A luminescent-magnetic nanocomposite for Hg(II) recognition and extraction: Preparation, characterization, sensing and removal performance

Gao Yu-qian [a,b], Song Jing [a,b], Zhao Xiaohang [a,b], Zhang Shimin [a,b], Xu Shuxia [a,b], Wu Kun [a,b,*], Mou Wanzhi [c]

[a] College of Life Sciences, Henan Agricultural University, 95 Wenhua Road, Zhengzhou 450002, China
[b] Key Laboratory of Enzyme Engineering of Agricultural Microbiology, Ministry of Agriculture, Henan Agriculture University, Henan 450002, China
[c] College of Chemistry and Molecular Engineering, Tsinghua University, Beijing 100871, China

ABSTRACT

The present paper constructed an organic–inorganic hybrid composite with core–shell structure for Hg(II) sensing, where superparamagnetic ferroferric oxide and silica molecular sieve MCM-41 were used as the inner core and the outer shell, respectively. A rhodamine derivative was firstly modified by sulfur substitution and then covalently connected to MCM-41 tunnels. This composite was supposed to recognize and extract Hg(II) ions. Electron microscopy images, X-ray diffraction analysis, IR spectra, thermogravimetry and N_2 adsorption/desorption analysis were performed on this composite, which confirmed its structure. It was found that emission of this composite increased with increasing Hg(II) concentrations, showing emission "off–on" effect. High selectivity, linear working curve and good recycling performance were obtained from this composite.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Composite materials, which are able to combine and maintain desired features from individual components, have drawn much research attention during last decade [1–3]. Organic–inorganic hybrid ones are particularly focused since their organic component can provide various features for multifunctional purpose, while their inorganic component is good at mechanical strength and high stability, serving as a perfect supporting matrix for organic component. To preserve individual features and minimize any potential side effects, various hybrid structures, such as core–shell, Janus and layer-by-layer, have been proposed and fabricated, showing great potential in optical sensing, catalysts, solar cells and optoelectronic devices [1–4].

As one of the most important applications, optical sensing has shown virtues such as instant response, low running cost and simple instrumentation. Particularly, optical sensing systems for Hg contamination recognition have been intensively studied owing

to its biological participation in vital life activities [5,6]. Inorganic Hg contaminations can be generated by both natural and anthropogenic activities. In addition, they can be eaten and transformed into organic ones by some bacteria and microbes [5–7]. Hg concentration can be increased to hazard level after being accumulated through food chains [5,7]. In other words, contamination removal should be equally considered as well as its recognition. However, traditional optical sensing systems usually focus on analyte recognition with no removal ability. It seems that the utilization of magnetic component which is specialized at site-specific targeting, sample sorting and isolating may well solve this issue [8–12].

Traditionally, optical sensing is based on probe emission quenching and/or energy transfer in the presence of analyte [13,14]. Unfortunately, some competing species and emission killers also quench probe emission, leading to limited signal reliability and accuracy. Emission "turn-on" probes are then proposed to overcome this problem [15]. Their emission generally increases with increasing analyte concentrations and remains constant upon other competing species, showing unique selectivity toward a specific analyte. Rhodamine and its derivatives are a class of representative emission "turn-on" probes for Hg(II) ions. In this case, the emission "turn-on" effect is finished by a structural transformation from a

non-emissive spirolactam structure to an emissive xanthene structure, making them shining candidates for Hg(II) sensing.

Guided by above consideration, it is assumed that the combination of magnetic component with a rhodamine derived probe may satisfy Hg(II) recognition and extraction well. In the following content, a core–shell structured luminescent-magnetic nanocomposite is designed with magnetic Fe_3O_4 as the core and silica molecular sieve MCM-41 as the shell, respectively. A rhodamine derived probe is modified by sulfur substitution and then connected to the shell, aiming at improved selectivity, as depicted in Scheme 1. This nanocomposite (denoted as Sensor 1) and its Hg(II) sensing performance are characterized and discussed in detail.

2. Experimental details

2.1. General information

All reagents used in this work can be summarized as follows. Rhodamine B (AR), anhydrous hydrazine (95%), cetyltrimethylammonium bromide (CTAB, AR), 4-hydroxybenzaldehyde (AR), tetraethoxysilane (TEOS, AR), 3-(triethoxysilyl)-propyl isocyanate (TESPIC, AR), odium dodecyl sulfate (SDS, AR), $FeCl_3$ (AR), $Hg(NO_3)_2$ and other inorganic salts were provided by Nanyun Chemicals and Reagents Company (Zhengzhou, China). Organic solvents used in this work, including glycol (AR), anhydrous ethanol, $CHCl_3$, n-hexane (AR), CH_3CN and tetrahydrofuran (THF), were obtained from Yingge'er Chemical Company (Zhengzhou, China) and redistilled before usage. Solvent water used in this work was deionized.

Apparatus information is summarized as follows: ^{1}H NMR, IR and mass spectra were recorded by a Varian INOVA 300 spectrometer, a Agilent 1100 MS series/AXIMA CFR MALDI/TOF MS spectrometer and a Bruker Vertex 70 FTIR spectrometer (400–4000 cm^{-1}, KBr pellet technique), respectively. XRD curves were obtained from a Rigaku D/Max-Ra X-ray diffractometer (λ = 1.5418 Å). A Hitachi S-4800 microscope and a JEOL JEM-2010 transmission electron microscope were used for sample morphology study. Magnetic features were analyzed by a MPM5-XL-5 superconducting quantum interference device. N_2 adsorption and desorption measurement was finished with a Nova l000 analyzer. Mesoporous parameters were calculated following Barrett–Joyner–Halenda (BJH) model. Thermal degradation measurement was completed on a Perkin-Elmer thermal analyzer. Fluorescence data were recorded by a Hitachi F-4500 fluorescence spectrophotometer. Standard Hg(II) concentrations were determined through an inductively coupled plasma (ICP) spectrometer (Perkin Elmer). All operations were carried out at room temperature without further specification.

2.2. Synthesis of RBS hydrazine

2-Amino-3′,6′-bis(diethylamino)spiro[isoindoline-1,9′-xanthene]-3-thione (RBS hydrazine) was synthesized following a three-step procedure described as follows [16,17]. First, rhodamine B (10 mmol) was dissolved in $CHCl_3$ (30 mL) under ice bath. Then $POCl_3$ (5 mL) was dropwise added. This solution was stirred at 0 °C for 1 h and then heated to reflex under N_2 atmosphere for 6 h. $CHCl_3$ solvent and excess $POCl_3$ were removed by rotary evaporation. Then, anhydrous hydrazine (10 mL) was mixed with acetonitrile (100 mL) and slowly added into above solid residue. The resulting mixture was stirred at 0 °C for 1 h and at 30 °C for another 10 h. Solvent acetonitrile and excess hydrazine were vaporized under reduced pressure. The resulting solid sample was collected and purified in mixed solvent of ethanol/water (v:v = 2:8). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.27 (t, 12H, NCH_2CH_3), 3. 13 (q, 8H, NCH_2CH_3), 3.56 (s, 2H, N-NH_2), 6.28 (dd, 2H, xanthene-H),

6.40 (d, 2H, xanthene-H), 6.52 (d, 2H, xanthene-H), 7.17 (dd, 1H, Ar-H), 7.49 (dd, 2H, Ar-H), 8.16 (dd, 1H, Ar-H). EI-MS m/e: calc. for $C_{28}H_{32}N_4O_2$, 456.2; found, 456.2 [m]$^+$.

Third, the above obtained sample was mixed with Lawesson's reagent (20 mmol) and toluene (50 mL) [17]. This mixture was heated to 120 °C under N_2 atmosphere overnight. After reaction, solvent was removed by thermal evaporation. The resulting solid residue was collected and purified through a silica column with $CHCl_2$ as eluent. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.24 (t, 12H, NCH_2CH_3), 3. 11 (q, 8H, NCH_2CH_3), 3.52 (s, 2H, N-NH_2), 6.24 (dd, 2H, xanthene-H), 6.36 (d, 2H, xanthene-H), 6.46 (d, 2H, xanthene-H), 7.14 (dd, 1H, Ar-H), 7.44 (dd, 2H, Ar-H), 8.13 (dd, 1H, Ar-H). EI-MS m/e: calc. for $C_{28}H_{32}N_4OS$, 472.2; found, 472.2 [m]$^+$.

2.3. Synthesis of RBS-OH

(E)-3′,6′-Bis(diethylamino)-2-((4-hydroxybenzylidene) amino) spiro[isoindoline-1,9′-xanthene]-3-thione (RBS-OH) was synthesized by the following procedure. RBS hydrazine (5 mmol), p-nitrobenzenesulfonic (0.1 mmol), 4-hydroxybenzaldehyde (6 mmol) and ethanol (50 mL) were mixed together and heated to 80 °C under N_2 atmosphere overnight. Then solvent ethanol was removed by thermal evaporation. Crude product was collected and recrystallized in the mixed solvent of ethanol/water (v/v = 7:3). ^{1}H NMR (DMSO), δ (ppm): 1.26 (t, 12H, NCH_2CH_3), 3.12–3.14 (q, 8H, NCH_2CH_3), 6.21 (s, 2H, xanthene-H), 6.38 (s, 2H, xanthene-H), 6.44 (s, 2H, xanthene-H), 7.12 (s, 1H, Ar-H), 7.29 (s, 1H, Ar-H), 7.36 (s, 1H, Ar-H), 7.50 (s, 2H, Ar-H), 7.55 (s, 2H, Ar-H), 8.16 (s, 1H, Ar-H), 8.26 (s, 1H, N=CH), 9.87 (s, 1H, Ar-OH). MS m/z: [m+1]$^+$ calc. for $C_{35}H_{36}N_4O_2S$, 576.3; found, 576.3.

2.4. Synthesis of RBS-Si

(E)-4-(((3′,6′-Bis (diethylamino)-3-thioxospiro [isoindoline-1,9′-xanthen]-2-yl)imino) methyl) phenyl (3-(triethoxysilyl) propyl)carbamate (RBS-Si) was synthesized by the following procedure. RBS-OH (2 mmol), Et_3N (10 drops) and TESPIC (3 mmol) were stirred in anhydrous THF (20 mL) at room temperature for 2 h and then heated to 80 °C under N_2 atmosphere overnight. After cooling, solvent THF was removed by thermal evaporation. Cold n-hexane was added to generate solid product. Crude product was collected and recrystallized in n-hexane. ^{1}H NMR (DMSO), δ (ppm): 1.14–1.16 (t, 9H, OCH_2CH_3), 1.23 (t, 6H, OCH_2CH_3), 1.27 (t, 12H, NCH_2CH_3), 3.12–3.14 (q, 8H, NCH_2CH_3), 3.42–3.44 (q, 6H, $Si(CH_2)_3$), 5.79 (s, 1H, CONH), 6.23 (s, 2H, xanthene-H), 6.37 (s, 2H, xanthene-H), 6.45 (s, 2H, xanthene-H), 7.15 (s, 1H, Ar-H), 7.28 (s, 1H, Ar-H), 7.37 (s, 1H, Ar-H), 7.51 (s, 2H, Ar-H), 7.56 (s, 2H, Ar-H), 8.14 (s, 1H, Ar-H), 8.25 (s, 1H, N=CH). MS m/z: calc. for $C_{45}H_{57}N_5O_6SSi$, 823.4; found, 823.4 [m]$^+$.

2.5. Fabrication of supporting matrix

The supporting matrix for RBS-Si was fabricated according to a three-step protocol. Fe_3O_4 nanoparticles were firstly fabricated following a literature procedure, serving as the core for supporting matrix [10]. SDS (2.0 g), $FeCl_3 \cdot 6H_2O$ (5.4 g) and NaAc (14.4 g) were mixed with glycol (100 mL) and stirred at room temperature for 30 min. This solution was transferred into a teflon flask and kept for 8 h at 200 °C. After natural cooling, the resulting solid product was collected and washed with deionized water. Then amorphous SiO_2 was coated onto these Fe_3O_4 nanoparticles, making the following MCM-41 planting procedure more easier to complete. Fe_3O_4 nanoparticles (0.2 g) were treated by ultrasonic bath in ethanol (40 mL), then mixed with $NH_3 \cdot H_2O$ (1 mL) and deionized water (20 mL). TEOS (0.2 g) was slowly added into this solution and stirred at room temperature for 6 h. The resulting product was collected