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A selective fluorescent bulk sensor for lutetium based on hexagonal mesoporous structures

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ABSTRACT

A novel Lu^{3+} sensitive fluorescent chemosensor is constructed by preparation of 8-hydroxyquinoline functionalized mesoporous silica with ordered hexagonal array structure (SBA-SPS-Q). The new synthesis material demonstrated a selective interaction with Lu^{3+} ion, most probably because of the presence of the fluorophore part at its surface. Fluorescence studies revealed that the emission intensity of the Lu^{3+}-bound mesoporous material increases significantly after addition of various concentrations of Lu^{3+}, while the mono-, di-, trivalent cations result in either no changes or weak changes in fluorescent intensities. The enhancement of fluorescence is attributed to the strong covalent binding of Lu^{3+} ion, evident from the large binding constant value ($2 \times 10^6\ M^{-1}$). The linear range of the fluorescent chemosensor covers a Lu^{3+} concentration from 1.6×10^{-7} to 2.6×10^{-6} M, with detection limit of 4.0×10^{-8} M. This chemosensor has been applied to determination of Lu^{3+} ion in some soil samples where domestic devices were stored.

1. Introduction

Mesoporous silica is a form of silica which can be consider as a recent development in nanotechnology. The most common types of mesoporous nanoparticles are MCM-41 and SBA-15. The large surface area of the pores allows the particles to be used in drug delivery; in catalyst applications and in sensor/biosensory systems. Also, the structure of these particles allows them to be filled with a fluorescent dye.

Mesoporous silica SBA-15 possesses a large average pore size, uniform channels and large surface area so it can act as an excellent support for constructing chemosensors. The straight channel of SBA-15 is beneficial for facilitating the entering and diffusion of target metal ions there-through. Though SBA-15 itself is non-fluorescence, it can supply a layer of abundant hydroxyl groups as the binding sites for covalent grafting of silylation reagents. Versatile silylation reagents can be used to enhance the rigidity of the silicon wall through the linkage with oxygen of the hydroxyl groups. Simultaneously reactive groups such as amino or halogens can be attached for further introducing some chromophore or fluorescent functional molecules as the signaling part. The rigidity of the siliceous wall and the spatial restriction of the mesopore also strictly affect the photic property of the encapsulated molecules. Moreover, using siliceous hosts as solid binding units has some advantages including favorable biocompatibility, optical transparency in the visible region and especially its satisfactory anti-swelling property in the solution, which enables the resulting materials to be promising sensor substrates [1–6]. Literature survey reveals that there are some reports on using mesoporous nanosilica for sensory applications [6–8].

The biological properties of lutetium as well as other lanthanide ions are primarily based on their similarity to calcium. This phenomena cause they have some potential therapeutic applications since the early part of the twentieth century. Lanthanide ions have similar ionic radii to calcium, but possessing a higher charge thus; they have a high affinity for Ca^{2+} sites on biological molecules, and a stronger binding to water molecules [9–11].

Lutetium can be found in houses and equipments such as color televisions, fluorescent lamps energy-saving lamps and glasses. Thus, lutetium compounds can be increasingly dumped in the environment mainly from petrol-producing industries or when household appliances are improperly disposed of. Lutetium will hence gradually accumulate in soil and water soil, eventually leading to increased concentrations in human and animal bodies. This can specially be a threat to the liver when it accumulates in the human body. As far as water animals are concerned, lutetium

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causes cell membrane damage, creating several negative influences on the reproduction and on the nervous system functions [12].

The conventional methods for determination of lutetium ions include activation analyses [13], photometric determination [14], resonance ionization spectroscopy determination [15], Extraction chromatography-atomic emission spectrometry [16], spectrofluorimetric determination [17], and inductively coupled plasma atomic emission spectrometry [18].

Furthermore, a number of potentiometric ion-selective electrodes for Lu^{3+} ion have recently been reported [19,20]. However, most of these methods suffer either one, two or, in some cases, all of the following drawbacks of (1) high limit of detection, (2) narrow working concentration range, and (3) serious interferences from various cations.

Development of chemosensors for the determination of metal ions has become a rapidly expanding area of analytical chemistry in the past decade, most probably because they offer certain advantages simple preparation, reasonable selectivity, improved sensitivity and no need for separate reference devices [21–28].

In the light of our previous experiences in the development of a number of chemosensors and optical sensors for ions such as Zn^{2+} [29], Hg^{2+} [30], $P_2O_7^{4-}$ [31], Tb^{3+} [32–34], Er^{3+} [35] and regarding the effective coordinating ability of 8-hydroxyquinoline with specific cations [36–38] and the excellent structure properties of SBA-15, we wish to introduce a functionalized mesoporous fluorescent material as a very simple and versatile chemosensor. 8-hydroxyquinoline has been grafted covalently to the surface of SBA-15 via formation of a sulfonamide bond between sulfonyl chloride derivative of 8-hydroxyquinoline and amine functionalized SBA-15 (designated as SBA-SPS-Q). Our experiments revealed that the used material, has high selectivity and sensitivity toward Lu^{3+} ion concentration over the other tested cations. Hence, it can be used as nano sensor to directly sense in some especial environments. To the best of our knowledge, there is no report on the assembly of a Lu^{3+} selective chemosensor based on mesoporous material SBA-15 by using fluorescence spectroscopy.

2. Experimental

2.1. Materials

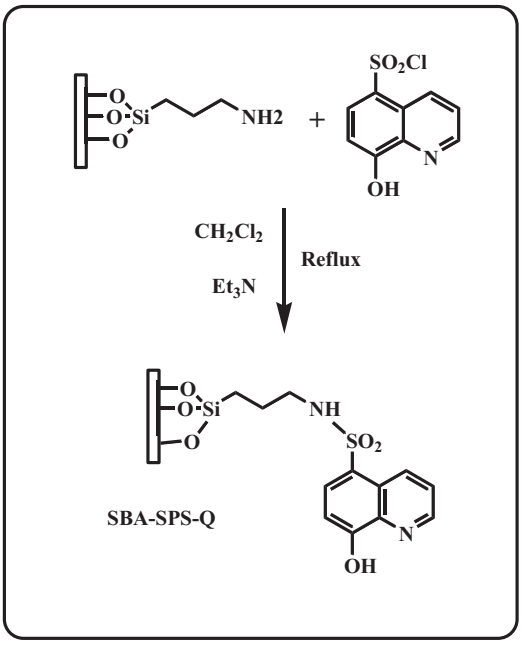
All Chemicals were of reagent grade from Merck Chemical Company (Germany). Nitrate and chloride salts of all the cations used were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Pluronic P123 with average molecular weight of 5800 was purchased from Aldrich. Tetraethyl orthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTES) were also purchased from Merck. All other reagents and solvents were of analytical grade and used as received.

2.2. Synthesis and aminopropyl functionalization of mesoporous silica SBA-15

SBA-15 type mesoporous silica was prepared according to the literature with slight modification [35]. The aminopropyl functionalization of SBA-15 was carried out by using APTES. In a typical synthesis, about 1.0 g of calcinated SBA-15 was added to 100 ml of dry toluene in a 250 ml flask and then 2 mmol of APTES was added and refluxed for 4 h. The resulting solid was then filtered, washed with a toluene and ethanol mixture, and dried in the air.

2.3. Synthesis of SBA-SPS-Q

SBA-SPS-Q was prepared as described elsewhere [39]; its synthesis route is depicted in Scheme 1. As can be seen in Scheme 1, 8-hydroxyquinoline was attached to the surface through the formation of a sulfonamide bond between 8-hydroxyquinoline-5-sulfonyl chloride and surface amine groups of aminopropyl functionalized SBA-15.



Scheme 1. Synthesis route of SBA-SPS-Q.

2.4. Instruments and Spectroscopic Measurements

Low-angle X-ray diffraction (XRD) patterns were recorded with a Philips X Pert MPD diffractometer using Cu K_α radiation (40 kV, 40 mA) at a step width of 0.02°. N_2 adsorption–desorption isotherms were measured using a BELSORP mini-II. FT-IR spectra were recorded within a 4000–400 cm^{-1} region on a Bruker Vector 22 infrared spectrophotometer. SEM analysis was performed on a Philips XL-30 field-emission scanning electron microscope operated at 16 kV.

The emission spectra were obtained on a Perkin-Elmer LS50 luminescence spectrometer. Fluorescence measurements were done in a 1 cm quartz cuvette containing a magnetic-stirred suspension of grafted mesoporous silica (0.08 g L^{-1}) in 3 mL of aqueous solution. This solution was titrated with a standardized Lu^{3+} ion solution and the fluorescence intensity of the system was measured. The emission intensity, at an excitation wavelength of 360 nm, was measured. Spectral bandwidths of monochromators for excitation and emission were 5 nm.

The fluorescence quantum yield was obtained by comparison of the integrated area of the emission spectrum and absorbance of the samples with the reference under the same excited wavelength. The concentration of the reference quinine sulfate ($\Phi_{ref} = 0.54$) in an aqueous solution was adjusted to match the absorbance of the test sample. The quantum efficiency of a metal-bound sample was measured using a suspension solution of 0.08 g L^{-1} SBA-SPS-Q and 2.0×10^{-6} mol L^{-1} Lu^{3+}. Emission for SBA-SPS-Q was integrated from 414 to 620 nm with excitation at 360 nm, whereas for SBA-SPS-Q, the emission area was integrated from 414 to 620 nm. The quantum yields were calculated with Eq. (1) [40].

$$\phi_{sample} = \phi_{reference} \frac{\int emission_{sample}}{\int emission_{reference}} \frac{A_{reference}}{A_{sample}} \quad (1)$$