Analytica Chimica Acta 804 (2013) 240–245

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Metal–organic frameworks of zeolitic imidazolate framework-7 and zeolitic imidazolate framework-60 for fast mercury and methylmercury speciation analysis

Fujian Xu[a], Lu Kou[a], Jia Jia[b], Xiandeng Hou[a,b], Zhou Long[a,b,*], Shanling Wang[b,*]

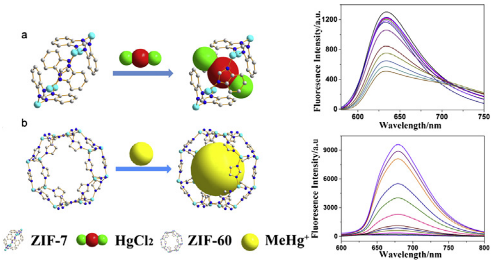
[a] College of Chemistry, Key Laboratory of Green Chemistry and Technology of MOE at Sichuan University, Chengdu, Sichuan 610064, China
[b] Analytical & Testing Centre, Sichuan University, Chengdu, Sichuan 610064, China

HIGHLIGHTS

- Speciation analysis of Hg with MOF as fluorescence sensing probe was firstly reported.
- The method was characterized with rapidness, high sensitivity and selectivity.
- The procedure for preparing small-sized MOF NPs was easy and fast.
- Good reproducibility (RSD ≤ 4.5%) and detection limit (≤6 ng mL^{-1}) were obtained.

GRAPHICAL ABSTRACT

Metal–organic frameworks employed as fluorescence sensing probe for fast, sensitive, reproducible and highly selective speciation analysis of Hg.



ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form
25 September 2013
Accepted 28 September 2013
Available online 12 October 2013

Keywords:
Fluorescence sensing
Metal–organic frameworks
Speciation analysis
Mercury
Methylmercury

ABSTRACT

A fluorescence sensing platform based on metal–organic frameworks (MOFs) nanoparticles (NPs) of both zeolitic imidazolate framework-7 (ZIF-7) and zeolitic imidazolate framework-60 (ZIF-60) was developed for speciation analysis of inorganic Hg [Hg(II)] and methylmercury (MeHg$^+$). Microwave-ultrasound assisted synthesis was employed for the preparation of ZIF-7 and ZIF-60 NPs, with short reaction time, easy procedure, and small particle size obtained. Based on strict cavity confinement of the ZIF-7 and ZIF-60 structures, the proposed method exhibited excellent selectivity for both Hg(II) and MeHg$^+$, even in the presence of the other Hg species or various cations or anions with the concentration of 50 times high. Effect of pH and ionic strength on sensing behaviour of the ZIF MOF was studied as well. The calculated detection limit is 3 ng mL^{-1} and 6 ng mL^{-1} for Hg(II) and MeHg$^+$, respectively. Furthermore, the application of the developed method to the analysis of local drinking water was demonstrated to be feasible, and the obtained recovery was 102% and 96.2% for Hg(II) and MeHg$^+$, respectively.

1. Introduction

The toxicological and biological effects and characters of mercury (Hg) species highly depend on their chemical forms [1]. For instance, organic forms of Hg, especially methylmercury (MeHg$^+$), have much higher toxicity than inorganic and elemental Hg, for its enhanced toxicity, bioaccumulation and volatility [2]. Moreover, inorganic mercury [Hg(II)] can be converted into MeHg$^+$ in the environment after a number of biological processes [3]. Hence, effective speciation analysis of Hg is more important than determination of total Hg, which has received much attention during recent years [4–6].

The most commonly used methods for Hg speciation analysis include atomic absorption spectroscopy (AAS) [4,7], atomic fluorescence spectrometry (AFS) [6,8], liquid chromatography (LC)

---

* Corresponding author.
E-mail address: longzhou@scu.edu.cn (Z. Long).

0003-2670/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.aca.2013.09.058

[9,10], gas chromatography (GC) [11,12], capillary electrophoresis (CE) [13–15], and inductively coupled plasma mass spectrometry (ICP-MS) [16,17]. Although these methods are powerful, either complicated pretreatment procedure or expensive instrumentation is needed, which makes it inconvenient for fast and facile determination of more than one Hg species.

Recently, because of high sensitivity and simple operation procedure, fluorescence (FL) sensors have become popular [18–23]. Nanoparticles (NPs) such as quantum dots (QDs) or Au NPs are usually employed as FL sensing probe due to their attractive characters including narrow emission bands, stability against photobleaching, high extinction coefficient, and broad absorption spectrum in a visible light [20,24–30]. NP-based FL sensing often follows the mechanism through FL signal changing (e.g. quenching) caused by interaction between target analytes and NPs. Especially for FL sensing of Hg species, Hg(II) has been the mostly concerned analyte and the NP-based probes were usually modified prior to sensing. For instance, Freeman et al. [31] modified QDs with thymine-rich nucleic acid and the FL quenching of QDs were caused by electron-transfer between QDs and the surface Hg(II)-thymine complexes. Yuan et al. [18] modified QDs with 2-hydroxyethyldithiocarbamate (HDTC) which dissociated from the QD surface upon exposure to Hg(II), leading to FL quenching.

During the past several years, metal–organic frameworks (MOFs) employed as FL sensing probe have become more attractive because of their unique properties compared with other NPs, such as high porosity, exceptional tunability, tremendous internal surface areas, structural diversity, and robust thermal stability [32–34]. Moreover, intrinsic topology, cavity confinement effect and conformational rigidity enable MOFs to have good size and shape selectivity for the sensing of specific analytes [35–39], even without extra modification or functionalization to accomplish selectivity like other NPs such as QDs or Au NPs. Up to now, various MOFs have been reported as FL sensing probes for specific target analytes such as NO_2^- [40], Hg(II) [41–43], Pd^{2+} [44], Fe^{3+} [45], Zn^{2+} [46], Ag^+ [47], and $MeHg^+$ [48]. However, all those reported methods involving MOF-based FL sensing focused on only one kind of analyte and no reports concerning Hg speciation analysis have been found to date. In this context, we herein reported a fast and facile method using MOF NPs of zeolitic imidazolate framework-7 (ZIF-7) and zeolitic imidazolate framework-60 (ZIF-60) for speciation analysis of Hg(II) and $MeHg^+$. ZIF-7 and ZIF-60 were synthesized using microwave-ultrasound assisted method, with short reaction time, easy procedure and small particle size obtained. Aqueous Hg(II) and $MeHg^+$ could be determined by using ZIF-7 and ZIF-60, respectively, in a fast, sensitive, reproducible and highly selective manner. Moreover, the developed method was further explored to real sample analysis, with good results obtained for the determination of both Hg(II) and $MeHg^+$ contained in local drinking water.

2. Experimental

2.1. Chemicals and reagents

All chemicals used in this work are AR grade or better. N,N-dimethylformamide (DMF), imidazole (IM), mercury dichloride ($HgCl_2$) and $ZnNO_3{\cdot}6H_2O$ were purchased from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). 2-methylimidazole (mIM) and benzimidazole (bIM) were purchased from Chengdu Juhui Chemical Technology Co. Ltd. (Chengdu, China). Methanol was purchased from Amethyst Chemicals (J&K Scientific, China). Standard solutions of $MeHg^+$ in methanol (76.6 ppm) were obtained from National Institute of Metrology China (Beijing, China). De-ionized water (18 MΩ-cm) used all through the experiments was obtained from a water purification system (PCWJ-10, Pure Technology Co. Ltd., Chengdu, China). The Hg(II) solutions were prepared by dissolving $HgCl_2$ in water. All standards and stock solutions were stored at 4 °C in a refrigerator until use.

2.2. Instrumentation

The Uwave-1000 microwave reactor (Sineo Microwave Chemistry Technology Co. Ltd., Shanghai, China) was used for synthesis of the ZIF MOF. The FL data were collected from an F-7000 FL spectrometer (Hitachi, Japan) using a 310 nm optical filter. The PXRD patterns were obtained with an X'Pert Pro MPD (Philips, the Netherlands) X-ray diffraction spectrometer using $Cu_{K\alpha}$ radiation. The scanning electron microscope (SEM) images were obtained from a JEOL JSM-7500F scanning electron microscope. FT-IR spectra were collected using a Nicolet IS10 FTIR spectrometer (Thermo Inc., USA). The concentration of Hg species was also determined with an inductively coupled plasma optical emission spectrometer (SPECTRO ARCOS, Germany) and an atomic fluorescence spectrometer (Model AFS-9600, Beijing Haiguang Instrument Co. Ltd., Beijing, China).

2.3. Synthesis of ZIF-7 and ZIF-60

For ZIF-7, $ZnNO_3{\cdot}6H_2O$ (0.11 g, 0.37 mmol) and bIM (0.06 g, 0.51 mmol) were dissolved in 50 mL of DMF and then stirred for 1 h. The obtained liquid was transferred into the microwave reactor and heated at 100 °C for 10 min. For ZIF-60, $ZnNO_3{\cdot}6H_2O$ (0.27 g, 0.91 mmol), IM (0.18 g, 2.65 mmol) and mIM (0.07 g, 0.85 mmol) were dissolved in 30 mL of DMF. The obtained liquid was stirred for 1 h then put in the microwave reactor and heated at 85 °C for 10 min. Subsequently, for both ZIF-7 and ZIF-60, the obtained suspension was centrifuged and the particles were collected from the bottom of the tube, which was then mixed with water under ultrasound for rinsing. The ultimately obtained particles were dried at 80 °C under vacuum until use. Characterization of the obtained ZIF particles was performed by comparing the FT-IR spectra of the particles with according precursors during the synthesis process.

2.4. Speciation analysis and interference studies

2.0 mg ZIF-7/ZIF-60 was added into 10 mL of water and then kept under ultrasound for 10 min, followed by a 15-min centrifugation at 8000 rpm. The supernatant was collected and aqueous Hg(II)/$MeHg^+$ was subsequently added into the collected suspension for FL measurement. For interference study, solution containing specific cation or anion was added into the aforementioned suspension, followed by the addition of aqueous Hg(II)/$MeHg^+$ and subsequent FL measurement. For the study of the effect of pH and ionic strength (IS), aqueous Hg(II)/$MeHg^+$ was added into the according ZIF suspension with varied pH or IS, followed by FL measurement.

3. Results and discussion

The size and shape of ZIF MOF particles were examined by SEM, and homogeneously sized ZIF-7 (Fig. 1a) and ZIF-60 (Fig. 1b) particles were observed. Moreover, the dominating peaks of the PXRD spectra of both ZIF-7 and ZIF-60 correlate with the previously reported (Fig. 1c and d) [49,50]. Moreover, the pore size of ZIF-7 and ZIF-6 NP was previously reported around 3 Å and 7 Å, respectively [51]. In order to further characterize the obtained MOF particles, according FT-IR spectra were collected. In Fig. 2, for bIM, IM and mIM used for the synthesis of ZIF-7 and ZIF-60, there is a sharp band around 3125 cm^{-1} due to C—H stretch, a weak band near 1820 cm^{-1}, as well as several strong and broad N-H bands between