation (RSD) of  $3.0\%$ . When the volume increased to  $15\text{ }\mu\text{L}$ , the ECL emission increased and the RSD became  $0.7\%$ . When the volume increased to  $20\text{ }\mu\text{L}$ , the ECL emission slightly decreased, having a RSD of  $8.9\%$ . However, when the volume decreased, the electrolyte solution did not cover the entire hydrophilic area of the patterned paper, so the ECL emission became lower. The volume of  $15\text{ }\mu\text{L}$  was optimal for the formation of thin-layer

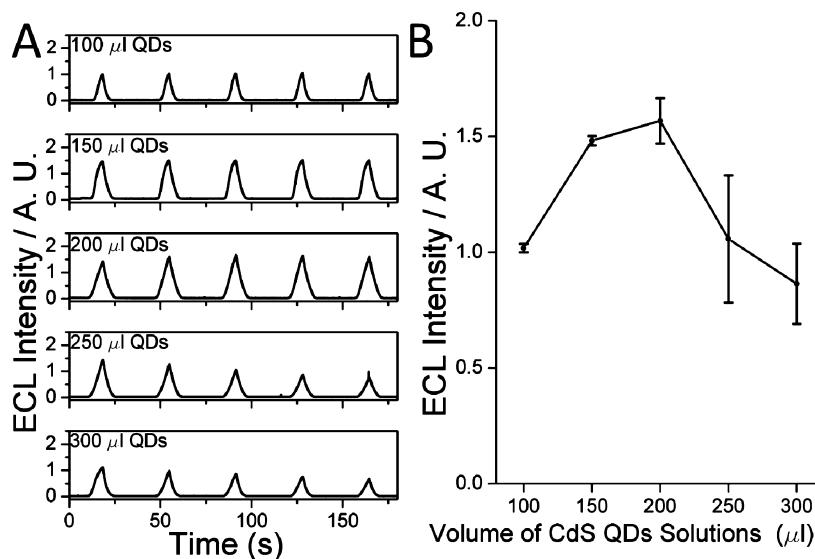


**Figure 4.** ECL–time curve of five cycles with various volumes of the electrolyte solution added in the patterned paper for ECL detection. Experimental parameters: the running solution,  $0.1\text{ M}$  phosphate buffer solution ( $\text{pH } 10.0$ ) consisting of  $1\text{ mM H}_2\text{O}_2$ ; the other conditions were the same as those given in Figure 3.

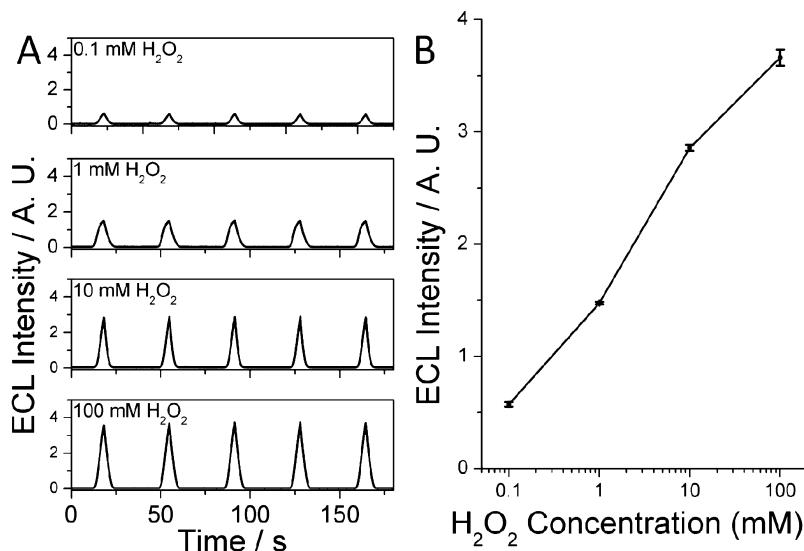
electrochemical cells with an area  $1.10\text{ cm}$  long and  $0.74\text{ cm}$  wide. The varied ECL emission with the increasing volume of the electrolyte solution was probably due to the leak of extra solution outside the thin-layer electrochemical cell.

Figure 5 shows the effects of different amounts of CdS QDs on the ECL signal. We applied suspensions of CdS QDs of the same concentration ( $0.1\text{ mg mL}^{-1}$ ) with various volumes. In this case, different amounts of CdS QDs are all confined in a circular area, because the carbon adhesive tape is hydrophobic. Our results showed that the circular area increased by  $\sim 60\%$  when the QD solution volume increased  $100\%$ . This could be attributed to the fact that the carbon tape is hydrophobic. Thus, greater amounts of QDs were coated on the carbon tape with increasing volume of the QD solution with the same concentration. Interestingly, ECL emission increased with an RSD value of  $<2.0\%$  when the volume of the QD solution was  $100$  and  $150\text{ }\mu\text{L}$ . When the volume increased to  $200\text{ }\mu\text{L}$ , the RSD increased to be  $6.2\%$ , although the ECL emission increased only slightly. Further increases in volume resulted in a decrease in ECL emission with much larger RSD values. Our results implied that there is a threshold of the amounts of CdS QDs for the generation of stable ECL emission. When the QD amount is over the threshold, ECL emission would decrease with worse reproducibility. This might be attributed to the fact that CdS QDs are semiconductors. The increasing amount of QDs could decrease the conductivity, so that electrochemical and ECL reactions could not occur very well.

Under the optimized experimental conditions, our approach was applied to quantify fresh  $\text{H}_2\text{O}_2$  solutions at various concentrations using ECL detection. It could be observed from Figure 6 that ECL emission increased as the  $\text{H}_2\text{O}_2$  concentration increased from  $0.1\text{ mM}$  to  $100\text{ mM}$ . ECL emission was linearly proportional to the logarithmic values of the  $\text{H}_2\text{O}_2$  concentrations ( $R = 0.985$ ). ECL emission for all  $\text{H}_2\text{O}_2$  concentrations was very stable within at least five cycles. Such stable ECL emission may allow investigation of ECL mechanism by coupling with other approaches, such as spectroscopic techniques.<sup>29</sup> The stable ECL emission could be mostly attributed to the strong attachment of CdS QDs on



**Figure 5.** (A) ECL–time curve of five cycles at the carbon tape electrodes modified with various amounts of CdS QDs and (B) the correlation of ECL emission with the amounts of CdS QDs modified on the carbon tape electrodes. Experimental parameters: the running solution, 0.1 M phosphate buffer solution (pH 10.0) consisting of 1 mM H<sub>2</sub>O<sub>2</sub> (volume of 15 μL); the other conditions are the same as those given in Figure 3.



**Figure 6.** (A) ECL–time curve of five cycles for various concentrations of H<sub>2</sub>O<sub>2</sub> and (B) the relationship of ECL emission and the H<sub>2</sub>O<sub>2</sub> concentrations with the CdS QD-modified carbon tape electrodes. Experimental parameters: the running buffer, 0.1 M phosphate buffer solution (pH 10.0) consisting of H<sub>2</sub>O<sub>2</sub> (volume of 15 μL); the other conditions were the same as those given in Figure 3.

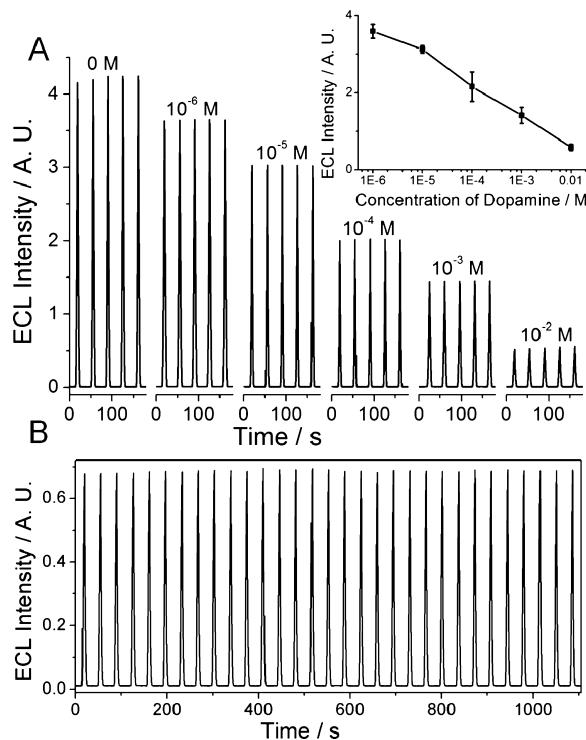
the carbon adhesive tape. Moreover, the paper-based thin-layer electrochemical cell facilitates the ECL reactions. The carbon tape electrode also offers a large surface area for efficient ECL emission.

The determination of dopamine has been studied based on ECL emission using QDs, based on the quenching effect of dopamine in QD-based ECL detection.<sup>20,21</sup> Figure 7A shows that, in our integrated system, the ECL intensity decreased with the increase in dopamine concentration from 1 μM to 10 mM. Such a relationship between ECL emission and dopamine concentration revealed that the detection mechanism was based on the quenching effect.<sup>20,21</sup> Figure 7B shows stable and reproducible ECL emission for 31 cycles or nearly 20 min with 10 mM dopamine under continuous potential scans. Note that a sample volume of 15 μL was used during this procedure. With such a low sample volume, our approach may open more

opportunities for the application of ECL detection in microdialysis and other bioanalytical applications.<sup>30,31</sup>

## CONCLUSION

In summary, here, we have demonstrated that double-sided carbon adhesive tape could be used as an ideal working electrode for quantum dots (QD)-based electrochemiluminescence (ECL) detection in paper-based devices. Stable ECL emission could be generated by simply immobilizing CdS QDs on the carbon adhesive tape without other treatment. With the robust attachment of CdS QDs on the carbon adhesive tape, stable ECL emission could be utilized for quantification of the H<sub>2</sub>O<sub>2</sub> concentrations. The determination of dopamine in low volumes suggested that our approach paved the way to a wide variety of bioanalytical applications and devices involving ECL detection.



**Figure 7.** (A) ECL–time curve of five cycles on the detection of dopamine with various concentrations (inset shows the relationship of ECL emission and the dopamine concentration) and (B) ECL–time curves of 31 cycles with dopamine at the concentration of 10 mM. The values and standard deviations were obtained based on three samples for every concentration. Experimental parameters: the running buffer, 0.1 M phosphate buffer solution (pH 10.0) consisting of 1 M  $\text{H}_2\text{O}_2$  and dopamine with specific concentrations (volume of 15  $\mu\text{L}$ ); the other conditions were the same as those given in Figure 3.

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### Notes

The authors declare no competing financial interest.

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