

Application of Nanopore and Porous Materials for Heavy Metal Ion Detection

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Abstract: Porous materials exhibit distinct advantages for heavy metal sensing after functionalization with corresponding ionosphere as compared to the direct utility of ionosphere in solution without porous materials substrate. In recent years, engineered protein nanopore and artificial nanopore emerged to be a promising platform to build sensors for analysis of metal ions. This article reviewed recent development and current status of detection of heavy metal ions using nanopore and porous materials. The emphasis was given to the mesoporous silica materials. Except silicate based porous materials which could be used for ionosphere embedment, there were several other kinds of porous materials including porous metallosupramolecular networks, porous metal oxide, porous carbon materials, porous polymer membrane and porous clays, which could also be employed to construct metal ion sensors. Finally, we discussed the contents and goal of further research in this field.

Key Words: Porous materials; Metal ion; Ion channel; Electrochemical approach; Optical approach

1 Introduction

At present, environmental pollution has been exacerbated because of the increasing usage of chemical pesticide, high level of industrialization and intense human activities. According to the survey of ministry of agriculture, around 64.8% of the sewage irrigation area of 1.4 million hectares suffers from heavy metal pollution, of which the light pollution area represents 46.7%, the moderate pollution represents 9.7% and the serious pollution represents 8.4%. Once being contaminated, recovery of the soil is highly challenging. These heavy metal ions are biological toxicity to living organisms and can be bioaccumulated through the food chain, which strongly threat human health. Therefore, it is significant to detect and come up with appropriate countermeasures and suggestions to prevent and relieve environmental pollution.

Porous materials include different inorganic and organic ones such as mesoporous silicate materials, porous

metallosupramolecular networks, porous metal oxide, porous carbon materials and porous polymer. Porous materials can be categorized into three types by their pore size: microporous (pore size < 2 nm), mesoporous (2 nm < pore size < 50 nm) and macroporous (pore size > 50 nm)^[1]. In the detection of metal ions, mesoporous materials are used as scaffolds for the modification of probe molecules that provide recognition and signal transduction. The pores can be used to immobilize optically active probe molecules. The specific surfaces can be used to provide sites for the adsorption and diffusion of targets and enhance the local concentration. Single nanopore materials include protein nanopore, glass nanopore and polymeric membrane. Single nanopore materials can be categorized into two types by their shape of nanopore: conically shaped nanochannels and cylindrical shaped nanochannels, which can be used to detect metal ions by resistive-pulse sensing and ion-current rectification.

Recently, nanopore and porous materials have attracted the most attention for the detection of heavy metal ions. The

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researchers have done a lot of work to improve sensitivity, selectivity, responsiveness and repeatability. Since the pore diameter of silicate based porous materials can be easily adjusted from 2 nm to 50 nm, fast responsive and high specificity toward metal ions can be achieved. In combination with electroanalytical methods or optical methods, various metal ions can be easily detected, such as Cd^{2+} , Hg^{2+} , Pb^{2+} , etc. The limit of detection (LOD) down to picomolar is achieved. Except silicate based porous materials, there are also several other kinds of porous materials that can be employed to construct metal ion sensors. This article reviewed the recent development and current status of detection of heavy metal ions using nanopore and porous materials.

2 Application of porous silicate materials for heavy metal ion detection

2.1 Synthesis of mesoporous silica

The synthesis of mesoporous silica requires silica precursors, acid or alkali, water and surfactant. At first, acid or alkali, surfactant and water were mixed together, and then silica precursors were added. After aging at room temperature or hydrothermal treatment, the sample was washed and filtered. At last, the mesoporous silica was obtained by subsequent removal of the surfactant by extraction or calcination.

Although the protocol for synthesis of mesoporous silica materials is similar, a slight change in the experimental conditions such as temperature, pH, silica precursors and surfactant, which lead to distinct morphologies and different pore sizes. Scientists at Mobil Oil Company^[2,3] synthesized mesoporous silica, known as M41S (Mobil Crystalline Material), which have high specific surface area (typically $1000 \text{ m}^2 \text{ g}^{-1}$) and pore sizes between 2 nm and 10 nm. The most well-known representatives of these materials are MCM-41, MCM-48 and MCM-50, which have 2D hexagonal, 3D cubic and lamellar mesostructures, respectively. Later on, Pinnavaia and his collaborators synthesized less-ordered Hexagonal Mesoporous Silica (HMS)^[4] and slightly higher ordered Michigan State University silica (MSU)^[5]. Zhao *et al.*^[6] achieved the synthesis of SBA-15 (Santa Barbara Amorphous silica) with even larger pores (up to 30 nm), which further expanded the applications of these materials. In 1999, Inagaki^[7], Stein^[8] and Ozin^[9] discovered periodic mesoporous organosilicas (PMOs), which led to a major breakthrough in materials science. El-Safty *et al.*^[10] synthesized highly ordered silica monoliths (HOM) by a lyotropic microemulsion of Brij 56 ($\text{C}_{16}\text{EO}_{10}$) as a template. This method was simple and versatile and HOM had a big pore size and good hydrothermal stability. The mesoporous materials with high surface area and open pore structure are widely used in the detection of heavy metal ions. Most efforts at metal ions sensing relied on either

optical or electrochemical sensing methods for detection.

2.2 Electrochemical sensing method

Stripping voltammetry (SV) is the most sensitive electroanalytical technique and widely used for determining heavy metal ions. The overall analysis involves a two-step procedure: preconcentration accumulation and voltammetry detection. In the first step, the working electrode is immersed in a solution of metal ions and then metal ions are accumulated onto the working electrode surface and reduced under an optimized voltage. In the second step, the potential is swept toward positive value to reoxidize the metal into metal ions and *i-E* voltammetry curves are recorded. Every peak current corresponds to a metal and the peak height is proportional to the concentration of the metal ion. There are a number of factors affecting the sensitivity and the detection limit of electrochemical sensors, for example functional method, synthesis method, working electrode, etc. In the past decade, many efforts were devoted into synthesizing mesoporous silica that was developed into miniaturized and portable sensors especially when in combination with electrochemical methods.

While unmodified silicate materials were directly used to accumulate metal ions through interactions with anionic silanol groups, the selectivity could not be warranted in this way. It is still highly desirable that surface functionalization is implemented to increase the selectivity of sensors. Two main approaches were developed to graft the functional groups onto the surface of silica: post-synthesis grafting method and co-condensation method. This conventional post-synthesis grafting method involved grafting a ligand onto the pore surface of the previously prepared mesoporous silica by single or multi step attachment. Hybrid mesoporous silica was also obtained directly in a “one-step” procedure by co-condensation and hydrolysis of organoalkoxysilanes with tetraalkoxysilanes in the presence of a structure-directing agent. Both these methods have advantages and disadvantages. Post-synthesis grafting method can protect the structure integrity and ordering of materials, but the content of functional groups is low. Co-condensation method overcomes the drawbacks and hybrid materials have higher density of functional groups. However, increasing too much the amount of organosilanes in the reaction mixture may greatly influence the level of mesoporous ordering and totally disordered the obtained materials.

Yantasee *et al.*^[11] developed metal ions sensors by assembling a composite of thiol-tagged monolayers on the mesoporous support (SH-SAMMSTM). In this method, the mesoporous silicate-functionalized electrode showed high loading capacity and stability and had the ability to be easily regenerated in acid solutions. For Cd^{2+} , Pb^{2+} and Cu^{2+} , SH-SAMMSTM showed dramatic selectivity in aqueous

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