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Ultrasensitive photoelectrochemical aptasensor for lead ion detection based on sensitization effect of CdTe QDs on MoS_2-CdS:Mn nanocomposites by the formation of G-quadruplex structure

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ABSTRACT

An ultrasensitive photoelectrochemical (PEC) aptasensor for lead ion (Pb^{2+}) detection was fabricated based on MoS_2-CdS:Mn nanocomposites and sensitization effect of CdTe quantum dots (QDs). MoS_2-CdS:Mn modified electrode was used as the PEC matrix for the immobilization of probe DNA (pDNA) labeled with CdTe QDs. Target DNA (tDNA) were hybridized with pDNA to made the QDs locate away from the electrode surface by the rod-like double helix. The detection of Pb^{2+} was based on the conformational change of the pDNA to G-quadruplex structure in the presence of Pb^{2+}, which made the labeled QDs move close to the electrode surface, leading to the generation of sensitization effect and evident increase of the photocurrent intensity. The linear range was 50 fM to 100 nM with a detection limit of 16.7 fM. The recoveries of the determination of Pb^{2+} in real samples were in the range of 102.5–108.0%. This proposed PEC aptasensor provides a new sensing strategy for various heavy metal ions at ultralow levels.

1. Introduction

Lead ions, one of the most toxic metallic pollutants, can cause various neurotoxic effects, such as memory loss, anemia, and retardation even at very low level [1]. And the more severe case is that exposure to high concentrations of Pb^{2+} can lead to death [2]. The sanitary standards for drinking water (GB5749-2006) has been fully implemented since 2007 in China, in which the limit value of state-specified standard of Pb^{2+} is 0.01 mg/L (about 50 nM). The traditional detection methods for Pb^{2+}, such as inductively coupled plasma mass spectrometry (ICP-MS) [3] and atomic absorption spectrometry (AAS) [4], suffers from expensive equipment, complicated sample pre-treatment and operation procedure. To overcome these problems, several measurements have been applied to detect the concentration of Pb^{2+}, such as fluorescence [5–7], colorimetry [8–10], electrochemistry [11,12]. Herein, electrochemical voltammetric [13,14], and electrochemiluminescent (ECL) [15–17] methods, have been proved to be a promising alternative in the determination of Pb^{2+} because of its high sensitivity, rapid response, easy data read-out and low cost. With the increase of demands for the trace amount detection of Pb^{2+} in complicated samples, ultrasensitive methods with highly selectivity for the detection of lead ions are urgently needed.

Photoelectrochemical (PEC) detection, where light is utilized to excite the photoactive species and photocurrent is employed as the detection signal, has attracted much attention, due to its advantages in terms of higher sensitivity and selectivity compared with conventional methods because of the total separation of the excitation source and detection signal. During the past decades, many PEC platforms have been used for detecting biomarkers [18], DNA sequences [19], enzymes [20], cells [21], and heavy metal ions [22–26]. In the detection of metal ions, most works concentrated on Hg^{2+} and K^+, few about Pb^{2+}. Aptamers are short single-stranded DNA or RNA oligonucleotides, generated by an in vitro process called systematic evolution of ligands by exponential enrichment (SELEX) [27,28]. Aptamers could bind to a wide range of targets, from small molecules to proteins, even whole cells [29]. They also exhibit unique advantages compared with other specific recognition elements, including good stability, ease of synthesis and modification, high affinity, and strong specificity [30]. Because of these unique characteristics, aptamers have received substantial attention as recognition probes in aptasensors. The G-quadruplex aptamer, generally stabilized by metal cations, has emerged as a specific identification element to build elegant and versatile devices [31,32]. Compare with K^+, Pb^{2+} has a higher G-quadruplex stabilizing efficiency resulted from the formation of a more compact structure. In the past decades, many works have been developed for the detection of metal ions using functional nucleic acids as recognition elements

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[33–36]. In this manuscript, a G-rich oligonucleotide was used for the detection of Pb^{2+}. To improve the sensitivity of the aptasensor, MoS_2-CdS:Mn nanocomposites and sensitized structure was introduced to the aptasensor.

Two dimensional (2D) nanomaterials have received more and more attention in recent years because of their ultrathin structure and novel mechanical, optical, and electronic properties [37]. Besides graphene, few inorganic 2D nanomaterials have been reported in PEC biosensor [38,39]. Molybdenum disulfide (MoS_2) is a typical member of the 2D nanomaterials, which has been explored for many applications in photocatalysis [40], hydrogen generation [41], and lithium batteries [42]. Graphene oxide (GO) has been used in PEC biosensor [21], supercapacitors [43], batteries [44,45], and solar cells [46] mainly due to the excellent electric conductivity. But the synthesis of GO is complicated and it only severed as a conductor, which is facilitating for electron transfer to the electrode. In order to suppress the recombination of the excited electron-hole pair and further enhance the photocurrent intensity, Mn^{2+} can be introduced into CdS to form Mn-doped CdS (CdS:Mn), because the lifetime of electron-hole recombination for CdS:Mn is up to hundreds of microseconds, which is much longer than that of CdS. MoS_2 is a semiconductor with a narrow energy band (~ 1.8 eV). The combination of MoS_2 with CdS: Mn, which has a higher conductive band than MoS_2 [47], is favor of increasing the photocurrent intensity and enhance the sensitivity of the biosensor.

Herein, we developed a novel PEC biosensor for ultrasensitive Pb^{2+} detection based on MoS_2-CdS:Mn nanocomposites and the sensitized effect of CdTe QDs. As the matrix of the aptasensor, MoS_2-CdS:Mn nanocomposites were modified on the ITO electrode through dropping method. Then, the pDNA was anchored on the electrode through the classic EDC coupling reaction. Next, tDNA was introduced to the electrode through the hybridization of pDNA and tDNA. Finally, CdTe QDs were modified on the electrode through the EDC coupling reaction between phosphate radical of the aptamer and the amino groups of CdTe QDs. The detection of Pb^{2+} was based on conformational change of the pDNA after incubating with Pb^{2+}. In the absence of Pb^{2+}, due to the DNA hybridization, the sensitization effect was inhibited. However, after incubating with Pb^{2+}, as the formation of the G-quadruplex, the labeled CdTe QDs move close to the electrode, leading to the enhancement of the sensitization effect, which evidently increased the photocurrent intensity. This aptasensor exhibited high sensitivity, specificity, reproducibility, and stability. The proposed aptasensor also provides a general model for detecting other heavy metal ions.

2. Experimental

2.1. Materials and reagents

ITO slices (type JH52, ITO coating 30 ± 5 nm, sheet resitance ≤ 10 Ω/square) were purchased from Zhongjingkeyi Technology Co. Ltd. (China). Cadmium chloride hemi(penhydrate) ($CdCl_2{\cdot}2.5H_2O$), Sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$), and sodium hydroxide (NaOH) were obtained from Shanghai Chemical Reagent Co. (China). 3-mercaptopropionic acid (MPA), 1-ethyl-3-(3-(dimethylamino) propyl) carbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), ethanolaimne (MEA) were all obtained from Sigma-Aldrich (USA). Molybdenum disulfide (MoS_2), Citric acid (CA) and ascorbic acid (AA) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). All other reagents were of analytical grade and used as received. All aqueous solutions were prepared with deionized water (DI water, 18 MΩ/cm), which was obtained from a Milli-Q water purification system. Tris-HCl buffer solution (pH 7.4, 10 mM) containing 0.1 M NaCl was used for preparation and hybridization of DNA stock solutions. The oligonucleotides used in this work were ordered from Shenggong Bioengineering Co., Ltd. (Shanghai, China) with the following sequences: probe DNA (pDNA, aptamer), 5′-NH_2-$(CH_2)_6$-TTG GGT GGG TGG GTG GGT-P-3′, target DNA (tDNA), 5′-ACC CAC CCA CCC ACC CAA-3′.

2.2. Apparatus

The morphology and particle size of the samples were characterized by high resolution transmission electron microscope (HRTEM) (JEOL-2100, Japan). The UV–visible (UV–vis) absorption spectra were obtained on a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan). Photoluminescence (PL) spectra were obtained on a RF-5301PC spectrophotometer (Shimadzu). Electrochemical impedance spectrum (EIS) was performed on an Autolab potentiostat/galvanostat (PGSTAT 30, Netherlands) with a three-electrode system in 0.1 M KCl solution containing 1.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) mixture as a redox probe, and recorded in the frequency range of 0.01 Hz–100 kHz with an amplitude of 50 mV. PEC measurements were carried out with a self-made PEC system. A 500 W Xe lamp was used as the irradiation source with the light intensity of 400 $\mu W/cm^2$ estimated by a radiometer (Photoelectric Instrument Factory of Beijing Normal University). Photocurrent was recorded on a CHI 660D electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China), and ITO modified electrode, saturated calomel electrode (SCE) electrode, platinum wire was used as working, reference, and counter electrode in this work, respectively.

2.3. Synthesis of MoS_2-CdS:Mn nanocomposites

The MoS_2 nanosheets were obtained through previous reports with slight modification [48,49]. In briefly, 1.0 g of bulk MoS_2 was added into DI water, and dispersed by ultrasonic for about 4 h. Then, 2.0 mg/mL homogenous nano-MoS_2 dispersion was obtained by centrifuged and re-dispersed in DI water.

The synthesis procedure of the MoS_2-CdS:Mn nanocomposites were similar with the synthesis of GO/CdS with appropriate modifications [50]. Briefly, 0.76 mmol of $CdCl_2{\cdot}2.5H_2O$ and 0.114 mmol of Mn $(CH_3COO)_2{\cdot}4H_2O$ was added into 30 mL of MoS_2-CdS:Mn nanocomposites. The solution was stirred at room temperature for 15 min. Then, 1 mmol of $Na_2S{\cdot}9H_2O$, which was dissolved in 30 mL DI water, was added to the above solution. After stirring for 20 min, the mixture was reacted at 70 °C for 2 h. The obtained mixture was centrifuged and re-dispersed in ethanol and DI water for two times. Finally, the solution of MoS_2-CdS:Mn nanocomposites were obtained.

2.4. Synthesis of CdTe-NH_2 QDs

The water-soluble CdTe-NH_2 QDs were prepared according to the previous work [19,51]. Typically, 3.6 mmol of CA was mixed with 100 mL of 12 mM $CdCl_2$ solution under stirring. The pH of the solution was then adjusted to 5.7 by dropwise addition of 1.0 M NaOH under stirring. After the solution was deaerated with highly pure N_2 for 30 min, 0.1 g of $NaBH_4$ and 0.06 mmol of Na_2TeO_3 were successively added in. The typical molar ratio of Cd^{2+}: Te^{2-}: CA was 1: 0.05: 3. The mixture solution was heated to 100 °C and refluxed for 1 h under N_2 protection, and eventually the CdTe-NH_2 QDs were acquired.

2.5. Fabrication process of the aptasensor

ITO electrodes were cleaned by ultrasonic treatment for 15 min in acetone, 1 M NaOH in a water/ethanol mixture (1:1, v/v), and water before use, then dried at 80 °C. Next, 20 μL of the obtained MoS_2-CdS:Mn nanocomposites homogeneous suspension was dropped onto an ITO electrodes with a fixed area of 0.25 cm^2. After air drying, aptamer was immobilized onto the ITO/MoS_2-CdS:Mn electrode via the classic EDC coupling reaction. The MoS_2-CdS:Mn modified electrode was activated with 20 μL DI water containing 20 mM EDC and 10 mM NHS for 1 h at room temperature, followed by rinsing with washing buffer (0.1 M PBS, pH 7.4) to remove any excess EDC and NHS. Next, 20 μL of 2 μM aptamer was dropped onto the electrode surface and incubated at 4 °C for 2 h. Then the electrode was rinsed with washing buffer to