Ultrasensitive determination of inorganic arsenic by hydride generation-atomic fluorescence spectrometry using Fe$_3$O$_4$@ZIF-8 nanoparticles for preconcentration

Zhirong Zou [a], Shanling Wang [a], Jia Jia [a], Fujian Xu [b], Zhou Long [a,*], Xiandeng Hou [a,b,**]

[a] Analytical & Testing Center, Sichuan University, Chengdu, Sichuan 610064, China
[b] College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

ABSTRACT

In this work, magnetic Fe$_3$O$_4$@ZIF-8 core-shell nanoparticles (MNPs) were employed for effective adsorption of inorganic arsenic for preconcentration, with adsorption mechanism thoroughly discussed. The adsorbed inorganic arsenic was easily separated by a magnet along with the MNPs from the sample matrix, with possible matrix interference eliminated. The MNPs were then completely dissolved in hydrochloric acid prior to the determination of inorganic arsenic by hydride generation-atomic fluorescence spectrometry. The Fe$_3$O$_4$@ZIF-8 MNPs were prepared with a facile step-by-step assembly method in aqueous solution at room temperature. Under the optimized conditions, the sensitivity for inorganic arsenic determination was significantly increased through preconcentration, with satisfactory analytical merits obtained.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

At present, arsenic contamination has become one of the most serious healthcare concerns all over the world [1–4]. Nowadays, intake arsenic through the food chain, especially the water system, could be morbigenous or even fatal as a carcinogen [4,5]. According to the regulations of the World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA), the upper-limit level of arsenic in drinking water is 10 µg/L [6–8]. Therefore, it is necessary to monitor and remove toxic arsenic species from the global environment and the food chain, especially inorganic arsenic which is much more toxic than organic arsenic ("arsenic" refers to "inorganic arsenic" all throughout this work unless specifically pointed out). Various techniques have been used for arsenic removal from water systems [6,9], and adsorption is considered to be one of the most effective approaches because of low cost and easy operation. Up to now, several kinds of nano-scale sorbents have been reported such as nanoparticles (NPs) of metal oxides [10–12], activated carbons [13] and other polymers [14,15].

Since the past decade, metal–organic frameworks (MOFs) have attracted significant research interest in the field of catalysis [16], separation [17], gas storage [18] and chemical sensors [19,20]. Moreover, rigorous topological structures and abundant internal cavities or channels

also make MOFs ideal sorbents with high surface area [21]. As far as arsenic adsorption is concerned, a few kinds of MOFs have been employed as effective sorbents [22–24]. For instance, zeolitic imidazolate framework-8 (ZIF-8), a member of a subclass (ZIF) of MOFs (structured with Zn^{2+} or Co^{2+} and imidazolate and its derivative [25]), has been selected as a good candidate recently [7,26]. Moreover, ZIF-8 has already demonstrated attractive characteristics including high surface area, permanent porosity, and good thermal and chemical stability [27], which make it a possibly ideal sorbent for arsenic.

Furthermore, it should be noted that intake arsenic could easily cause intracorporal accumulation, so it is important to monitor even the trace-level arsenic in real water samples, which could be accomplished by pre-concentration via adsorption prior to determination. At present, methods of analytical atomic spectrometry have turned out to be most popular for arsenic determination [28–30]. Of all, hydride generation-atomic fluorescence spectrometry (HG-AFS) has a fairly long usage history and is still in widespread use for the same purpose because of its cost-effective instrumentation, high sampling efficiency and sensitivity, and low matrix interference [31]. Moreover, the elution procedure for the adsorbed arsenic species prior to determination might be complicated or might bring in extra interference for the HG process, so avoidance of this procedure might provide a shortcut between preconcentration and HG-AFS determination. In the work presented herein, we employed a magnetic material, Fe$_3$O$_4$ which could be easily separated from water matrix by a magnet, to accomplish effective arsenic adsorption [32] together with ZIF-8 as a core-shell sorbent (Fe$_3$O$_4$@ZIF-8). The nano-hybrid magnetic nanoparticles (MNPs) were

* Corresponding author.
** Correspondence to: X. Hou, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China.
E-mail addresses: longzhou@scu.edu.cn (Z. Long), houxd@scu.edu.cn (X. Hou).

Table 1
Instrumental parameters for the HG-AFS.

Parameters	Values
High voltage of PMT (V)	−350
Atomizer observation height (mm)	8
Lamp current (mA)	60
Auxiliary current (mA)	30
Flow rate of the carrier gas (mL/min)	400
Flow rate of the shielding gas (mL/min)	1000

synthesized with a simple, fast and facile step-by-step assembly strategy in aqueous solution at room temperature. After arsenic adsorption and then separation from water by a magnet, the Fe_3O_4@ZIF-8 NPs were dissolved in hydrochloric acid, followed by arsenic determination by HG-AFS, with satisfactory analytical merits obtained.

2. Experimental

2.1. Instrumentation

The powder XRD (PXRD) patterns were obtained with an X'Pert Pro MPD (Philips, the Netherlands) X-ray diffraction spectrometer using $Cu_{k\alpha}$ radiation. The microscope images were collected with a JEOL JSM-7500F (JEOL, Tokyo, Japan) scanning electron microscope (SEM) and a Tecnai G2F20 S-TWIN (FEI Co., USA) transmission electron microscope (TEM), respectively. Elemental characterization of the prepared NPs was accomplished with an X-ray photoelectron spectrometer (XPS, AXIS Ultra DLD 800 X, Kratos, UK). FT-IR spectra were obtained from a Nicolet IS10 FTIR spectrometer (Thermo Inc., USA). A commercial double-channel HG-AFS system (Model AFS-2202, Beijing Haiguang Instrument Co., Beijing, China) was used for arsenic determination, and the system was described in detail in our previous work [33,34].
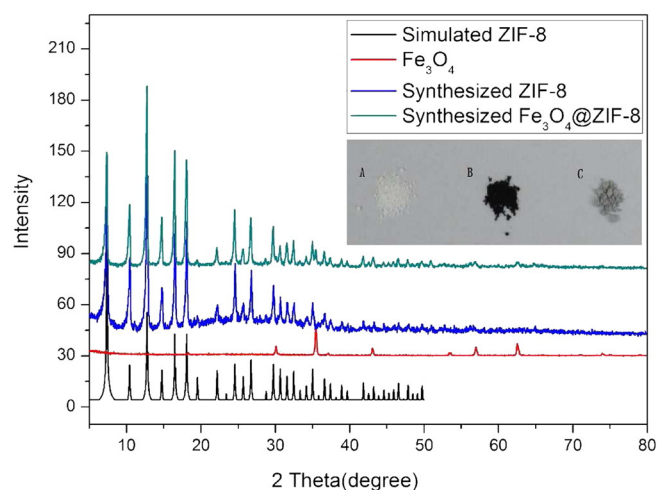
Fig. 2. PXRD spectra of Fe_3O_4, ZIF-8 and Fe_3O_4@ZIF-8. Inset pictures: NPs of ZIF-8 (A), Fe_3O_4 (B) and Fe_3O_4@ZIF-8 (C).

2.2. Materials and reagents

All reagents were analytical grade or better and were used without further purification. All used deionized water (DIW) of 18.2 MΩ-cm in conductivity was obtained from a water purification system (Chengdu Ultrapure Technology Co., LTD, China). The stock solution (1000 mg L^{-1} of arsenic) was purchased from the National Research Center of China (NRCC, Beijing, China), with further dilution to prepare other working solutions of As. L-ascorbic acid, thiourea, HCl, NaOH, KBH_4, 2-methylimidazole and triethylamine (TEA) were purchased from Kelong Chemical Reagents Co. (Chengdu, China). $Zn(NO_3)_2 \cdot 6H_2O$ was purchased from Sinopharm Chemical Reagent
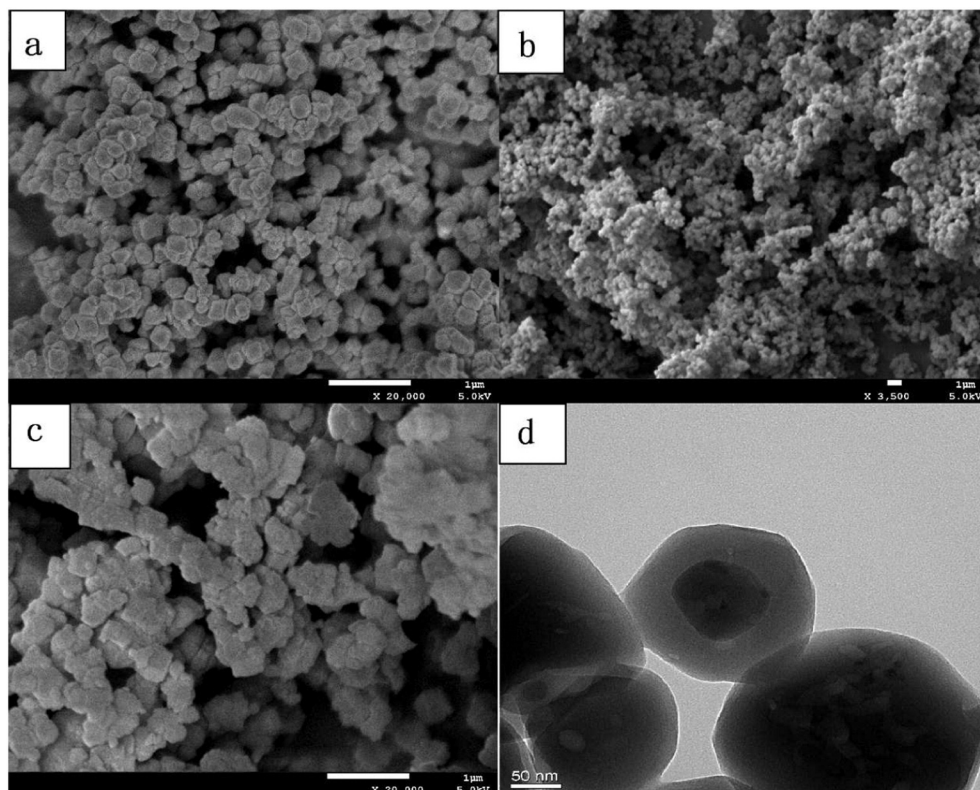
Fig. 1. SEM images of Fe_3O_4 (a) and Fe_3O_4@ZIF-8 (b, c), and TEM image of Fe_3O_4@ZIF-8 (d).