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Nanomaterials-Based Electrochemical Sensors for Heavy Metal Ions Detection

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Abstract. The emission and accumulation of heavy metals have been damaging our living situation. The ultrasensitive detection for heavy metal ions is an important area as it can alarm for pollution to protect the environment and help individual health. Electrochemical sensors known as the potential detecting methods attract the researcher's attention and combined with nanomaterial constitute an active research area that could give opportunities for further development in heavy metal detection performance. To this end, this research gives a brief introduction to nanomaterials-based electrochemical sensors developed in recent years and focuses on the detection mechanism, advantages of using certain materials, the reason to achieve specific detection, and the electrochemical performances including their advantages and drawbacks. Whether individual detection of Hg(II), Pb(II), or the simultaneous detection of multiple heavy metals, all of those electrode systems show a bright future in actual environmental monitoring with high sensitivity, good repeatability and chemical stability.

Keywords: electrochemical sensors; heavy metal ions; nanomaterials; detection.

1. Introduction

Electrochemical sensors first discovered in the 1950s have quite a long developing history. Advantages like highly developed theory make it still an ideal analytical instrument in the present era. The main mechanism is converting the received signal from the analytes into an electronic one, which can be put out for further analysis. Compared with other traditional sensing technologies, electrochemical sensors have relatively higher selectivity to the analyte. Therefore, electrochemical sensing methods are used in a diverse of different applications such as harmful gas detection. To optimize the performance of electrochemical sensors, scientists tried many different materials to make improvements including nanomaterials. Since nanomaterials require that the size in at least one dimension must be 1-100 nm, they tend to have special physicochemical properties with a large surface area. In addition, a high electron transfer rate and excellent stability also make nanomaterials one of the most famous directions in the electrochemical sensors research field. Electrochemical sensors constructed of nanomaterials have huge amounts of applications in different areas including biotechnology (virus and bacteria detection), pharmacy industry (organic compound analysis), and environmental pollutants analysis like heavy metals detection.

With the development of industry and the high level of society's requirements, lots of pollutants are produced and released into the environment. As one of the major pollutants, heavy metals have caused serious effects on both the environment and human health. Heavy metals cannot be degraded through bacteria so an increasing amount will be left in the environment. This phenomenon will impact soil and water quality and further cause huge destruction in the ecosystem. The amounts of heavy metals can continuously accumulate in plants and animals which can eventually enter the food chain and end up going back to an individual's body. Heavy metals harm human health badly since they can cause poisoning and even worse make people have cancer. Thus, detecting and monitoring the heavy metals in the environment is important and has raised increasing attention. Traditional sensing methods are no longer suitable for current detection since they always have complex operations, require high cost and some of them may be easily influenced by another environment in the samples. Nowadays, society needs novel and convenient equipment with excellent properties like high sensitivity to catch up with the rapid development of techniques and get accurate results.

Using nanomaterials-based electrochemical sensors to detect heavy metals has an important implication and a promising future. Therefore, there are quite a large number of previous research focused on it. Various kinds of nanomaterials such as carbon nanomaterials and composite materials can be used in electrochemical sensing [1]. Carbon nanomaterials occupy a large amount in electrochemical sensing technology. The specific structure of graphene and carbon nanotube brings a relatively high surface area which provides a large combination with analytes. For instance, a well-organized idea of using single-walled carbon nanotubes to make a single-used electrochemical sensor was achieved, and this detector can strip and analyze lead ions [2]. Instead of carbon nanomaterials, composite nanomaterials also play an important role in electrochemical sensor detection. By using MoS_2, a new nanocomposite material has been used for detection of Hg (II) in samples with significant selectivity [3]. Previous research also gives another way to monitor heavy metals in addition to direct detection. For example, if a compound has a special interaction with Hg (II), then it can be used in Hg (II) monitoring. Mao et al. built an electrochemical sensor using graphene oxide combined with cysteamine which has the mercapto group that can react with Hg (II) and make accurate detection [4]. From the previous studies, there are quite wide detecting types in the electrochemical sensing technology and each of them has special superiority. Therefore, this research mainly focuses on examples of single detection for Hg (II), Pb (II), and simultaneously for various heavy metal ions through using an electrochemical sensor built by nanomaterials.

2. Application of electrochemical sensors for detecting heavy metals

2.1. Single heavy metal ion detection

2.1.1. Hg (II) detection

Bismuth sulfide nanorods inlaid with palladium nanoparticles were used to prepare nanocomposite to design a new electrochemical sensor [5]. This electrochemical sensor has a simple structure and is easy to build. Bi_2S_3-based materials are excellent modified electrodes due to their catalytic proficiency, and palladium nanoparticles further improve that. In addition, the combination of Pd and Bi_2S_3 provides a rapid transfer rate of electrons, contributing to its electro-catalytic performance. The electrochemical sensor can selectively detect Hg (II) since the sulfur has a good affinity for Hg (II). Thus, the disturbance of other metal ions had no obvious current response in the detector. The high surface area and the synergistic effect of the nanocomposite electrodes made sensing Hg (II) more effective. The sensor also had good photoreduction activity under visible-light conditions. It also has a wide range for detection and a limit of detection (LOD) of 41.85 nM. The electrodes also have advantages in reusability and stability in the sample. This electrochemical sensor with a high recovery rate is successfully applied to monitor the amount of Hg (II) in sea, and river water samples and fish with different environments.

Introducing bismuth molybdate (BiM) into graphene (GR) can be used to prepare nanocomposite [6], as shown in Fig. 1. As one of the transition binary metal oxides, metal molybdates have excellent sensing properties and cycling stability. Since two-dimensional nanomaterials like GR provide high catalytic activity, the flexible electrode was structured by the combination of GR and BiM. This nanocomposite had high electrocatalytic performance including good conductivity and synergistic interfacial contact. In addition, for Hg (II) detection, the electrostatic interaction between them could significantly improve the electron transfer rate and the intrinsic activity. The BiM/GR nanocomposite created a huge amount of surface defects and active sites to increase its activity further and could avoid the agglomeration of the electrocatalyst. A stable matrix was formed by Hg (II) binding with BiM/GR nanocomposite through $\pi-\pi$ interaction to monitor mercury content. This electrochemical sensor has good recovery values, little current change in disturbance of other metal ions, and acceptable repeatability. The practical application of electrochemical sensors was achieved in some samples like corn and fish.

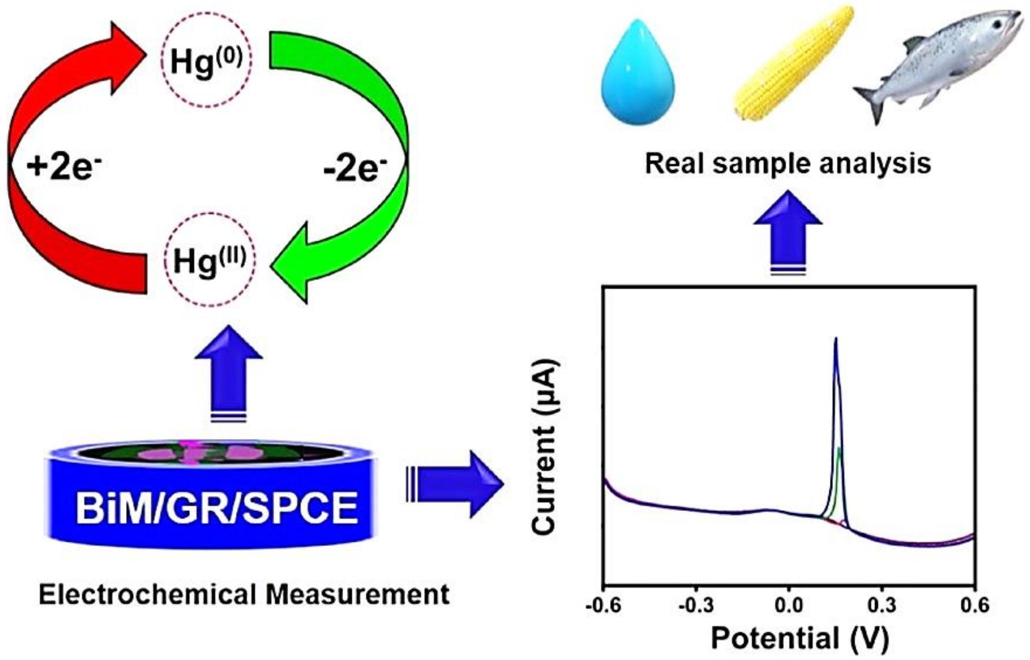

Fig. 1 Application of BiM/GR-based nanocomposite for electrochemical detection of Hg (II) [6].

There is another research on nanocomposite electrochemical sensors for Hg (II) detection. Single-walled carbon nanotubes and Sr-doped FeNi-S nanoparticles (Sr@FeNi-S/SWCNTs) were used to build a modified glassy carbon electrode [7]. Bimetallic sulfides have good electrochemical activity mixed with alkaline-earth metal strontium (Sr) could further develop its electrical conductivity. Meanwhile, electrocatalytic activity and stability are improved by adding single-walled carbon nanotubes. This design has lots of advantages like excellent durability, more active reaction sites, and a higher electron transfer rate due to synergetic effects. The kinetic charges transportation of nanocomposite is better than both Sr@FeNi-S and SWCNTs. The electrochemical sensor has good Hg (II) detecting performance with a wide linear range and LOD of 0.52 nM. Although other metal cations have small interference in Hg (II) monitoring, there is a drawback that nitro compounds with high concentrations largely decrease the current signal. However, not only the excellent repeatability and reproducibility but also the chemical stability of the sensor was successfully achieved in the practical lake and river water sample detection of Hg (II).

A three-dimensional sulfur-doped porous reduced graphene oxide (pS-rGO) electrochemical sensor was built [8]. The 3D porous structure and high doping degree made the large surface area of the nanostructured material which led to the higher capacitive property. Moreover, carbon-based materials like graphene oxide could provide suitable binding sites for Hg (II) detection. The soft-soft interaction made the sulfur-doped electrode have a significant affinity with Hg (II) and formed a monolayer coverage on pS-rGO. These two factors allowed the excellent uptake capacity of Hg (II). This electrochemical sensor showed a good selectivity to Hg (II) compared to the presence of other metal cations due to the strong binding interaction between the sulfur and Hg (II) on pS-rGO. It could absorb huge amounts of Hg (II) within a short time. The sensor has the advantage of long-term storage stability and is highly reproducible. The practical application using the pS-rGO packed column to detect Hg (II) of drinking water was achieved which proves the prospect of the pS-rGO electrochemical sensor.

In addition, an effective nanohybrid sensor for Hg (II) detection was proposed, where this work used cationic cyclodextrin carbon nanotubes (CNT-CDs) cast on the screen-printed carbon electrodes (SPCEs) and combined with ferrocenylcarnosine (FcCAR) [9]. This electrochemical sensor uses CNTs since the electrical conductivity and surface area of the electrode can be increased significantly.

CNTs with cationic β-cyclodextrins (CDs) showed a great recognition capability. CNT-CD layered on SPCEs could improve the current responses, electrocatalytic activity, and sensitivity for Hg (II) monitoring. FcCAR has a high affinity to Hg (II) which lets the modified electrode detect Hg (II) selectively with a large current signal. This senor shows a rapid response ability. SPCE/CNT-CD/FcCAR sensor has excellent electrochemical characterization for Hg (II) detection including a linear concentration range and a high sensitivity. After the experiment, this report pointed out that although the sensor has good reproducibility, there is an undesirable repeatability.

An aptasensor can be used to monitor Hg (II) [10]. In the Ag/Au core-shell structure, the use of Au nanoparticles (NPs) could provide covalent attachment support on the electrode surface and improve the stability of Ag NPs. Ag with high conductivity gives a high surface electron transfer rate and increases the detecting signal to make an electrochemical sensor having excellent electrocatalytic performance. Moreover, the aptamers modified by thiol have a strong interaction with Au and Ag NPs which helps the immobilization of aptamers on the electrode surface. While ZIF-8 as the substrate is easy to prepare and can increase surface area to load enough aptamers, it also can change the distribution and avoid the Ag/Au NPs agglomeration happening at the aptasensor surface to further improve the detection limit. The chemical stability of ZIF-8 leads to a potential application for Hg (II) detection in environmental analysis. This electrochemical sensor allows higher Hg (II) selectivity than other metal cations since the formation of a complex between Hg(II) and T-rich aptamers. It also shows advanced properties like high precision, repeatability, and stability in both tap water and wastewater detection. A result of a wide linear range and lower detection limit was reported after using two different monitor methods.

2.1.2. Pb (II) detection

Nanomaterials-based electrochemical sensor was built for Pb (II) detection. The researchers synthesized a nanocomposite sensor (GCE/ZnO-L-cys) by modifying a glass carbon electrode using L-cysteine which was fixed on the surface of ZnO nanofibers (ZnO_L-cys) [11]. ZnO was selected due to its excellent properties in both non-toxicity and stability. The ZnO nanofiber provided a porous structure leading to a larger specific surface area and making ion transference easier. L-cys, as a surface modifier, not only increased the active site and the detecting current signal for Pb (II) due to the high chelating capacity but also maintained the structure of the ZnO crystal. After the functionalization of L-cys, the electrochemical sensor shows good sensitivity and low LOD of about 0.397 μg/L in the linear range of 10–140 μg/L. Within an environment with interfering ions, the change of current signal can be ignored. Furthermore, the excellent stability, reproducibility, and repeatability make this electrode a bright prospect in real sample monitoring applications.

2.2. Simultaneous detection of multiple heavy metal ions

Some researchers achieved the detection of various heavy metal ions simultaneously. A potential nano-size material $ZnFeO_4$ was used to modify the glass carbon electrode as an electrochemical sensor (ZFO/GCE) for both Pb (II), Hg (II), and Cu (II) detection [12]. Researchers designed the small grain size ZFO material to increase the active sites and improve the contacting chance between nanoparticles and the electrode surface to achieve better detection performance. The large surface area leads to an excellent adsorption and desorption ability and a higher current value. The novel sensor has excellent electrochemical detecting properties in both individual and simultaneous monitoring. In single detection, the LOD of Hg (II), Pb (II), and Cu (II) with 1.61 nM, 7.38 nM, and 12.03 nM respectively. Hg (II) is more sensitive than others. The sensitivity of Cu (II) is improved while Hg (II) and Pb (II) are stable when simultaneous detection. Therefore, this electrode can detect Hg (II), Pb (II), and Cu (II) with low LOD and high sensitivity. This electrochemical sensor successfully achieved high repeatability, reproducibility, and chemical stability in actual water sample monitoring. What is more, the interfering ions have a negligible change in current indicating a good selectivity.

3. Conclusion

This research discusses the performance of electrochemical sensors constructed using different types of nanomaterials in detection of heavy metal ions. This research specifically discusses the detection effect of mercury and lead ions, and also analyzes the performance of electrochemical sensors for simultaneous detection of multiple heavy metal ions. In summary, this research aims to introduce how different sensors detect target heavy metal ions and show their excellent detecting properties in real sample detection such as high sensitivity. This research also analyzes the reasons behind the excellent performance of each electrochemical sensor in detecting heavy metal ions. Therefore, whether detecting heavy metal ions individually or simultaneously, using nanomaterials-based electrochemical sensors provides a promising and hopeful future in actual environmental analysis.

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