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Highly sensitive biosensor based on target induced dual signal amplification to electrochemiluminescent nanoneedles of Ru(II) complex

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ABSTRACT

Here, electrochemiluminescent nanoneedles of Ru(II) complex were synthesized to fabricate an "off-on" electrochemiluminescence (ECL) biosensor in assistance with target Pb^{2+} induced dual signal amplification. Firstly, new needle-like nanostructures of luminous Ru(II) complex (RuNDs) different from the previous ones were prepared through solvent evaporation induced self-assembly on the electrode, which processed high ECL efficiency due to massive Ru(II) complexes in those structures, giving a strong initial ECL signal. To further improve the stability of the RuNDs film, silver nanowires (AgNWs) with excellent electric-conductivity dispersed in Nafion solution were modified by film formation, which was also convenient for subsequent modification. Through Ag-S bond, the DNA duplex formed by ssDNA with -SH (S1) and ssDNA modified with ferrocene (S2-Fc) was immobilized, leading to an obvious decrease of the ECL signal because of the effective quenching effect of Fc (off state). With the presence of target Pb^{2+}, G-quadruplex structure was formed owing to the high specific affinity between S1 and Pb^{2+}, making S2-Fc fall off from the electrode. Interestingly, the ECL signal not only could be recovered due to the abscission of Fc, but also improved by the generation of Pb^{2+}-G-quadruplex (on state). Based on the effective dual signal amplification, a sensitive ECL biosensor was constructed for Pb^{2+} determination with a low estimated detection limit down to 0.33 pM. The strategy using luminous Ru(II) complex as precursor to directly prepare needle-like nanostructure was a convenient and effective way to enhance the ECL efficiency. Meanwhile, the simple and efficient target Pb^{2+} induced dual signal amplification would provide new thought for signal enhancement in the fabrication of biosensors.

1. Introduction

Heavy-metal pollution has always been a serious and still growing threat to environmental safety and human health, which is continuously caused by industry and human activities, such as fertilizer usage, electronic waste disposal, gasoline processing, and so on (Lin et al., 2017). Lead ions (Pb^{2+}), as one of the most toxic heavy-metal pollutants, could cause pollution of water, air, and soils, arousing extensively public concern. Owing to its non-biodegradability nature and high toxicity, Pb^{2+} could accumulate in various food chains and cause severe damage to digestive, immune, nervous and reproductive systems (Wen et al., 2017). Thus, sensitive and accurate monitoring of Pb^{2+} has become a significant issue. Current methods like inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), fluorescence and electrochemistry are utilized for Pb^{2+} analysis (Mandlate et al., 2017; Willis and Sturman, 2004; Liang et al., 2017; Xiao et al., 2007) Nevertheless, electrochemiluminescence (ECL), a favorable and popular analytical technique, is becoming one of the most promising and convenient method for Pb^{2+} determination, benefited from its advantages of outstanding controllability, simplified optical setup, high accuracy and sensitivity (Lv et al., 2018; Zhu et al., 2018; Liu et al., 2018; Carrara et al., 2017).

During the fabrication of ECL biosensors, enhancement of the luminous efficiency is vital for the sensitive analysis, which is directly associated with the efficient immobilization of luminophore (Liu et al., 2015). For the Ru(II)-based complex, a classical kind of ECL reagent that has been widely applied in various areas, several immobilized ways are included through doping, crosslinking, embedding, adsorption and film forming (Wang et al., 2017, 2018; Feng et al., 2017; Ni et al., 2018). Although those methods possess obvious advantages in cost saving and efficiency enhancing compared with the early method of directly adding Ru(II)-based complex into the detection solution, it is

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still essential to investigate new means with higher efficiency and more convenience. Thus, Ru(II)-based nanostructures (such as nanowires, nanobelts and nanorods) prepared by directly using Ru(II)-based complexes as precursors were proposed, which not only have extreme high luminous efficiency due to the accumulation of massive Ru(II)-based complexes, but also avoid tedious immobilized process (Li et al., 2012; Yu et al., 2008; Wang et al., 2016). In the further ECL analysis, they deserve more concern due to the simple prepared process, high specific surface area and excellent luminous property. However, the preparation of the Ru(II)-based nanostructures were easily effected by the solvents or the branched chain structure of ruthenium complexes, which limited their further development. Inspired by the nanoneedles preparation in the previous work, here, a new needle-like nanostructure of tris(2,2′-bipyridyl)ruthenium (II) with high ECL efficiency was synthesized on the electrode and applied to construct an ECL biosensor with high sensitivity (Togashi et al., 2014; Subhramannia et al., 2007).

Currently, ECL biosensors with different signal output modes were fabricated, for instance, “off-on”, “on-off” and “on-off-on” (Shao et al., 2018; Liu et al., 2017; Xu et al., 2017). The main advantages of those kinds of biosensor are simple design, wide linear detection range, low background signal, high detection sensitivity and so on, making them be applied various areas. Taking the “off-on” mode for example, Hallaj's group fabricated a sensitive ECL aptasensor for analysis of Hg^{2+} based on the signal recovering from “off” state to “on” state (Babamiri et al., 2018). Our group also constructed an “off-on” ECL biosensor for telomerase activity monitoring via the releasing of quencher accompany with the signal switching from “off” state to “on” state (Xiong et al., 2017). However, in most of those previous works, the ECL signal increased just through signal recovering when the “off” state switched to the “on” state, which would limit the detected sensitivity because of the different recovery efficiency. In this work, we found that Pb^{2+} based G-quadruplex had a favorable enhancement to the ECL of Ru(II)-based nanostructure, based on which a dual signal amplified strategy was designed to construct an “off-on” ECL biosensor. Particularly, in the switching process of “off” state to “on” state, ECL quenching directly switched to ECL enhancing, which was more effective in ECL signal increasing than simple signal recovery, resulting in a higher detected sensitivity.

Herein, tris(2,2′-bipyridyl)ruthenium (II) (Ru $(bpy)_3^{2+}$) dispersed in the mixture solution of acetonitrile and acetone (5:1, v/v) was used as precursor to prepare new needle-like luminous nanostructures (RuNDs) by solvent evaporation induced self-assembly. Owing to the large amount of Ru $(bpy)_3^{2+}$ in the structure, the as-obtained RuNDs processed high luminous efficiency and stability, generating a strong initial ECL signal on the electrode. Then, silver nanowires (AgNWs) with excellent electric-conductivity dispersed in Nafion solution were dropped on the electrode for film formation, improving the stability of the RuNDs film and making it convenient for subsequent modification. Thus, ssDNA with -SH (S1) was immobilized, which could further capture the ssDNA modified with ferrocene (S2-Fc), leading to an obvious decrease of the ECL signal because of the effective quenching effect of Fc (off state). When target Pb^{2+} was added, Pb^{2+}-G-quadruplex with upstanding enhancement to the ECL of RuNDs was formed, and S2-Fc with obvious quenching effect to the ECL signal was released from the electrode, leading to great improvement of the final ECL intensity (on state). As a result, a sensitive “off-on” ECL biosensor was fabricated for Pb^{2+} monitoring with excellent selectivity, stability and sensitivity. The strategies of the synthesis of Ru(II)-based nanostructure with high luminous property and target induced dual signal amplification gave a new mean for construction of biosensor with high sensitivity.

2. Experimental section

Reagents and apparatus. Lead nitrate ($Pb(NO_3)_2$), poly-(vinyl pyrrolidone) (PVP), silver nitrate ($AgNO_3$) and trimethylamine (TPrA) were obtained from Sigma Chemical (St. Louis, MO, USA). Tris (2,2′-bipyridyl)ruthenium (II) (Ru $(bpy)_3^{2+}$) was purchased from Suna Tech Inc. (Suzhou, China). Tris-HCl buffer (20 Mm, pH 7.4) and deionized water were used in this work. All the oligonucleotides were got from Shanghai Sangon Biological Engineering Technology and Services Co., Ltd. (Shanghai, China), which were listed as follows:

S1: 5′–SH–$(CH_2)_6$-GGT TGG TGT GGT TGG-3′

S2: 5′-Ferrocene-AAC CAC ACC AA-3′

The reference electrode (Ag/AgCl (sat. KCl)), the counter electrode (platinum wire), and the working electrode (the modified glassy carbon electrode (GCE, $\Phi = 4$ mm)) made up the classical three-electrode system that was applied in the detection. The ECL monitoring and electrochemical characterization were performed on MPI-E ECL analyzer (Xi'an Remax Electronic science & Technology Co. Ltd., China) and CHI 660E electrochemical workstation (Shanghai Chenhua Instrument, China), respectively. For characterization of nanomaterials, scanning electron microscopy (SEM, S-4800, Hitachi, Japan) was used.

Preparation of silver nanowires (AgNWs). AgNWs were prepared based on the literature with some modifications (Sun and Xia, 2002). Firstly, 30 mL anhydrous ethylene glycol was placed into a flask and further heated at 160 °C for 1 h. After that, ethylene glycol solution (10 mL) containing PVP (0.2 M) and ethylene glycol solution (3.5 mL) containing $AgNO_3$ (0.29 M) were added into the hot solution above. Under sustained magnetic stirring, the mixture solution was refluxed under 160 °C for 40 min. Through centrifugation, washing and redispersion, AgNWs were obtained.

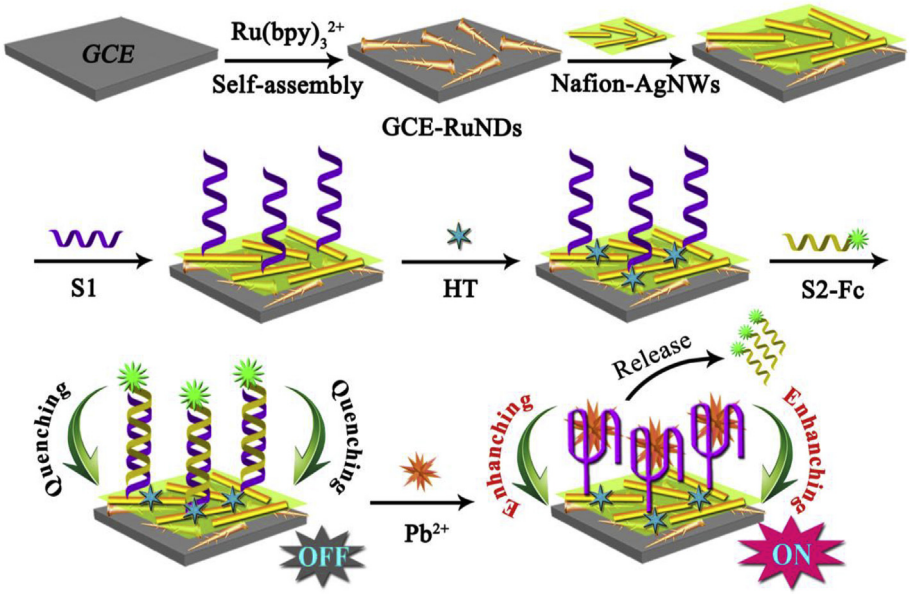
Fabrication of the ECL biosensor. First of all, the GCE was pretreated by polishing, rinsing and sonicating to obtain a mirror-like surface. Then, 5 μL Ru $(bpy)_3^{2+}$ dispersed in the mixture solution of acetonitrile and acetone (5:1, v/v) was dropped onto the cleaned GCE. The electrode was transferred into the oven with 37 °C, resulting in the evaporation of the solution and the formation of the RuNDs on the electrode surface. After that, 5 μL AgNWs dispersed in Nafion solution (0.25%) was dropped onto the electrode for film formation after drying in air. Through Ag-S bond, ssDNA with -SH (S1, 0.2 μM) was immobilized, which could further capture the ssDNA modified with ferrocene (S2-Fc, 0.2 μM). Owing to the quenching effect of Fc to the ECL of RuNDs, the ECL intensity of the electrode decreased sharply. After blocking the nonspecific adsorption sites with hexanethiol (HT, 96%), Pb^{2+} with different concentrations were added, which could interact with S1 to form G-quadruplex structure and release the S2-Fc. The ECL intensity of the electrode increased obviously because of the abscission of Fc and the enhancement of Pb^{2+}-G-quadruplex. Furthermore, the ECL signal improved continuously as the concentration of Pb^{2+} increased, by which Pb^{2+} was sensitively monitored. The fabricated process of the biosensor was presented in Scheme 1.

Measurement procedure. The biosensors incubated with Pb^{2+} with different concentrations were put in the ECL detector cell. Then, in the detection, the voltage of the photomultiplier tube (PTM) was set as 800 V, and the potential scanning range was set as 0.2-1.25 V. As the concentration of Pb^{2+} increased, the ECL signal increased accordingly, realizing the sensitive detection of Pb^{2+}.

3. Results and discussion

Morphology characterization of nanostructures. SEM was applied to characterize the obtained nanostructures in this study, which was presented in Fig. 1. According to Fig. 1A, large amount of structures with needle-like shape were uniformly distributed in the SEM image of the RuNDs. Meanwhile, the AgNWs with wire structure were also obviously observed in Fig. 1B. The SEM results above confirmed the successful preparation of the nanostructures used in this work.

Fabrication characterization for the ECL biosensor. In 5 mM $[Fe(CN)_6]^{4-/3-}$ solution, electrochemical impedance spectroscopy (EIS) was performed to verify the successful stepwise modified process. The obtained EIS profiles were shown in Fig. S1A in the Supporting



Scheme 1. The fabricated process of the ECL biosensor.

Information. Firstly, curve a showed a small impedance value for the bare GEC. After the modification of RuNDs and AgNWs dispersed in Nafion solution, the impedance value greatly increased due to the blocking effect to the electron transfer (curve b). Then, the impedance values further increased after the modification of S1 and S2-Fc because DNA with negatively charge could hinder the diffusion of the negatively charged $[Fe(CN)_6]^{4-/3-}$ (curve c and d). When Pb^{2+} was added, Pb^{2+}-G-quadruplex structure was formed on the electrode and S2-Fc fell off from the electrode, resulting in the decline of the impedance value (curve e). That was because of the fact that the negatively charged DNA strand would hinder the diffusion of $[Fe(CN)_6]^{4-/3-}$ to the electrode surface, and the falling of S2-Fc would reduce the hindrance to the diffusion of $[Fe(CN)_6]^{4-/3-}$. The above EIS results suggested the successful fabrication of the biosensor.

The ECL signal was also monitored in the fabricated process (Fig. S1B in the Supporting Information). Owing to the high luminous efficiency of RuNDs, there was a strong ECL signal after the modification of RuNDs and AgNWs dispersed in Nafion solution (curve a). Then, the ECL signal declined after the modification of S1 and blocking with HT because of their hindrance to electron transfer (curve b). Because Fc had strong quenching effect to the ECL of RuNDs, the ECL signal further decreased sharply when S2-Fc was modified on the electrode (curve c, off state). However, after adding of target Pb^{2+}, Pb^{2+}-G-quadruplex with upstanding enhancement to the ECL of RuNDs was formed, and S2-Fc with obvious quenching effect to the ECL signal was released from the electrode, leading to great improvement of the final ECL intensity (curve d, on state).

Analysis performance of the proposed biosensor for Pb^{2+}. Using the proposed biosensor, Pb^{2+} with different concentrations was determined and the obtained results were listed in Fig. 2. As increasing the concentration of Pb^{2+}, the ECL signal continuously improved (Fig. 2A, curve a-g). Moreover, as shown in Fig. 2B, the ECL intensities possessed obvious linear relationship with the logarithm of corresponding concentrations of Pb^{2+}. And the linear equation was $I = 787.3 \lg c + 10569.6$ (c was the concentration of Pb^{2+} and I was the ECL intensity) with a correlation coefficient of 0.9984. The estimated limit of detection (LOD) (defined as LOD = $3S_B/m$, where S_B is the standard deviation of the blank, and m is the slope of the corresponding calibration curve (Radi et al., 2006)) was 0.33 pM. Compared to the previous work for Pb^{2+} detection, the proposed biosensor also exhibited more excellent performace (Table S1 in the Supporting Information), suggesting the great applied promising of this proposed biosensor (Yu et al., 2016, 2018; Fang et al., 2017; Liao et al., 2017; Huang et al., 2017).

Other performance of the obtained biosensor. Firstly, selectivity, as one important aspect, was explored. Several interference ions, for instance Ag^+, Cd^{2+}, Co^{2+}, K^+, Mg^{2+} and Ni^{2+} were chosen to do the comparative experiment and the obtained results were presented in Fig. 3. After the incubation of 10 mM Ag^+, Cd^{2+}, Co^{2+}, K^+, Mg^{2+} Ni^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+} and Ca^{2+} respectively, the ECL signals of the biosensor were almost similar with that of the blank sample. And the ECL response increased obviously when the mixture containing 10 mM Ag^+, Cd^{2+}, Mg^{2+}, Ni^{2+} and 10 nM Pb^{2+}, which was almost the same

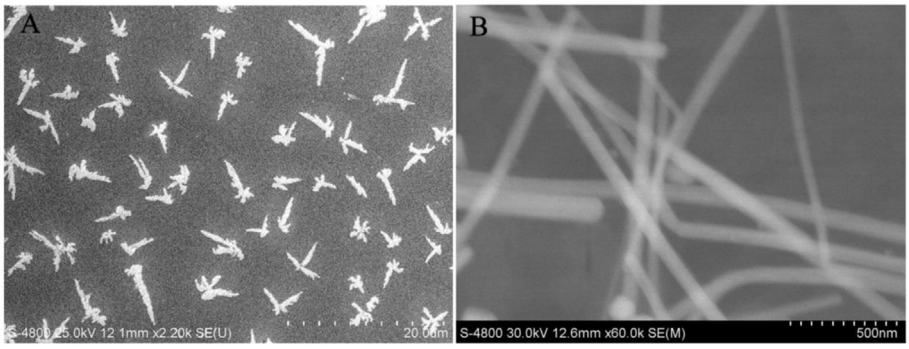


Fig. 1. SEM images of the prepared RuNDs (A) and AgNWs (B).

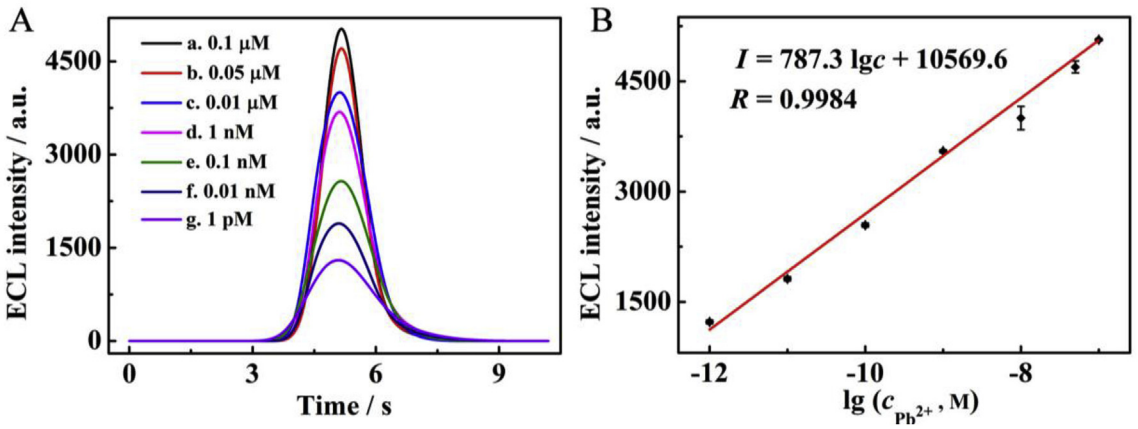


Fig. 2. (A) ECL signals for Pb^{2+} detection with different concentrations of (a-g): 0.1 μM, 0.05 μM, 0.01 μM, 1 nM, 0.1 nM, 0.01 nM and 1 pM. (B) Standard curve of the biosensor for Pb^{2+} detection.

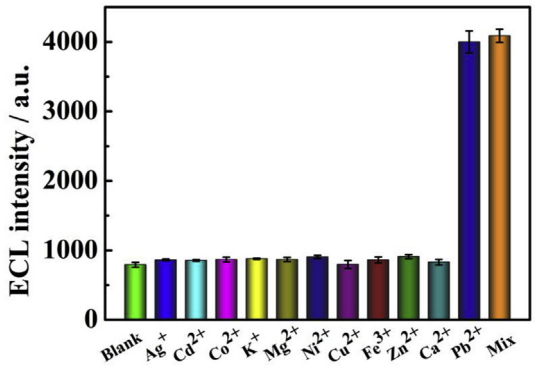


Fig. 3. The ECL signals of the biosensor incubated with different targets: Blank; Ag^+ (10 mM), Cd^{2+} (10 mM), Co^{2+} (10 mM), K^+ (10 mM), Mg^{2+} (10 mM), Ni^{2+} (10 mM), Cu^{2+} (10 mM), Fe^{3+} (10 mM), Zn^{2+} (10 mM), Ca^{2+} (10 mM), Pb^{2+} (10 nM) and the mixture (Mix) containing Ag^+ (10 mM), Cd^{2+} (10 mM), Mg^{2+} (10 mM), Ni^{2+} (10 mM) and Pb^{2+} (10 nM).

with that incubated with pure 10 nM Pb^{2+}. The obtained results above proved the outstanding selectivity of the obtained biosensor for Pb^{2+} detection, showing a promising application possibility.

Meanwhile, the reproducibility accessed through intra- and inter-assays was further investigated. As presented in Fig. 4A, the calculated R.S.D. of the intra-assays of six biosensors fabricated in the same batch was 3.77%, while that of the inter-assays of six biosensors fabricated in the different batches was 5.37%. The obtained results demonstrated the good reproducibility of the obtained biosensor. In addition, the stability was also another important aspect for the performance, which was investigated by consecutive cyclic potential scans. From Fig. 4B, the ECL signal of the proposed biosensor incubated with Pb^{2+} (0.1 μM) exhibited a steady trend and the R.S.D. of the ECL intensity under 17 cycle potential scans was 0.993%, indicating excellent stability in ECL detection of this biosensor.

Application of the obtained biosensor. To evaluate the feasibility, the obtained biosensor was applied for preliminary analysis of real samples. Using the ECL biosensor, Pb^{2+} with several different concentrations (actual concentration) in drinking water was measured. Recovery, the ratio between the determined concentration and the actual concentration, was calculated, which directly reflected the analysis accuracy. From Table 1, we could see that the recoveries were between 94.45% and 104.5%, indicating a good detected accuracy and an outstanding promising in environmental application for the ECL biosensor.

4. Conclusions

In summary, a sensitive "off-on" ECL biosensor was fabricated for Pb^{2+} measurement based on RuNDs with high luminous efficiency and target Pb^{2+} induced dual signal amplification. The proposed biosensor exhibited excellent performance in sensitivity, stability, selectivity and accuracy, which was mainly ascribed to the follow aspects. First, RuNDs obtained by solvent evaporation induced self-assembly on the electrode with Ru(II) complex as precursor processed high luminous efficiency due to the accumulation of massive Ru(II) complexes in those structures. And the modification of AgNWs-nafion film further enhanced the stability of RuNDs in ECL detection. Second, the strategy of target Pb^{2+} induced dual signal amplification that was quite effective because the ECL signal not only could be recovered due to the abscission of Fc, but also could be improved because of the generation of Pb^{2+}-G-quadruplex. Both the aspects above had very positive reference significance

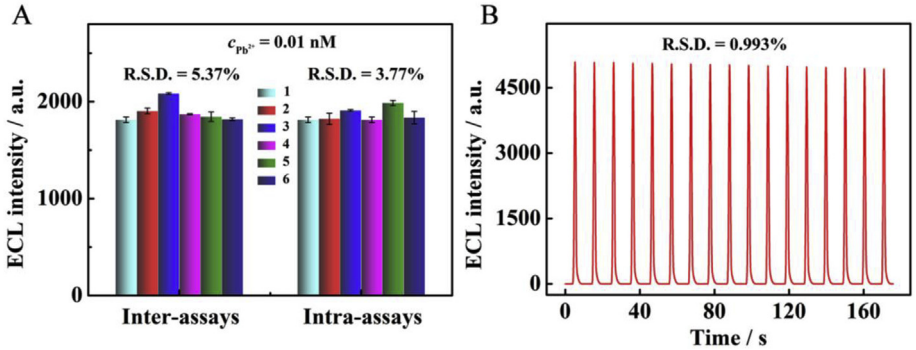


Fig. 4. (A) The reproducibility (intra- and inter-assays) of the proposed biosensor (0.01 nM Pb^{2+}), (B) The stability of the proposed biosensor incubated with Pb^{2+} (0.1 μM) under consecutive cyclic potential scans.

Table 1
Determination of Pb^{2+} with different concentration in drinking water.

Sample number	Actual/nM	Detected/nM (n = 3)	Recovery/%
1	10.00	9.445	94.45
2	1.000	1.045	104.5
3	0.1000	0.1026	102.6
4	0.01000	0.009904	99.04

in construction ECL biosensor with outstanding performance. And the proposed biosensor also held new promising in sensitive monitoring of environmental or clinic Pb^{2+}, improving the timely prevention and treatment.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Haijun Wang: Conceptualization, Data curation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Yuhang Song:** Data curation, Investigation. **Yaqin Chai:** Funding acquisition, Resources, Project administration, Supervision. **Ruo Yuan:** Funding acquisition, Resources, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bios.2019.111344.

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