Biosensors and Bioelectronics 87 (2017) 157–163

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

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

Dendritic structure DNA for specific metal ion biosensor based on catalytic hairpin assembly and a sensitive synergistic amplification strategy

Jianmin Zhao, Pei Jing, Shuyan Xue, Wenju Xu *

Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, School of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715 PR China

ARTICLE INFO

Article history:
Received 12 May 2016
Received in revised form
19 July 2016
Accepted 11 August 2016
Available online 12 August 2016

Keywords:
Electrochemical biosensor
Pb^{2+} detection
Catalyzed hairpin assembly
Dendritic structure DNA
Pb^{2+}-specific DNAzymes

ABSTRACT

In this work, a sensitive electrochemical biosensing to Pb^{2+} was proposed based on the high specificity of DNAzymes to Pb^{2+}. The response signal was efficiently amplified by the catalytic hairpin assembly induced by strand replacement reaction and the formation of dendritic structure DNA (DSDNA) by layer-by-layer assembly. Firstly, in the presence of Pb^{2+}, the substrate strand (S1) of the Pb^{2+}-specific DNAzymes was specifically cleaved by Pb^{2+}. Secondly, one of the two fragments (rS1) introduced into the electrode surface was hybridized with a hairpin DNA (H1) and further replaced by another hairpin DNA (H2) by the hybridization reaction of H1 with H2. The released rS1 then induced the next hybridization with H1. After repeated cycles, the catalytic recycling assembly of H2 with H1 was completed. Thirdly, two bioconjugates of Pt@Pd nanocages (Pt@PdNCs) labeled with DNA S3/S4 and electroactive toluidine blue (Tb) (Tb-S3-Pt@PdNCs and Tb-S4-Pt@PdNCs) were captured onto the resultant electrode surface through the hybridization of S3 and H2, S3 and S4, resulting in the formation of DSDNA triggered by layer-by-layer assembly. This formed DSDNA greatly facilitated the immobilization of manganese(III) *meso*-tetrakis (4-N-methylpyridiniumyl)-porphyrin (MnTMPyP) as mimicking enzyme. Under the synergistic catalysis of Pt@PdNCs and MnTMPyP to H_2O_2 reduction, the effective signal amplification of the developed Pb^{2+} biosensor was achieved. As a result, the sensitive detection of the proposed electrochemical strategy for Pb^{2+} was greatly improved in the range of 0.1 pM–200 nM with a detection limit of 0.033 pM.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

All the time, the sensitive, fast and cost-effective detection of toxic heavy metal ions such as Hg^{2+}, Pb^{2+}, Ag^{+}, and Cr^{3+} at trace or ultra-trace level was focused in environment control (Sobin et al., 2011; Gao et al.; 2016). Up to now, sensitive, rapid and inexpensive sensing system for different metal ions have already been reported, which were involved in electrochemistry (Gao et al., 2012; Zhang et al., 2015a), fluorimetry (Ju et al., 2014; Zhang and Chen, 2014; Gao et al., 2015a) and colorimetry (Huang et al., 2014; Gao et al., 2015b). To some extent, these proposed platforms showed desirable improvement of analytical performance.

As well known, DNAzymes (also called deoxyribozymes), isolated via in vitro selection technique, are capable of performing a specific chemical and biological reactions (Cuenoud et al., 1995; Liu et al., 2009). Interestingly, among them, metal ion-specific DNAzymes possess really high specificity to a particular metal ion. And the metal-binding specificity, binding site, and binding strength can be tuned. In the presence of certain metal ion, its specific DNAzymes could be specifically identified and cleaved at ribonucleotide site (rA). So using of such DNAzymes specific to different metal ions, such as Cu^{2+}, Pb^{2+}, Zn^{2+} and $UO_2{}^{2+}$, in different detection systems is very desirable for improving the selectivity and specificity of analytical methods (Carmi et al., 1998; Carmi et al., 2001; Santoro et al., 1997; Li et al., 2000; Liu et al., 2007). Accordingly, 8–17 DNAzyme, a kind of metal ion-specific DNAzymes, is a DNA metalloenzyme catalyzing RNA transesterification in the presence of Pb^{2+} and exhibit high binding specificity to Pb^{2+} through selective cleavage at rA by Pb^{2+}. Meanwhile the activity of DNAzymes is positively correlated to the concentration of Pb^{2+} (Li and Lu, 2000). Therefore, some facile methods based on this reaction have been reported to specifically detect Pb^{2+} (Yin et al., 2009a, 2009b). Meanwhile, the sensitive detection of Pb^{2+} is always of significance. Currently, it has been reported that many electrochemical biosensors for detecting Pb^{2+} were constructed by combining Pb^{2+}-specific DNAzymes with different signal amplification strategies, and

* Corresponding author.
E-mail address: xwju@swu.edu.cn (W. Xu).

http://dx.doi.org/10.1016/j.bios.2016.08.032
0956-5663/© 2016 Elsevier B.V. All rights reserved.

showed high specificity and sensitivity in analytical performance (Li et al., 2013; Tang et al., 2013; Cui et al., 2015).

As well known, catalytic hairpin assembly (CHA), as a kind of nucleic-acid amplification strategies, can be obtained simply by mixing hairpin probes and DNA species without the involvement of exogenous primer and enzyme (Hun et al., 2015; Li et al., 2011). CHA is simpler, lower-cost and more stable over other amplification methods such as polymerase chain reaction (PCR) and rolling circle amplification (RCA) (Yin et al., 2008; Jiang et al., 2013). So, many biosensors for the assay of metal ion, proteins, DNA and microRNA were widely reported by using CHA to amplify response signal (Chen et al., 2013; Liu et al., 2015; Tao et al., 2015; Zhang et al., 2015b; Wu et al., 2016).

More interestingly, dendritic structure DNA (DSDNA) based on layer-by-layer assembly triggered by the hybridization reaction of DNA (Xu et al., 2014; Zhang et al., 2014b), was an efficient immobilizing method for biomolecules and nanomaterials. Owing to the excellent stability (Astruc et al., 2010), DSDNA has received particular attention in developing biosensors based on different analytical methods (Meng et al., 2014). Meanwhile, due to the in situ assembly of DSDNA, nanomaterials or biomolecules with excellent electrocatalytic capacity can be effectively captured, which are very favorable for the response signal amplification. Benefited from this, the efficient improvement of analytical performance of the biosensing platforms for different targets can be successfully achieved. Sun et al. used nanoscale DNA-Au dendrimer as signal amplifier to construct a sensitive surface-enhanced Raman scattering biosensor for Pb^{2+} detection (Sun et al., 2011). While, our research group constructed a sensitive aptasensor for thrombin determination by employing three-dimension DNA-Au@Pt nanoparticles as nanocarriers (Zheng et al., 2016). Besides MnTPP, manganese(III) meso-tetrakis (4-N-methylpyridyl)-porphyrin (MnTMPyP) was also reported to show excellent peroxidases-like activity (Groves., 2000). Importantly, mimicking enzyme MnTMPyP molecules can be efficiently captured into double-strand DNA (dsDNA) scaffold by binding with AT and GC base pairs without requiring specific sequence, which can greatly avoid the limitation of binding amount of MnTMPyP in the labeling process (Pasternack et al., 1983; Nitta et al., 2006). Undoubtedly, MnTMPyP as mimicking enzymes exhibited more desirable catalytic activity in developing electrochemical biosensors (Xie et al., 2014; Liu et al., 2014), compared with traditional enzymes such as horseradish peroxidase or glucose oxidase.

Inspired by the above observations, herein a new electrochemical biosensing strategy for the sensitive detection of Pb^{2+} was proposed based on Pb^{2+}-specific DNAzymes as recognition element, the catalytic hairpin assembly and in situ assembly of DSDNA labeled on Pt@Pd nanocages (Pt@PdNCS), which possessed large surface area and splendid catalytic performance (He et al., 2012). Meanwhile, mimicking enzyme MnTMPyP molecules were embedded into the formed dsDNA scaffold. Under the synergistic catalysis of Pt@PdNCs and MnTMPyP with outstanding catalytic activity to the decomposition of H_2O_2, the electrochemical response signal could be significantly amplified. As a result, coupling with the high specific identification of Pb^{2+}-specific DNAzymes, the effective improvement and the great promotion of sensitivity and specificity, as well as other analytical performances were successfully achieved.

2. Experimental

2.1. Reagents and materials

Hexanethiol (96%, HT), toluidine blue (Tb), palladium potassium chloride (K_2PdCl_4), chloroplatinic acid (H_2PtCl_6), gold chloride ($HAuCl_4$), poly (vinyl pyrrolidone) (PVP, MW $\approx$55 000), potassium bromide (KBr), L-ascorbic acid (AA) were brought from Sigma (St. Louis, MO, USA). We purchased manganese(III) *meso*-tetrakis (4-*N*-methylpyridyl)-porphyrin (MnTMPyP) from J&K Chemical Technology Co., Ltd. (Beijing, China). Roche (Switzerland) provided Tris (hydroxymethyl) aminomethane hydrochloride (Tris-HCl) for use. The single-strand DNA oligonucleotides were synthesized by Sangon Biotech (Chongqing, China), the sequences of which are listed as followed:

Hairpin DNA H1: 3′-NH_2-$(CH_2)_6$-*CCTTCTCTACTCTGAGTCATCTG-TAGAGAA GG*-5′;.

Hairpin DNA H2: 3′-**TTCCACAAAT***CCTTCTCTACAGATGACTCA-GAGTAGA GAAGG*-5′;.

Pb^{2+}-specific DNAzymes substrate strand (S1): 3′-CTCA-GAGTAGAGAAGGrA TATCACTCA-5′ (the sequence marked with underlined letters refers to rS1);.

Pb^{2+}-specific DNAzymes catalytic strand (S2): 3′-TGAGTGA-TAAAGCTGGCCG AGCCTCTTCTCTAC-5′;.

DNA strand (S3): 3′-NH_2-$(CH_2)_6$-TCTTAACATGA**ATTTGTGGAA**-5′;.

DNA strand (S4): 3′-NH_2-$(CH_2)_6$-**TTCCACAAAT**TGTACAATTCT-5′.

These base sequences marked with italic letters of H1 and H2, underlined letters of H1 and S1, and bold letters of H2, S3 and S4, respectively were complementary each other.

In this work, 0.1 M phosphate-buffered solution (PBS, pH 7.0) was used as working buffer consisted of 0.1 M Na_2HPO_4, 0.1 M KH_2PO_4, 0.1 M KCl. All oligonucleotide solutions for DNA hybridization reaction were prepared by using 10 mM Tris-HCl (pH 7.0) containing 1 M NaCl and 1 mM EDTA. Deionized water (DI water) was used throughout the experiment process.

2.2. Instrumentation

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were carried out with a CHI 660D electrochemical workstation (Shanghai Chenhua Instruments, China), which was equipped with a conventional three-electrode system: a saturated calomel reference electrode as reference electrode, a platinum wire as supporting electrode and a modified glass carbon electrode (GCE) as working electrode. The pH of all used solutions was detected with a pHS-3C meter (MP 230, Mettler-Toledo, Switzerland). The scanning electron micrographs (SEM) of synthesized nanocomposites were tracked by the scanning electron microscopy (S-4800, Hitachi, Tokyo, Japan) at an acceleration voltage of 30 kV and by the thermal field emission scanning electron micrographs (JSM-7800F, JEOL, Japan) at an acceleration voltage of 5 kV.

2.3. Preparation of Pt@Pd nanocages (Pt@PdNCs)

According to the reported method (Zhang et al., 2011), Pt@Pd nanocages (Pt@PdNCs) were prepared. Firstly, 8 mL mixture containing 105 mg PVP, 60 mg AA, 600 mg KBr and KCl was heated to 80 °C under stirring for 10 min, then 3 mL K_2PdCl_4 (57 mg) was added slowly. After kept at 80 °C for 3 h, the product Pd nanocubes (PdNCs) were centrifuged and washed three times using DI water to remove excess PVP, and redispersed in 10 mL DI water. Next, 33.3 mg PVP, 300 mg KBr, and 300 mg AA were dissolved in 7 mL DI water, in which 1 mL PdNCs was added, and the resulting mixture was heated to 90 °C under stirring. After that, 1 mL H_2PtCl_6 (1%, *w/w*) was slowly added at a rate of 1 mL/min, and kept at 90 °C for 12 h. Finally, the obtained Pt@PdNCs were collected by centrifugation and redispersed in 2 mL of DI water for further use.

2.4. Preparation of two bioconjugates of Pt@PdNCs with S3 and S4 (Tb-S3- Pt@PdNCs and Tb-S4-Pt@PdNCs)

100 μL S3 (2.5 μM) or S4 (2.5 μM) added in 1 mL Pt@PdNCs was

Download English Version:

https://daneshyari.com/en/article/866173

Download Persian Version:

https://daneshyari.com/article/866173

Daneshyari.com