



Immobilization of a non-aqueous soluble probe onto mesoporous silica for utilization in highly sensitive and selective detection and removal of Hg²⁺ in pure aqueous media



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ABSTRACT

An efficient strategy to immobilize a non-aqueous soluble Hg²⁺ probe onto mesoporous silica is developed, and this immobilization is subject to several advantages regarding Hg²⁺ detection, such as improving sensing sensitivity and selectivity, extending application from an organic/aqueous mixture to a pure aqueous medium, and achieving removal of Hg²⁺ ions while detection. The selected Hg²⁺ probe, rhodamine B thiohydrazide, can be readily covalently immobilized onto mesoporous silica through a simple amide reaction and subsequently exhibits more than 10 times enhancement of sensitivity for Hg²⁺ (limits of detection are of 0.81 ppb in immobilized form versus 10 ppb in free form), and an adsorption capacity of 192 mg/g. Brunauer–Emmett–Teller and TEM characterizations demonstrate that the mesoporous structure can be well remained after Hg²⁺ probe modification and this feature is believed to be responsible for improved Hg²⁺ sensing properties.

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1. Introduction

With the development of economy, heavy metals were found in waste waters originating from chemical manufacturing, coating and painting, extractive metallurgy, mining, nuclear, and other industries [1]. Such heavy metal ions in waste water have serious deleterious effects on the environment and human health [2]. Therefore, the monitoring and removal of metal ions in environment, particularly in aquatic ecosystems, became an urgent issue [3]. Especially, as one of the most toxic and dangerous heavy metal ions and a serious environmental pollutant, mercuric ion (Hg²⁺) has high affinity for thiol group in proteins and enzymes, leading to dysfunction of cells and consequently causing serious health problems [4,5]. Although numerous techniques for toxic metal ions detection have been developed, such as traditional inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption/emission spectroscopy, and been broadly applied as standard analysis methods for metal ions, the high cost, non-portable and

sophisticated sample preparation significantly limit the range of their applications.

Due to the high sensitivity and non-destructive, fluorometric method is regarded as a promising technique for potentially rapid and on-site detection of metal ions [4]. In recent years, great deal of efforts have been devoted to the development of sensitive and selective fluorescent probes which are capable of detecting metal ions in an inexpensive, convenient, reliable, and rapid manner [6,7]. Up to now, many fluorescent probes have been designed and synthesized to serve as powerful tools for detection of metal ions [7–11], but a commonly encountered problem is their water solubility, and thus an organic solvent has to be added to help dissolve probe molecules.

Because of the unique properties, such as high surface area, uniform open pores, high stability, optical transparency and good dispersibility in water, mesoporous silica have been proven as excellent supports for lots of applications [12–15]. The high surface area and open pore structure of mesoporous materials provide an amplified target–receptor interface and thus making them desirable for sensing applications. Mesoporous silica offer not only open ordered mesoporous channels for conveniently grafting fluorescent probes in high density, but also enable rapid diffusion of analytes, thereby yielding a rapid response [13]. The properties cited above

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made us believe that immobilized fluorescent probe in mesoporous silica may provide numerous advantages in comparison to its free form in solution, i.e. circumventing water soluble problem, improving sensing sensitivity, removing metal ions while detection, and easily recycling and disposing sensing material.

Inspired by the above, herein, a rhodamine derivative based Hg^{2+} probe, i.e. rhodamine B thiohydrazide (RBTH), was immobilized onto mesoporous silica for utilization in highly sensitive and selective detection of Hg^{2+} in a pure aqueous medium rather than an organic/aqueous mixture. Meanwhile, the obtained organic–inorganic hybrid sensing material also displays high adsorption capacity for Hg^{2+} . Since rhodamine derivatives have been well demonstrated as ideal candidates to construct OFF–ON molecular fluorescent switch for metal ions detection in the past decades [7,16–19], the described strategy in this work may be readily extended into other detection systems.

2. Experimental section

2.1. Chemicals and materials

Rhodamine B, 3-isocyanatopropyltriethoxysilane (NCO-silane), triblock copolymer PEO-PPO-PEO (P123), and Lawesson's reagent were purchased from Aldrich. Tetraethyl orthosilicate (TEOS), anhydrous toluene, anhydrous ethanol, hydrazine hydrate, hexane, methanol, sodium chloride and magnesium perchlorate were obtained from Sinopharm Chemical Reagent Co., Ltd. Other metal salts (as their perchlorates) were acquired from J & K Technology Co. Ltd. All reagents and solvents were of at least analytical grade and used without further purification unless otherwise noted. Deionized water was used throughout the experiments. Rhodamine B hydrazide and mesoporous silica SBA-15 were prepared according to the reported methods [20,21].

2.2. Synthesis of RBTH

A slightly modified literature procedure was taken to synthesize rhodamine B thiohydrazide (RBTH) [20]. Simply, rhodamine B hydrazide (0.90 g, 2.0 mmol) and Lawesson's reagent (0.80 g, 2.0 mmol) were dissolved in anhydrous toluene (25 mL), and the reaction mixture was heated and refluxed for 6 h under N_2 atmosphere; after removal of toluene, the residue was purified by silica chromatography with dichloromethane/n-hexane = 1/1 as eluant to afford a pale yellow powder after evaporating solvents and drying under vacuum (312 mg, 30% yield). ^1H NMR (400 MHz, CDCl_3):

$\delta = 1.17$ (t, 12H), 3.33 (q, 8H), 6.28 (d, 2H), 6.35 (s, 2H), 6.44 (d, 2H), 7.12 (d, 1H), 7.48 (m, 2H), 8.09 (d, 1H), 8.10 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 12.596$, 29.704, 44.440, 73.291, 98.069, 103.396, 108.107, 123.081, 124.565, 128.083, 128.583, 132.034, 136.409, 149.222, 153.513, 182.945. ESI-MS: $[(\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_5)(\text{H})]^+$, calcd. $m/z = 473.2$, found $m/z = 473.2$.

2.3. Synthesis of RBTH modified SBA-15

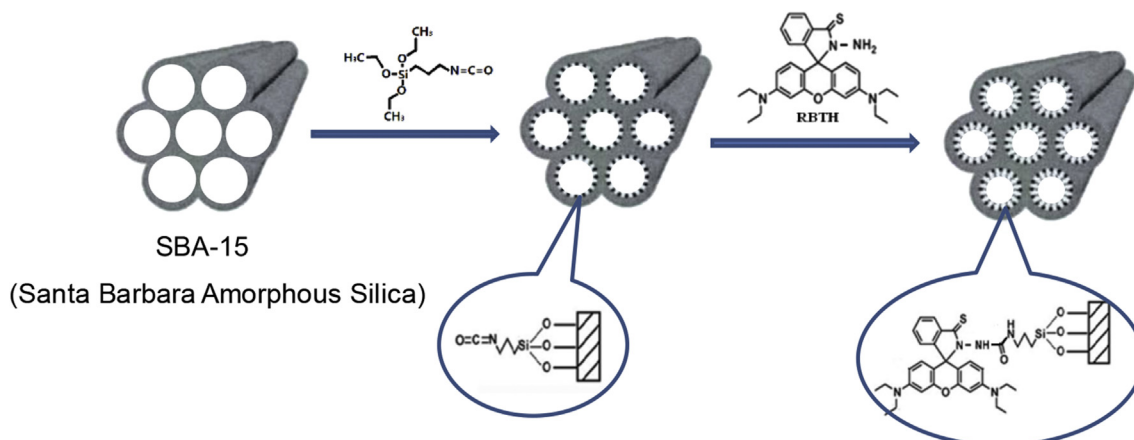
The RBTH modified mesoporous silica, named RBTH-SBA-15, was prepared by a step-by-step immobilization approach as illustrated in Scheme 1 [22,23]. Briefly, SBA-15 (0.10 g) was dispersed in anhydrous toluene (10 mL) and 3-isocyanatopropyltriethoxysilane (0.40 mL, 1.6 mmol) was added. The mixture was then heated and refluxed for 24 h under N_2 atmosphere. After removal of the unreacted reagent through three cycled washing and centrifuging with ethanol and acetone, the mesoporous silica SBA-15-NCO (50 mg) was then dispersed in dry toluene and compound RBTH (15 mg, 0.03 mmol) was added at room temperature under middle agitation. The mixture was stirred and refluxed under N_2 for 24 h. After cooled to room temperature, the modified mesoporous silica was collected by filtration and washed by methanol and acetone several times, and finally dried under vacuum at 50°C overnight.

2.4. Preparation of solutions for fluorometric tests

The dispersion solution of RBTH-SBA-15 (0.02 g/L) was prepared in a phosphate ($\text{Na}_2\text{HPO}_4\text{--NaH}_2\text{PO}_4$) buffer solution (PBS, 10 mM) at pH 7.0. Stock solutions of metal ions of K^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Ni^{2+} , Ag^+ , Pb^{2+} , Co^{2+} , Cd^{2+} , Fe^{3+} and Hg^{2+} were prepared at 0.1, 0.01 and 0.001 M, respectively. For a fluorometric measurement, 3.0 mL of dispersion solution of RBTH-SBA-15 was firstly filled into a quartz cell of 1 cm optical path length, and then added an appropriate concentration and amount of metal ions stock solution to obtain the desired concentration (the total volume change of solution was kept <1% in order to eliminate the effects of concentrations change).

2.5. Adsorption test

RBTH-SBA-15 adsorption tests were performed in an aqueous solution by the classical batch equilibration method [24]. Typically, 50 mg of RBTH-SBA-15 was firstly dispersed in 45 mL PBS buffer solution at pH 6 (10 mM). Then 5 mL of Hg^{2+} stock solution (0.01 M)



Scheme 1. A schematic illustration of the step-by-step approach for preparation of RBTH modified SBA-15.

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