Sensors and Actuators B 210 (2015) 56–68

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Chalcone isothiocyanate-mesoporous silicates: Selective anchoring and toxic metal ions detection

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ARTICLE INFO

Article history:
Received 5 September 2014
Received in revised form
13 December 2014
Accepted 18 December 2014
Available online 26 December 2014

Keywords:
Nanosensor
KIT-6
SBA-15
Probe carriers
Chalcone isothiocyanate

ABSTRACT

Nanosensors are one of the important applications of mesoporous materials used for toxic metal ions detection. Here, a rational strategy aimed at designing 2D and 3D nanosensors using SBA-15 and KIT-6 types of mesoporous silicates as probe carriers. A novel ligand of chalcone analogue namely, chalcone isothiocyanate, CITC has been synthesized. Covalent anchoring of CITC into mesoporous silicates was performed through two methods: (i) loading via the coupling agent (3-aminopropyl) trimethoxysilane (APS) into calcinated mesoporous silicates, (ii) alkaline loading into amino-functionalized mesoporous silicates. The obtained mesoporous silicates and their CITC anchored forms were characterized using different spectroscopic techniques. The results indicated the higher efficiency of KIT-6 and APS loading method than both SBA-15 and alkaline loading method. Therefore, a highly sensitive nanosensor used for toxic metal ions detection was successfully designed by the anchoring of CITC into KIT-6 via the more efficient APS method. Among of metal ions, the most widely toxins, Cd(II), Co(II) and Sb(III) were studied. The optical sensing of these metal ions was performed using electronic absorption and emission techniques. The absorption spectra increase gradually upon increasing the concentrations of the used metal ions, with significant color changes. Also, a great enhancement in the fluorescence intensity was observed upon adding these metal ions. The spectral changes can be rationalized in terms of the formation of $[M(CITCs\text{-}KIT\text{-}6)_n]^{2+}$ complexes. These results suggested that CITC/KIT-6 nanosensor is suitable for the on-line analysis and in situ detection of these toxic ions in potable and environmental water samples.

1. Introduction

Mesoporous silicates with 2- and 3-dimensional (2D and 3D, respectively) structures have unique properties including high surface areas, narrow pore size distribution, large pore volume and high thermal stability [1–3]. Therefore, these nanostructured materials have been used for nanotechnological applications such as catalysis, adsorption, separation, sensing, medicine, lasers, drug/gene delivery and intrapore inclusion chemistry [4–6].

The synthesis strategy of mesoporous silicates depends on hydrolysis of various types of silica source such as tetraethoxysilane (TEOS) in the presence of surfactant as a template, forming an amorphous silica wall around the template micelle assemblies, followed by template removal using appropriate methods such as calcination to leave the open ended mesoporous structure as shown in Scheme 1 [7]. So, the surfactant type and synthesis conditions control the pore structure i.e., the pore diameter and dimensions of the resulting mesoporous materials [8].

In 1998, Santa Barbara Amorphous (SBA) materials of mesoporous silicates were synthesized using a triblock co-polymer as structure-directing agent instead of commonly used cationic tetraalkylamine surfactant to enhance the structural quality of the mesoporous silicates [9,10]. Among of SBA family, SBA-15 is used due to its excellent properties including: large pore size (up to 10 nm), 2D hexagonal structure, open-ended cylindrical channel and higher thermal stability relative to that of the MCM family [11,12].

Direct templating of surfactant is one of several methods which were used to enlarge the pores diameter and dimension of mesoporous materials [13]. In this method, the block copolymer-water solutions were mixed with alcohol as co-surfactant and swelling agent. In the case of the Korean Advanced Institute of Science and Technology (KIT-6) mesoporous silicates, butanol was used with P123 to synthesize large cubic-pores and 3Dmesoporous silicates as shown in Scheme 2 [14]. The large pore diameter and usage of inexpensive non-ionic surfactants in the synthesis of KIT-6 and SBA-15 suggested them a high potential as drug

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http://dx.doi.org/10.1016/j.snb.2014.12.079
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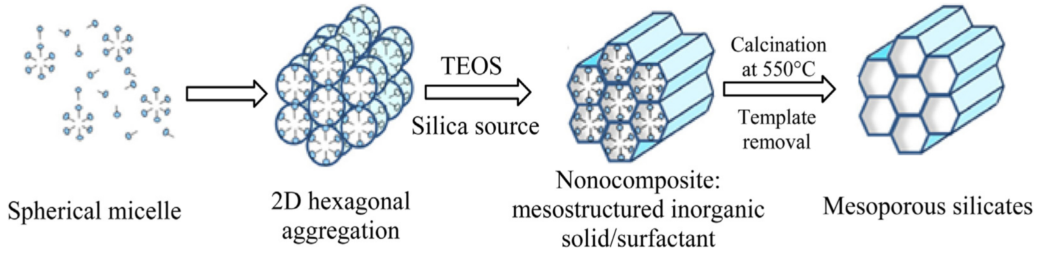
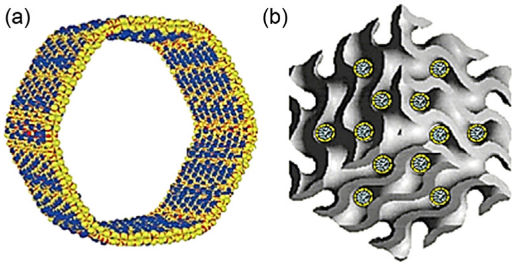


Scheme 1. General outlines for the synthesis of mesoporous silicates through a surfactant template method [9].



Scheme 2. (a) SBA-15 (large-pore 2D hexagonal) and (b) KIT-6 (large-pore 3D gyroid cubic) [15].

delivery media and hard templates for other nanostructured materials [15].

In addition, their internal and external surfaces could be chemically functionalized by many approaches. These were achieved by connecting a functional group via post-synthesis or one-step method. The post-synthesis method is related to the grafting of the functional group into calcinated mesoporous silicates. The one-step method was carried out by co-polymerization of an organosilane with a silica source in the presence of surfactant template, in which the functional groups of the resultant product were decomposed at high temperature. Therefore, the post-synthesis method has been commonly employed due to the high loading achievement of functional groups [16].

In liquid solutions, the quantum efficiencies of most organic dyes are strongly reduced. This is so-called self-quenching effect which results from the non-radiative energy transfer between dye molecules. Solid host materials isolate the dye molecules from each other, thus, reduces unwanted energy transfer. Therefore, the anchoring of dye molecules into solid host increases the photostability, fluorescence yield and water solubility besides easy surface modification compared to the free dye solutions itself [17].

Many researchers have used fluorescein isothiocyanate (FITC) and tetramethyl rhodamine isothiocyanate (TRITC) as guests for mesoporous materials, based on isothiocyanate group, as amino-reactive group which is covalently attached to the amino group of APS coupling agent [18,19]. This prompted us to anchor a new class of chalcones namely chalcone isothiocyanate (CITC) into mesoporous silicates.

The importance of chalcones are due to their wide applications in laser dyes, photopolymer imaging systems, metal ions sensing, high biological activities, photoactive and electroactive materials in molecular electronics. Anchoring of CITC into mesoporous hosts produces hybrid organic–inorganic nanocomposite materials with novel optical properties, which could be attractive as an optical sensing device for heavy metal ions detection [20].

Recently, the development of selective and sensitive imaging tools capable of rapidly monitoring heavy metal ions have attracted considerable attention due to their environmental and biological relevance. In this regard, Cd(II), Co(II) and Sb(III) are the most significant metal ions and have deleterious effects on the environment and living organisms, particularly at high levels of concentration [21,22]. Cd(II) is an extremely toxic and contributes to a large number of health conditions including the major killer diseases such as heart disease, cancer and diabetes [23]. Also, Co(II) is not highly toxic, but large doses will produce adverse clinical manifestations. Acute symptoms are pulmonary edema, allergy, nausea, renal failure, skin disorders, and thyroid abnormalities [24]. In addition, antimony and its compounds are considered as priority pollutants by the United States Environmental Protection Agency (US-EPA), due to their high toxicity [25]. The oxidation state of antimony Sb(III) is reported to be considerably more toxic and mobile than Sb(V). Therefore, there is a significant demand for accurate and specific determination of these toxic ions at low concentration levels in potable and environmental water samples [26].

In this work, the synthesis of a novel probe, chalcone isothiocyanate, via protection technique was reported. Also, two types of mesoporous silicates, KIT-6 and SBA-15 were prepared. The selective anchoring of CITC molecules into the host of KIT-6 and SBA-15 mesoporous materials via two loading methods was performed. Different spectroscopic techniques were used to characterize the investigated nanocomposite and assessment the two loading methods. Cd(II), Co(II) and Sb(III) sensing response were performed quantitatively using electronic absorption and emission techniques, as well as qualitatively using naked-eye color changes. Finally, the binding constants of the formed $[M(CITCs\text{-}KIT\text{-}6)_n]^{2+}$complexes were determined.

2. Experimental

2.1. Materials and reagents

Tetraethoxysilane (TEOS, 98%) was purchased from Across. Benzaldehyde and triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, molecular weight = 5800, where EO = ethylene oxide, PO = propylene oxide) were purchased from Sigma-Aldrich. 4-Acetylphenyl isothiocyanate (97% trans world chemicals incorporated), dimethyl amine (40% Oxford Laboratory), and benzene crystalline (BHD Laboratory) were used without further purification. 3-Amino propyltriethoxysilane was purchased from MB Biomedicals, inc. Ethanol and methanol (HPLC grade) were purchased from Fisher. Toluene and butanol were purchased from Tedia. Cobalt(II) chloride, antimony(III) chloride and cadmium(II) chloride were purchased from Wako Pure Chemicals, Osaka, Japan. Potassium chloride, sodium hydroxide, hydrochloric acid (35%) and acetic anhydride (98%) were purchased from Beijing Chemical Int. Distilled water was used for the preparation of all aqueous solutions.

2.2. Synthesis of CITC

It is well known that, chalcone has been synthesized via aldol condensation in the presence of alcoholic sodium hydroxide. The situation is very complicated in the case of chalcone isothiocyanate synthesis: where, the hydroxyl ion could react directly with