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Photoelectrochemical sensing of catechol based on CdS-DNA-pristine graphene nanocomposite film

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ABSTRACT

A photoelectrochemical (PEC) sensing platform was designed for catechol determination using CdS quantum dots (QDs), DNA and pristine graphene (PGR) nanocomposite film-modified electrode. In such a composite film-based PEC sensor, CdS QDs served as the photoelectric conversion element which produced photocurrent signal under visible light illumination; and DNA was designed as the biological recognition element which improved the PEC response of sensor toward catechol due to the interaction between DNA and catechol. To improve the electron transfer of the composite film, PGR with high electrical conductivity was doped, which significantly amplified the photocurrent signal of sensor. Based on such a CdS-DNA-PGR composite film-modified electrode, catechol showed a linear PEC response proportional to its concentration from 1.0×10^{-8} to 1.0×10^{-6} mol L^{-1}. The detection limit (3S/N) was estimated to be 4.9×10^{-9} mol L^{-1}. The developed PEC sensor was successfully applied to determine trace catechol in water samples.

1. Introduction

Photoelectrochemical (PEC) sensor is a newly emerging but dynamically developing analytical technique owing to its inexpensive photoelectric devices and high sensitivity [1,2]. The principle of PEC sensing is based on photocatalytic oxidation or reduction of molecules to produce enhanced electron transfer between analyte and semiconductor electrode under light irradiation [3]. Compared with electrochemical analysis, PEC detection has very low background due to the separation of excitation source (light) and detection signal (photocurrent). During the PEC process, light is utilized to excite the photoactive species and photocurrent is typically employed as the detection signal. To fabricate PEC sensors, photoactive materials are usually utilized as the substrates for the immobilization of recognition elements [4]. Among various photoactive materials, quantum dots (QDs) have been intensively introduced as popular visible-light active materials [5–8].

DNA, carrying the biological genetic information, is the main component of chromosome. It is a biomacromolecule composing of two nucleotide chain double helix structure. Due to the phosphate backbone, bases and pentose ring, there are non-covalent interactions of van der Waals force, ionic bond, hydrogen bond, hydrophobic function and space mutual matching between DNA and some compounds [9]. The biochemical sensor employing DNA as identifying center can be used for detecting various target analytes including organic pollutants, metal ions, biomolecules, and pharmaceutical molecules [10–14].

Recently, graphene (GR) has been demonstrated as an outstanding nanomaterial to improve the photoelectrocatalytic activity of semiconducting materials such as TiO_2, ZnO and QDs [15–19]. GR has been mainly obtained via chemical oxidation of graphite, especially according to Hummers [20] or modified Hummers methods [21]. However, chemical oxidation-based strategies have some intrinsic drawbacks, such as consumption of a large amount of strong oxidizing reagents, complicated and rigorous treatments, and potential destruction of intrinsic structure of graphite. Moreover, the GR obtained by reduction of graphene oxide (GO) still remains some epoxy groups and hydroxyl groups in GR sp^2 carbon layer. In addition, the terminal carboxyl and carbonyl are also not completely reduced. Thus, the presence of these groups and the newly produced defects will dramatically decrease conductivity of GR [22]. Liquid stripping is a method for preparation of few defective pristine graphene (PGR) by means of adding a certain amount of high purity graphite into organic solvent or aqueous dispersants, followed by a long time ultrasonic treatment [23–27]. Compared with Hummers method, liquid phase stripping method

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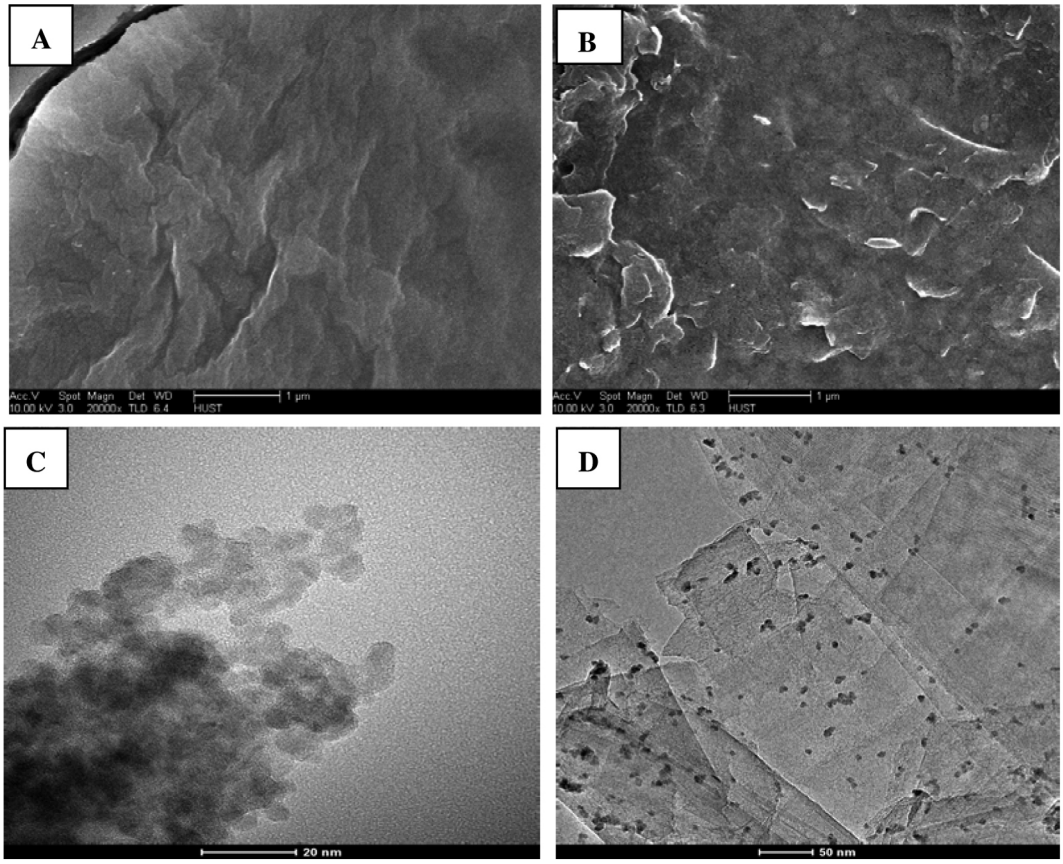

Fig. 1. FE-SEM images of (A) CdS-DNA and (B) CdS-DNA-PGR. TEM images of (C) CdS-DNA and (D) CdS-DNA-PGR.

has the advantages of simplicity and low cost, and the obtained PGR has fewer defects and better conductivity [28].

As a typical phenol derivative, catechol has been primarily used in various fields such as pesticide, medicine, eikonogen and disinfectant [29]. However, catechol is very harmful to human body due to its irritation to skin and biotoxicity. Therefore, it is necessary to develop new type of high-performance catechol sensors [30–32]. Our group had prepared DNA electrochemical sensor using carbon nanotubes and GO modified electrodes for catechol monitoring based on the interaction between DNA and catechol [33,34]. However, the sensitivity remains to be further improved.

In the present work, we fabricated a FTO electrode modified with the composite film of CdS QDs, DNA and PGR. The modified electrode was used as a highly sensitive PEC sensor for catechol determination according to the PEC activity of CdS QDs (producing photocurrent) and biochemical activity of DNA (interacting with catechol). Furthermore, the addition of PGR can significantly improve the photocurrent response performance of composite film due to the excellent conductivity of PGR. The developed sensor showed a linear PEC response toward catechol in the concentration range from 1.0×10^{-8} to 1.0×10^{-6} mol L^{-1}.

2. Experimental

2.1. Chemicals

Herring sperm DNA was purchased from Sigma. Cadmium perchlorate hexahydrate ($Cd(ClO_4)_2 \cdot 6H_2O$) and Nafion solution were provided by Alfa Aesar Chemical Co. Ltd. (Tianjin, China). Poly (diallyldimethylammonium chloride) (PDDA) was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Other reagents of analytical grade were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Distilled water was used throughout the investigation.

2.2. Preparation of PGR and water soluble CdS QDs

PGR was prepared via ultrasonic exfoliation as described previously [35]. Five-gram graphite powder was added into 500.0 mL N-methyl-2-pyrrolidone (NMP), and then sonicated for 48 h. The resulting suspension was centrifuged, washed with ultrapure water and ethanol several times, and finally dried in vacuum at 60 °C for 5 h. The resultant PGR was dispersed in 0.3% Nafion solution to obtain 2 g L^{-1} PGR suspension by sonication at least for 1 h.

Water soluble CdS QDs with a size of ca. 4 nm were synthesized by a hydrothermal method [36]. Briefly, 1.5 mL of mercaptoacetic acid was added into 100 mL of 0.2 mol L^{-1} $Cd(ClO_4)_2$ solution, followed by adjusting the solution pH to 10 with 2.0 mol L^{-1} NaOH. The obtained mixture was then transferred into a 250 mL round-bottomed flask and heated at boiling point under constant passage of high purity nitrogen gas. Thirty minutes later, 100 mL of 0.2 mol L^{-1} Na_2S solution was added into the mixture. After 4-h reaction, the product was collected by centrifugation, washed several times with ethanol, and dried at 50 °C.

2.3. Fabrication of PEC sensor

An F-doped SnO_2 conducting glass (FTO, Dalian Heptachroma SolarTech Co. Ltd., China) was cleaned by sonication in acetone, ethanol and water for 10 min and dried with nitrogen gas. The cleaned FTO electrode with controlled exposed geometry area of 0.096 cm^2 was immersed into 2% PDDA solution containing 0.5 mol L^{-1} NaCl for 1 h, followed by thoroughly rinsing with distilled water and dried with nitrogen gas. Then the FTO surface