

# 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)<sup>[1]</sup>. 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  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ , 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<sup>[2,3]</sup> 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)<sup>[4]</sup> and slightly higher ordered Michigan State University silica (MSU)<sup>[5]</sup>. Zhao *et al.*<sup>[6]</sup> 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<sup>[7]</sup>, Stein<sup>[8]</sup> and Ozin<sup>[9]</sup> discovered periodic mesoporous organosilicas (PMOs), which led to a major breakthrough in materials science. El-Safty *et al.*<sup>[10]</sup> 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 great influence the level of mesoporous ordering and totally disordered the obtained materials.

Yantasee *et al.*<sup>[11]</sup> developed metal ions sensors by assembling a composite of thiol-tagged monolayers on the mesoporous support (SH-SAMMS<sup>TM</sup>). 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  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , SH-SAMMS<sup>TM</sup> showed dramatic selectivity in aqueous

solutions. The results showed a good linear response over a range of concentrations from 0 to 10 ppb. Besides thiol functionalized mesoporous silica, 2-benzothiazolethiol functionalized mesoporous silica was also evaluated as a working electrode in the determination of  $\text{Cu}^{2+}$  ions with the limit of detection of 39 nM<sup>[12]</sup>.

Walcarius *et al.*<sup>[13]</sup> recently described the one-step generation of thiol modified silica thin films in the presence of the cetyltrimethylammonium (CTAB) surfactant on electrodes. The amount of surfactant (CTAB) was varied to optimize the pore sizes and improve the sensitivity and preconcentration properties of target metal ions. Many other factors affecting the detection of metal ions on the electrode surface included electrolysis potential, stripping solution composition and functional groups content. The LOD achieved was 6 nM for  $\text{Ag}^+$  under the optimized conditions. Mesoporous silica films functionalized with 5-mercapto-1-methyl-1H-tetrazole (MTTZ) groups were deposited in one step onto glassy carbon electrodes for selective detection of  $\text{Hg}^{2+}$ <sup>[14]</sup>. After template extraction, the film was highly porous and achieved effective  $\text{Hg}^{2+}$  accumulation at low pH value (pH 1). MTTZ content in the film had dramatic influence on the sensitivity of the electrode. The 10%-MTTZ film electrode was the best condition. After 20 min of accumulation time, the electrode response was linear in the nanomolar concentration range, with a detection limit of 2 nM.

Carbon paste electrodes (CPEs) are one of the most popular mercury-free electrodes and have widely applied in electrochemistry research. Mesoporous silica modified carbon paste electrodes (MCPEs) are often widely used in stripping voltammetry due to their advantages including low cost, ease of preparation, and easy to be regenerated. The experimental conditions play an important role in properties of heavy metal ion sensors, which are great influence the characteristics of mesoporous silica materials, such as particle size, morphology, surface area, pore diameter, etc.

Sierra *et al.*<sup>[15]</sup> synthesized four types of ordered mesoporous silicas with different surfactants, and incorporated these materials into carbon paste electrodes to obtain sensors for the determination of  $\text{Pb}^{2+}$  ions in aqueous. The CPE modified with silica, which had a pore diameter of 37 Å and pseudo-spherical morphology, exhibited the best reproducibility and sensitivity, a linear range between 1 and 30 ppb with a limit of detection of 0.8 ppb. The CPE modified with silica, which had a pore diameter of 58 Å and cylindrical morphology, exhibited the poorest reproducibility and sensitivity, a linear range between 5 and 100 ppb with a limit of detection of 2.6 ppb. It demonstrated that the characteristics of electrodes are greatly influenced by order/disorder structure, pore diameter and particle morphology.

Except that the property of surfactants plays a very important role in the synthesis of mesoporous silicas, different catalysts can lead to distinct morphology and pore sizes of silica

materials, which are highly critical to the sensitivity and selectivity of the sensors based on mesoporous silica. In the presence of  $\text{NH}_3$  catalyst, the mesostructured silica materials were spherical and showed excellent sensing efficiency. By comparison, in the presence of HCl or NaOH catalyst, the mesostructured silica materials were non-spherical and gave rise to lower sensitivity<sup>[16]</sup>. Huang *et al.*<sup>[17]</sup> synthesized a multifunctional microsphere with a mesoporous silica shell and a magnetic core ( $\text{Fe}_3\text{O}_4$ ). The  $\gamma\text{-AlOOH@SiO}_2/\text{Fe}_3\text{O}_4$  electrode was utilized for the detection of various concentrations of each metal ion in the presence of the other metal ions.

SBA-15 modified with functional groups was used to prepare carbon paste electrodes with high selectivity. SBA-15 functionalized with phenylthiourea was used to prepare an MCPE for determination of  $\text{Ag}^+$  and the factors affecting the performance of the electrode were studied. Higher concentrations of modified silica showed a decrease in the peak current due to the reduction of conductive area at the electrode surface. The optimum condition was 10% modified silica in the paste.  $\text{Ag}^+$  could be sensitively determined with an LOD of 5 pM<sup>[18]</sup>. Similarly, SBA-15 functionalized with cyclam derivatives was incorporated into carbon paste electrodes and used for the determination of  $\text{Cu}^{2+}$  with a limit of 0.05  $\mu\text{g L}^{-1}$ <sup>[19]</sup>. Figure 1 illustrates the overall uptake/release process involves Cu(II) binding to cyclam-functionalized materials. The selective and sensitive detection of  $\text{Cu}^{2+}$  was due to the attractive binding properties of these macrocyclic ligands. Ionic liquid could also be immobilized on the surface of ordered mesoporous silica<sup>[20]</sup>. The electron transfer ability of the electrode was improved because of the high surface area of the SBA-15. The poor conductivity of silica decreased the sensitivity of the determination. However, this shortcoming was offset by ionic liquid. This sensor was used to simultaneous determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ . Under the optimized conditions, the detection limits for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  were 80, 40, 60 and 10 nM, respectively.

Besides SBA-15, carbon paste electrodes were also modified with MCM-41<sup>[21,22]</sup>, HMS<sup>[23,24]</sup> and MSU<sup>[25]</sup>. Yantasee *et al.* developed a novel sensor for simultaneous detection of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by anodic stripping voltammetry. This carbon paste electrode was modified with carbamoyl phosphonic acid (acetamide phosphonic acid) self-assembled on MCM-41. The surface area and the narrow pore size of MCM-41 were 989  $\text{m}^2 \text{g}^{-1}$  and 5.0 nm. The silica showed the open-parallel mesopores that made easy to access metal ions. The detection limits were 10 ppb after a 2-min preconcentration period and improved to 0.5 ppb after a 20-min preconcentration period<sup>[21]</sup>.

Most recently, the research on the modification of screen-printed working electrodes (SPCEs) with mesoporous silica materials has made significant progress. Lin *et al.*<sup>[26]</sup> achieved voltammetric analysis of  $\text{Eu}^{3+}$  at screen-printed electrodes

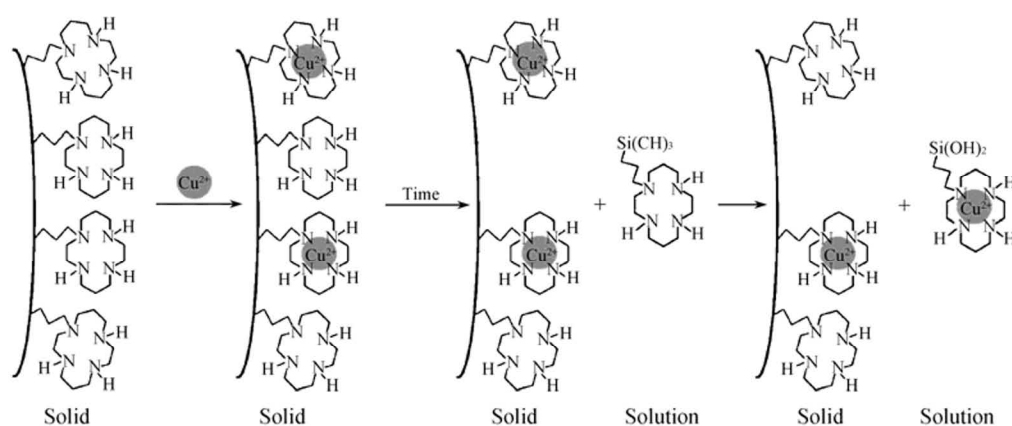


Fig.1 Illustration of Cu (II) binding to cyclam-mono-grafted silica and subsequent evolution while aging<sup>[19]</sup>

modified with salicylamide self-assembled on mesoporous silica (MCM-41). The experimental detection limit was 10 ppb after 10 min preconcentration. In comparison with carbon paste electrodes, screen-printed working electrodes were simple, low cost and easy to establish the calibration curve. To detect lanthanide, other ligands were also used, such as acetamide, phosphonate, propionamide phosphate, glycyl urea and hydroxypyridonates. Screen-printed electrodes modified with acetamide phosphonic acid self-assembled monolayer on mesoporous silica (Ac-Phos SAMMS) were used for the detection of  $\text{Pb}^{2+}$  with the detection limit of 0.91 ppb<sup>[27]</sup>. The Ac-Phos SAMMS showed high affinity for  $\text{Pb}^{2+}$  with the descending order of affinity of metal ions as  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Ca}^{2+} > \text{Na}^+$ . The advantages of screen-printed electrochemical sensors for heavy metal ions determination were miniaturization and hand-held field analyzers. A screen-printed working electrode modified with functionalized mesoporous silica nanoparticles (MTTZ-MSU-2) was used for the detection of  $\text{Pb}^{2+}$  ions. This work was extended to analyze the real samples by applying SPCEs to real natural water samples. This electrode showed a LOD of  $0.1 \mu\text{g L}^{-1}$  after 5 min of preconcentration time<sup>[28]</sup>.

### 2.3 Optical sensing method

The second popular method is based on the combination of mesoporous silica materials and spectrometric methods which normally involve absorbance or fluorescence measurement. The unique feature of this approach lies in that color change due to the interaction between porous silicate and target metal ion, it can be easily observed by naked eyes, which is very useful for field application. There are several factors that may influence the quality of sensors, which are summarized as following: (1) the different mesostructure and pore diameters of the mesoporous silica; (2) the flexibility and conformation of a dye molecule in a pore; (3) the experimental conditions, cation and other interference factors.

Many types of mesoporous silicas, such as SBA-15<sup>[29–43]</sup>,

MCM-41<sup>[44–47]</sup>, MCM-48<sup>[48,49]</sup>, HMS<sup>[50–53]</sup> and PMOs<sup>[54,55]</sup>, were used as solid supports for immobilizing the dye. Mesoporous aluminosilica materials were also used as carriers for designing optical metal ions sensors<sup>[56–59]</sup>. Silica monoliths with ordered or disordered mesostructures (HOM type)<sup>[37,60–68]</sup> were prepared by using a simple and fast method by using Brij 76 ( $\text{C}_{18}\text{EO}_{10}$ ) as templates. HOM materials have a very robust, open, tunable structure and large cage channel that can show fascinating properties in the visual detection of metal ions.

The most frequently reported such silica is SBA-15 which has a 2D hexagonal arrangement of the mesopores and well-controlled particle size (5–30 nm). SBA-15 was widely used in catalysis, separation and sensors. Azobenzene-coupled acyclic receptor functionalized SBA-15 recognized  $\text{Hg}^{2+}$  by color change from light yellow to red. The sensor was fully reversible by the addition of EDTA (Ethylene Diamine Tetraacetic Acid)<sup>[29]</sup>. SBA-15 functionalized with other more ligands was extensively used to detect  $\text{Hg}^{2+}$ <sup>[30–36]</sup>. Similarly, SBA-15 modified with a variety of functional groups was also prepared to detect a wide range of heavy metal ions, for example,  $\text{Sb}^{3+}$ <sup>[37]</sup>,  $\text{Zn}^{2+}$ <sup>[38]</sup>,  $\text{Cu}^{2+}$ <sup>[39]</sup>,  $\text{Pb}^{2+}$ <sup>[40]</sup>,  $\text{Cr}^{3+}$ <sup>[41]</sup> and  $\text{Fe}^{3+}$ <sup>[42,43]</sup>.

Mobil Oil Company synthesized highly ordered mesoporous silica, known as M41S silica. MCM-41 has a hexagonal arrangement of the mesopores and pore diameters from 2 nm to 10 nm. MCM-48 has a cubic arrangement of the mesopores and pore diameters from 1.5 nm to 20 nm. However, only limited examples of both these materials have been reported to detect  $\text{Zn}^{2+}$ <sup>[44,45]</sup>,  $\text{Hg}^{2+}$ <sup>[46,47]</sup> and  $\text{Cu}^{2+}$ <sup>[48,49]</sup>, mainly because the pore diameters of two materials are smaller than that of SBA-15, the flexibility or freedom of functional molecules in nanopore is limited.

Hexagonal mesoporous silica (HMS) was synthesized by using a long-chain as the template at ambient temperature. Compared with MCM-41 and SBA-15, HMS has less ordered structure. HMS-based optical sensors were successfully used for detecting  $\text{Hg}^{2+}$ <sup>[50, 51]</sup> and  $\text{Cu}^{2+}$ <sup>[52, 53]</sup>. Silica nanoparticles modified with DNA were used for the detection of  $\text{Hg}^{2+}$ . This

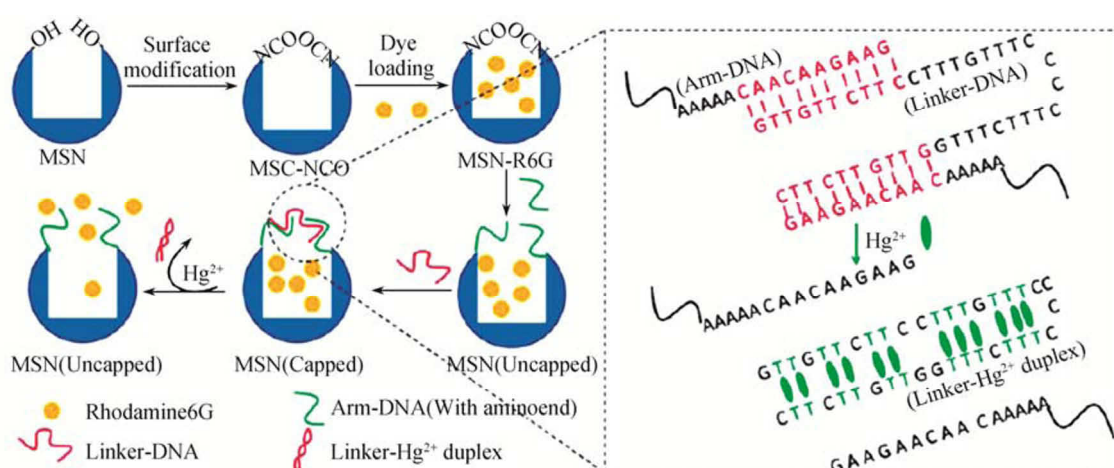


Fig.2 (A) Schematic representation of synthesis, surface modification, dye loading, and DNA binding of the MSN (mesoporous silica nanoparticles), as well as the release of dye from MSN in the presence of mercuric ion. (B) Hybridization of the arm-DNA and linker-DNA in the absence and presence of mercuric ion<sup>[51]</sup>

method was rapid, sensitive, and selective. In the presence of Hg<sup>2+</sup><sup>[51]</sup>, one DNA strand with higher affinity to Hg<sup>2+</sup> was dehybridized from the other two strands to open the pore and release dye (Fig.2). Mesoporous silica nanoparticles based sensor was also applied to monitor Cu<sup>2+</sup> in living cells<sup>[53]</sup>.

The functionalization of mesoporous materials mainly depends on the covalent modification to modify small molecules of dyestuff combined with heavy metal ion with high selectivity on the inner surface of mesoporous materials. This method was used widely, but the modification of functional groups was mainly dependent on the size of pore diameter and the physical and chemical properties of inside surface. The discovery of PMOs accelerated the chemical sensing process. Compared with mesoporous materials, PMOs showed more intense photoabsorption and stronger fluorescence intensity. Rhodamine-6G Schiff-base bridged periodic mesoporous organosilicas (RSPMOs) were successfully synthesized by using the ionic liquid 1-hexadecyl-3-methylimidazolium bromide (C<sub>16</sub>mimBr) as a structure-directing agent. The sensor was used for the highly sensitive and selective determination of Cu<sup>2+</sup> in real sample<sup>[54]</sup> and Zn<sup>2+</sup><sup>[55]</sup>.

The incorporation of aluminum into the silica framework was reported to increase the thermal stability and impose more acidic sites for mesoporous silicas<sup>[56]</sup>. These aluminosilica materials were reported to detect Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup> and Pb<sup>2+</sup><sup>[56–59]</sup>. El-Safty *et al.*<sup>[58]</sup> designed an optical chemical sensor for simple, fast detection and removal of toxic Cr<sup>3+</sup> ions. Mesoporous aluminosilica monoliths enhanced sensing characteristics in terms of sensitivity, selectivity, and response time due to their unique morphologies, active surface sites, and physical properties.

Among the nanosensors developed here, the large pore surface of highly ordered monoliths (HOM) exhibited

considerable structural stability against longer hydrothermal treatment times and higher thermal temperature. In recent years, some nanostructure composite silica monoliths, such as HOM-11<sup>[60,61]</sup>, HOM-9<sup>[62–65]</sup>, HOM-2<sup>[37,63,66]</sup>, HOM-10<sup>[64]</sup>, HOM-C10<sup>[67,68]</sup> and HOM-13<sup>[62,64]</sup>, were used to detect heavy metal ions (e.g. Sb<sup>3+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, Pd<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Bi<sup>3+</sup>, Cu<sup>2+</sup>, etc.).

The monoliths with open-pore structure, high surface area and high pore volume might enhance the fast distribution of the metal ions onto pore surfaces, leading to high sensitivity of metal ion sensors. El-Safty *et al.*<sup>[63]</sup> reported that HOM-2 and HOM-9 sensors had higher sensitivity and regeneracy than that of SBA-15 powder sensors. The response time of 3D monoliths was shorter than that of 2D monoliths (Fig.3).

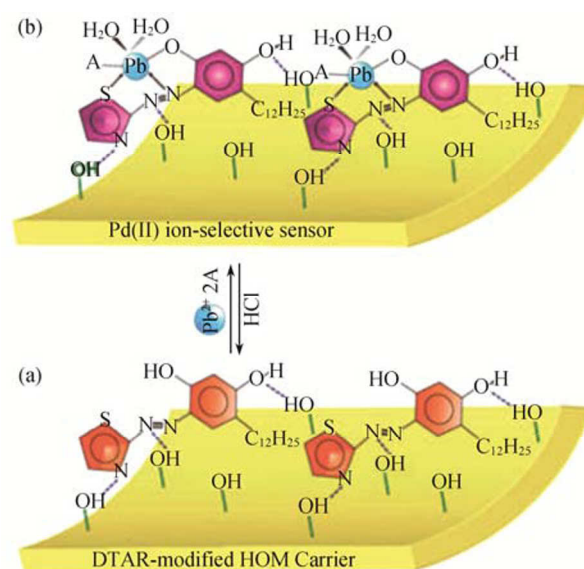


Fig.3 Mechanism of probe with possible interactions into HOM (highly ordered mesoporous)<sup>[63]</sup>

A research reported by the same group showed that an extreme selectivity of nanoscale membrane strips toward detection of  $\text{Hg}^{2+}$ <sup>[61]</sup>. When a series of metal ions and anionic interferences were added to the membrane sensors, the strips showed no significant changes in the colorimetric spectra and visible color patterns. The stability of the sensor allowed for stable detection without any structural damage, even after several numbers of repeated cycles. The strips were easily portable and storable, which were well suited to on-site areas and to in-situ field analyses.

### 3 Application of artificial ion channel for heavy metal ion detection

Stochastic sensing via nanopore showed that divalent metal ions such as  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  could be identified using a mutant  $\alpha$ -hemolysin ( $\alpha$ HL) pore containing histidine residues<sup>[69]</sup>. However, too much hypothesis and inaccuracy existing in the data processing and analysis impede the further development. Nevertheless, this work is an important milestone in the development of metal ion sensors. Wen *et al*<sup>[70]</sup> reported a highly sensitive and selective detection method for  $\text{Hg}^{2+}$  with  $\alpha$ HL-based single-channel recording in the presence of designed DNA oligomers. The results are shown in Fig.4. Both these methods above used resistive-pulse sensing to detect metal ions.

Ion current rectification is another approach to report the changes in surface charge when the dimensions of nanopore are comparable to the Debye length. The accumulation and depletion of metal ions in the nanopore can be reflected by the changes in current-versus-voltage curve. Imidazole-modified nanopipettes were used to detect  $\text{Co}^{2+}$ <sup>[71]</sup>; protein-modified nanopipettes were also used to detect  $\text{Ca}^{2+}$ <sup>[72]</sup>; polyelectrolyte- functionalized nanopores were used to detect  $\text{Cu}^{2+}$ <sup>[73]</sup>. The mechanism of these methods was that the interactions between probe and inside wall of the nanochannel and their binding affinities were derived from Langmuir absorption model<sup>[74,75]</sup>.

Synthetic nanochannels embedded in polymer membrane have attracted great attention due to their easy functionalization and facile fabrication. Han *et al* prepared conically shaped nanochannel by embedding in polyethylene terephthalate (PET) membrane. At the neutral pH value, the channel walls were negatively charged due to the presence of inherent ionized carboxyl groups ( $\text{COO}^-$ ), which, in combination with the conical shape of the channel, led to ion- current rectification. 2,2'-Dipicolylamine (DPA)-modified PET membrane was applied to detect  $\text{Zn}^{2+}$ . This method could be extended to detect anions<sup>[76]</sup>. There is still a lot of space to develop in the detection of heavy metal ions based on single nanopore.

### 4 Application of other kinds of porous materials for heavy metal ion detection

There are several other kinds of porous materials including porous metallosupramolecular networks, porous metal oxide, porous carbon materials, porous polymer membrane and porous clays, which can also be employed to construct metal ion sensors. Hou *et al*<sup>[77]</sup> used porous coordination polymers to detect dangerous metal ions, such as  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Cu}^{2+}$ . The mechanisms of sensor were ion sorption and exchange, which occurred directly by suspending such frameworks in a solution containing metal salts. The polymers could be employed as a fluorescent chemosensor and an electrochemical probe for multi-ion detection. A significant characteristic of these frameworks is their large well defined pore size and pore shape. These features mean that these frameworks have dramatic applications in metal ions detection and hopefully remove heavy metals from the body. A specific color change in the crystals of a metal-organic framework in response to Pd species was reported by He *et al*<sup>[78]</sup>. Different contents of  $\text{Pb}^{2+}$  appeared different colors. This method was much cheaper and more convenient than previous instrumental methods. Simply placing the crystal into the metal ions solution was followed by the color change of the crystal for detection (Fig.5).

In comparison with the relatively flat surface of the carbon, the ordered mesoporous carbon has a very high surface area and conductive area. They have been widely used as working electrodes for detection of metal ions by electrochemical methods. For instance, anodic stripping voltammetry was used for the determination of  $\text{Pb}^{2+}$  at nmol levels<sup>[79]</sup> and porous clay modified carbon paste electrode was used for the sensitive and effective determination of  $\text{Pb}^{2+}$ <sup>[80]</sup>. The study on the determination of metal ions using porous metal oxide  $\text{MgO}$ <sup>[81]</sup>,  $\text{NiO}$ <sup>[82]</sup> and  $\text{Co}_3\text{O}_4$ <sup>[83]</sup> was also reported. Compared with these methods above, the porous polymers achieved better selectivity by ion-imprinting method<sup>[84,85]</sup>. In general, polymerization is carried out in the presence of a print ion, which forms a complex with the constituent monomers. After ion imprinting polymerization, the imprint metal ion is removed from the polymeric particles by leaching. The “imprinted sites” was leaved in the polymeric particles that were complementary in shape of the imprint metal ion. Such an imprinted polymeric material shows an affinity for the template ion over other structurally related compounds. This method can combine with quartz crystal microbalance (QCM)<sup>[86]</sup> and electrochemical method<sup>[87]</sup>.

## 5 Outlooks

Research into the synthesis and characterization of mesoporous materials were developed for almost twenty years, but the application of them for heavy metal ions detection was just begun in the late decade. Some promising porous materials could be reliably used as sorbents for the detection of various toxic metal ions from environmental waters due to

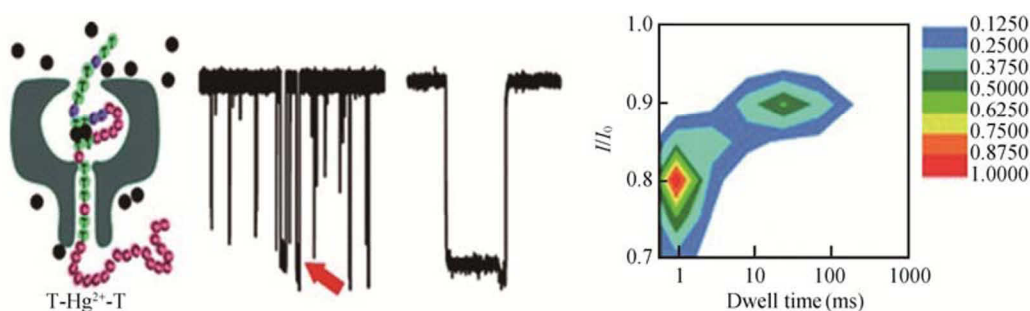


Fig.4 Representation of translocation of T-Hg<sup>2+</sup>-T containing DNA hairpin through a single  $\alpha$ HL ( $\alpha$ -hemolysin) nanopore<sup>[70]</sup>

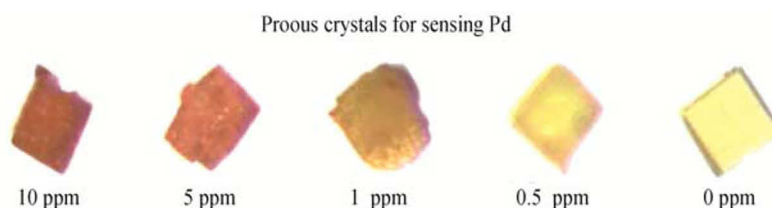


Fig.5 A highly specific, distinct color change in crystals of a metal-organic framework with pendant allyl thioether units in response to Pd species was discovered<sup>[78]</sup>

their unique characteristics, such as large surface area, ease of functionalization, high adsorption capacity, excellent mechanical resistance and excellent stability. Except porous materials, engineered protein nanopore and artificial nanopore emerged to be a promising platform to build sensors for the analysis of metal ions in recent years. Despite the great success in the detection of various metals ions by porous materials and single nanopore materials, there are also some problems in terms of sensitivity and selectivity, interference, recoverability, and long term stability.

In the future, several directions deserving more efforts are listed as followings: (1) synthesizing new dye which can specifically interact with metal ions; (2) designing integral system which can be used for on-site application. With the emergence of new technique and new materials, it is envisioned that the detection of metal ions by single nanopore and nanoporous metals will find value in commercial applications.

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