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Electrochemical Determination of Carbendazim in Water Base on Carbon Dots Modified Glassy Carbon Electrode

Linyan Bian[1], *Chunli Li*[1] *and Haitao Zong*[2,*]

[1] School of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454000, China
[2] School of Physics and Electronic Information Engineering, Henan Polytechnic University, Jiaozuo 454000, China
[*]E-mail: haitaozong@163.com

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Through the urea and sodium citrate electrochemical carbonizing, one-pot method which is convenient and economical, is employed to fabricate the water soluble carbon dots (designated as C-Dots). By developing electrochemical sensor with high sensitivity, where the glassy carbon electrode was decorated by C-Dots, the carbendazim was then determined by different pulse voltammetry. The $[Fe(CN)_6]^{3-/4-}$ was used as an electrochemical probe to investigate the electrochemical specific property of the decorated electrode. The electron transfer on larger surface of electrode demonstrated faster rate in C-Dots/GCE than that on electrode with any functionalization. On the decorated electrode, the cycle voltammetry was employed to investigate the electrochemical carbendazim actions. The excellent performance in electrochemically oxidizing carbendazim is exhibited by C-Dots/GCE. With optimized condition, excellent linearity was observed in the well-established sensor of C-Dots/GCE by combining the peak current and carbendazim concentration, where the 10 nM was considered to be the limitation with the range (0.1-10 μM). The carbendazim can be successfully and effectively determined in the water sample by using this proposed sensor.

Keywords: Carbon dots; Electrochemical sensor; Oxidation; One-pot; Electroanalysis

1. INTRODUCTION

As a potential harm to environment and human health, pesticide residues have attracting much attention. For controlling the environment pollution and protecting human health, it is definitely urgent to determine the residues with trace level in the samples of environment and food. . For controlling the wide fungal diseases including blight, mold, mildew, rot, spot and scorch in the corps, as a pesticide of toxic class IV, methyl-1H-benzo[*d*]imidazol-2-ylcarbamate (designated as carbendazim) behaves widely as a benzimidazole fungicide. [1]. Due to its slow degradation and long-time persistence, which resulted from the difficulty of breaking its benzimidazolic ring, carbendazim harmed the health of human-beings and environment [2, 3]. Hence, in order to control the environment pollution and protect the health of human beings, it should be very essential to build a well-established method to detect the trace carbendazim sensitively, facilely and quickly. Because this electrochemical method is simple, selective and cost-effective with on-field detection and time-saving, it recently has been attracted much attention. Various materials with different functions have been employed to decorate the interface of electrode with sensors of carbendazim, where nanosheets of cyclodextrin with graphene hybrid (designated as CD–GNs) [4], clay of sodium montmorillonite (designated as NaMM) [5], carbon nanotubes with multiwall (designated as MWNTs) [6], polymeric methyl red (designated as PMRE) [7], tricresyl phosphate [8], graphite oxide (designated as GO) [9], and tricresyl phosphate (designated as TCP) [10-12] are included. However, there are barely reports about C-Dots which was used to functionalize the interface electrode for electrochemical effective sensors, to determine the trace carbendazim.

Due to strong chemical inertness, excellent properties in optics and character of low-toxicity, much attention has been paid to C-Dots [13]. various methods including arc discharge [14], ablating with laser [15, 16], pretreated by oxidative acid [17], synthesized by hydrothermal[18], etching with electrochemical way [19, 20], pyrolysis [20], and synthesized under microwave assistance [21] have been employed to fabricate C-Dots. A method for fabricating fluorescence C-Dots with argon carrying water vapor, was reported by Sun and co-workers [15]. Meanwhile, a method of preparing the C-Dots was reported from the combustion soot of candles by Liu and co-workers [17], where the samples were pretreated by oxidative acid and purified by PAGE (short for polyacrylamide gel electrophoresis). Meanwhile, a one-pot method of fabricating C-Dots was reported from Pan’s group [20] by pyrolysis of EDTA with the presence of nitrogen. Even though there are a lot of methods for preparing the C-Dots, the reported C-Dots demonstrated poor interaction with analytes which was result from extremely low functionalization, and confine its real application. In recent years, there are some efforts to be made to functionalize and control the surface characteristic. *N*-(2-aminoethyl)-*N*,*N*,*N′*tris(pyridin-2-ylmethyl)ethane-1,2-diamine coating the C-Dots combined with CdSe/ZnS quantum dots was applied to detect intracellular Cu^{2+} by Zhu and co-workers [22]. A system with FRET was established by Yu and his co-workers to detect NO by combining C-Dots with phenylenediamine, which contained naphthalimide and behaved as an actor to recognize the NO. [23]. Sun et al. [24] functionalized the C-Dots by the employment of cyanine dye, which exhibited special activity to the bisulfite, to achieve a fluorescence probe to detect SO_2 selectively and quantitatively. But complicated surface functionalization and special receptors are required in these methods always. It is definitely urgent to find out a convenient and efficient method to fabricate the functionalized C-Dots. Here, we report an easy, efficient and cost-effective one-step idea to fabricate functionalized C-Dots which is water-soluble by carbonizing the urea with sodium citrate under electrochemical way. This method is simpler, faster and cheaper, and can be conducted under more benign condition in contrast to previous report. The synthesized C-Dots showed excellent ability to electrochemically recognize the carbendazim, where it was used to detect he carbendazim under electrochemistry condition.

2. EXPERIMENTS

2.1. Materials:

Carbendazim (99.0 %) was obtained from Sigma. NaH_2PO_4, urea, Na_2HPO_4 and sodium citrate were purchased from cooperation limited of Sinopharm chemistry (Shanghai, China). No chemicals is further purified. The ultrapure H_2O was used in all experiments, and the purification machine was purchased from Millpore Co. in USA.

2.2. Synthesis of C-Dots:

The efficient one-pot electrochemical method was employed to synthesize the C-Dots. After the stirring mixture of urea and sodium citrate with appropriate ration were transferred into the 10 ml ultrapure water, a transparent solution was formed. After 1 hour for the reaction, where the potential was 5 V, the whole solution color changed from transparent to brown. To get the carbon dots, the obtained solution was purified by dialysis membrane, which was used with 1000 Da MWCO together. This purification was performed by using ultrapure water. The electrode couples of negative and positive were two Pt sheets ($1.5*2cm^2$), where there was almost a distance of 1 cm between two Pt sheets.

2.3. Characterizations

Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 F20 S-Twin microscope (FEI, USA). Fourier transform infrared (FTIR) spectroscopy was performed using a Perkin Elmer FTIR spectrometer (RX) in a frequency range of 4000–500 cm^{-1}. The samples were prepared using the KBr disk method. The fluorescence spectra were obtained on a Varian Cary Eclipse Fluorescence Spectrophotometer.

2.4. Experimental measurements:

By using the microsyringe, PBS of 0.1 M (5 ml, pH 7.0) and specific concentration carbendazim were moved to an airtight electrochemical cell. The 0.1 M PBS (where the pH was equal to 7.0) was employed to pretreat the decorated electrode for 90 minutes. After tuning the pulse anodic stripping voltammetry (designated as DPV) from 0.3 to 1.2 V, the performance of detecting the carbendazim with voltammetry was investigated. The following was the measurement condition: 0.2 second is pulse interval, pulse width is about 0.05 second, and amplitude and potential increase were about 0.05 and 0.004 V, respectively. Ahead of all experiments, the nitrogen was purged for 10 minutes to remove the oxygen.

3. RESULTS AND DISCUSSION

TEM was employed to characterize the morphology of obtained C-Dots. Excellent dispersion of C-Dots was observed by TEM images which was illustrated in Figure 1A. The size distribution of C-Dots is about from 5.1 to 2.5 nm, and the size is almost 3.3 nm in average. Through FTIR spectroscopy, the groups exhibiting different functions on the carbon dots surface were studied. The specific absorption peaks which are at 3267, 3423 and 3334 cm^{-1} represent the vibrations of oxygen-hydrogen stretching and nitrogen-hydrogen stretching as illustrated in Figure 1B. Meanwhile, the peak at 1668 cm^{-1} represents the carbonyl group vibration. The peaks at 1395 and 1596 cm^{-1} were assigned to COO- vibration under symmetric and asymmetric stretching. [16] The results of these measurements indicate that the durability and hydrophilicity of C-Dots are promoted by nanoparticles, which are functionalized by –OH$^-$, COO$^-$ and amino group.

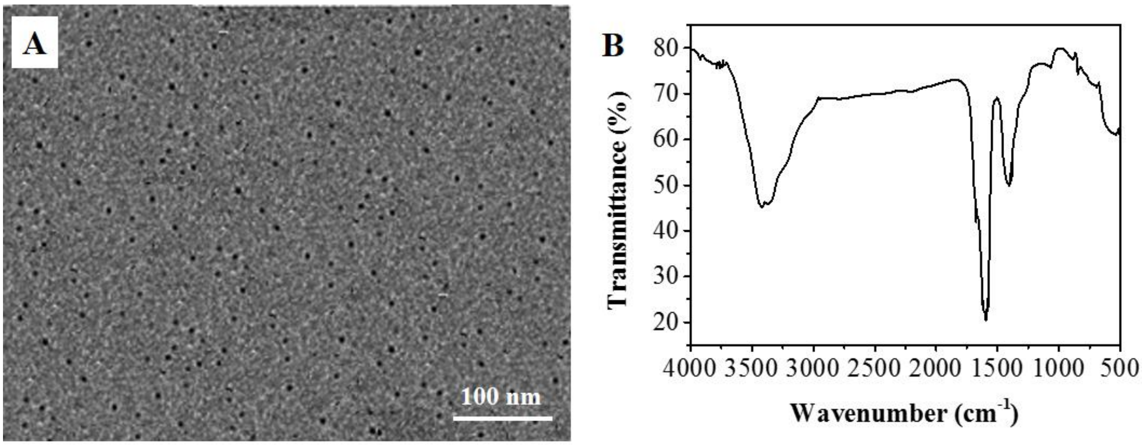

Figure 1. (A) Transmission electron microscopy image of carbon dots. (B) FTIR spectrum of carbon dots.

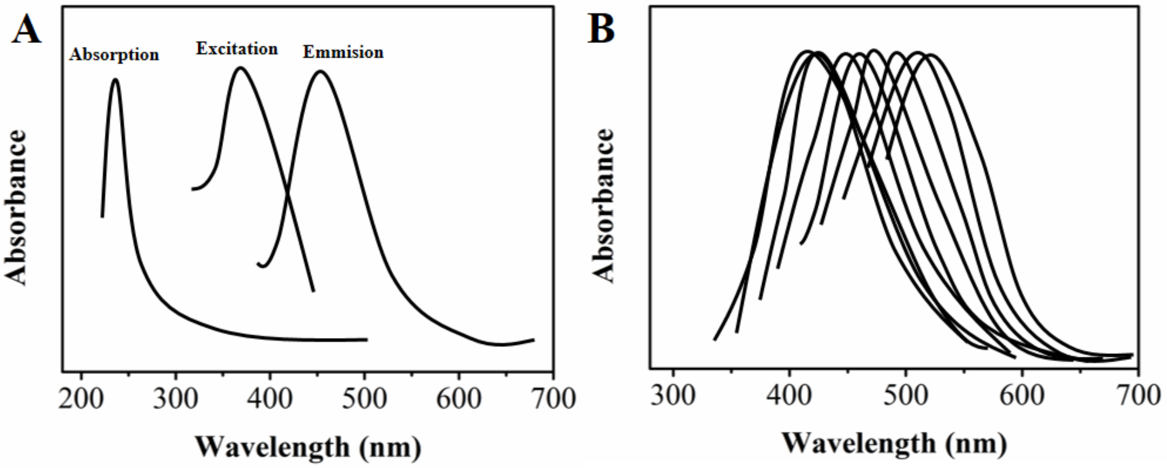

Figure 2. (A) The fluorescence spectrum and UV-visible absorption of as-synthesized carbon dots. Inset: photos of as-prepared carbon dots irradiated by UV light. (B) Normalization of fluorescence emission spectrum where the longer excitation wavelength is increasing from 300 with 20 nanometer increments.

The fluorescence and UV-vis absorption were employed to investigate the optical characters of the obtained carbon dots. The C-Dots solution exhibits a spectrum with wide absorption as illustrated in Figure 2A. The absorption peak at 240 nm is ascribed to the typical absorption of an aromatic π system or the n–p$*$ transition of the carbonyl [25-27]. The emission wavelength of solution with C-Dotsis 440 nm, and the maximum excitation wavelength of that is 360 nm. By taking the UV light of 365 nanometers for the excitation of C-Dots solution, blue luminescence of high brightness was observed definitely, which was shown in the Figure 2A. As shown in Figure 2B, the fluorescence wavelength of carbon dots depended on the excitation wavelength, where the emission wavelength from 517 to 410 nanometers corresponded to the excitation wavelength about 460~300 nanometers. Various size and distribution of the carbon nanoparticles should be responsible for this behavior. Compared with 54% quantum yield of quinine sulfate at H_2SO_4 (0.1 M), the quantum yield measured about fluorescence of C-Dotsis 11.9%, which compares well with previous work [28]. The higher quantum yield may be ascribed to the chemical nature and abundant surface defects of the as-synthesized C-Dots [29].

As a molecular probe, the behavior of the $[Fe(CN)_6]^{3-/4-}$ redox was performed to study why the active surface of functionalized electrode was enhanced. As illustrated in Figure 3, the peak currents in anode acted as the functions to $v^{1/2}$ (v represents scanning rate) for 1.0 mM $[Fe(CN)_6]^{3-}$. In a funtionalized electrodes and bare GCE, the i_{pa} (representing the peak currents of anode) showed linearity to $v^{1/2}$. Based on the equation of Randles–Sevick, the surface area of active electrode could be figured out.

$$i_{pa} = 0.446nFCA(\frac{DnF}{RT})^{1/2}v^{1/2}$$

In this equation, n represents the number of e (short for electron) which meant the shifted electron in this redox reaction. D, C and A represent the coefficient of diffusion, concentration and active area of electrode respectively. T, F and R have their own meanings, which represent 298 K, 96,480 C/mol and 8.314 J mol/K respectively. The specific surface area of bare GCE was 0.103 ± 0.005 cm^2 from calculation. The active area of electrode functionalizedby C-dots (0.195 ± 0.014 cm^2) showed that electrode decoration could effectively increase the specific surface area, make the active sites increased and lead to the decrease of detection limit and enhancement of the electrochemical response [30].

In the PBS of 0.1 M and pH 7.0, cycle voltammetry of carbendazim (5 uM) on both C-Dots functionalized and bare GCE as shown in Figure 4A. All electrode exhibited the electrochemical oxidation about carbendazim, where the potential range is 0-1.2 V. On bare GCE, there was a weak peak of anode compared to the broad and increased current peak which was observed in the C-Dots functionalized GCE, where the peak was single irreversible, and this was assigned to the chain of side issue about carbendazim and carbon dots.

Illustrated by Figure 4B, DPV performance with C-Dots/GCE and no decorated GCE under carbendazim loading, was conducted to investigate the special electrochemical action of carbendazim with various support electrodes in the PBS solution (0.1M, the pH was equal to 7.0). The large specific surface area and good conductivity were the main reasons why the current peak was increasing with carbendazim on C-Dots/GCE compared with so weak peak of that on bare GCE.

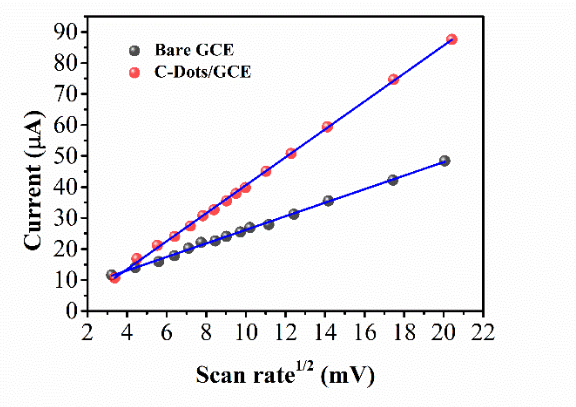

Figure 3. Plots of 1mM $[Fe(CN)_6]^{3-}$ anodic peak current *versus* $v^{1/2}$ including C-Dots/GCE and bare GCE.

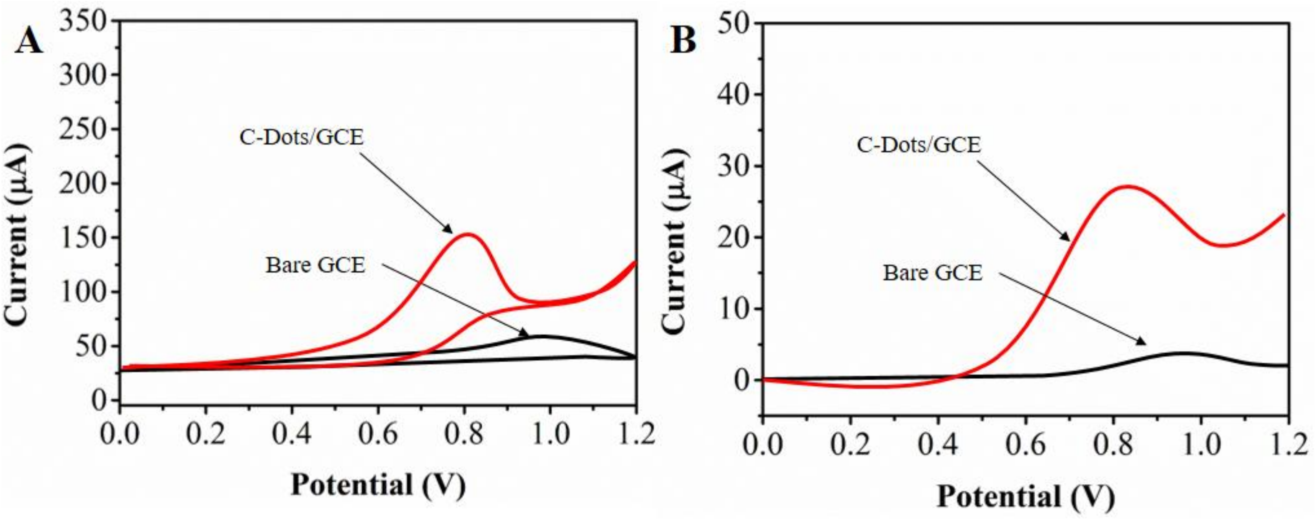

Figure 4. (A) Cycle voltammetry and (B) DPV of C-Dots/GCE and no decorated GCE which were both modified by 5uM carbendazim in PBS (pH was equal to 7.0) with the concentration of 0.1 M.

During the experiment, the parameters have been selected to detect the carbendazim with high sensitivity, such as pH, *V*, *t* and the electrolyte for support. The buffer pH can affect electrochemical actions with carbendazim, which is investigated at Figure 5A. The relationship between pH (0.5-0.9) and the current response, where 5uM carbendazim was present, is shown in the Figure 5B. In Figure 5B, the response of carbendazim peak current of anode on C-Dots/GCE to pH was just like a volcanic form, where the maximum was obtained at pH 7.0, and the reaction of degrading carbendazim under basic media was the main reason for the decrease. As a result, the pH of 7.0 was selected to determine the voltammetry due to its high sensitivity. As shown in Figure 5B, the E_p responded to pH as a function, where equation of E_p $(V) = -0.051\text{pH} + 1.532$ ($R^2 = 0.99$) showed the real relationship, and E_p decreased under increasing pH. Based on the formula following behind:

$$dEpa / dpH = (-2.303mRT) / nF$$

In which m and n represent the number of participation protons and transferring number in specific reaction of electrochemistry. The amounts of moved proton are equal to that of electron, which results from the *m/n* value of 1.

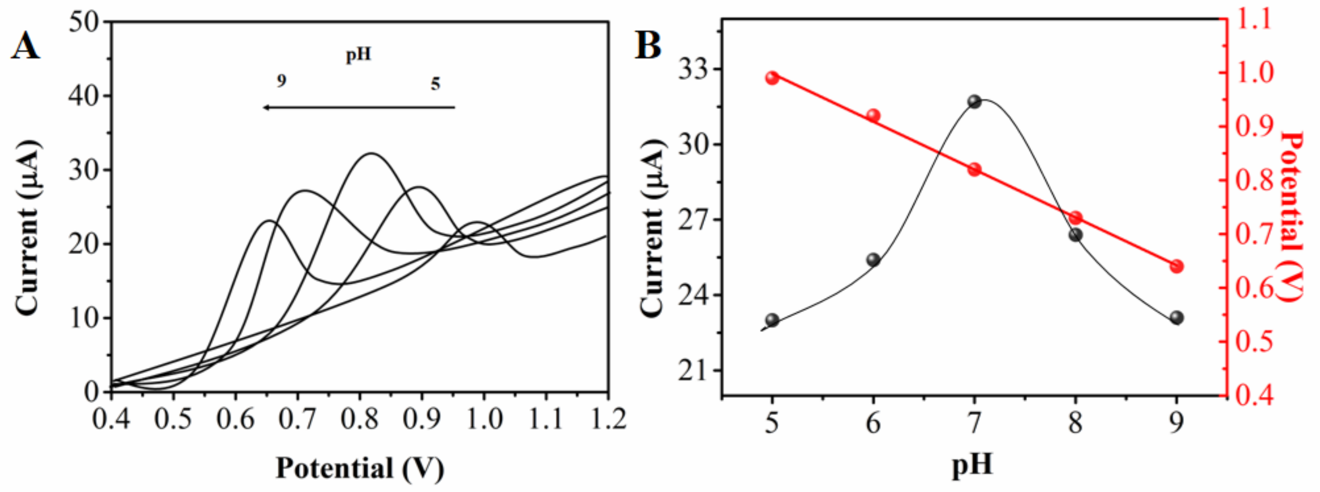

Figure 5. DPV on GCE decorated by carbon dots in 5 uM carbendazim under various pH (A); pH influence at peak potential and currents of anode (B).

The carbendazim concentration which was absorbed at the electrode is improved by the accumulation, and the decrease of detecting limit and improvement of sensitively determining are both achieved. Thus, the effect of accumulating time and potential were both studied. In Figure 6, the effect of accumulating potential to the response of current was shown from 0.2 to 1.0 V, which was performed in the PBS of 0.1 M with carbendazim of 5 uM at pH 7.0. Due to the 0.8V as the maximum peak current, this value was the optimal accumulating potential to detect cabendazim. The relationship between accumulating time and current was studied too as shown in Figure 7B, where carbendazim (usually 5 uM) was employed to decorate the C-Dots/GCE with various accumulating times. Because increase of current of peak with time stopped at 90 minutes, the condition with 90 minutes and 0.8 V was used for the experiments.

There are a lot of advantages about this method, such as excellent sensitivity and simplicity, low cost, low limitation detection and on field, where the performance of separating and treating the sample before using are not needed. The relationship between the different concentration and carbendazim on GCE decorated byC-Dots, was tested with optimal condition as shown in Figure 7 (0.1~10 uM), where the deviation of response from good linearity would happen if the concentration achieved 10 uM.

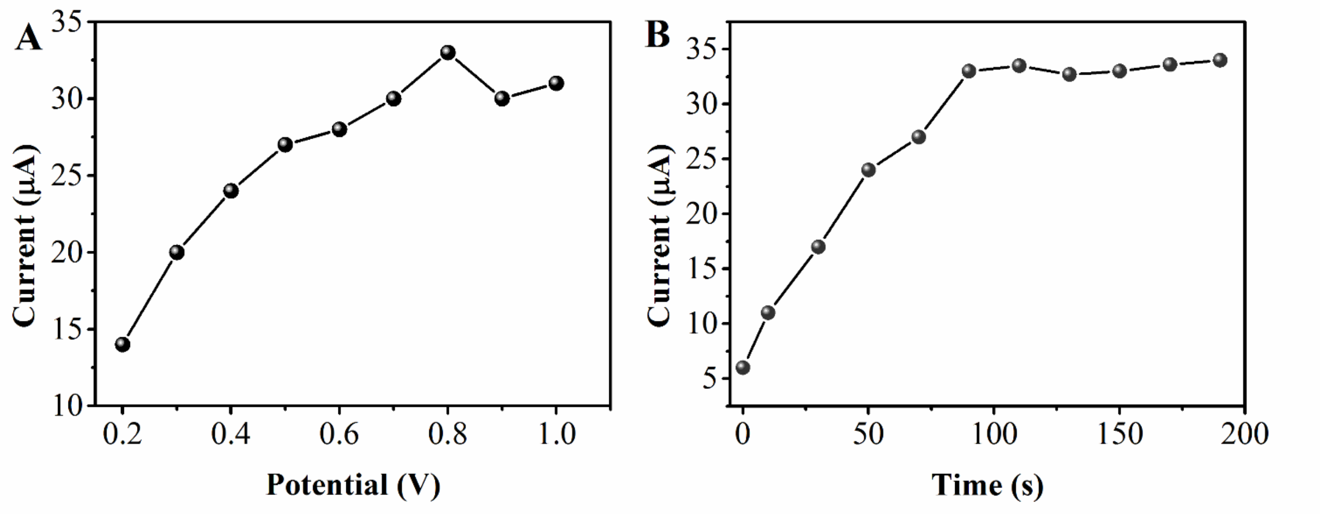

Figure 6. The plots of accumulating potential (A) and time (B) vs current, which 5uM carbendazim is used in PBS (the pH was equal to 7.0 and the concentration was 0.1M).

Due to lower competition, the coverage of active surface which was accessible from outside became larger in the condition at low concentration, which made the caibendazim more effective, faster and more sensitive under the condition at lower concentration. Thus, switching in the slope in two linear equation was observed. The concentrations are in good proportion to the peak of current ranging from 0.1 to 10 uM, where the equation showed as I (μA) = 5.447+ 1.077 C (μM) (R^2 = 0.99). The limit of quantitation (designated as LOQ) and limit of detection (designated as LOD) were noticed to 10 nM and 0.05 μM respectively, which were much lower than the well-established limit. Table 1 shows the comparison of our proposed carbendazim electrochemical sensor with some previously reported sensor.

Table 1. Comparison of proposed carbendazim electrochemical sensor with other reports.

Electrode	LDR (μM)	LOD (μM)	Reference
Graphene oxide/GCE	1-100	0.5	[31]
Pyrrolidinium ionic liquid modified ordered mesoporous carbon	1.25-800	0.5	[12]
SiO_2/MWCNT	0.2-4	0.056	[32]
Diamond electrode	0.5-15	0.03	[33]
Electrochemically reduced graphene oxide/GCE	0.002-0.4	0.001	[34]
GO–MWNT/GCE	0.01-10	0.005	[8]
MWCNT-polymeric methyl red film	0.2-100	0.009	[7]
Cyclodextrin–graphene/GCE	0.005-0.25	0.002	[4]
C-Dots	0.1-10	0.001	This work

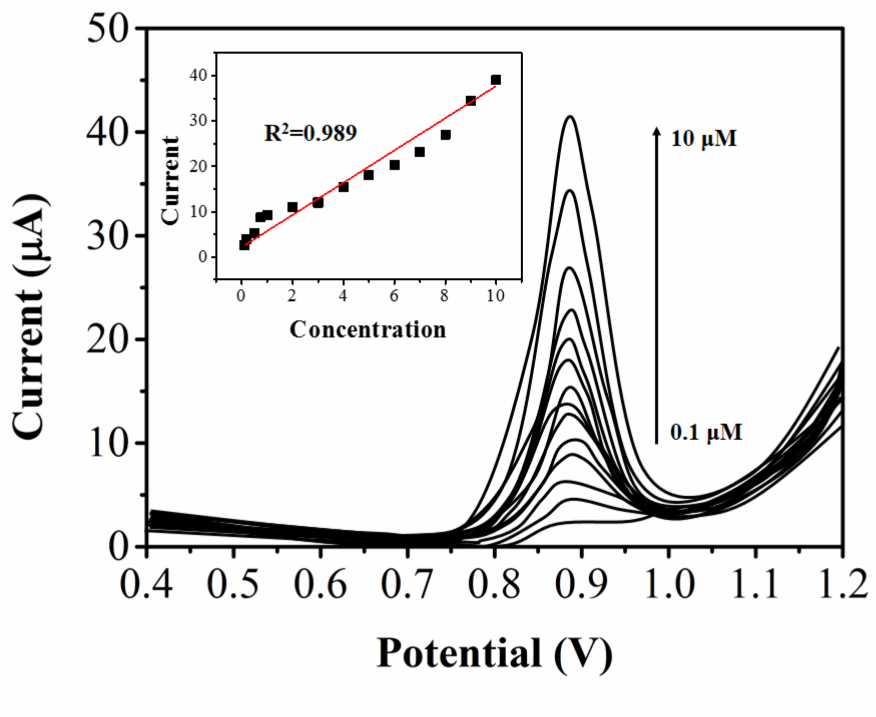

Figure 7. Plots of various amounts on C-Dots of carbendazim vs DPV signal. Accumulating time, potential, increment of potential and support electrolyte were 90 minutes, 0.8 V, 4 mV and PBS (the concentration was 0.1 M, and the pH was equal to 7.0).

Other measurements for prepared sensor were performed to identify the method whether it was precise and practical. By successively measuring it for 20 times, the stability performance of C-Dots functionalizedGCE to the electrochemical response was obviously excellent, where there was only 2.5% of RSD (short for relative standard deviation). The long time durability of the prepared electrode was tested at pH 7.0 by 5 uM carbendazim with PBS of 0.1 M , where the decorated electrode should be kept at 4 °C refrigerator and the measurement was performed one time per two days in the one month. No obvious decrease of current was observed in the first week, but there was gradual decrease after that. The long time durability of GCE decorated by C-Dotsshowed great due to the 89.4% remains of initial response. Five prepared C-Dots/GCE were tested to compare the peak current of oxidation, where the results showed that it was high reproducible due to its low RSD of 5 samples (4.2%). Reproducibility, long term durability and stable operation indicated that this prepared sensor was in good performance.

Furthermore, to detect the carbendazim in the tap water, the prepared sensor was employed, which was optimized through standard addition idea. As shown in Table 2, the sensor demonstrated excellent properties in real application with barely purification due to its high recovery ranges (93.2% ~104.1%). What is more, this well-established method can detect the trace carbendazim owing to its accuracy, suitability and efficiency from the satisfactory results.

Table 2. Data of determining the carbendazim in the samples of tap water through C-Dots/GCE ($n = 5$).

Sample	Added (μM)	Found (μM)	Recovery (%)
1	0.1	0.097	97
2	0.5	0.466	93.2
3	1	1.035	103.5
4	3	3.122	104.1

4. CONCLUSIONS

In conclusion, we reported that the carbonization of sodium citrate with urea under electrochemistry was an efficient way to produce the decorated C-Dots, which have been applied to determine the carbendazim by electrochemistry. It was worth to note that the detecting wideness was ranging from 0.1 to 10 uM and the limit was about 10 nM. What is more, the sensor synthesized by electrochemistry method was used to detect the carbendazim of the tap water successfully.

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