

# Supporting Information

## **A novel DNA-quantum dot nanostructure electrochemiluminescence aptamer sensor by chain reaction amplification for rapid detection of trace Cd<sup>2+</sup>**

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## 1. Experimental section

### Reagents and Materials

All the high-performance liquid chromatography (HPLC)-purified oligonucleotides (Table 1), SA and sodium sulphide ( $\text{Na}_2\text{S}$ ) were purchased from Shanghai Sangon Biological Engineering Co., Ltd. The oligonucleotides were dissolved in Tris-EDTA (TE) buffer (pH 8.0, containing 10 mM Tris-HCl, and 1 mM EDTA), and stored at  $-20\text{ }^\circ\text{C}$ . The diluted phosphate buffer solution (PBS, pH 7.4) contained 0.1 M  $\text{Na}_2\text{HPO}_4$ , 0.1 M  $\text{NaH}_2\text{PO}_4$ , and 0.1 M KCl. Ethanol, Sodium hydroxide (NaOH), Cadmium chloride ( $\text{CdCl}_2$ ), 1-(3-(dimethylamino)-propyl)-3-ethylcarbodiimide hydrochloride (EDC), N-hydroxysuccinimide:1-hydroxypyrrolidine-2,5-dione (NHS), tetrachloroauric acid ( $\text{HAuCl}_4$ ) were purchased from Aladdin Co., Ltd. (Shanghai, China). Mercaptopropionic acid (98.0%, MPA) was purchased from Beijing Balinwei Technology Co., Ltd. All reagents were of analytical grade and used as received. Ultrapure water from a Millipore water purification system ( $\geq 18\text{ M}\Omega$ , Milli-Q, Millipore) was used throughout the experiment.

**Table 1. Sequences of DNA used in this work**

Oligonucleotide	Sequence (5'-3')
cpDNA	ATACCACAACAGTTTTT-NH <sub>2</sub>
Cd <sup>2+</sup> Aptamer DNA	ACTGTTGTGGTATTATTTTTGGTTGTGCAGT
H1	ATAAAAACCAACACGTCAACTGCACAACCAAAAATA-Biotin
H2	TGACGTGTTGGTTTTTATTATTTTTGGTTGTGCAGT-Biotin

### Apparatus

Transmission electron micrograph (TEM) image was acquired using a JEM-2100 instrument (JEOL, Japan). UV-vis absorption spectra were measured with Lambda 35 UV Visible Spectrometer (Japan). Polyacrylamide gel electrophoresis (PAGE) analysis was performed on the Beijing JUNYI electrophoresis analyzer and imaged on the Biorad ChemDoc XRS (USA). Scanning electron microscopy (SEM) image was acquired using a S-4800 instrument (Hitachi, Japan) with the voltage of 20 kV. The

fluorescence spectrum was obtained from the F-4500 fluorescence spectrometer (Japan). The ECL signal was acquired by a model MPI-E ECL analyzer (Remex Electronic Instrument Lt. Co., Xi'an, China) with three-electrode system containing a Pt wire counter electrode, saturated calomel (saturated KCl) reference electrode, and a glassy carbon electrode working electrode. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured on CHI 660E electrochemical workstation (Chenhua Instrument Co., Ltd. Shanghai, China).

### **Synthesis of CdS QDs**

CdS QDs were synthesized by the classical aqueous synthesis method. In summary, 250  $\mu\text{L}$  of mercaptopropionic acid and 50 mL of  $\text{CdCl}_2$  (0.01 M) were first added to a three-necked flask and  $\text{N}_2$  was promptly passed through for 30 min to deoxygenate. Then 1.0 M NaOH was slowly added to adjust the pH of the solution to 11, and 5.0 mL of  $\text{Na}_2\text{S}$  (0.1 M) was quickly added to the above solution, followed by heating to boiling and refluxing for more than 4 h. The prepared CdS QDs solution was stored at 4  $^\circ\text{C}$  and protected from light. Purification by centrifugation is required before use. Specifically, CdS QDs were mixed with an equal volume of ethanol and the supernatant was removed by high speed centrifugation. The resulting precipitate was dissolved in an equal volume of secondary water and set aside.

### **Analysis of PAGE**

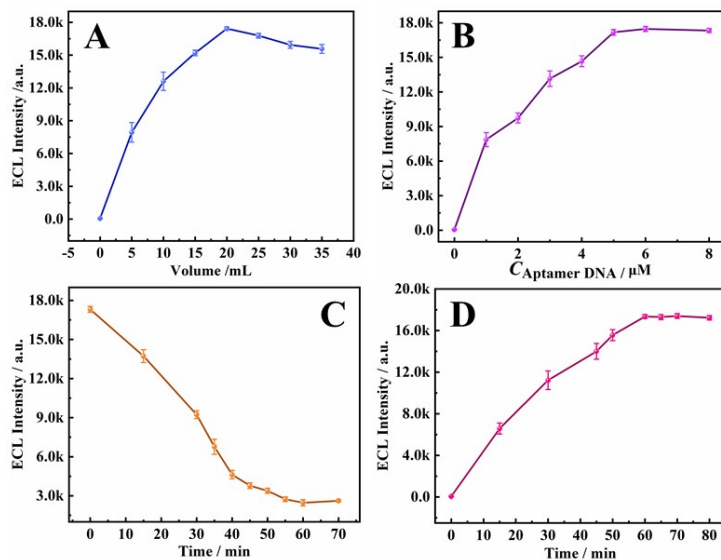
The DNA hybridization during the HCR and electrode assembly process were analyzed by PAGE experiments. In a 1 $\times$ triacetic acid-ethylenediaminetetraacetic acid (TAE) (pH 8.0) buffer solution, the experiment was carried out. A voltage of 180 V was first applied for 3 min at room temperature, then a voltage of 135 V was continuously applied for 1.5 h. Finally, ethidium bromide (EB) was used for staining for 20 min, the gel was scanned, and UV imaged with a gel imaging system (Biorad ChemDoc XRS).

### **ECL measurements**

The ECL measurements were performed in a three-electrode system containing  $\text{K}_2\text{S}_2\text{O}_8$  (0.05 M) and KCl (0.1 M) phosphate buffer solution. The voltage setting range

of the MPI-E analyzer was 0 to  $-1.5$  V, and the scan rate was controlled at 100 mV/s. The voltage of the photomultiplier tube (PMT) was 800 V.

## 2. Results and discussion



**Figure S1.** (A) The volume of SA connected to CdS QDs, (B) the assembly concentration of  $\text{Cd}^{2+}$  Aptamer DNA, (C) the incubation time of  $\text{Cd}^{2+}$  with the electrode, and (D) the assembly time of the CdS QDs-SA complex affect the detection performance.

**Table S2. Comparison of different methods for  $\text{Cd}^{2+}$  determination**

methods	linear range	LOD	ref
ECL	10 nM-2.5 $\mu\text{M}$	4.0 nM	S1
Colorimetry	5.0 $\mu\text{M}$ -5.0 mM	2.0 $\mu\text{M}$	S2
Electrochemistry	15 nM-0.1 pM	4.34 fM	S3
PEC	1.0 pM-10 nM	0.36 pM	S4
OCP	2.5 pM-2.5 $\mu\text{M}$	0.17 pM	S5
FL	1.0 $\mu\text{M}$ -40 $\mu\text{M}$	546 nM	S6
FL	10 pM-1.0 $\mu\text{M}$	2.5 pM	S7
ECL	10 fM-10 nM	2.6 fM	This work

**Table S3. The result of measuring  $\text{Cd}^{2+}$  in the actual water sample**

Sample	Add (pM)	Found (pM)	Recovery (%)	RSD (% , n=3)
<b>Tap water</b>	0	1.32		3.89
	3	4.45	104.33	4.29
	5	6.63	106.20	2.81
	10	11.08	97.60	2.27
<b>River water</b>	0	213.6		3.63
	500	745.1	106.3	2.55
	1000	1251.8	103.8	2.93
	3000	3164.5	98.4	3.32

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