Label-free detection of lead(II) ion using differential phase modulated localized surface plasmon resonance sensors

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Abstract

A label-free differential phase modulated localized surface plasmon resonance (LSPR) sensor is developed for specific detection of lead (II) ions (Pb(II)) in aqueous solution. The Pb(II) selective sensing receptor, poly(m-phenylenediamine-co-Aniline-2-sulfonic acids) (mPD-co-ASA) copolymer was fabricated through oxidative copolymerization, and was functionalization onto the LSPR self-assembly gold nanoislands (SAM-AuNIs) chip. The sensor exhibits specific response to Pb(II) ion rather than other metallic ions over a wide range of concentrations. The limit of detection (LOD) is estimated as 0.15 ppb, which is much lower than 10 ppb, the recommended threshold of Pb concentration in drinking water by the World Health Organization. Furthermore, the label-free advantage is combined with fast detection response. Therefore, the plasmonic sensor has great potential for highly sensitive and specific detection of Pb(II) ions in drinking water.

Keywords: label-free, lead(II) detection, LSPR, phase measurement

1. Introduction

Drinking water safety has become a global issue with reported lead (Pb) contamination crises in the metropolitan city of Hong Kong [1] and the developed states of Flint, Michigan [2]. As Pb is particularly poisonous to infants and children, continuous consumption of Pb-containing water is known to affect the intellectual development of these age groups. The World Health Organization (WHO) Guidelines and the United States National Primary Drinking Water Regulations (NPDWR) stipulate the threshold of Pb concentration in drinking water as 10 part-per-billion (ppb) [3] and 15 ppb [4] respectively. These are equivalent to 10 and 15 microgram of Pb per liter of water (µg/L).
Existing state-of-the-art analytical techniques including ICP-MS [5] and HPLC [6] reported Pb detection limits from ng/L to µg/L. Recent progress in electrochemical [7], luminescent assay [8] and colorimetric [9] approaches has also reported detection limits of comparable performance. However, laborious sample preparation is necessary for all these techniques and the measurement has to be performed in laboratory to achieve the ultimate sensitivity. This is far from satisfactory to meet the global demand for a rapid, sensitive and accurate inspection that allows on-site detection of Pb(II) ions in drinking water.

Recently, we have developed a robust differential phase modulated localized surface plasmon resonance interferometer based on common-path spectral interferometry and self-assembly gold nanoislands [10]. We have also established a novel dielectric functionalization protocol for detection of IgG antigen in human serum to picomolar sensitivity with the LSPR interferometer [11]. With locally confined electromagnetic field to nanometric scale, the molecular mass of detectable analyte has also been reduced substantially to about 200 g/mole, which is attainable by conventional surface plasmon resonance (SPR) devices. Therefore, we were also able to identify 3-nitro-L-tyrosine biomarker to subpicomolar resolution in human serum with doped graphene receptor for early diagnostics of Alzheimer’s diseases [12]. With these establishments, we believe the LSPR interferometer is capable to detect Pb(II) in drinking water provided that Pb(II) specific receptors are functionalized onto the gold nanoislands.

2. Materials and Methods

M-Phenylenediamine (mPD), Aniline-2-sulfonic acid (ASA), ammonium persulfate (APS, (NH₄)₂S₂O₈), HCl (1.0 M) were purchased from Sigma Aldrich (Shanghai, PR China). Lead nitrate (Pb(NO₃)₂) and other metal cations (Sigma Aldrich) are all in analytical grade and used to prepare the solution based on WHO suggested threshold concentration without any further purification. A series of Pb(II) solutions were obtained by repeatedly diluting 10 ppm Pb(II) with 18.2 MΩ deionized water.

Poly(mPD-co-ASA) copolymer was synthesized by chemical oxidation copolymerization of mPD and ASA monomers using the APS oxidizer. The optimized molar ratio of 95:5 between mPD and ASA was found to provide the best sensitivity. For the oxidation reaction, the oxidizer to monomer molar ratio was kept at 1:1 and 1.0 M of HCl was used as solvent. The mixed monomer solution was placed in water bath at 30°C, and then the oxidizer solution was then added drop by drop within 30 min. The reaction mixture was constantly stirred at 30°C for 24 hours. The steps of synthesis were similar to those reported by Huang et al [13]. The resultant copolymer solution was further filtered to retain the optimal size for the best Pb(II) sensitivity.

The LSPR chip with self-assembly gold nanoislands was fabricated and installed into the common-path spectral interferometer with a LED source as reported previously [10]. Diluted poly(mPD-co-ASA) solution was injected into the flow chamber with a peristaltic pump at a constant flow rate of 200 µL/min. The SO₃⁻ functional group of the poly(mPD-co-ASA) binds to the gold nanoislands and plays the role as Pb(II) receptor. Sequentially, the sensing chip was rinsed by deionized water to remove excessive copolymer and the functionalized LSPR chip was ready for label-free Pb(II) detection.

3. Results and Discussion

There were three steps in the overall detection procedure, namely, i) deionized water was injected to the flow cell for the first 200 s to establish the baseline reference, ii) Pb(II)-containing water sample was injected for the next 600 s, iii) deionized water was injected again for 200 s again to rinse the flow cell. The final step was necessary to remove nonspecific binding on the copolymer receptor and prevent false-positive results. The total time to complete the test was about 1000 s and the flow rate was kept constant at 200 µL/min. The total sample volume required was about 2 mL. The phase sensorgram of different Pb ion concentrations from the time of Pb(II) sample injection is shown in Fig. 1a, i.e. deionized buffer water, 3 ppb, 7 ppb, 10 ppb and 20 ppb Pb(II) ion solution. By observation of Fig. 1a, the phase increased in accordance with Pb(II) concentration and by rinsing with deionized water did not alter the final phase reading from 600 to 800 s. It is clear that the WHO threshold for Pb(II) concentration in drinking water, i.e. 10 ppb, is easily distinguished with the present system. The limit of detection (LOD) is estimated with linear fitting toward Pb(II) concentration from 10 ppb to 1 ppb, as shown in Fig. 1b. Each concentration was repeated for at least three times to determine the standard deviations shown as error bar in each data point. The
linear fitting equation was \( y=0.04447x+0.02358 \) (R-square=0.9919), and was used to calculate the LOD according to the definition by the International Union of Pure and Applied Chemistry. This gives the LOD of 0.15 ppb, which is two orders of magnitude better than the WHO threshold.

![Fig. 1](image1.png)

**Fig. 1.** (a) Phase sensorgram of different Pb ion concentration; (b) Linear regression of lead ion ranging from 0 to 10ppb for estimating the detection limit.

The poly(mPD-co-ASA) functionalized LSPR sensor also exhibits excellent selectivity to Pb(II) when compared that with other common metallic ions such as Cu(II) and Fe(III) which are usually found in drinking water, as shown in Fig. 2a. The WHO limit for Cu(II) is 2 ppm, but there was no limit for Fe(III) [3]. The copolymer has the best response toward 10 ppb Pb(II) with 0.47 radian, and comparatively weaker responses of 0.042 radian and 0.020 radian toward 40 ppm Fe(III) and 200 ppm Cu(II), respectively. It is noted that the concentrations of Cu(II) and Fe(III) ions were exaggerated to show that the sensor is specific to Pb(II) ions. The similar phase response (0.46 radian) obtained for Pb(II)-Cu(II)-Fe(III) coexist solution also demonstrates its robustness for Pb(II) detection in drinking water. Fig. 2a also shows a phase drop of the co-exist solution after 700 s. This is due to the nonspecific binding of the coexisted ions being removed by rinsing with deionized so that the final phase reading is the about the same as Pb(II) solution alone. The selectivity of the LSPR sensor is further illustrated in the bar chart of Fig. 2b.

![Fig. 2](image2.png)

**Fig. 2.** (a) Phase sensorogram of 10 ppb lead ions, 200 ppm copper ions, 40 ppm iron ions and co-exist solution; (b) is the selectivity of the mPD-co-ASA receptor to 10 ppb Pb(II) in comparison to other metallic ions of various concentrations.
4. Conclusions

In comparison with other Pb(II) detection systems, the present sensor is label-free, and has better selectivity, sensitivity and cost-effectiveness for on site Pb(II) detection with minimum sample volume requirement. Its estimated LOD of 0.15 ppb (0.15 μg/L) is much better than the values of 62 ppb [7] and 58 ppb [13] with electrochemical methods, 0.62 ppb with colorimetric method [9]. Such LOD is even comparable with existing ICP-MS and HPLC standard practice. Thus, the present novel LSPR sensor is a strong candidate for cost effective, fast and ultrasensitive Pb(II) detection.

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