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ORIGINAL PAPER

Magnetic $ZnFe_2O_4$ nanotubes for dispersive micro solid-phase extraction of trace rare earth elements prior to their determination by ICP-MS

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Abstract

Magnetic $ZnFe_2O_4$ nanotubes (ZFONTs) with numerous pores on their walls were synthesized and characterized. They are shown to be a viable sorbent for dispersive micro-solid phase extraction of the trivalent ions of rare earth elements (REEs), specifically of lanthanum, praseodymium, europium, gadolinium, holmium and ytterbium. The specific surface area of ZFONTs is large (57 $m^2·g^{-1}$) and much bigger than that of $ZnFeO_4$ nanoparticles (16 $m^2·g^{-1}$). It is shown that REEs are quantitatively retained on ZFONTs in the pH range of 7.0–9.0. The separation of the sorbent from the aqueous phase was achieved by an external magnetic field. Following elution with 0.5 $mol·L^{-1}$ HNO_3, REEs were quantified by inductively coupled plasma mass spectrometry. The main parameters influencing preconcentration and determination of the REEs were studied. Under optimum conditions, detection limits for REEs range from 0.01 (Ho) to 0.75 (La) $pg·mL^{-1}$. Relative standard deviations are less than 6.5% (for $n = 9$; at 1.0 $ng·mL^{-1}$). The method was applied to the determination of trace REEs in spiked biological and environmental samples and gave satisfactory results.

Keywords Water samples · Tea leaves · Human hair · Magnetic separation · Scanning electron microscopy · X-ray diffractometer

Introduction

Owing to their unique characteristics, rare earth elements (REEs) have attracted considerable interest in high-technology fields, including electronics, superconductors, super-magnets, ceramics, catalysts and laser materials [1–3]. Moreover, because REEs can promote the growth of plants and animals, they are also widely used as feed additives and microelement fertilizer in agricultural production [4]. As a result, more and more REEs are spread in the environment, and may enter human bodies via food chain. It was reported that long-term intake of low dose REEs may result in the aberration of bone structure and tissue, and even bring about the generation of genetic toxicity in bone marrow cells [5]. REEs can invade the central nervous system because they are susceptible to cerebral cortex and cause subclinical damage [6]. Therefore, it is of great importance to develop new methods for the determination of trace/ultra-trace REEs in environmental and biological samples.

Various analytical techniques have been used for the determination of REEs in real samples, such as neutron activation analysis, X-ray fluorescence, isotopic dilution mass spectrometry, inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry (ICP-MS). Relatively, ICP-MS is the most favorable choice because of its advantages, including high sensitivity, wide linear range and multi-elemental detection capability. However, direct determination of REEs in environmental and biological samples by ICP-MS is sometimes restricted due to very low concentration of REEs and high contents of matrices. This is the reason why sample pretreatment techniques are often necessary prior to analysis [7, 8]. Among the preconcentration method, solid phase extraction (SPE) is a preferred procedure because of its advantages, such as simple operation, low cost, high enrichment factor

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and the ability to combine with other detection techniques [9–11]. However, this technique suffers from certain shortcomings, including solvent loss, large secondary wastes and a long procedure [12]. In addition, a liquid sample is passed through a column containing an adsorbent in conventional SPE. Small-size adsorbent such as nanoparticles can escape from SPE column, and can cause high pressure in SPE system.

In order to overcome the above-mentioned drawback of SPE, many researches have focused on developing simplified and miniaturized sample pretreatment methods. Among them, dispersive micro-solid phase extraction (DMSPE) has received an increasing attention. Compared with traditional SPE, DMSPE has many merits of reduced solvent consumption, less adsorbent usage, short extraction time and high extraction efficiency [13–15]. In DMSPE, physicochemical properties of sorbents are very important to achieve an accurate, sensitive and selective determination of analytes. Therefore, development of new adsorbent materials has become a focus of interests to analysts.

Due to their unique properties, nanomaterials are attracting more and more attention in analytical sciences [16–21]. Among them, magnetic nanoparticles have shown great potential as adsorbent because of their smaller particle size, large surface area, high adsorption activity and magnetic property. Some magnetic nanomaterials have been employed for the preconcentration and separation of inorganic and organic substances in DMSPE [22–27]. Magnetic $ZnFe_2O_4$ nanotubes (ZFONTs) not only possess tubular structure, but also exhibit many pores on their wall, which result in their larger specific surface area. These features reveal that ZFONTs maybe have a great analytical application as an adsorbent in DMSPE. To the best of our knowledge, however, study on this topic has received little attention so far.

In this work, ZFONTs were investigated as adsorbent for the first time in DMSPE for the preconcentration of REEs before their determination by ICP-MS. The experimental results showed that ZFONTs have a strong adsorption capacity for REEs due to their large specific surface area. DMSPE using ZFONTs coupled to ICP-MS provides the merits of high enrichment factor, large dynamic capacity, low detection limits. In addition, the separation of the sorbent containing target analytes from aqueous phase was achieved by an external magnetic field to avoid time consuming column passing or filtration/centrifugation process. The accuracy and applicability of this were validated by analyzing REEs in environmental water samples and two certified reference materials.

Experimental

Instrumentation

An X Series 7 ICP-MS system (Thermo Fisher Scientific, USA, www.thermofisher.com) with a Babington nebulizer was applied in this work. 1.0 $ng\cdot mL^{-1}$ ^{115}In was used as internal standard to compensate for signal error. The optimal conditions for ICP-MS are listed in Table S1. A pH meter with a combined electrode was used to control the pH values of solutions (Thermo Fisher Scientific, USA, www.thermofisher.com). The mixture was sonicated using a KQ-50E ultrasonic bath (Kunshan Ultrasonic Instrument Co., Ltd., Suzhou, China, www.kscsyq.com). A strong neodymium-iron-boron ($Nd_2Fe_{12}B$) magnet was used for phase separation. Sample digestion was performed by an Ethos T microwave digestion device (Milestone, Italy, www.milestonesci.com).

Reagents and solutions

Stock standard solutions of REEs (1.0 $mg\cdot mL^{-1}$) were purchased from the National Analysis Center of Iron & Steel (Beijing, China, www.nacis cn.com). Working solutions were prepared by stepwise dilution of the above stock solutions just before use. All reagents used in this experiment were of analytical grade unless otherwise noted and bought from Shanghai Reagent Factory (Shanghai, China, www.zardzfp.cn.gtobal.com). High purity deionized water was obtained from Milli-Q® A10 service (Millipore Corporation, USA, www.millipore.com) and used during this work. The synthesis of ZFONTs was carried out in our laboratory. All plastic and glass containers in this work were stored in 20% (*v*/v) nitric acid over 24 h and rinsed with high purity water prior to their use.

Dispersive micro-solid phase extraction procedure

The model solution of 30 mL containing REEs was placed in a 50 mL test tube and adjusted to pH 8.0 with diluted $NH_3\cdot H_2O$. Afterwards, 10 mg of ZFONTs was immediately added to the test tube. The mixture was dispersed by ultra-sonication for 1.5 min at room temperature, followed by a strong magnet placed at the bottom of the test tube to separate ZFONTs from the aqueous solution. The aqueous phase was discarded, and ZFONTs remained in the test tube. To desorb the analytes, 1.0 mL of 0.5 $mol\cdot L^{-1}$ HNO_3 solution was added to the test tube containing ZFONTs, and the test tube was ultra-sonicated for 1 min. Finally, the eluate was isolated by the magnet again. The analytes in the eluent was determined by ICP-MS. A blank solution was also run by the same procedure.

Sample preparation

The water samples, including lake water and wastewater water (collected from Wuhan, China), were filtered through a 0.45 μm membrane filter, and then acidified to a pH of 5.0 for their storage. Prior to use, the sample solution was adjusted to a pH 8.0 with 0.1 $mol\cdot L^{-1}$ $NH_3\cdot H_2O$.

Two certified reference materials of tea leaf (GBW 07605, Institute of Geophysical and Geochemical Exploration, Langfang, China) and human hair (GBW 09101a, NRCSM, Beijing, China) were used to validate this method. An accurately weighed sample portion of 0.1000 g was mixed with 4.0 mL of HNO_3 (65–68%, *w*/w) and 2.0 mL of H_2O_2 (30%, w/w) in a PTFE pressure vessel. The PTFE vessel was closed and left to stand overnight. Then, the vessels were placed into a microwave digestion device. After that, the samples were digested at 180 °C (ramp, 10 $°C·min^{-1}$; hold, 15 min) with a power of 1.0 kW. After cooling, the vessels were opened and heated to near dryness on a hot plate at 200 °C. The residues were dissolved with 0.1 $mol·L^{-1}$ HNO_3, diluted to a required volume with ultrapure water, and kept in a refrigerator at 4 °C for future analysis. The blanks were prepared exactly as the samples without addition of target ions.

Results and discussion

Preparation of magnetic magnetic $ZnFe_2O_4$ nanotubes (ZFONTs)

Magnetic ZFONTs were fabricated by a facile electrospinning and direct annealing method. Firstly, a certain amount of $Zn(Ac)_2·2H_2O$ and $Fe(acac)_3$ with molar ratio of 1:2 were completely dissolved in 6 mL N, N-dimethylformamide with vigorous stirring to form homogeneous solution. Then, 1 g poly(vinyl pyrrolidone) (PVP, Mw~1,300,000) powder was added into the above solution, followed by stirring for 6 h at ambient temperature to obtain uniform brown-red precursor solution. Finally, the mixture precursor was loaded into a syringe equipped steel needle, a high voltage of 11 kV was supplied by a direct-current power supply, and the collector was placed 15 cm away from the tip of steel needle. Magnetic ZFONTs were fabricated by direct annealing of as-spun $ZnFeO_4$ precursor nanofibers mat at 550 °C for 3 h with a heating rate of 1 $°C \cdot min^{-1}$. For comparison, $ZnFeO_4$ nanoparticles were prepared by a hydrothermal method [28].

Choice of materials

Among various materials such as RGO, γ-Fe_2O_3-SiO_2, MIPs, LDH, Ni-doped $CoFe_2O_4$, magnetite @MOFs and ZnO, ZFONTs can stand above due to its remarkable advantages. Preparation of ZFONTs is facile, and used precursors possess no drastic toxicity. However, the materials like MIPs are too complex, and in some cases use toxic precursors such as vinyl compounds. For magnetite @MOFs, MOFs were activated at a required temperature under vacuum condition. Thus, their synthesis is also an extremely tedious work. The separation of the non-magnetic adsorbents such as RGO, LDH and ZnO from aqueous phase was achieved using time-consuming filtration or centrifugation process.

Compared with the magnetic γ-Fe_2O_3-SiO_2 and Ni-doped $CoFe_2O_4$ nanoparticle, ZFONTs exhibit hollow tubular structure and many pores on their wall. This unique structure results in the great increase of specific surface area and active sites of ZFONTs, which is beneficial for adsorbing more ions or molecules. Besides, ZFONTs is polar, unlike some polymers and mesoporous carbon materials, and can highly disperse in water, which leads to more contact between the adsorbent and analytes.

Characterization of ZFONTs

The formation of ZFONTs was evaluated by an X-ray diffractometer with Cu Kα radiation (XRD 7000, Shimazu, Japan, https://www.shimadzu.com). It can be seen from Fig. 1a that the sharp and intense diffraction peaks located at 2 Theta of 29.9°, 35.3°, 42.9°, 53.2°, 56.7°, 62.2° and 73.5° corresponded to the (220), (311), (400), (420), (511), (440) and (533) planes of ZFONTs, respectively. It is demonstrated that ZFONTs possessed standard spinel structure after calcination treatment.

The surface morphology and composition of ZFONTs was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS, attached to SEM) (MAIA 3 LMH, TESCAN, Czech Republic, www.tescan.com). In Fig. 1b, it is vividly indicated that ZFONTs possess a mean outer diameter of about 258 nm and many nanopores on their walls which consist of $ZnFeO_4$ nanoparticles. Moreover, the hollow structure of ZFONTs with mean inner diameter of approximate 150 nm can be detected from the transection image (Fig. 1c). Additionally, ZFONTs maintain the 1D nanotube morphology. The formation of the nanopores can be attributed to the void space between the stacking $ZnFeO_4$ nanoparticles during annealing process. The results of EDS spectrum indicate that ZFONTs were composed of Zn, Fe and O except for Au from the sample treatment, which suggests that the pure ZFONTs were obtained in this work.

Sorption isotherm and pore size distribution of ZFONTs were measured by a Micromeritics ASAP 2010 analyzer (Norcross, GA, USA, www.micromeritics.com). Fig. 1d indicates that the sorption isotherm belongs to the type IV with a distinct hysteresis loop, illustrating the presence of mesoporous structures on ZFONTs. In addition, the pore size distribution of ZFONTs was examined by Barrett-Joyner-Halenda method (Fig. 1e). The specific surface area and pore volume of ZFONTs were measured to be 57.42 $m^2·g^{-1}$ and 0.16 $cm^3·g^{-1}$ by Barrett-Emmett-Teller method, respectively. It is noting that the specific surface area of ZFONTs is much bigger than that of $ZnFeO_4$ nanoparticles (16.09 $m^2·g^{-1}$) reported in the literature [28].

The experimental facts mentioned above suggest that ZFONTs not only possess tubular structure, but also have

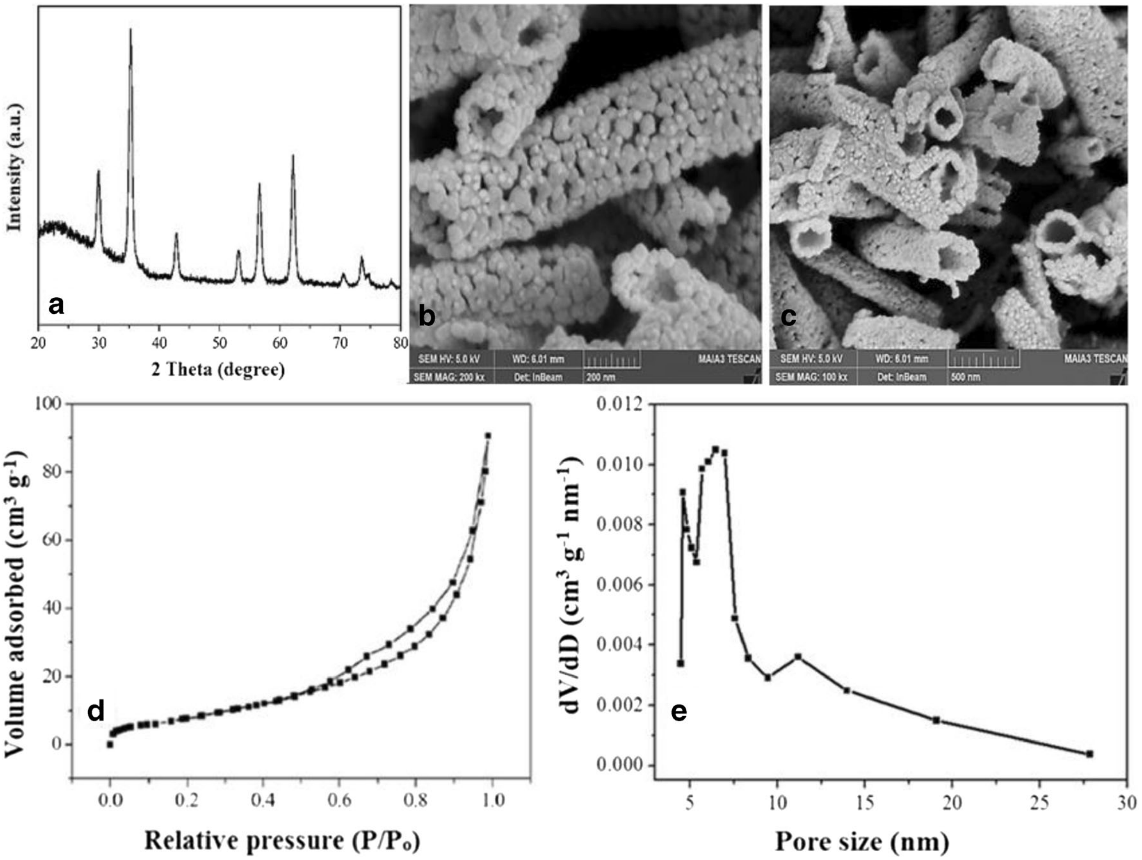

Fig. 1 XRD pattern of ZFONTs (**a**). SEM images of ZFONTs with many pores on their walls (**b**). SEM transection image of ZFONTs (**c**). Nitrogen sorption isotherm of ZFONTs at 77 K (**d**). Pore size distribution of ZFONTs based on Barrette-Joynere-Halenda method (**e**)

many nanopores on their wall, which result in their large specific surface area. ZFONTs may be likely to become an excellent adsorbent.

Optimization of experimental conditions

To achieve good analytical results, the following parameters were optimized: a sample pH of 8.0 (Fig. S1), 10 mg of ZFONTs as an adsorbent, 1.5 min as an extraction time, 1.0 mL of 0.5 mol·L^{-1} HNO_3 as an eluent, and 1.0 min as an elution time. Relevant experimental steps, respective data, Tables and Figures were given in the Electronic Supplementary Material.

Study of memory effect

Memory effect as a significant parameter was investigated in DMSPE. The results revealed that all analytes retained on ZFONTs can be completely desorbed under the selected conditions, and no carryover is observed in the next analysis. The reason for this fact is that DMSPE allow a close contact between the sorbent and the eluent in the elution step, which favors the kinetics of elution.

Effect of sample volume

To explore its capability of extracting analytes at very low content levels from large volume of real sample, the effect of sample volume on the extraction of the analytes was investigated by different sample volumes ranging from 10 to 150 mL containing 6.0 ng of REEs. It is found from the results that 120 mL is the largest sample volume at which quantitative extraction of analytes was achieved. However, the recovery of analytes slightly decreased with further increase of sample volume to 150 mL. Thus, an enrichment factor of 120 was obtained by 1.0 mL of 0.5 mol·L^{-1} HNO_3 as the elution solution.

Influence of diverse ions

In order to investigate the selectivity of ZFONTs for DMSPE of REEs, the effect of various interfering anions and cations, most probably present in biological and environmental samples, on the recoveries of analytes was examined. In this experiment, solutions containing 3.0 ng·mL^{-1} analytes and various amounts of the interfering ions were treated according to this procedure. The tolerance limit of coexisting ions is defined as the largest amount making the recovery of the analyte

Table 1 Characteristic data for this method

Isotope	DL ($pg{\cdot}mL^{-1}$)	RSD (%)	LR ($pg{\cdot}mL^{-1}$)
^{139}La	0.75	2.5	0.65–10,000
^{141}Pr	1.2	3.8	0.25–10,000
^{151}Eu	0.06	4.1	0.35–10,000
^{157}Gd	0.37	5.0	0.20–10,000
^{165}Ho	0.01	5.9	0.10–10,000
^{172}Yb	0.31	6.3	0.15–10,000

maintained in the range of 90–110%. It was found that 10,000 $mg{\cdot}L^{-1}$ Cl^- and NO_3^-, 8000 $mg{\cdot}L^{-1}$ SO_4^{2-}, SiO_3^{2-} and PO_4^{3-}, 10,000 $mg{\cdot}L^{-1}$ K^+ and Na^+, 5000 $mg{\cdot}L^{-1}$ Ca^{2+} and Mg^{2+}, 10 $mg{\cdot}L^{-1}$ Al^{3+} and Fe^{3+} did not influence on recoveries of the analytes. Based on the experimental results, it can be concluded that this method has an excellent selectivity for the adsorption of REEs, and is suitable for the analysis of samples with complicated matrix.

Adsorption capacity

Adsorption capacity is an important parameter to evaluate the performance of sorbent. In this work, the adsorption capacity of REEs on ZFONTs was measured by the procedure reported in the literature [29]. 30 mL aliquots of sample solutions containing the analytes in the concentration range of 10–40 $\mu g{\cdot}mL^{-1}$ were preconcentrated and eluted under the selected conditions. The amount of the analytes adsorbed on ZFONTs ($mg{\cdot}g^{-1}$) at each concentration level was determined by this method. Breakthrough curves were plotted by concentration of analytes versus their amount adsorbed on per gram of adsorbent. The adsorption capacities for La, Pr, Eu, Gd, Ho and Yb calculated from the breakthrough curves were found to be 31.2, 27.6, 28.9, 26.1, 25.9 and 32.7 $mg{\cdot}g^{-1}$, respectively.

Analytical performance of method

The analytical performances of DMSPE using ZFONTs coupled with ICP-MS for the determination of trace REEs were evaluated under the optimum conditions, including precision, detection limits, and linear range of calibration. The detection limits (DLs), defined as the concentration of the analytes equal to 3 times the standard deviation for nine replicate detections of the blanks, were in the range of 0.01(Ho) - 0.75 (La). The relative standard deviations (RSDs) ranged from 2.5% (La) to 6.3% (Yb) ($n = 9$, $c = 1.0$ $ng{\cdot}mL^{-1}$). The linear range (LR) of calibration covered over four orders of magnitude with correlation coefficient (R^2) higher than 0.9986. The relative data were listed in Table 1.

Table 2 gives the data of the analytical performances of this method and other methods reported in the literatures [30–35]. The results in Table 2 indicate that DLs of this method are lower than those reported in the literatures. The RSDs, LR and R^2 are superior or similar to other methods. In addition, this method has a higher enrichment factor.

Validation and application of method

The accuracy and reliability of this method were examined by the determination of REEs in environmental water samples, including lake water and wastewater. The results were listed in Table S2. The recoveries for the spiked samples were in the range of 93–107%. To further validate this method, two certified reference materials of tea leaf (GBW 07605) and human hair (GBW 09101a) were also analyzed by this method (Table 3). The analytical results in Table 3 showed that the determined values agreed well with the certified values.

Conclusions

Magnetic $ZnFe_2O_4$ nanotubes (ZFONTs) were used as a new adsorbent for dispersive micro-solid phase extraction

Table 2 Comparison of this method with other techniques

Method	Element	EF	LR ($pg{\cdot}mL^{-1}$)	ET (min)	R^2	DL ($pg{\cdot}mL^{-1}$)	RSD (%)	Reference
ETV-ICP-MS	Lanthanides	–	3MO	–	–	0.20–0.91	2.5–9.1	[40]
LLE-ICP-MS	La, Eu, Gd	8.6	20–10,000	2	>0.993	0.2–3.7	8.1–3.2	[41]
CME-ICP-MS	Lanthanides	–	4MO	6	>0.99	0.16–0.85	2.7–9.8	[42]
SPE-ICP-MS	Lanthanides	25	–	–	>0.9985	0.31–1.2	<5%	[43]
DLLME-ICP-MS	Lanthanides	16	50–5000	9	>0.9973	0.085–3.33	–	[44]
MSPE-ICP-MS	Lanthanides	50	0.3–10,000	–	>0.9998	0.04–1.49	1.7–6.5	[45]
DMSPE-ICP-MS	Lanthanides	120	0.1–10,000	1.5	>0.9986	0.01–1.2	2.5–6.3	This work

ETV electrothermal vaporization, *LLE* liquid-liquid extraction, *CME* capillary microextraction, *SPE* solid phase extraction, *DLLME* dispersive liquid-liquid microextraction, *MSPE* magnetic solid phase extraction, *EF* Enrichment factor, *MO* magnitude orders, *ET* extraction time

Table 3 Analytical results of REEs in certified reference materials

Element	Tea leaves ($\mu g \cdot g^{-1}$)		Human hair ($ng \cdot g^{-1}$)	
	Determined [a]	Certified	Determined [a]	Certified
La	0.71 ± 0.06	0.60 ± 0.03	14.5 ± 1.0	13.4 ± 1.8
Pr	0.10 ± 0.09	0.12[b]	2.1 ± 0.13	2.4[b]
Eu	0.016 ± 0.001	0.018 ± 0.002	0.78 ± 0.06	0.6[b]
Gd	0.097 ± 0.008	0.093[b]	1.7 ± 0.11	1.8[b]
Ho	0.021 ± 0.002	0.019[b]	0.21 ± 0.01	0.3[b]
Yb	0.041 ± 0.003	0.044 ± 0.004	0.95 ± 0.07	0.8[b]

[a] Mean value ± standard deviation, $n = 3$

[b] Reference values

(DMSPE) of rare earth elements followed by ICP-MS detection. Compared with traditional SPE, DMSPE allow a close contact between the sorbent and the analytes in the preconcentration step, which greatly improves the extraction efficiency. Moreover, ZFONTs exhibit hollow tubular structure and many pores on their wall. This unique structure results in the great increase of specific surface area and adsorptive sites of ZFONTs. The mechanism for extraction of target ions mainly attributes to the different surface charges of ZFONTs at different pH values. Thus, ZFONTs have a great application potential in preconcentration, separation and analysis of metal ions, speciation of elements, non-metal ions and polar organic compounds. At the same time, it should be pointed out here that the structure of ZFONTs may be destroyed in harsh acidic or basic media. Thus, this material suffers from limited tolerance for an eluent with a high concentration level of strong acid or base.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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