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# Cyclodextrin–graphene hybrid nanosheets as enhanced sensing platform for ultrasensitive determination of carbendazim

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ABSTRACT

In this paper, cyclodextrin–graphene hybrid nanosheets (CD–GNs) for the first time have been used as an enhanced material for ultrasensitive detection of carbendazim by electrochemistry method. The peak currents of carbendazim on the GNs modified glassy carbon electrode (GNs/GCE) and the CD–GNs/GCE are increased by 11.7 and 82.0 folds compared to the bare GCE, respectively. This indicates the nanocomposite film not only shows the excellent electrical properties of GNs but also exhibits high supramolecular recognition capability of CDs. At the CD–GNs/GCE, the peak currents increase linearly with the concentration of carbendazim in the range of 5 nM–0.45 μM. The detection limit of carbendazim reached to 2 nM on the basis of the signal-to-noise characteristics (S/N = 3) and the recoveries were between 98.9% and 104.5%. The developed electrochemical sensor exhibited good stability and reproducibility for the detection of carbendazim. And the CD–GNs based electrochemical sensor was also successfully demonstrated for the detection of carbendazim in water sample with satisfactory results. Furthermore, this simple sensing platform can in principle be extended to the detection of other benzimidazole fungicide which can form host–guest complexes with cyclodextrin.

## 1. Introduction

Carbendazim is a sort of benzimidazole fungicide. It is widely used in agriculture for protecting from and eradicating a variety of pathogens which affect fruits and vegetables [1]. This compound, when applied on soils, can persist for a long time, because the benzimidazolic ring is difficult to break and consequently its degradation is slow [2]. Therefore, the ability to rapidly and accurately determine trace amount of carbendazim has become increasingly important for the environment and health protection. The methods most frequently used for measuring benzimidazole fungicides were high-performance liquid chromatography [3,4], mass spectroscopy [5,6], UV–vis, fluorescence spectroscopies [7–13] and electrochemical techniques [14–16]. Among all these techniques mentioned above, electrochemical methods have received considerable attention for carbendazim analysis due to their sensitivity, simplicity, low cost and easy for on-site determination. However, the redox reaction of carbendazim at bare electrode is generally difficult due to the poor sensitivity and reproducibility. The rapid development of nanoscience and nanotechnology provided new avenues to the area of electrochemical sensor for improving the sensitivity and selectivity. At present, some functional nanomaterials have been synthesized to develop sensitive carbendazim electrochemical sensors. Typical examples are carbon nanotubes (CNTs) and their hybrids [17–21] modified electrode. Although the above mentioned sensors have improved the electrochemical response of carbendazim, the design of new nanomaterials is still needed to further accelerate the development of highly sensitive pesticide sensing platform.

Graphene, a two-dimensional lattice of carbon only a single atom thick, has attracted enormous attention owing to its remarkable electronic, optical, and thermal properties, chemical and mechanical stability [22,23]. This unique nanostructure holds great promise for potential applications in many technological fields such as nanoelectronics [24], nanophotonics [25], nanocomposites [26], supercapacitors [27] and sensors [28] etc. In particular, it is an excellent candidate for electrodes material to prepare electrochemical sensors or biosensors due to its excellent conductivity, electrocatalytic activity and large surface area [29]. For instance, Worden's group [30,31] has reported the use of the exfoliated graphite nanoplatelets to fabricate a high-performance glucose biosensor as a viable and inexpensive alternative to carbon nanotubes. Dong's group [29] demonstrated an advanced electrochemical sensing and biosensing platform based on GNs, which showed much higher electrocatalytic activity towards β-nicotinamide adenine dinucleotide (NADH), neurotransmitters and other biological molecules than that of graphite. Hong's group [29] reported that free-standing flexible conductive reduced graphene

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oxide/nafion hybrid films obtained the excellent figure of merit as a sensing platform for organophosphate detection. Weiller et al. [31] developed a simple, practical, and effective method for producing chemical sensors for $NO_2$, $NH_3$, and dinitrotoluene by chemically converted graphene. Li's group [32,33] has demonstrated the use of the graphene nanosheets to develop a high-performance electrochemical sensor for dopamine and electrocatalytic oxidation of methanol. These results indicate that graphene shows a grand potential as enhanced materials to fabricate the electrochemical sensing interface.

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven or eight glucose units called α-, β- and γ-CDs. These CDs are toroidal in shape with a hydrophobic inner cavity and a hydrophilic outer side [34]. The interesting characteristic can enable them to bind selectively various organic, inorganic and biological guest molecules into their cavities to form stable host–guest inclusion complexes or nanostructured supramolecular assemblies in their hydrophobic cavity, showing high molecular selectivity and enantioselectivity. So the combination of CDs and GNs simultaneously possesses the unique properties of GNs (large surface area and high conductivity) and CDs (high supramolecular recognition capability), which provide good opportunities for applications in the fields of sensors, electrocatalysis, luminescence and electronics, etc. [35].

Herein, a sensing platform for ultrasensitive determination of carbendazim was firstly presented based on the CD–GNs modified glassy carbon electrode (CD–GNs/GCE). The electrochemical behavior of carbendazim at the CD–GNs/GCE exhibited much higher electrochemical performance than at those of GNs/GCE and bare GCE, revealing that the CD–GNs film not only shows the excellent electrical properties of GNs but also exhibits high supramolecular recognition properties of CDs through the formation of inclusion complexes between CDs and the carbendazim molecules [36].

## 2. Experimental

### 2.1. Materials

Graphite was purchased from Alfa Aesar. β-Cyclodextrin (β-CD), hydrazine solution (50 wt.%), ammonia solution (25–28 wt.%) were obtained from Beijing Chemical Reagent Factory (Beijing, China). Carbendazim was obtained from Sigma. Other chemicals were of analytical grade and used without further purification. Tap water sample were obtained from the local place and used without any treatment. Water used throughout all experiments was purified with the Millipore system.

### 2.2. Apparatus

AFM image was taken by using an SPI3800N microscope (Seiko Instruments Industry Co., Tokyo, Japan) (Seiko Instruments, Inc.) operating in the tapping mode with standard silicon nitride tips. Typically, the surface was scanned at 1 Hz with the resolution of 256 lines/image. Fourier transform infrared spectroscopy (FTIR) was recorded on a Bruker Vertex 70 spectrometer ($2\,cm^{-1}$). UV–vis absorption spectra were recorded on a Cary 500 UV-vis-NIR spectrometer (Varian, U.S.A.). Electrochemical measurements were carried out on CHI832B electrochemical workstation (ChenHua Instruments Co., Shanghai, China). A three-electrode system was used in the experiment with the bare and the modified glassy carbon electrode (3 mm in diameter) as the working electrode, respectively. An Ag/AgCl electrode (saturated KCl) and a Pt wire electrode were used as reference and counter electrode, respectively.

### 2.3. Synthesis of CD–graphene hybrid nanosheets and pure graphene

Graphene oxide (GO) was synthesized from natural graphite by Hummers' method with little modification [37]. CD–GNs were synthesized according to our previous work [35]. Briefly: 20.0 mL of the homogeneous graphene oxide dispersion (0.5 mg/mL) was mixed with 20.0 mL of β-CD aqueous solution (80 mg) and 300.0 μL of ammonia solution, followed by the addition of 20 μL of hydrazine solution. After being vigorously shaken or stirred for a few minutes, the vial was put in a water bath (60 °C) for 3.5 h. The stable black dispersion was obtained. The dispersion was filtered with a nylon membrane (0.22 μm) to obtain CD–GNs that can be redispersed readily in water by ultrasonication. Additionally, the preparation of pure graphene was similar with CD–GNs except no addition of CD.

### 2.4. Preparation of the CD–GNs/GCE or GNs/GCE

Prior to the modification, the glassy carbon electrode was polished with 1, 0.3 and 0.05 μm alumina slurry and rinsed thoroughly with doubly distilled water between each polishing step. Then, it was washed successively with 1:1 nitric acid, acetone and doubly distilled water in an ultrasonic bath and dried in air. Lastly, 5 μL of 0.25 mg/mL CD–GNs or GNs was carefully cast on the surface of the well-polished GCE and dried in air. The CD–GNs/GCE or GNs/GCE electrode was thus obtained.

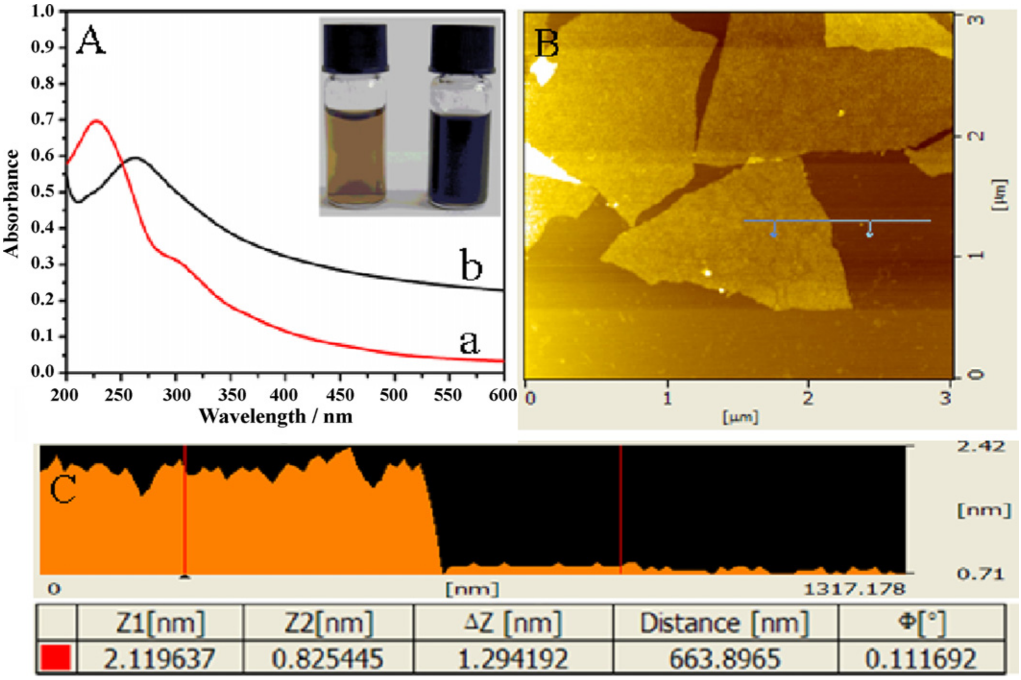
## 3. Results and discussion

### 3.1. Characterization of the CD–GNs

As shown in Fig. 1A, the GO dispersion displays a maximum absorption at 231 nm which is due to the $\pi-\pi^*$ transition of aromatic C=C bonds. After reduced by hydrazine, the absorption peak of the GO dispersion at 231 nm shifts to 264 nm and the color of the dispersion changed from pale-yellow to black (inset in Fig. 1A), suggesting that the electronic conjugation within the GNs was restored upon the reduction by hydrazine [38,39]. Particularly, the dispersion was stable and no obvious precipitates were observed after stored for six months (Fig. 1A, inset). FT-IR spectra of CD–GNs exhibited typical CD absorption features which clearly confirmed that CD molecules were attached to the surface of GNs [35]. Fig. 1B shows the AFM image of CD–GNs. A number of flake-like nanostructures are obviously found. The corresponding cross-sectional view, as shown in Fig. 1C, indicates that the average thickness of CD–GNs was about 1–2 nm, typical characteristic of single-layer graphene [40].

### 3.2. Electrochemical behavior of carbendazim on the surface of various electrodes

Fig. 2A depicts cyclic voltammograms (CVs) for the electrochemical characterization of 50 μM carbendazim at the bare GCE (a), the GNs/GCE (b) and the CD–GNs/GCE (c) in 0.1 M phosphate buffer solution (pH 7.0). A pair of well defined redox peaks of carbendazim was observed within the potential window from 0.2 to 1.2 V revealing that carbendazim underwent a quasi-reversible redox process on the electrodes. The peak currents of carbendazim are very small at the bare GCE. At the GNs/GCE, the peak currents of carbendazim increased by a factor of 11.7 relatively to bare GCE. The signal enhancement may be ascribed to the excellent conductivity and large surface area of GNs. While at the CD–GNs/GCE, the peak currents show a remarkable increase by a factor of 82 compared to the bare GCE. This illustrates that β-CD molecules on



|  | Z1[nm] | Z2[nm] | ΔZ [nm] | Distance [nm] | Φ[°] |
|---|---|---|---|---|---|
| 🟥 | 2.119637 | 0.825445 | 1.294192 | 663.8965 | 0.111692 |

**Fig. 1.** (A) UV–vis absorption spectra of GO (a) and CD–GNs (b) inset: photographs of GO (left) and CD–GNs (right) dispersion in water. (B) AFM image of CD–GNs and (C) the cross section identified by the line in D shows the height of CD–GNs.

the surface of GNs with high supramolecular recognition capability can form host–guest complexes with carbendazim. Accordingly, the concentration of carbendazim on the surface of the modified electrode is increased, which results in pronounced peak currents enhancement. These phenomena suggest that the CD–GNs not only show the excellent properties of GNs but also exhibit the excellent supramolecular recognition capability of CDs. The greatly enhanced electrochemical reactivity of carbendazim at the CD–GNs/GCE compared with that at the other two electrodes makes the CD–GNs/GCE a better choice for the electrochemical sensing of carbendazim at pH 7.0.

The effect of scan rates vs. the peak currents of carbendazim at the CD–GNs/GCE was investigated. The redox processes of the carbendazim gave roughly symmetric anodic and cathodic peaks at relatively slow scan rates. When the scan rate increases, the redox potentials ($E_{\mathrm{pa}}$ and $E_{\mathrm{pc}}$) of carbendazim shift slightly. At the same time, the redox peak currents are proportional to the square root of the scan rate in the range of 0.05–0.5 V s$^{-1}$. The linear regression equations are $i_{pa}(\mathrm{A}) = -8.992\times10^{-5} + 4.82\times10^{-4}\,\nu^{1/2}\,(\mathrm{V\,s^{-1}})^{1/2}$ ($r = 0.9990$) and $i_{pc}\,(\mathrm{A}) = 1.19\times10^{-4} + 5.32\times10^{-4}\,\nu^{1/2}\,(\mathrm{V\,s^{-1}})^{1/2}$ ($r = 0.9966$) (inset, Fig. 2B) indicating a diffusion-controlled process.

### 3.3. *Optimization of the determination conditions*

#### 3.3.1. *Effect of pH*

The effect of pH on the electrochemical behavior of carbendazim was performed in the pH range of 5.0–10.0 using 0.1 M of phosphate buffer solutions. The peak currents increased by varying pH from 5.0 to 7.0 and then decreased when the pH exceeded to 7.0 (Fig. 3A). Therefore, phosphate buffer with pH 7.0 was used as the supporting electrolyte in all voltammetric determinations.

#### 3.3.2. *Effect of the amount of CD–GNs*

The relationship between the peak currents of carbendazim and the amount of CD–GNs on the GCE was investigated. The peak currents of 50 µM carbendazim on the CD–GNs/GCE increased

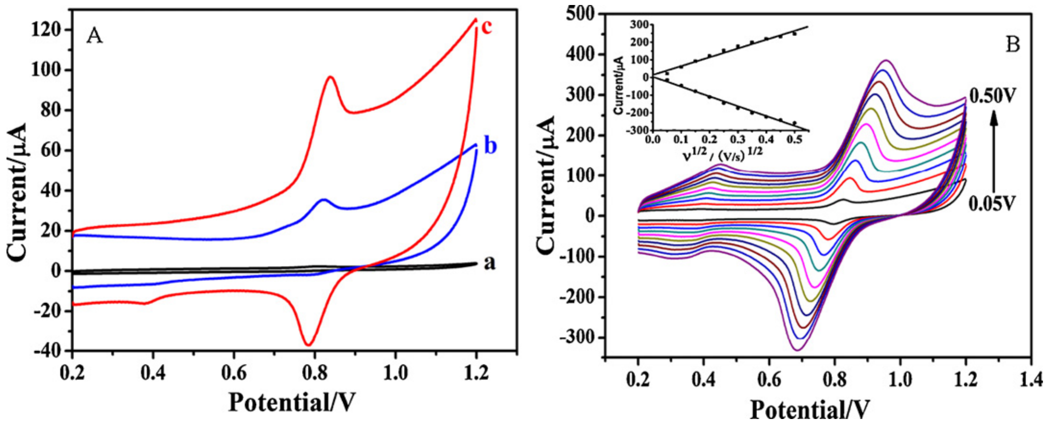


**Fig. 2.** (A) CVs of 50 µM carbendazim at GCE (curve a), GNs/GCE (curve b) and CD–GNs/GCE (curve c) in 0.1 M phosphate buffer (pH 7.0). Scan rate: 50 mV s$^{-1}$. (B) Cyclic voltammograms of 50 µM carbendazim in 0.1 M phosphate buffer (pH 7.0) at CD–GNs/GCE with different scan rates. Inset: the peak current of carbendazim vs. the square root of the scan rate.

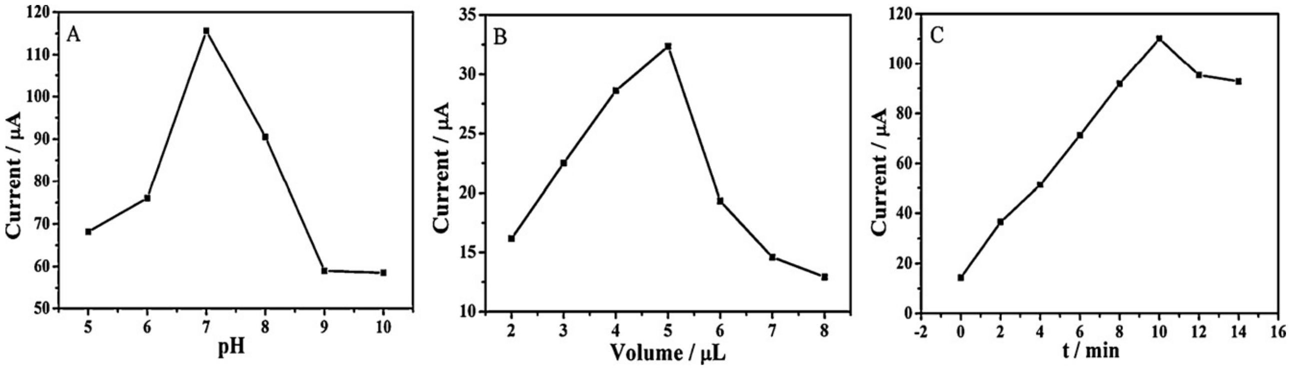


**Fig. 3.** Effects of pH (A), amount of CD–GNs (B) and accumulation time (C) on the electrochemical response of 50 μM carbendazim in 0.1 M phosphate buffer (pH 7.0) at the CD–GNs/GCE.

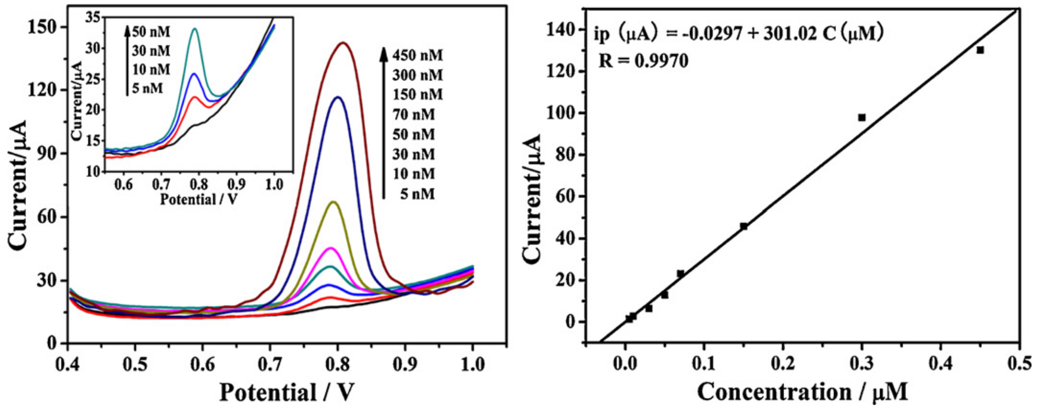


**Fig. 4.** (Left) DPV response for the different concentrations of carbendazim at CD–GNs/GC electrode 0.1 M phosphate buffer (pH 7.0). The pulse period: 0.2 s, amplitude: 50 mV. (Right) The calibration curve of carbendazim.

remarkably when the amount of CD–GNs suspension (0.25 mg/mL) increased from 2 to 5 μL. However, when the amount of CD–GNs exceeded 5 μL, the peak current decreased dramatically (Fig. 3B). The results may be attributed to the thicker film of CD–GNs, which blocked the electrical conductivity. Consequently, a CD–GNs suspension of 5 μL was utilized to modify the GCE.

### 3.3.3. Effect of the accumulation time

The sensitivity of the proposed method was undoubtedly improved by the accumulation time. As shown in Fig. 3C, with the accumulation time increased from 0 to 10 min, the peak currents of carbendazim increased linearly, owing to the increased amount of carbendazim on the CD–GNs/GCE. After that, no further increase was observed due to the surface saturation, therefore, 10 min was chosen as the optimal accumulation time.

## 3.4. Determination of carbendazim by differential pulse voltammetry

The differential pulse voltammetric (DPV), as a highly sensitive and a low detection limit electrochemical method, was used for the determination of trace amounts of carbendazim under the optimum conditions. The DPV responses for different concentrations of carbendazim were illustrated in Fig. 4. The resulting calibration plots are linear over the range from 5 nM to 0.45 μM. The linear equation is $i_p$ (μA) = −0.0297 + 301.02$C$ (μM) with a correlation coefficient of 0.9970. The detection limit is 2 nM (S/N = 3). Comparing with the method reported previously [16–19], the proposed method in this work has wide linear range and low detection limit. This further confirmed the synergetic effect of GNs and CDs. The detailed specific features are shown in Table 1. It indicated that this method was preferable in the determination of trace amount of carbendazim.

The influences of some common ions and pesticides on the determination of carbendazim (0.1 μM) were studied in the experiment. The results indicated that the concentration of 100 times of $Cu^{2+}$, $Zn^{2+}$, $NH_4^+$, $Na^+$, $K^+$, $Ca^{2+}$, $SO_4^{2-}$, $CO_3^{2-}$, $NO_3^-$, 200 times of $Cl^-$ and 100 times of endodulfan, ametryn, fenamiphos did not affect the determination of carbendazim.

## 3.5. Determination of carbendazim in spiked water samples

The spiked water samples were prepared by adding known amount of carbendazim solution in tap water. The pesticide percentage of recovery and relative standard deviation were determined and presented in Table 2. The good recoveries of the samples indicate that the proposed method can be successfully applied in the detection of carbendazim concentration in water sample.

**Table 1**
Characteristics of comparable voltammetric methods for determination of carbendazim.

| Method | Detection limit (mol/L) | Linear range (mol/L) | References |
|---|---|---|---|
| MC/GCE | $9.6 \times 10^{-7}$ | $9.6 \times 10^{-7}$–$9.6 \times 10^{-5}$ | [16] |
| MWNT-PMRE/GCE | $9.0 \times 10^{-9}$ | $2.0 \times 10^{-7}$–$1.0 \times 10^{-5}$ | [17] |
| MWNTs/GCE | $5.2 \times 10^{-8}$ | $5.2 \times 10^{-8}$–$2.6 \times 10^{-6}$ | [18] |
| Silicone OV-17/GE | $4.8 \times 10^{-8}$ | $2.6 \times 10^{-8}$–$2.6 \times 10^{-7}$ | [19] |
| CD-GNs/GCE | $2.0 \times 10^{-9}$ | $5.0 \times 10^{-9}$–$4.5 \times 10^{-7}$ | Present work |

MC, montmorillonite clay; PMRE, polymeric methyl red film; GE, graphite electrode.

**Table 2**
The recoveries of carbendazim from water samples.

| Samples | Added (μM) | Found (μM) | Recovery% | RSD% |
|---|---|---|---|---|
| 1 | 0.07 | 0.071 | 101.4 | 0.52 |
| 2 | 0.11 | 0.115 | 104.5 | 0.48 |
| 3 | 0.15 | 0.151 | 100.7 | 0.42 |
| 4 | 0.18 | 0.178 | 98.9 | 0.36 |
| 5 | 0.20 | 0.199 | 99.5 | 0.40 |

### *3.6. The repeatability and stability of carbendazim assay on the CD–GNs/GCE*

The reproducibility of the modified electrode was evaluated by detecting the current response of 0.1 μM carbendazim with the same electrode. The results revealed that the electrode possessed a satisfying reproducibility with a relative standard deviation (RSD) of 4.67% for 30 successive measurements. When detecting 0.1 μM carbendazim for several times in 7 days, the modified electrode kept 96.5% of its initial current response. The storage stability of the sensor was also investigated. After the modified electrode was stored at room temperature for 15 days, only a small current decrease (about 3.2%) was observed. The results demonstrated that the sensor exhibited excellent stability.

## 4. Conclusion

In this work, a new and highly enhanced electrochemical sensing platform based on CD–GNs was established for the determination of carbendazim by DPV. The new nanomaterial combining the advantages of graphene and cyclodextrin dramatically enhanced the sensitivity of carbendazim assay. The high sensitivity and improved detection limit of the CD–GNs/GCE are promising for the determination of trace amounts of carbendazim in water sample. Furthermore, this simple sensing platform in principle can be extended to the detection of other benzimidazole fungicide which can form host–guest complexes.

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