1. As one of the most hazardous heavy metal contaminant, lead ion can cause serious impact on human health and environment (1).

Kaur G , Singh H P , Batish D R , et al. Lead (Pb)-induced biochemical and ultrastructural changes in wheat (Triticum aestivum) roots[J]. Protoplasma, 2013, 250(1):53-62.

Exposure to lead ion mainly through contaminated water in the environment, leaded gasoline, coal combustion, ceramic production and so on.

Long F , Zhu A , Wang H . Optofluidics-based DNA structure-competitive aptasensor for rapid on-site detection of lead(II) in an aquatic environment[J]. Analytica Chimica Acta, 2014, 849:43-49.

It can accumulate in the body through skin absorption, digestive tract or food chain, leading to nerve disorder, memory decay, or anemia even at very low level exposure, particularly in children().

Kayhanian M . Trend and concentrations of legacy lead (Pb) in highway runoff[J]. Environmental Pollution, 2012, 160(none):169-177.

Wang F , Wu Z , Lu Y , et al. A label-free DNAzyme sensor for lead(II) detection by quantitative polymerase chain reaction[J]. Analytical Biochemistry, 2010, 405(2):168-173.  
The World Health Organization (WHO) regulate that the maximum acceptable concentration of lead ion in drinking water are 10μg/L.

Gupta V K , Rastogi A . Biosorption of lead from aqueous solutions by green algae Spirogyra species: Kinetics and equilibrium studies[J]. Journal of Hazardous Materials, 2008, 152(1):407-414.

Thus, the construction of simple, sensitive and rapid methods for the detection lead ion is of great value.

There are many methods to analyze lead ion, such as atomic absorption spectrometry (AAS),

Ghaedi M , Ahmadi F , Soylak M . Simultaneous Preconcentration of Copper, Nickel, Cobalt and Lead Ions Prior to Their Flame Atomic Absorption Spectrometric Determination[J]. Ann Chim, 2007, 142(1):272-278.

inductive coupled plasma atomic emission spectrometry (ICP-AES)

He Q , Chang X , Huang X , et al. Determination of trace elements in food samples by ICP-AES after preconcentration withp-toluenesulfonylamide immobilized on silica gel and nanometer SiO2[J]. Microchimica Acta, 2008, 160(1-2):147-152.

and inductively coupled plasma mass spectrometry (ICP-MS)

Vojtěch Ettler, Mihaljevi? M , Michael Komárek. ICP-MS measurements of lead isotopic ratios in soils heavily contaminated by lead smelting: tracing the sources of pollution[J]. Analytical and Bioanalytical Chemistry, 2004, 378(2):311-317.

have been reported for detection of lead ion.

Although these conventional analytical methods are highly sensitive and accurate, they are labor-intensive, time-consuming, expensive equipment, which restrict their wide applications.

Conversely, electrochemical sensor has been widely utilized in detection of lead ion owing to simple instrument, high selectivity, fast detection and low cost.

Long F , Zhu A , Wang H . Optofluidics-based DNA structure-competitive aptasensor for rapid on-site detection of lead(II) in an aquatic environment[J]. Analytica Chimica Acta, 2014, 849:43-49.

2. Aptamer, an artificial synthetic single-stranded DNA or RNA oligonucleotides, is selected in vitro through a SELEX (systematic evolution of ligands by exponential enrichment).

Zhang Z Z , Zhang C Y . Highly Sensitive Detection of Protein with Aptamer-Based Target-Triggering Two-Stage Amplification[J]. Analytical Chemistry, 2012, 84(3):1623-1629.

Due to binding stability to targets, it has been employed in biosensors to analyze small molecules, heavy metal, proteins or cells.

1. Cao X , Xu J , Xia J , et al. An electrochemical aptasensor based on the conversion of liquid-phase colorimetric assay into electrochemical analysis for sensitive detection of lysozyme[J]. Sensors and Actuators B: Chemical, 2017:S0925400517316830.

2. Lv Y, Yang L, Mao X, et al. Electrochemical detection of glutathione based on Hg 2+ -mediated strand displacement reaction strategy[J]. Biosensors & Bioelectronics, 2016, 85:664-668.

3. Yu H , Han J , An S , et al. Ce(III, IV)-MOF electrocatalyst as signal-amplifying tag for sensitive electrochemical aptasensing[J]. Biosensors & Bioelectronics, 2018, 109.

4. Kara P , Erzurumlu Y , Kirmizibayrak P B , et al. Electrochemical aptasensor design for label free cytosensing of human non-small cell lung cancer[J]. Journal of Electroanalytical Chemistry, 2016:S157266571630296X.

There are different specific aptamers can be used in lead ion aptasensor design.

Zahra K , Reza H M , Asma V , et al. Simultaneous detection and determination of mercury (II) and lead (II) ions through the achievement of novel functional nucleic acid-based biosensors[J]. Biosensors and Bioelectronics, 2018, 116:130-147.

Because all of lead ion aptamer contain lots of guanines, they can product stable G-quadruplex structure when the presence of lead ion.

Li T , Dong S , Wang E . A Lead(II)-Driven DNA Molecular Device for Turn-On Fluorescence Detection of Lead(II) Ion with High Selectivity and Sensitivity[J]. Journal of the American Chemical Society, 2010, 132(38):13156-13157.

Based on this unique property, many electrochemical sensors were fabricated for ultrasensitive detection of lead ion.

Taghdisi S M , Danesh N M , Lavaee P , et al. An electrochemical aptasensor based on gold nanoparticles, thionine and hairpin structure of complementary strand of aptamer for ultrasensitive detection of lead[J]. Sensors and Actuators B: Chemical, 2016:S0925400516306852.

Gao F , Gao C , He S , et al. Label-free electrochemical lead (II) aptasensor using thionine as the signaling molecule and graphene as signal-enhancing platform[J]. Biosensors & Bioelectronics, 2016, 81:15-22.

（DNA传感器到DNAzyme，到适体）

3. Recently, catalytic hairpin assembly (CHA) as an enzyme-free signal and isothermal nucleic acid amplification strategy have been broadly applied to detection of RNA or DNA in electrochemical sensing platforms, but it has been rarely seen in the detection of heavy metal.   
Cai W , Xie S , Tang Y , et al. A label-free electrochemical biosensor for microRNA detection based on catalytic hairpin assembly and in situ formation of molybdophosphate[J]. Talanta, 2016:S0039914016308426.

Shuai H L , Huang K J , Xing L L , et al. Ultrasensitive electrochemical sensing platform for microRNA based on tungsten oxide-graphene composites coupling with catalyzed hairpin assembly target recycling and enzyme signal amplification[J]. Biosensors and Bioelectronics, 2016, 86:337-345.

加一个DNAzyme 检测铅

材料介绍

Pt nanomaterials have unique properties such as large surface, excellent biocompatibility, good redox activity and excellent ability to catalyze H2O2. But it will aggregate, resulting in a gradual decrease in catalytic activity.

Porous carbon supported platinum ( Pt -CS)

5. In this work, a novel electrochemical sensor based on catalytic hairpin assembly (CHA) has been developed to detect lead ion. We select T30695 aptamer as lead ion specific aptamer.

As shown in Scheme 1, the signal amplification strategy was conducted as follows: firstly, in the presence of lead ion, lead ion aptamer was transformed stable G-quadruplex structure with lead ion, leading to the release of cDNA. Then, the released cDNA opened and hybridized with thiol-modified hairpin probes (HP1) that were immobilized on the Au electrode. After another hairpin probes (bio-HP2) was added electrode, cDNA liberated from HP1 for the next cycle process and HP1/bio-HP2 duplex structure are formed. When the cyclic process completed, there are a large number of capture probe (HP1/bio-HP2) left on the electrode. Finally, amounts of PtNPs@CS-SA by the specific recognition between HP2 modified biotin and streptavidin (SA) were immobilized on the electrode. Thus, a significantly amplified current is obtained.

CHA

Recently, catalytic hairpin assembly (CHA) as an enzyme-free signal and isothermal nucleic acid amplification strategy have been broadly applied to detection of RNA or DNA in electrochemical sensing platforms, but it has been rarely seen in the detection of heavy metal.

1. CHA not only overcomes the disadvantage of enzymatic amplification, such as complex operations, specific reaction conditions, and reaction-time dependent enzymatic activity，but exhibits the high sensitivity, simplifies the reaction conditions and reduces the experimental costs.

Liu J , Zhang Y , Zhao Q , et al. Bifunctional aptamer-mediated catalytic hairpin assembly for the sensitive and homogenous detection of rare cancer cells.[J]. Analytica Chimica Acta, 2018, 1029:58.

Zhang H , Wang K , Bu S , et al. Colorimetric detection of microRNA based on DNAzyme and nuclease-assisted catalytic hairpin assembly signal amplification[J]. Mol Cell Probes, 2018. 比色，CHA

3. Hundred-fold catalytic amplification can be achieved by CHA reactions. CHA is powerful for amplifying and transducing signals at the terminus of nucleic acid amplification reactions [10-12].

[10] S. Tang, Y. Gu, H. Lu, H. Dong, K. Zhang, W. Dai, X. Meng, F. Yang, X. Zhang, Highly-sensitive microRNA detection based on bio-bar-code assay and catalytic hairpin assembly two-stage amplification, Anal. Chim. Acta 1004 (2018) 1e9.

[11] Y.S. Jiang, B. Li, J.N. Milligan, S. Bhadra, A.D. Ellington, Real-time detection of isothermal amplification reactions with thermostable catalytic hairpin assembly, J. Am. Chem. Soc. 135 (2013) 7430e7433.

[12]P. Yin, H.M. Choi, C.R. Calvert, N.A. Pierce, Programming biomolecular selfassembly pathways, Nature 451 (2008) 318e322.

4. This overcomes the limitations of enzymatic amplification and the utilization of materials, such as complex operations, specific reaction conditions, and reaction-time dependent enzymatic activity.

However, most of these methods are confined to nucleic acid detection for the innate character of CHA is nucleic acid strand displacement.

1. Bifunctional aptamer-mediated catalytic hairpin assembly for the sensitive and homogenous detection of rare cancer cells CHA介绍，双功能，荧光

CHA is programmed with DNA self-assembly and disassembly reactions, the two hairpin structures can stably coexist without initiator presence. When a single strand DNA as initiator is added, the hairpin structure H1 is opened by base pairing with DNA. Then, due to the hairpin structure H2 has more complementary sequence with opened H1 compared to DNA, H1-H2 complexes are formed and the DNA is displaced participating in another assembly reaction. CHA not only overcomes the disadvantage of enzymatic amplification, but exhibits the high sensitivity, simplifies the reaction conditions and reduces the experimental costs.