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Label-free and enzyme-free strategy for sensitive electrochemical lead aptasensor by using metal-organic frameworks loaded with AgPt nanoparticles as signal probes and electrocatalytic enhancers

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ABSTRACT

Herein, based on G-rich lead-specific aptamer (LSA) as the recognition element of target lead ion (Pb^{2+}), a label-free and enzyme-free electrochemical aptasensor for Pb^{2+} was developed by using metal-organic frameworks (MIL-101(Fe)) decorated with AgPt nanoparticles (AgPtNPs) as electrochemical probes and signal enhancers. The as-prepared AgPtNPs/MIL-101(Fe) that presented both inherent redox activity from MIL-101(Fe) and excellent electrocatalytic activity was further conjugated with single-strand DNA partially complementary to LSA (CS). In the presence of Pb^{2+}, the G-rich LSA, being incubated onto the modified electrode surface, was specifically folded to be stable G-quadruplex structure. Through the DNA hybridization reaction between LSA and CS, the unfolded G-rich LSA captured the proposed signal probes CS-immobilized AgPtNPs/MIL-101(Fe) in the electrode surface. As a result, the detectable electrochemical signal generated by MIL-101(Fe) was dependent on Pb^{2+} concentration. The cooperative electrocatalysis of AgPtNPs and MIL-101(Fe) effectively enhanced the response signal and greatly improved the detection sensitivity. Thus, the developed aptasensor for Pb^{2+} displayed a wide linear range from 0.1 pM to 100 nM with a detection limit of 0.032 pM, as well as excellent specificity, good stability, and acceptable reproducibility. This would make the proposed label-free and enzyme-free method be promising and potential candidate for sensitive and cost-effective detection of Pb^{2+} in real samples.

1. Introduction

Lead ion (Pb^{2+}), one of the well-known toxic heavy-metal elements, has been considered as a serious source of environment problem and healthy disease owing to its wide application [1,2]. Thus, highly sensitive and selective detection of Pb^{2+} is of considerable significance. Traditional analytical methods, such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectroscopy/optical emission spectrometry (ICP-MS/OES), atomic fluorescence spectrometry (AFS), colorimetry, surface plasmon resonance and etc. have been reported for determining Pb^{2+} [1–7]. Many of them, however, suffered from the drawbacks of sophisticated and expensive instruments, complicated treatment and low sensitivity, which in turn limited their practical application capability, particularly the detection of low abundant Pb^{2+}. Comparatively, various electrochemical methods have shown simplification, sensitivity and cost-effectiveness [1,2,7–11]. In order to further improve the selectivity of electrochemical detection platforms, special recognition elements like Pb^{2+}-specific DNAzymes have been used to specifically recognize the target Pb^{2+} [2,7,12–15]. Recently, based on the cooperative catalysis of flower-like MnO_2, hollow AuPd and hemin, our group used Pb^{2+}-specific DNAzymes as the recognition probes of Pb^{2+} to develop an electrochemical Pb^{2+} biosensor with high selectivity and sensitivity [16]. Similarly, by utilizing the specific recognition of Pb^{2+} DNAzymes, a highly selective and sensitive electrochemical Pb^{2+} biosensor was also constructed on the basis of the catalytic hairpin assembly and the dendritic structure DNA formation to improve the analytical performance [17]. As well-known, the selective interaction between Pb^{2+} and its specific DNAzymes with a substrate strand and a catalytic strand is based on a specific cleavage process at a certain site of substrate strand, which would cause a relatively complicated fabrication process of sensors [18,19]. Compared with Pb^{2+}-specific DNAzymes, G-rich lead-specific aptamer (LSA) as a kind of short, single-strand DNA or RNA possesses desirable properties such as high stability, simple

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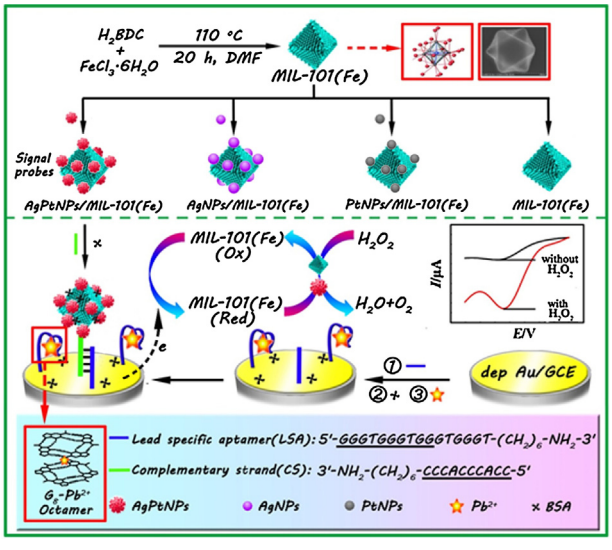
synthesis and good binding affinity [20,21]. It has been reported that, in the presence of Pb^{2+}, G-rich LSA folds into a hydrogen-bonded G-quartet (G_4) conformation, and contiguous G_4 stacks to be G-quadruplex structure [20,22]. Pb^{2+} is sandwiched between two G_4 layers, forming a G_8-Pb^{2+} octamer with strong stability (see the inset in Scheme 1) [23]. Thus, G-rich LSA with affinity and selectivity could be used as a specific and convenient recognition element for constructing Pb^{2+} sensors. To the best of our knowledge, using G-rich LSA to construct electrochemical Pb^{2+} aptasensor has received little attention [2,24,25].

Metal-organic frameworks (MOFs) with such desirable properties as good stability, enormous porosity, and large surface area have received tremendous attention in gas storage, drug delivery and sensors [26–29]. Especially, MOFs with intrinsic peroxidase-like catalytic activity have shown increasing interests in electrochemical biosensors [10,28,29]. For example, Ling and coworkers developed an electrochemical DNA sensor based on mimetic catalysis of functional MOFs by encapsulating iron porphyrin into a prototype MOFs, HKUST-1(Cu) [28]. Recently, a typical type of MOF with iron as central metal (MIL-101(Fe)) was reported to show special excellent mimicking peroxidase activity, which is desired for the immobilization of biomolecules and the catalytic amplification of response signal [30–32]. More interestingly, some MOFs with both intrinsic redox activity and electrocatalytic ability could be greatly promising for sensitive electrochemical biosensors [33,34]. Furthermore, the targeted modification of MOFs with different metal and/or bimetal nanoparticles with excellent conductivity and catalytic activity, such as AuPd clusters Pd@Co and core-shell nanoparticles, would be especially favorable and helpful to improve the analytical performance of electrochemical platforms for analytes [35,36]. Among them, bimetallic AgPt nanoparticles (AgPtNPs) were attractive to the functionalization of MOFs, due to large surface area, good electrical conductivity and electrocatalytic activity beyond the sole counterparts [37,38].

In this work, based on G-rich LSA as the recognition probes of the target Pb^{2+}, a label-free and enzyme-free electrochemical aptasensor for Pb^{2+} was proposed by using MIL-101(Fe) decorated with AgPtNPs (AgPtNPs/MIL-101(Fe)) as signal probes and electrocatalytic enhancers. In the presence of Pb^{2+}, the G-rich LSA incubated in the modified electrode surface was specifically folded to be stable G-quadruplex structure [20,23]. And the unfolded LSA captured the proposed signal probes AgPtNPs/MIL-101(Fe) through the DNA hybridization reaction. In the resulting electrode interface, the detectable electrochemical signal from MIL-101(Fe) was further amplified by the electrocatalysis of AgPtNPs/MIL-101 (Fe), effectively avoiding the involvement of additional electron mediators and enzymes. The proposed electrochemical system with significantly improved analytical performance would be a promising and potential alternative to the determination of Pb^{2+} in real samples.



Scheme 1. Schematic illustration of the fabrication process of the proposed Pb^{2+} electrochemical aptasensor, together with the preparation of different signal probes, and the mechanism of the signal amplification in the electrode interface.

2. Experimental

2.1. Reagents and materials

Lead nitrate ($Pb(NO_3)_2{\cdot}3H_2O$), silver nitrate ($AgNO_3$), chloroplatinic acid (H_2PtCl_6), bovine serum albumin (BSA, 96-99%), poly (ethylenimine) (PEI) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Hexadecyl trimethyl ammonium bromide (CTAB), N,N-dimethylformamide (DMF), terephthalic acid (H_2BDC), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ascorbic acid (AA) were received from Chengdu Kelong Chemical Reagent Company (Chengdu, China). 2-Aminoterephthalic acid was obtained from Tokyo Chemical Industry Co., Ltd. Trishydroxymethylaminomethane hydrochloride (Tris-HCl) was supplied by Roche (Switzerland). 20 mM Tris-HCl buffer (pH 7.4) which contains 140 mM NaCl, 5 mM KCl, 1 mM $CaCl_2$ and 1 mM $MgCl_2$, was served as buffer solution. Phosphate buffered solution (PBS, 0.1 M, pH 7.0) containing 0.1 M KCl, 0.1 M KH_2PO_4 and 0.1 M Na_2HPO_4 was used as working buffer. All oligonucleotides used in this work were received from Sangon Biotech. Inc (Shanghai, China). The base sequences of the oligonucleotides were as follows [24]: Pb^{2+} specific aptamer (LSA): 5'-**GGGTGGGTGG**GTGGGT-$(CH_2)_6$-NH_2-3' and a complementary single-strand DNA to the bolded sequence of LSA: 3'-NH_2-$(CH_2)_6$- **CCCACCCACC**-5' (CS). All aqueous solutions were prepared by using double-distilled water (DD water) obtained from a Milliporewater purification system (≥18.2MΩ, Milli-Q, Millipore). All other chemicals were of analytical grade and used as received.

2.2. Apparatus

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were conducted with a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument, China), which contains a three-electrode system by using modified glassy carbon electrode (GCE, 4 mm in diameter) as the working electrode, platinum wire as the auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. The scanning electron micrographs (SEM) were conducted by using a scanning electron microscope (SEM, S-4800, Hitachi Instrument, Japan). The Fourier transform infrared (FT-IR) spectrum was carried out by using a DIGILAB FTS 7000 spectrometer (Varian, Cambridge, MA, USA). Powder X-ray diffraction (PXRD) pattern was collected on a D8 ADVANCE X-ray diffractometer (Bruker, Germany).

2.3. Preparation of AgPtNPs/MIL-101(Fe) and AgPtNPs/MIL-101(Fe) conjugated with complementary strand (CS)

Firstly, MIL-101(Fe) was synthesized according to a previous literature with minor modification [30]. Briefly, H_2BDC (0.412 g, 2.48 mM) and $FeCl_3{\cdot}6H_2O$ (1.35 g, 4.9 mM) were dissolved in DMF (15 mL) to form a clear solution. Then, the solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 110 °C for 20 h. After that, the resulting brown solid MIL-101(Fe) was collected by centrifugation and washing with water and ethanol, and finally dispersed in 10 mL water for next use.