Int. J. Electrochem. Sci., 15 **(2020)** 8710 – 8720, doi: 10.20964/2020.09.32

International Journal of
ELECTROCHEMICAL
SCIENCE
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High Sensitive Electrochemical Luminescence Sensor for the Determination of Cd^{2+} in Spirulina

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Received: 5 April 2020 / *Accepted:* 8 June 2020 / *Published:* 10 August 2020

The determination of cadmium ions in Spirulina is very important in food safety. In this work, stable CdTe quantum dots (QDs) were synthesized in the aqueous phase with thioglycolic acid as a protective agent. Based on the enhancement effect of cadmium ions on the electrochemiluminescence (ECL) signal of the TGA-modified CdTe QDs, a signal-enhanced ECL sensor was constructed to detect cadmium ions under the optimal experimental conditions. The linear range was 2 nM-0.5 μM, and the detection limit was 1.1 nM. In addition, the system can also be used to determine the pH. In the pH range of 4.5-7.4, the electrochemiluminescence intensity increased linearly with increasing pH. This method can be used not only to detect cadmium ions but also to determine the pH of the solution. It can be applied to the detection of cadmium ions in Spirulina samples.

Keywords: Electrochemiluminescence; Electrochemistry; Cadmium ions; Thioglycolic acid; Spirulina

1. INTRODUCTION

Spirulina is one of the oldest green single-celled organisms in the world. The main components of Spirulina are proteins, saccharides, a few lipids and abundant micronutrients, such as vitamins and mineral substances [1,2]. Spirulina decreases blood pressure, improves immunity and has antioxidant and anticancer activities. Because of these nutritional and functional values, Spirulina can provide great economic benefits [3,4]. The quality of Spirulina products is the top concern for consumers. Thus, the development of a fast and effective detection method for Spirulina products is actively demanded for market management [5,6].

Cadmium ions have a biological half-life of 20-30 years. They have toxic effects on the kidneys, bones, lungs and cardiovascular system and may cause cancer and damage to human tissues and organs [7–10]. Therefore, the detection of cadmium ions is one of the important items for food standards in China. Currently, the main methods for the determination of cadmium are inductively coupled plasma mass spectrometry, atomic absorption spectrometry, electrochemical analysis, fluorescence spectroscopy, mass spectrometry and their combined technologies [11–16]. However, these methods have many disadvantages, such as multiple steps, the high price of pharmaceutical instruments, the high costs of analysis and experimentation, low sensitivity, etc. Therefore, it is of great significance to study a rapid, simple and highly sensitive method for detecting cadmium in food [17–21].

Electrochemiluminescence (ECL) is a kind of light radiation that occurs when a certain voltage is applied to an electrode, causing reaction products between or at the electrodes to react with each other or with a certain component in the solution [22–24]. Similarly, chemiluminescence is produced by a substance involved in an electron energy transfer reaction, but the difference is that electrochemiluminescence is excited and controlled by the voltage, whereas the latter is excited and controlled by the mixture of substances involved in the reaction [25–27]. Electrochemiluminescence has the advantages of chemiluminescence, such as high sensitivity, a wide linear range, simple instrumentation and equipment, etc. At the same time, it has the advantages of good electrochemical reproducibility, reagent stability, strong controllability, etc. Therefore, ECL analysis is widely studied and applied. As an important analytical method, ECL analysis is currently used in many scientific research fields, such as environmental detection, food analysis, biological immunological analysis and drug analysis [28–33].

Quantum dots (QDs), which are also known as semiconductor nanocrystals and have a diameter of 1-10 nm, have a stable three-dimensional structure and unique optical and electrical properties [34–36]. Currently, cadmium telluride, cadmium sulfide and cadmium selenide are mainly studied [33,37–42]. Because the size of QDs is no larger than the exciton Bohr radius of the corresponding bulk materials, the electrons and holes generated under excitation are limited to a narrow three-dimensional space, resulting in the quantum confinement effect, which gives QDs their unique photoelectric properties [43–46]. To date, electroluminescent sensors based on the quenching or signal enhancement effect of quantum dots have been widely used in the fields of organic small molecule detection, immunoassays, and hydrogen peroxide and inorganic ion detection and biosensors. In this work, stable CdTe QDs were synthesized in the water phase with thioacetamide as a protective agent [47–50]. The hydrolysis of the thioacetamide coating the surface of CdTe and the combination of sulfur ions with cadmium ions in solution cause a change in the ECL intensity of the QDs, and the detection of cadmium ions is successfully realized. In addition, the system can also be used to determine the pH in the range of 4.5-7.4; the ECL intensity increases linearly with increasing pH. This method exhibits high sensitivity and good selectivity and is successfully applied to the determination of cadmium ions and the pH of the solution in Spirulina samples.

2. MATERIALS AND METHODS

Instruments: F-4500 fluorescence spectrophotometer (Hitachi, Japan); U-3010 ultraviolet-visible spectrophotometer (Shimazu, Japan); 78-1 magnetic heating mixer (Jintan Jieruier Electric Co., Ltd.); KQ-100 ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd.); CHI760 electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.); pHS-C meter (Shanghai Weiye Instrument Co., Ltd.); IFFE-E flow injection chemiluminescence analyser (Xi'an Ruimai Analytical Instrument Co., Ltd.); quartz sub-boiling high purity water distiller (Jintan Jieruier Electric Co., Ltd.); three-electrode system with ITO, Ag/AgCl and Pt electrodes as the working, reference and counter electrodes, respectively.

Reagents: cadmium chloride ($CdCl_2·2.5H_2O$, China Tingxin Chemical Co., Ltd.); tellurium powder (TE, Tianjin Afaeisa Chemical Co., Ltd.); disodium hydrogen phosphate (Na_2HPO_4, Shanghai Lingfeng Chemical Co., Ltd.); sodium dihydrogen phosphate (NaH_2PO_4, Shanghai Lingfeng Chemical Co., Ltd.); thioglycolic acid (TGA, Sinopharm Group Shanghai Chemical Reagent Co., Ltd.); thioacetamide (CH_3CSNH_2, Sinopharm Chemical Reagent Co., Ltd.); sodium hydroxide (NaOH, Sinopharm Chemical Reagent Co., Ltd.); sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd.). The reagents were analytically pure and were not purified before use. Spirulina samples were supplied by the Otog Banner Research Centre of Spirulina Engineer and Technology.

Synthesis of CdTe QDs: Tellurium powder (14.0 mg) and sodium borohydride solid (30.0 mg) were placed in a 5 mL small bottle. Water (1 mL) was quickly added to the small bottle. The reaction system was placed beside an incandescent lamp and heated. The colour change of the whole reaction process was as follows: black → purple → light pink → colourless. When the solution was colourless and transparent, heating was stopped, and the resulting solution was the precursor of sodium telluride. Then, 50 mL water, 100.4 mg of cadmium chloride solid and 55 μL of mercaptoacetic acid were placed in a three-neck round bottom flask, and the pH was adjusted to 11 with 1 M sodium hydroxide under magnetic stirring. After deaeration, the sodium telluride precursor solution was rapidly injected into the mixed solution. The mixture was heated and refluxed in a 145 ℃ oil bath for 4 h. The obtained QDs were stored in the refrigerator in the dark.

ECL detection: Certain amounts of a phosphate buffer solution, the cadmium telluride quantum dot solution and thioacetamide were added to the reaction tank, mixed evenly and reacted for 10 min (denoted TGA-CdTe QDs). Then, cadmium ions were successively added in different concentrations, and after each reaction, the ECL detection experiments were conducted for 10 min using a three-electrode system.

3. RESULTS AND DISCUSSION

Figure 1 shows a schematic of cadmium ion detection using the QD-based ECL method.

Figure 2A shows the UV absorption and fluorescence spectra of the TGA-modified CdTe QDs after a 4 h reflux time. As shown in the figure, the UV absorption spectrum of the CdTe QDs has a characteristic absorption peak at 516 nm [51]. The fluorescence emission wavelength of the CdTe QDs is 556.5 nm. According to the empirical formula, the particle size is 2.22 nm.

The effect of the QD concentration on the ECL intensity was investigated in a phosphate buffer solution at pH 8.0. Figure 2B shows that when the concentration of CdTe QDs is low, the ECL intensity is weak. With increasing quantum dot concentration, the ECL intensity increases and reaches a maximum value at a quantum dot concentration of 11 μM. When the quantum dot concentration is higher than 11 μM, the intensity of the electrochemiluminescence decreases with increasing quantum dot concentration. These results are explained by the increase in the number of QDs in the excited state and thus the intensity of the ECL as the concentration of QDs increases [52,53]. The later weakening may be due to the self-absorption phenomenon of QDs, which inhibits the generation of excited QDs, thus weakening their ECL intensity, at high concentrations. Based on the changes in the curve of the ECL intensity with the concentration of the QDs, it can be concluded that the optimal concentration of quantum dots in this experiment is 11 μM. These results are consistent with literature reports [54,55].

It is well known that compared to other analytical method techniques, ECL has remarkable advantages, such as high accuracy and sensitivity, low background from unselective photoexcitation, no need of an external light source and relatively convenient temporal and spatial control [56–58]. To investigate the influence of the pH on the luminescence intensity of the QDs, the pH of the QD solution was adjusted to 4.5, 5.0, 5.5, 6.0, 6.5, 7.4, 8.0, 8.5, and 9.0. The results are shown in Figure 2C. The pH is in the range of 4.5-7. With increasing pH, the luminescence intensity increases. When the pH is greater than 7, the ECL intensity decreases as the pH increases. Therefore, pH 7 is selected as the optimal experimental condition.

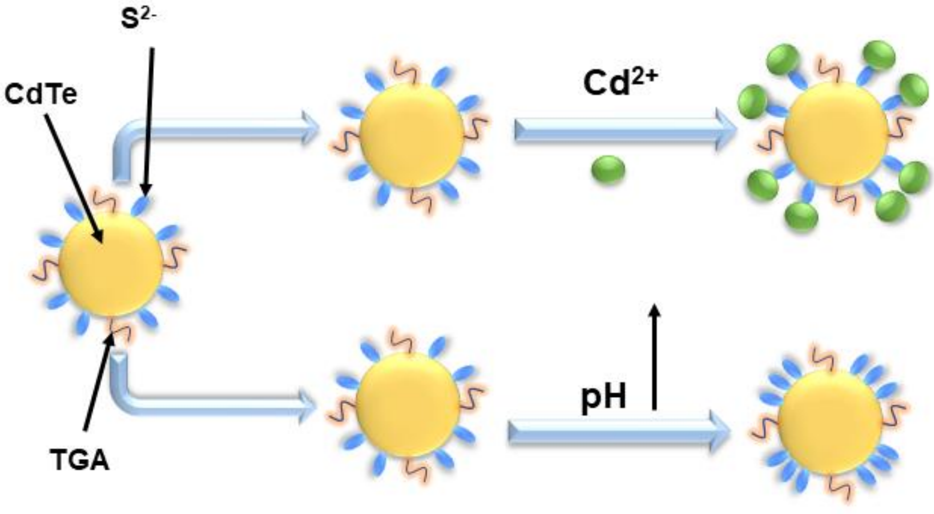

Figure 1. Scheme of the cadmium ions detection based on CdTe QDs assisted ECL method.

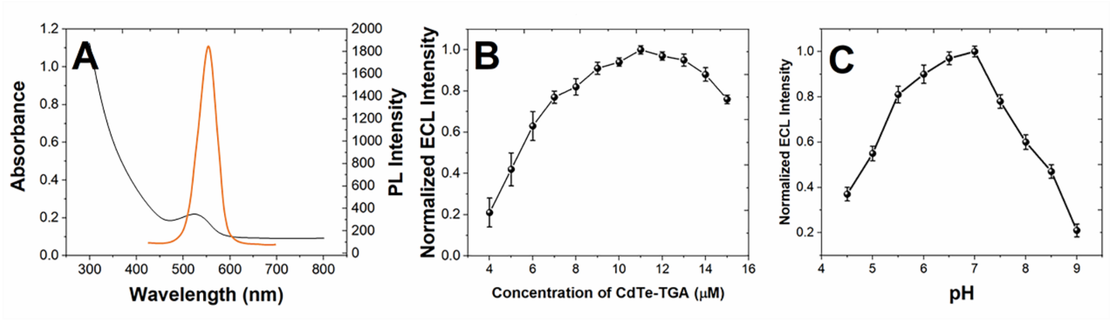

Figure 2. (A) UV–vis and PL spectra of TGA-CdTe QDs. (B) Effect of concentration of TGA-CdTe QDs on the ECL properties. (C) Effect of pH on the ECL properties of TGA-CdTe QDs.

To study the effect of TGA on the ECL intensity of the CdTe QDs, different concentrations of TGA were added to the same amount of CdTe QD solution, and the ECL intensity of the CdTe QDs was detected and recorded. The experimental results are shown in Figure 3A. The figure reveals that with increasing TGA, the ECL intensity of the CdTe QDs decreases gradually, because the sulfur ions produced by TGA hydrolysis in solution cover the surface of the QDs, thus affecting their ECL intensity and stability. When 0.1 mM TGA is added, the ECL intensity is higher, and the stability is the best. Therefore, 0.1 mM TGA is the optimal condition.

Figure 3B shows the ECL time curves of the CdTe QDs in TGA in the presence and absence of cadmium ions. When a certain concentration of TGA is added, the corresponding ECL intensity is significantly reduced, and it is obvious that TGA has a quenching effect on the ECL. After mixing a certain amount of cadmium ions with TGA for 10 min, the corresponding ECL intensity increases, which indicates that adding cadmium ions can increase the ECL intensity of the CdTe QDs.

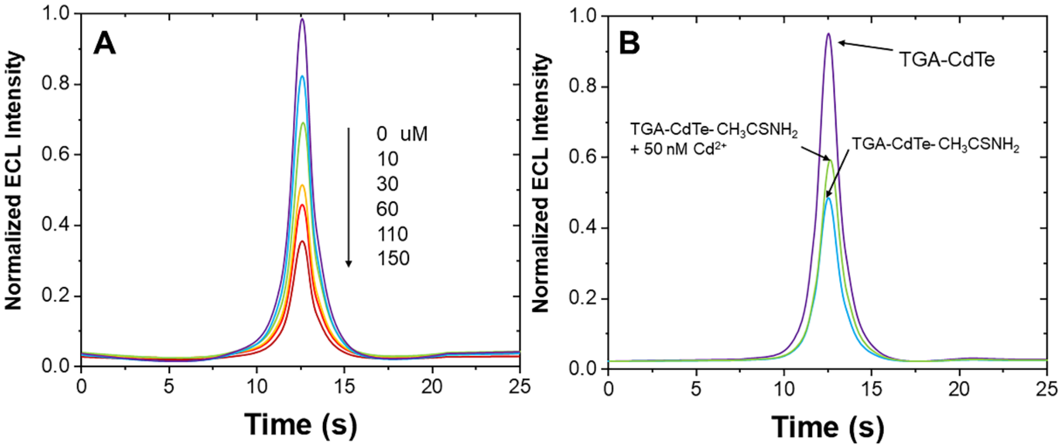

Figure 3. (A) ECL-Time curves of TGA-CdTe QDs to various concentration of CH_3CSNH_2. (B) ECL-time curves of TGA-CdTe, TGA-CdTe- CH_3CSNH_2, TGA-CdTe-CH_3CSNH_2+50 nM Cd^{2+}.

As shown in Figure 4A, when a certain concentration of TGA is added, the corresponding ECL intensity of CdTe is significantly reduced. Obviously, TGA can quench the ECL of CdTe. After mixing

TGA with a certain amount of cadmium ions for 10 min, the ECL intensity of CdTe increases. As shown in Figure 4B, when a certain concentration of TGA is added, the corresponding peak current of CdTe oxidation decreases very little, and after adding a certain amount of cadmium ions to the sulfur in TGA for 0 min, the corresponding peak current of CdTe oxidation increases slightly. These results show that it is feasible to use TGA-modified CdTe QDs to detect cadmium ions. Before coordination with Cd^{2+}, the TGA-modified CdTe QDs exhibit a weaker fluorescence due to the lone pair of electrons, which induce an intramolecular reaction. Furthermore, the lone electron pairs of the nitrogen atoms give rise to a non-radiative process through the n-π* state, which also leads to a high degree of fluorescence quenching. Conversely, after the TGA-modified CdTe QDs are coordinated to Cd^{2+}, the radiation process primarily occurs via the π-π* state, and the coordination compound is more rigid [59].

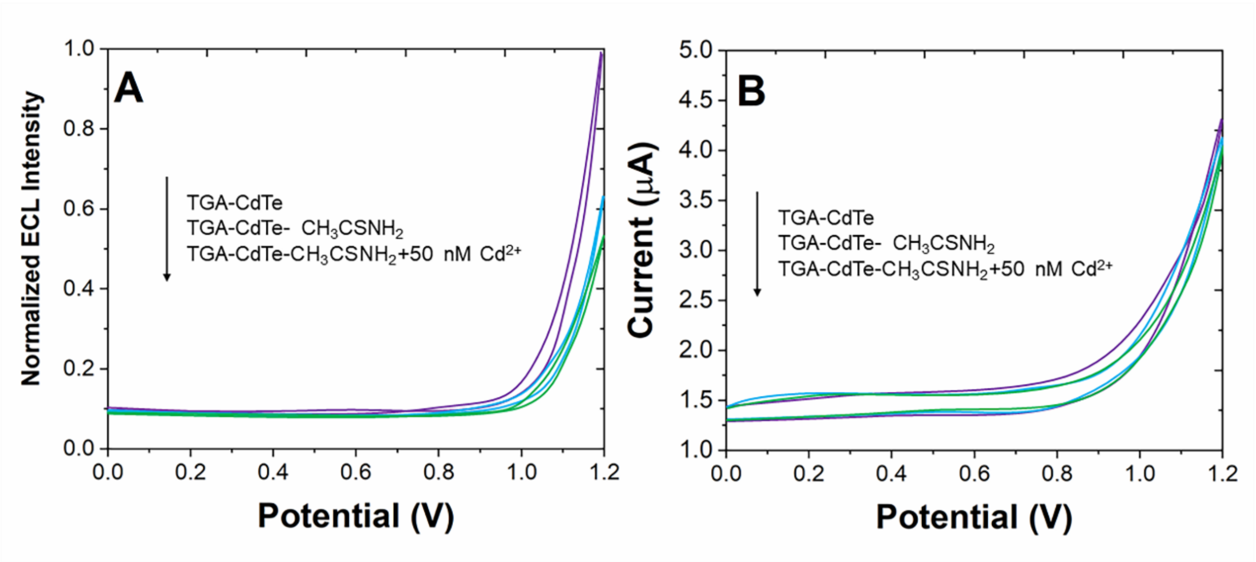

Figure 4. (A) ECL-Potential curves of TGA-CdTe, TGA-CdTe- CH_3CSNH_2, TGA-CdTe-CH_3CSNH_2+50 nM Cd^{2+}. (B) Cyclic voltammograms of TGA-CdTe, TGA-CdTe-CH_3CSNH_2, TGA-CdTe-CH_3CSNH_2+50 nM Cd^{2+}.

As shown in Figure 5, under the optimal experimental conditions, the ECL intensity of the CdTe QDs modified by TGA exhibits a linear relationship with the concentration of cadmium ions in the range of 2 nM-0.5 μM, and the detection limit is 1.1 nM (s/N = 3). As shown in Table 1, this method has a lower detection limit and a wider linear range than other methods.

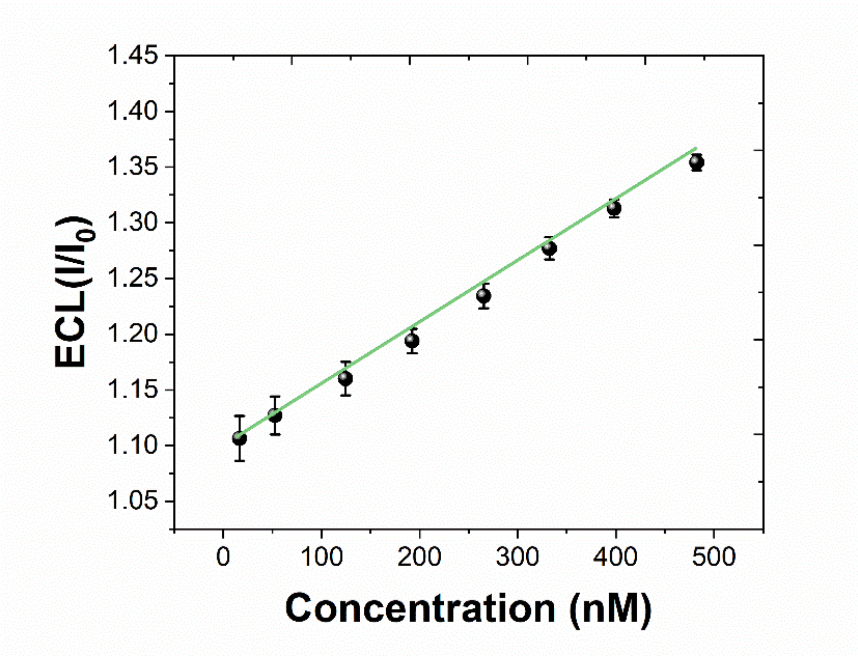

Figure 5. Linear calibration plot of ECL toward concentration of Cd^{2+} (nM).

Table 1. Comparison of Cd^{2+} sensing using proposed method with previous reports.

Method	Linear of Detection (nM)	Limit of Detection (nM)	Reference
Fluorescence	0.1 μM-2 μM	6 nM	[60]
Colormetric	0.2 μM-1.7 μM	0.1 μM	[61]
Paperlater flow immunodevice	3.6 nM-89 nM	0.89 nM	[62]
Ratiometric fluorescence	0.1 μM-15 μM	12 nM	[63]
TGA-CdTe-CH_3CSNH_2	2 nM-0.5 μM	1.1 nM	This work

As shown in Figure 6A, in the absence of cadmium ions, the ECL intensity of the TGA-modified CdTe QDs increases with increasing solution pH. As shown in Figure 6B, in the absence of cadmium ions, the ECL intensity of the TGA-modified CdTe QDs exhibits a linear relationship with the pH of the solution in the range of 4.5-7.4. Therefore, this method can also be used for pH determination.

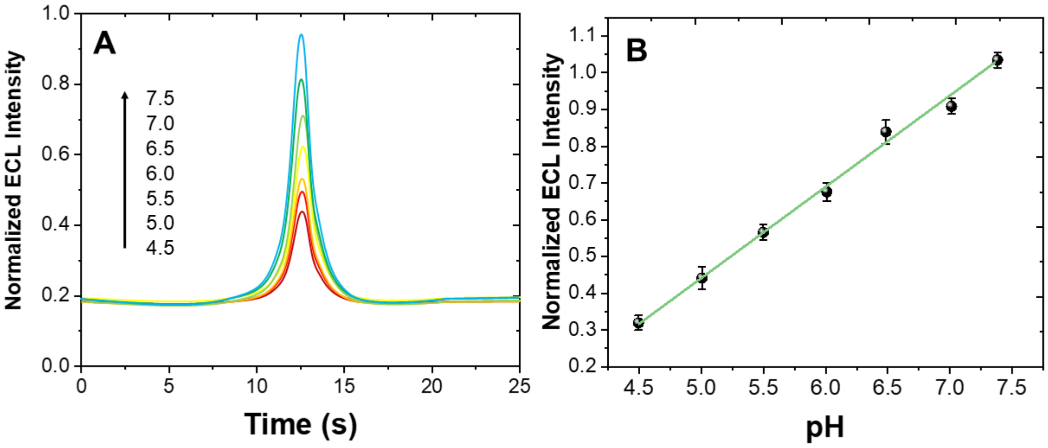

Figure 6. (A) ECL-time curve of TGA-CdTe QDs to various pH without Cd^{2+}. (B) Corresponding plots.

To determine the selectivity of the ECL method based on CdTe QDs modified by TGA, 13 common metal ions that may interfere with the actual detection of CdTe are studied in this experiment, as shown in Figure 7. The results show that when the concentrations of sodium, potassium, copper, manganese, cobalt, magnesium, mercury, zinc, lead, nickel, barium, aluminium and chromium ions are 10 times higher than that of cadmium ions, no obvious interference with the actual detection of cadmium ions is observed. Therefore, the proposed sensor exhibits an excellent anti-interference property.

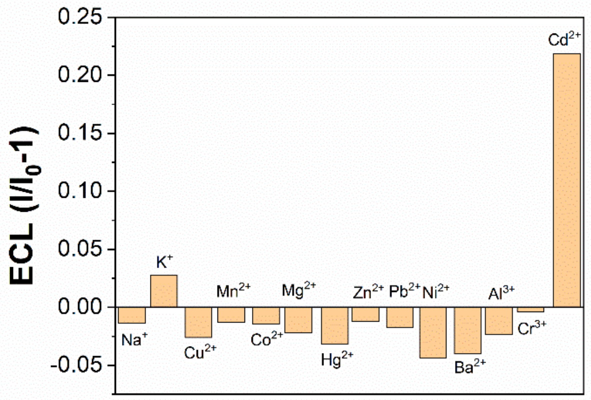

Figure 7. Anti-interference property of the proposed sensor.

The proposed sensor was then used to determine the content of Cd^{2+} in Spirulina samples supplied by the Otog Banner Research Centre of Spirulina Engineer and Technology. All Spirulina samples were sonicated for 30 min for extraction. Then, a certain amount of extract was injected into the electrochemical cell for analysis. A standard amount of Cd^{2+} was added. Table 2 shows the performance of the sensor in real sample analysis. No Cd^{2+} is detected in any of the Spirulina samples. In addition, an excellent recovery performance is observed in each test, indicating that the proposed sensor can be employed for real sample sensing.

Table 2. ECL determination of Cd^{2+} content in Spirulina samples.

Sample	Detected (nM)	Added (nM)	Detected (nM)	Recovery (%)
1	0	10.00	9.88	98.80
2	0	20.00	20.79	103.95
3	0	50.00	50.24	100.48
4	0	100.00	99.71	99.71

4. CONCLUSION

Stable CdTe QDs were synthesized in the aqueous phase with thioglycolic acid as a protective agent, and their UV, fluorescence and ECL properties were characterized. Based on the enhancement effect of cadmium ions on the ECL signal of TGA-modified CdTe QDs, a signal-enhanced ECL sensor was constructed to detect cadmium ions under the optimal experimental conditions. The linear range is 2 nM-0.5 μM, and the detection limit is 1.1 nM. In addition, the system can also be used to determine the pH. In the pH range of 4.5-7.4, the electrochemiluminescence intensity increases linearly with increasing pH. This method can be used not only to detect cadmium ions but also to determine the pH of the solution. It can be applied to the detection of cadmium ions in Spirulina samples.

ACKNOWLEDGEMENTS
This work was supported by National Natural Science Foundation of China (31660151) and Ordos City Science and Technology Project (YY201820076).

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