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Synthesis of 1,10-phenanthroline functionalized periodic mesoporous organosilicas as metal ion-responsive sensors

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The periodic mesoporous organosilicas with 1,10-phenanthroline (Phen) integrated in the framework (Phen-PMOs) were synthesized by co-condensation of tetramethoxysilane (TMOS) and the phenanthroline bridged organosilicas (Phen-Si) using triblock copolymer P123 as a template in weak acidic medium. The FT-IR, ^{13}C CP-MAS and ^{29}Si MAS NMR characterizations confirmed the integration of phenanthroline ligand in material. The Phen-PMOs have ordered 2-D hexagonal mesostructure though the structural order decreases with the increment in Phen content based on XRD and TEM characterizations. The hybrid materials exhibited specific surface area of 328–106 m^2/g and total pore volume of 0.43–0.17 cm^3/g. These Phen-functionalized PMOs, with strong blue fluorescent emission originated from phenanthroline group in the framework, have potential application in recognition of different metal ions, with luminescence intensity sensed to the type and concentration of the metal ions.

1. Introduction

Periodic mesoporous organosilicas (PMOs) synthesized from bridged silane precursors, $(R'O)_3Si–R–Si(OR')_3$, have attracted great research interest due to their unique physical and chemical properties, including high surface areas, large pore volume, high hydrothermal and mechanical stability, as well as uniform distribution of organic and inorganic moieties at the molecular level within the framework [1–3]. So far, different types of organic groups and even chiral ligands/catalysts have been incorporated in the framework of PMOs, such as methylene, ethydene, ethylene, ethinyl, phenylene, biphenylene, thiophene, norbornane, ferrocene [4–7], chiral alkane [8], chiral amine [9], benzylic ether [10], VO(Salen) [11,12], L-tartardiamide [13], norbornane [14], chiral 1,1′-bi-2-naphthol [15], 2,2′-bis(diphenylphosphino)-1,10-binaphthyl [16], etc. The incorporation of these functional organic groups widely extends the application scopes of PMOs, such as catalysis, adsorption, chiral separation, sensors, drug delivery [4,17–19] and so on.

Through integrating organic units with photoelectric properties in the framework, PMOs could be endowed optical and electronic characteristic. Corriu reported the synthesis of PMOs containing azobenzene moieties within the framework and showed that a sizable fraction of the azobenzene groups is reversibly photoisomerized [20]. Garcia and co-workers found that the PMOs with 4,4′-bipyridinium in the framework could act as electron acceptors. Later, they also reported a periodic mesoporous MCM-41 organosilica containing *trans*-1,2-bis(4-pyridyl)ethylene incorporated in the silica walls, which undergoes photochemical isomerization to the *cis* configured bis(4-pyridyl)ethylene [21]. Highly fluorescent and visible-light-responsive mesostructured organosilica films were successfully obtained by acidic sol–gel polycondensation of oligo(phenylenevinylene)-bridged organosilane and tetraethoxysilane precursors by Inagaki's group. Meanwhile, they reported the PMOs consisting of naphthalene–silica hybrid frameworks, which exhibit unique fluorescence behavior that reflects molecular-scale periodicity in the framework [22,23].

As a class of important fluorescent molecules, 1,10-phenanthroline (Phen) and its derivatives, which exhibited pronounced photochemical, electrochemical and biological activities, can be used in many fields. Incorporation of Phen and its derivatives in the framework of PMOs will be very interesting due to the combined effect of uniformly distributed Phen groups, ordered pore structure and high surface area. However, the PMOs with Phen as an integral part of the framework have seldom been reported.

As we all known, heavy transition metal ions are very harmful environment pollutants because they are widely distributed in the air, water and soil, which may cause serious human health risks. Detection, adsorption and removal of metal ions have been obtained extensive research interest due to their important roles

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in environmental protection. Many current techniques for metal ions detection, such as atomic absorption/emission spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS), and atomic fluorescence spectrometry, require expensive and sophisticated instrumentation and/or complicated sample preparation processes [24,25]. Unlike these techniques, chemosensors offer a promising approach for simple, low-costly and rapid tracking of metal ions in biological, toxicological and environmental samples [26–28]. Fluorescence-based sensors appear as one of the most promising candidates for metal ions detection, because fluorescence techniques are highly sensitive and easily operated. Several organic dye molecules have been demonstrated to be selective for the detection of metal ions based on fluorescence quenching [29,30]. For example, phenanthroline and its derivatives have been widely utilized for analytical and technological applications, and are efficient fluorescent probes for detecting metal ions. Incorporation of phenanthroline and its derivatives into porous solid materials will provide great application prospects for detecting heavy metal ions.

In this work, we reported the direct synthesis of ordered mesoporous Phen-PMOs with high content of phenanthroline in the framework by co-condensation method. The application potential of Phen-PMOs as luminescence sensor for detecting different kinds of heavy metal ions was investigated.

2. Experimental

2.1. Chemicals and reagents

Triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer Pluronic P123 (Mw = 5800, $EO_{20}PO_{70}EO_{20}$) was purchased from Sigma–Aldrich Company Ltd. (USA). 3-(Triethoxysilyl)propyl isocyanate was obtained from ABCR GmbH & Co.KG. Hydrazine hydrochloride was purchased from Sinopharm Chemical Reagents Limited Company (SCRC). NaCl, tetramethoxysilane (TMOS), and other reagents were purchased from Shanghai Chemical Reagent Company of Chinese Medicine Group. The solvents were of analytical quality and dried by standard methods. Other reagents were of analytical grade and used as purchased without further purification.

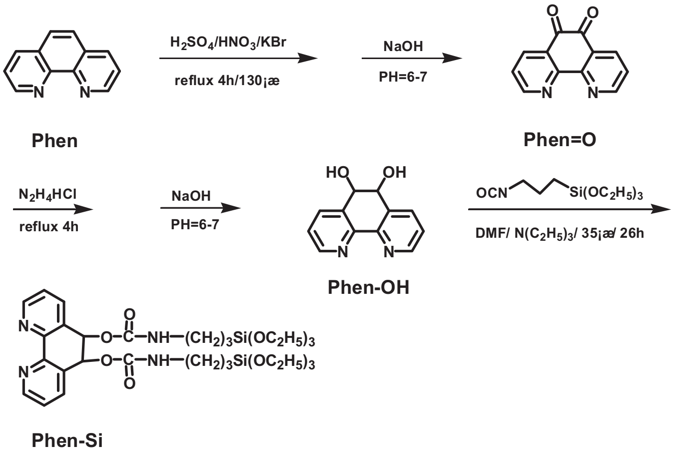
2.2. Synthesis

2.2.1. Synthesis of 1,10-phenanthroline-5,6-diol (Phen-OH)

1,10-Phenanthroline-5,6-diol (Phen-OH) was synthesized according to literature method [31,32].

2.2.2. Synthesis of phenanthroline bridged organosilane precursor (Phen-Si)

Under argon atmosphere, 3-(triethoxysilyl) propyl isocyanate (11 mmol) were added to the mixture of 1,10-phenanthroline-5,6-diol (5 mmol), DMF (70 mL) and triethylamine (2.5 mL) by syringe at room temperature over a period of 10 min. The mixture was stirred over 26 h at room temperature. The coupling reaction can easily be monitored by infrared spectroscopy. After reaction, the solvent was pumped off and the crude product was dissolved in hexane. The solvent was evaporated and the excess of 3-(triethoxysilyl)propyl isocyanate was distilled in vacuo. The crude product was dissolved in DMF and filtered. Evaporation of the solvent gave the pure 1,10-phenanthroline-bridged organosilane precursor (Phen-Si) as a wine red and highly viscous liquid. The general synthesis procedure for Phen-Si was outlined in Scheme 1. Yield: 2.13 g (93%). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.90 (4H), 8.33 (2H), 7.85 (2H), 5.70 (2H), 3.75 (12H), 3.08 (4H), 1.58 (4H), 1.15 (18H), 0.62 (4H).



Scheme 1. General synthesis procedure for phenanthroline bridged organosilane precursor (Phen-Si).

2.2.3. Synthesis of periodic mesoporous organosilicas with phenanthroline in the framework (Phen-PMOs)

The periodic mesoporous organosilicas with phenanthroline in the framework were synthesized by the co-condensation of TMOS and Phen-Si with block copolymer P123 as a templating agent (Scheme 2). In a typical synthesis, P123 (1.06 g) was dissolved in a mixture of NaCl (1.92 g), 0.25 M NH_4F (0.32 mL) and 0.1 M HCl (32.8 mL) with stirring at 40 °C for 6 h to obtain a clear solution. The mixture of TMOS and Phen-Si in ethanol was added to the above solution under vigorous stirring. The molar ratio of the reactants was (TMOS + Phen-Si)/H_2O/P123/NH_4F/NaCl/HCl = 1:163: 0.016:0.007:2.748:0.029. The resultant mixture was further stirred at 40 °C for 46 h. The product was recovered by filtration, washed with deionized water, and dried in air under ambient conditions. The surfactant was extracted by refluxing 1.0 g of the as synthesized material in 200 mL of ethanol for 12 h. The materials obtained were denoted as PST-*n*, where *n* (*n* = 5, 10, 20, 30) is the molar percent of Phen-Si/(TMOS + Phen-Si).

2.2.4. Adsorption of metal ions on PST-10

At room temperature, 50 mg of PST-10 was immersed in 5 mL H_2O solution containing different kinds of $M(NO_3)_2$ (M = Mg^{2+}, Ni^{2+}, Pb^{2+}, Cr^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, or Cd^{2+}) or $Cu(NO_3)_2$ with concentration in the range of 10^{-5}–10^{-2} M and the mixture was stirred for 12 h. The solid product was recovered by centrifugation and washed with 3 mL deionized water for 3 times for removal the excess $M(NO_3)_2$. After dried at room temperature, metal-ion-incorporated PST-10 (denoted as M-PST-10) was obtained as solids for luminescence studies.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max 2500 powder diffraction system using CuKα radiation of wavelength 0.15406 nm. The nitrogen sorption experiments were performed at 77 K on an ASAP 2020 system. Samples were degassed at 333 K for 5 h prior to the measurements. BET surface area was calculated from the adsorption data at a relative pressure P/P_0 ranging from 0.05 to 0.25. Pore size distribution was determined from the adsorption branch using the Barret-Joyner-Halenda (BJH) method. Pore volume was estimated at a relative pressure P/P_0 of 0.99. FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer with KBr pellets. Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2 at an acceleration voltage of 120 kV. Solid-state ^{13}C (100.5 MHz) CP-MAS NMR and