Biosensors and Bioelectronics 101 (2018) 146–152

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Reduced graphene oxide/$BiFeO_3$ nanohybrids-based signal-on photoelectrochemical sensing system for prostate-specific antigen detection coupling with magnetic microfluidic device

Qian Zhou, Youxiu Lin, Kangyao Zhang, Meijin Li*, Dianping Tang*

Key Laboratory of Analysis and Detection for Food Safety (Ministry of Education and Fujian Province), Institute of Nanomedicine and Nanobiosensing, Department of Chemistry, Fuzhou University, Fuzhou 350108, PR China

ARTICLE INFO

Keywords:
Photoelectrochemical sensing
$BiFeO_3$
Reduced graphene oxide
Prostate-specific antigen
Magnetic microfluidic device

ABSTRACT

A novel magnetic controlled photoelectrochemical (PEC) sensing system was designed for sensitive detection of prostate-specific antigen (PSA) using reduced graphene oxide-functionalized $BiFeO_3$ (rGO-$BiFeO_3$) as the photoactive material and target-triggered hybridization chain reaction (HCR) for signal amplification. Remarkably enhanced PEC performance could be obtained by using rGO-$BiFeO_3$ as the photoelectrode material due to its accelerated charge transfer and improved the visible light absorption. Additionally, efficient and simple operation could be achieved by introducing magnetic controlled flow-through device. The assay mainly involved in anchor DNA-conjugated magnetic bead (MB-aDNA), PSA aptamer/trigger DNA (Apt-tDNA) and two glucose oxidase-labeled hairpins (H1-GOx and H2-GOx). Upon addition of target PSA, the analyte initially reacted with the aptamer to release the trigger DNA, which partially hybridized with the anchor DNA on the MB. Thereafter, the unpaired trigger DNA on the MB opened the hairpin DNA structures in sequence and propagated a chain reaction of hybridization events between two alternating hairpins to form a long nicked double-helix with numerous GOx enzymes on it. Subsequently, the enzymatic product (H_2O_2) generated and consumed the photo-excited electrons from rGO-$BiFeO_3$ under visible light irradiation to enhance the photocurrent. Under optimal conditions, the magnetic controlled PEC sensing system exhibited good photocurrent responses toward target PSA within the linear range of 0.001 − 100 ng/mL with a detection limit of 0.31 pg/mL. Moreover, favorable selectivity, good stability and satisfactory accuracy were obtained. The excellent analytical performance suggested that the rGO-$BiFeO_3$-based PEC sensing platform could be a promising tool for sensitive, efficient and low cost detection of PSA in disease diagnostics.

1. Introduction

With the fast development of society and unceasing improvement of living conditions, more and more attention has been attracted to life science, environmental protection and food safety. It is very essential to develop rapid and effective methods for the monitoring of trace analytes. Photoelectrochemical (PEC) sensing technique has received great attention as a useful analytical tool due to its natural advantages (Zhang et al., 2015; Shu et al., 2016b; Li et al., 2017). Typical PEC sensing process often use the light as the excitation source, and current generated from the photoelectrode as the response signal (Ye et al., 2016; Liu et al., 2016). By combining electrochemical detection with light irradiation, the merits of both electrochemical and optical methods could be achieved for PEC sensors (Tu et al., 2016). The application of different energy source forms (light for input and electricity for output) in PEC sensors could bring it high sensitivity and low background signal (Lin et al., 2017; Zhao et al., 2011). Moreover, advantages such as low cost and easy miniaturization of PEC instrument could be achieved by using electrochemical readout signal (Zhuang et al., 2015b). Photoactive material always plays an important role in the PEC sensing system because that effective separation of electron-hole pairs and enhanced photocurrent intensity could be beneficial for the high sensitivity (Fan et al., 2016; Wang et al., 2017). Among the reported PEC sensors, metallic semiconductors such as TiO_2, CdS and ZnO have been widely applied as photoactive materials due to their unique merits, e.g., good biocompatibility and effective photoelectric conversion (Kang et al., 2010; Liang et al., 2012; Wang et al., 2014a). However, most of them have been restricted in potential practical application because of large band gap, bio-toxicity or poor charge transport (Zhuang et al., 2015a). Therefore, photoactive materials with visible-light response,

* Corresponding authors.
E-mail addresses: mjli@fzu.edu.cn (M. Li), dianping.tang@fzu.edu.cn (D. Tang).

http://dx.doi.org/10.1016/j.bios.2017.10.027
Received 30 August 2017; Received in revised form 9 October 2017; Accepted 13 October 2017
Available online 16 October 2017
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low toxicity and low cost are greatly desirable for the construction of PEC sensing systems.

Bismuth ferrite ($BiFeO_3$), a typical multiferroic material, has attracted much attention owing to its ferromagnetism at room temperature, high ferroelectric Curie temperature (Tc ≈ 1100 K) and G-type antiferromagnetic Neel temperature (TN ≈ 643 K) (Zhang et al., 2016b; Gao et al., 2007). Fascinating properties of $BiFeO_3$ have made it one of the main candidates for room-temperature-based applications including data storage, magnetoelectric devices, light-emitting diodes and spintronics (Sun et al., 2014; Catalan and Scott, 2009; Shirolkar et al., 2012). Recently, it has been demonstrated that $BiFeO_3$ could be applied as a promising photocatalyst for both organic pollutants degradation and water splitting (Cao et al., 2014). The relatively narrow band gap (~ 2.2 eV) allows carrier excitation in $BiFeO_3$ with visible light irradiation (Li et al., 2013). However, the PEC performance of $BiFeO_3$ remains poorly rated because of the fast recombination of electron-hole pairs (Zhang et al., 2016b; Ren et al., 2017). To overcome the shortcoming, efforts have been made to improve the PEC properties of $BiFeO_3$ such as elemental doping and hybrid structures (Zhang et al., 2016b; Quynh et al., 2016; Luo and Maggard, 2006; Cho et al., 2015). Graphene can accelerate the transfer of photogenerated charge carriers in photoactive materials, and thus improve the efficiency of the PEC process (Xiang et al., 2012). However, the hydrophobicity makes graphene difficult to disperse well in water, which has limited its further application in PEC systems. Reduced graphene oxide (rGO) shows both good conductivity and high dispersion in water as the intermediate state between graphene and graphene oxide (GO), providing great opportunities for the development of rGO based photoactive materials (Ren et al., 2017; Ng et al., 2010; Zhou et al., 2017). Therefore, it can be a good choice to combine rGO with $BiFeO_3$ for improving PEC performances.

Herein, rGO-$BiFeO_3$ nanohybrids with excellent PEC performance is employed as photoelectrode materials for the construction of PEC sensing system towards target prostate specific antigen (PSA, a kind of tumor marker for prostate cancer) (Dey et al., 2012). By introducing rGO, more effective separation of photo-excited charge carriers compared to pure $BiFeO_3$ can be achieved due to the facilitated charge transfer and enhanced visible light absorption in rGO-$BiFeO_3$ nanohybrids. Meanwhile, target triggered HCR process is carried out for signal amplification. The competitive combination of PSA and its aptamer leads to the release of trigger DNA (tDNA), which is used for triggering the formation of long double-stranded DNA to integrate large amount of glucose oxidase (GOx) onto the surface of magnetic bead (MB). PSA with a higher concentration leads to more GOx on MB, and more catalytic product H_2O_2 served as the photoelectron acceptor is generated to enhance the cathodic photocurrent of rGO-$BiFeO_3$ nanohybrids under the visible light irradiation. In this way, the quantitative detection of PSA could be simply achieved by monitoring the photocurrent change of the system.

2. Experimental section

2.1. Reagents and chemicals

Iron nitrate [$Fe(NO_3)_3{\cdot}9H_2O$], bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$], 2-methoxyethanol and citric acid were acquired from Sinopharm Chem. Re. Inc. (Shanghai, China). Carboxylated magnet beads (MBs) was purchased from Aladdin (Shanghai, China). Avidin-glucose oxidase (GOx) conjugates (2.0 mg/mL by UV absorbance at 280 nm; lyophilized; Buffer: 0.02 M potassium phosphate + 0.15 M sodium chloride, pH 7.2) were obtained from Rockland Immunochemicals Inc. (Limerick, Ireland). Graphene oxide (GO; 4.0 mg/mL, in H_2O), N-hydroxysuccinimide (NHS) and N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) were purchased from Sigma-Aldrich (Saint Louis, MO 63103, USA). All oligonucleotides used in this study were synthesized by Dingguo Biotech. Inc. (Beijing, China). The sequences are listed as follows:

PSA aptamer: 5′-ATTAA AGCTC GCCAT CAAAT AGC-3′
Anchor DNA (aDNA): 5′-NH_2-TCGCC ATCAA ATAGC-3′
Trigger DNA (tDNA): 5′-AGTC TAGGA TTCGG CGTGG GTTAA GCTAT TTGAT GGCGA-3′
Hairpin DNA1 (H1): 5′-TTAAC CCACG CCGAA TCCTA GACTC AAAGT AGTCT AGGAT TCGGC GTG-biotin-3′
Hairpin DNA2 (H2): 5′-biotin-AGT CTAGG ATTCG GCGTG GGTTA ACACG CCGAA TCCTA GACTA CTTTG-3′

Note: All sequences of the above-mentioned oligonucleotides were designed referring to the previous works (Huang et al., 2011; Zhang et al., 2012), and the designed sequences should be theoretically evaluated and simulated by using RNA folding prediction software (*Software: RNA structure, version 5.3, University of Rochester Medical Center, Mathews Lab,* http://rna.urmc.rochester.edu/software.html). All other reagents were of analytical grade and used without any further purification. Ultrapure water obtained from a Millipore water purification system (18.25 MΩ cm^{-1}, Milli-Q, Millipore) was used in all runs. All buffers including phosphate-buffered saline (PBS) solution were the products of Sigma-Aldrich.

2.2. Preparation of rGO-$BiFeO_3$ nanohybrids

First of all, $BiFeO_3$ nanoparticles were prepared through typical sol-gel method referring to literature with minor modification (Luo et al., 2010). 4.0 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ and 4.0 mmol of $Fe(NO_3)_3{\cdot}9H_2O$ were initially dissolved into 2-methoxyethanol (20 mL, original concentration), followed by adjusting the pH to about 4–5 with HNO_3. Subsequently, citric acid (4.0 mmol; as complexing agent) and ethylene glycol (10 mL, original concentration; as the dispersant) were added into the mixture and stirred at 60 °C for 30 min until the formation of a sol mixture. Following that, the sol was aged at 80 °C to form the gel, which was dried at 150 °C and calcined at 500 °C for 2 h (2 °C/min) to get $BiFeO_3$ nanoparticles.

Next, the rGO-$BiFeO_3$ nanohybrids were synthesized from GO and $BiFeO_3$ via a simple hydrothermal process. Graphene oxide (GO) nanosheets with different concentrations in H_2O (5.0 mL) were dispersed into $BiFeO_3$ aqueous suspension (25 mL, 10 mg/mL) under sonication and stirring. Following that, the resulting mixture was transferred to 50-mL autoclaves and heated at 150 °C for 6 h, and then cooled to room temperature naturally. Finally, the as-prepared rGO-$BiFeO_3$ nanohybrids were washed with ultrapure water and dried at 60 °C for the following use.

2.3. Conjugation of MBs with aDNA (MB-aDNA)

Aminated anchor DNA strands were conjugated with carboxylated magnetic bead via a typical carbodiimide couple (Zhang et al., 2014). The carboxylated MB (100 μL, 1 mg/mL, aqueous suspension) were mixed with MES buffer (800 μL, 0.1 M, pH 6.0) containing EDC (2.5 mg/mL) and NHS (2.5 mg/mL). The resultant mixture reacted for 15 min at 37 °C to activate the carboxyl groups on MB. Then, the aminated aDNA (100 μL, 200 μM) was added into and the mixture, and kept shaking for 12 h at 37 °C. The product was magnetically collected and washed several times with PBS (0.01 M, pH 7.4) to remove unbound biomolecules. Finally, the MB-aDNA conjugates were dispersed in PBS (1.0 mL, 0.01 M, pH 7.4) and stored at 4 °C when not in use.

2.4. Hybridization of PSA aptamer with trigger DNA (Apt/tDNA)

PSA aptamer (5.0 μL, 100 μM) and trigger DNA (5.0 μL, 100 μM) were initially mixed into PBS (90 μL, 0.01 M, pH 7.4). Thereafter, the mixture was annealed for 5 min at 95 °C, and finally cooled to room temperature. During this process, the added aptamer partially

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