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A nanostructured LUS-1 based organic–inorganic hybrid optical sensor for highly selective sensing of Fe^{3+} in water

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ABSTRACT

An organic–inorganic hybrid optical sensor (LQS) was prepared with post grafting of 8-hydroxy-5-quinoline sulfonic acid onto the surface of LUS-1. Its structure was characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FT-IR), N_2 adsorption/desorption, and thermogravimetry analysis (TGA). The fluorescence evaluation of LQS toward a wide range of cations including Na^{+}, Mg^{2+}, Al^{3+}, K^{+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} revealed that LQS was a highly selective optical sensor for Fe^{3+} in a wide range of pH in pure water.

1. Introduction

Ordered mesoporous silica (OMS) materials such as LUS-1, SBA-15, and MCM-41 having high specific surface area, well-defined pore size, and uniform open channels have attracted a growing interest for their potential applications in different fields [1–4]. Since their surface is covered with abundant Si–OH active groups, they are considered as an excellent inorganic scaffold for constructing organic–inorganic hybrid materials via simple silanol chemistry. As a new emerging methodology, OMS materials have been used as matrices in hybrid optical sensors which can be prepared by immobilization of various organosilanol functionalities followed by the subsequent attachment of appropriate fluorophores onto the surface of these materials [5–10]. Hybrid optical sensors work based on translating the changes in fluorescent emission into tangible analytical signals. Indeed, they can be considered as an efficient and economic tool for detecting hazardous agents in environment. Moreover, these sensors offer direct aqueous media applicability as well as simplicity. In particular, LUS-1 can offer better distinction among various targets because its narrower pore diameter allow diffusion of targets with the given sizes.

Iron is one of the most important trace elements in biological systems and is essential for cellular metabolism, provides the oxygen-carrying capacity of heme and acts as a co-factor in many enzymatic reactions [11,12]. Nevertheless, recent studies have indicated that increased iron availability in serum or tissues is associated with an increased risk of several tumors and may promote carcinogenesis [13]. It could also be involved in the underlying mechanisms of many neurodegenerative diseases such as Alzheimer's disease [14] and Parkinson's disease [15]. Therefore, seeking an effective and convenient method for detection of low level concentrations of iron is an important task.

Up to now, various molecular sensors have been successfully developed for the detection of low-level of Fe^{3+} ions [16–22], however, many of these sensors suffer from some disadvantages including interference problems caused by other transition metal cations such as Cr^{3+} [23–26] and Cu^{2+} [27] and poor direct applicability in 100% aqueous solution [28,29]. Therefore, there is room for introducing a novel hybrid optical sensor to overcome these drawbacks.

In this sense and as a part of our continuing interest in the development of optical sensors for ions [30–33], we have followed

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here a new approach for the preparation of a fluorescent probe for the detection of Fe^{3+}. The Literature survey reveals that only limited examples of such hybrid mesoporous chemosensors for Fe^{3+} have been reported [34–36].

Herein, 8-hydroxy-5-quinoline sulfonic acid was chosen as both the chelating agent and fluorescent organic moiety and LUS-1 as the support to form the hybrid material LQS. 8-Hydroxy-5-quinoline sulfonic acid was covalently grafted to iodopropyl functionalized mesoporous support LUS-1 and resulted in the construction of a new fluorescent Fe^{3+} sensor in water.

2. Experimental

2.1. Materials and reagents

Hexadecyltrimethylammonium p-toluenesulfonate, 3-iodopropyltriethoxysilane (IPTES) (Fluka), 8-hydroxy-5-quinoline sulfonic acid (QS), triethylamine and metal salts (Merck) were used as received. Toluene was dried prior to use.

2.2. Synthesis of LQS

LUS-1 type mesoporous silica was prepared according to the literature [37]. To the dispersion of 2 g LUS-1 in 100 ml dried toluene, 10 mmol IPTES was added dropwise under vigorous stirring. After refluxing the mixture for 24 h, the resulting solid was filtered, washed repeatedly with toluene and ethanol, and finally dried overnight (I-LUS-1).

Afterward, 1 g I-LUS-1 was dispersed in 50 ml dried methanol/water (3:1), and then 5 mmol 8-hydroxy-5-quinoline sulfonic acid and 10 mmol triethylamine were added under stirring and the mixture was refluxed for 24 h. Finally, the product was filtered, washed with an excess amount of ethanol to give a pale pink solid (LQS). To make sure that there is no unreacted fluorophores within the channels, the sensor was sonicated, washed and dried. The overall procedure is depicted in Fig. 1

2.3. Instruments and spectroscopic measurements

Low-angle X-ray scattering measurements were performed on X'Pert Pro MPD diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). N_2 adsorption–desorption isotherms were obtained using BELSORP-mini II instrument at liquid nitrogen temperature (−196 °C). All samples were degassed at 100 °C before performing measurements. The Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) equations were applied on sorption data using BELSORP analysis software to calculate physical properties of materials including specific surface area, pore diameter, pore volume, and pore size distribution. The Fourier transform infrared (FT-IR) spectra of samples were recorded on a RAYLEIGH WQF-510A apparatus. SEM analysis was performed on a Philips XL-30 field emission scanning electron microscope operated at 16 kV. TEM was performed on Zeiss EM900 instrument at an accelerating voltage of 80 kV. Samples were dispersed in ethanol using an ultrasonic bath and a drop of the ethanol mixture was placed on a lacey carbon-coated copper grid for analysis. Thermogravimetric analysis (TGA) was carried out in a TGA Q50 V6.3 Build 189 instrument from ambient temperature to 1000 °C with a ramp rate of 20 °C/min in air. Fluorescence spectra were recorded on Agilent G980A instrument.

3. Results and discussion

3.1. Low-angle X-ray diffraction

Fig. 2 shows low-angle XRD patterns of LUS-1 and LQS. The observation of the four reflections, located at nearly $2\theta = 2°$ (single intense reflection), 4° (two weak reflections), and 5° (single weak reflection) are attributed to the diffraction from (1 0 0), (1 1 0), (2 0 0), and (2 1 0) planes, respectively, confirming the mesoporous structure of LUS-1 (Fig. 2a). As it is observed in Fig. 2b, the reflections except for one at 5° were also emerged in XRD pattern of LQS sample implying original mesoporous structure was preserved after modification steps. Moreover, the disappearing of reflection at 5° and the reduction in intensity of the rest reflections were resulted from the attached organic groups into the LUS-1 walls causing differences between the scattering features of the pores and the walls [32]. Fig. 2(c and d) gives the SEM and TEM images of LUS-1. SEM image showed long rod shape particles and TEM image demonstrated the parallel channels, which resembled the configuration of the pores in LUS-1.

3.2. N_2 adsorption–desorption

Fig. 3 shows the N_2 adsorption–desorption isotherms of LUS-1 and LQS. As it can be seen, LUS-1 showed a characteristic "type IV" isotherm with "H1-type" hysteresis indicating cylindrical structure of mesoscale pores. Moreover, the presence of similar isotherm in LQS sample implied that original structure of LUS-1 was preserved after functionalization steps by organic moieties. Table 1 provides the textural parameters of the samples including specific surface area (BET method), pore diameter (BJH method), and total pore volume. Decreasing in those three parameters confirmed successful attachment of organic moieties on the inner surface of the silica wall.

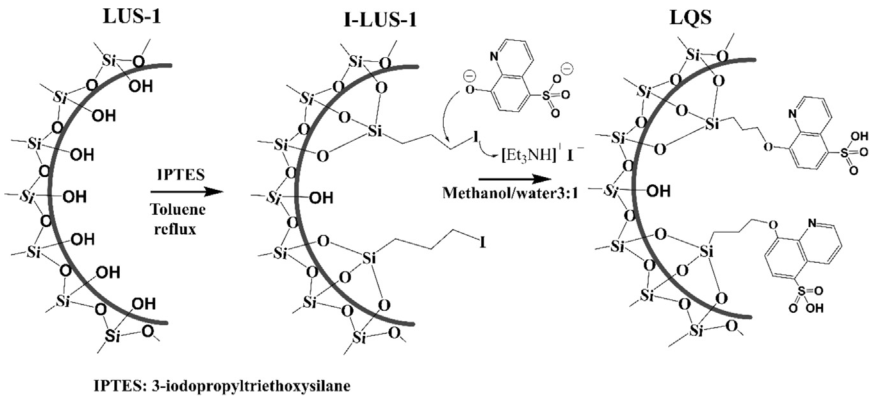

Fig. 1. Synthesis procedure of LQS.