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Short Communication

Mesoporous hybrid from anionic polyhedral oligomeric silsesquioxanes (POSS) and cationic surfactant by hydrothermal approach

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ABSTRACT

In this paper, we report one novel kind of organic–inorganic mesoporous hybrid from octa-anionic polyhedral oligomeric silsesquioxanes (POSS) and cationic surfactant. The mesoporous hybrid was achieved by two steps: first, lamellar precursor made of POSS and surfactant was prepared by template-directed synthesis; then mesoporous structure was obtained via the reformation of lamellar precursor under hydrothermal treatment. According to our experimental results (XRD, TEM and SEM), the lamellar-to-hexagonal mesophase transformation process and its mechanism was suggested. The thermal stability and degradation behavior of the mesoporous hybrid was also discussed based on TGA curves obtained under nitrogen atmosphere.

1. Introduction

The synthesis and applications of nanomaterials with porous structure have been one popular topic in materials research due to their attractive features such as high pore volume, large surface area, etc. [1,2]. Ordered mesoporous (2–50 nm) materials seems more attractive, which can be utilized in the storage of small molecules or larger molecules (such as nucleotides and proteins), or be employed as carriers for drug delivery [3–5]. Compared with amorphous colloidal and porous silica, mesoporous materials modified by functionalisation exhibit higher loading of drugs and provide a controlled drug release [6]. The discovery of a new family of highly ordered mesoporous siliceous materials designated as M41S which processes uniform pore diameter [7] has been regarded as a breakthrough in mesoporous materials research [8,9]. Generally speaking, there are four different mesostructures in the M41S, such as hexagonal MCM-41, cubic MCM-48, lamellar M41S, and cubic octamer $[(CTAB)SiO_{2.5}]_8$ [10]. Among them, the hexagonal MCM-41 is very useful as practical material because it has mesopores of uniform size and shape with one-dimensional channels of hexagonal array, high thermal and hydrothermal stability, and ease of fuctionalisation by other elements. These kinds of mesoporous materials can be prepared by silica and surfactant via template-directed synthesis following co-operative assembly pathways, in which surfactant works as soft template to induce the self-assembly, while silica are used as framework in building the materials.

Polyhedral oligomeric silsesquioxanes (POSS), with their sizes ranged from 1 to 3 nm in diameter, can be regarded as the smallest possible units of silica. POSS are one type of hybrid materials with the general formula $(RSiO_{3/2})_n$, whose organic substituents are connected with a silicon–oxygen core. The most common POSS cage is T_8 (cubic structure), and other POSS cages with well-defined geometries include T_n (where $n = 6$, 10, 12, 14, etc.) [11–13]. Since its first synthesis reported in 1946 [14], numerous POSS and POSS compounds with different organic substituents have been prepared by chemists. Now they are becoming novel building block with immense potential for generating hybrid materials: POSS cages can be used in forming novel composite materials with improved or special properties [15,16]; POSS themselves are one kind of hybrid materials with low toxicity, stability, good biocompatibility; ionic POSS nanoparticles can be used in drug delivery [17] and DNA detection [18]; POSS based nanocomposites or nanohybrids are valuable or potentially valuable in biomedical application [19].

It is of great interests to design novel POSS based nanomaterials with defined mesoporous structure and specific properties. In this paper, we present one kind of mesoporous hybrid obtained from octa-anionic POSS and cationic surfactant by self-organization and hydrothermal approach.

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2. Experimental

2.1. Materials

Tetramethylammonium hydroxide (Me_4NOH), Phenyltrichlorosilane, benzene, chlorosulfonic acid, and alkyltrimethylammonium bromide ($C_{16}H_{33}NH_4Br$, C_{16}TAB), they were commercially available and were of analytical grade.

2.2. Techniques

Bruker EQUINOX 55 FT-IR spectrophotometer; Rigaku K/max-γA X-ray diffractometer with a Cu Ka (λ = 1.5415 A) at the scanning rate of 0.02/s; JSM-6700F Field Emission Scanning Electronic Microscope system; JEOL2010 Transmission Electronic Microscope system; Netzsch STA-409c Thermal Analyzer under a 50 mL/min nitrogen flow.

2.3. Synthesis and preparations

Octaphenyl Polyhedral Oligomeric Silsesquioxane (Ocp-POSS) was synthesized via the hydrolysis and condensation of phenyltrichlorosilane ($PhSiCl_3$) and the subsequent rearrangement reaction catalyzed by tetramethylammonium hydroxide according to the published literature [20]. $PhSiCl_3$ (100.00 g, 0.48 mol) was dissolved in 1000 mL of benzene with vigorous stirring and then 50 mL of water was added. The hydrolysis was carried out at room temperature for 48 h. Thereafter, the benzene layer was isolated and washed several times with deionized water to remove the hydrochloric acid. The above benzene solution and 20 mL methanol solution of tetramethylammonium hydroxide (50 wt.%) were charged to a flask equipped with a mechanical stirrer. The mixture was refluxed for 48 h to attain a complete rearrangement reaction. After that, the mixture was cooled to room temperature and afforded about 58 g white microcrystalline powders. The product was extracted, using benzene in a Soxlet extractor, to remove the soluble resin and further dried in vacuum.

Octa(sulfonic phenyl) POSS (Osp-POSS) was obtained by the sulfonation of Ocp-POSS. Fifteen grams Ocp-POSS was further dissolved in sufficient chlorosulfonic acid under slow electromagnetic stirring and the liquid becomes clear and transparent after several minutes. In this way, sulfonic groups can be introduced to Ocp-POSS. After half an hour the solution was transferred into a separating funnel, then the mixture was dropped in water at an extremely slow rate and white solid appeared simultaneously accompanied with certain amount of heat release. The white solid product was then collected and washed for further neutralization reaction. Five grams Osp-POSS (3 mmol) was dissolved in 240 mL NaOH aqueous solution (0.1 mol/L) and colorless transparent Na_8Osp-POSS solution (0.0125 mol/L) was formed.

Lamellar precursor was prepared by ion-exchange reaction between Na_8Osp-POSS and cetyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$, C_{16}TAB). When the solution was mixed by sufficient aqueous solution of C_{16}TAB (0.1 mol/L), ion-exchange reaction occurred and white deposition appeared. It was washed by distilled water and further dried in vacuum in order to get pure Osp-POSS–C_{16}TAB hybrid powder. These were reported and discussed in our previous work [21]. POSS cages and the organic chains of surfactant were connected by electrostatic forces and lamellar structure was formed for the different compatibility between the organic part (alkyl chain) and the inorganic part (POSS cage) of the hybrid.

The mesoporous Osp-POSS–C_{16}TAB hybrid was obtained by the reformation of lamellar precursor under hydrothermal treatment: 1 g lamellar powder together with 5 mL Na_8Osp-POSS solution (0.0125 mol/L) was dispersed in aqueous solution system under a 20-min ultrasonic treatment with controlling pH = 8–9. Thereafter, it was placed in a sealed high-pressure kettle under 120 °C for 48 h (2-day sample) and 240 h (10-day sample) respectively. The final products were separated and washed for the following characterization.

3. Results and discussion

FTIR, Solid ^{29}Si NMR and MALDI-TOF Characterizations of Ocp-POSS are showed in Fig. 1, and detailed data are as following:

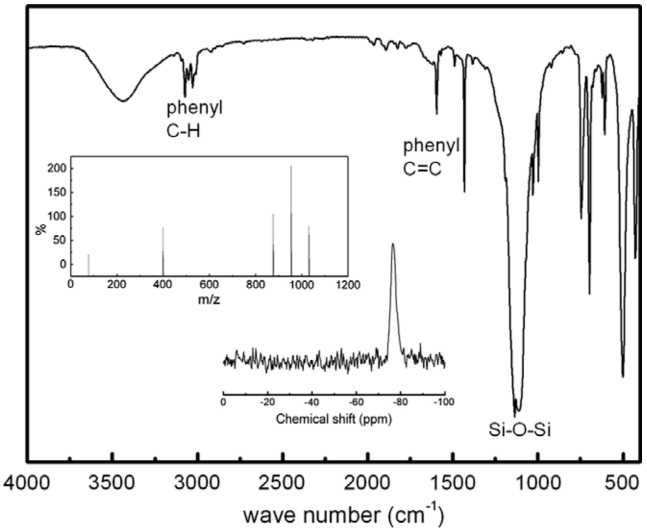

Fig. 1. FT-IR spectrum, ^{29}Si NMR spectrum and mass spectrum of Octaphenyl POSS.

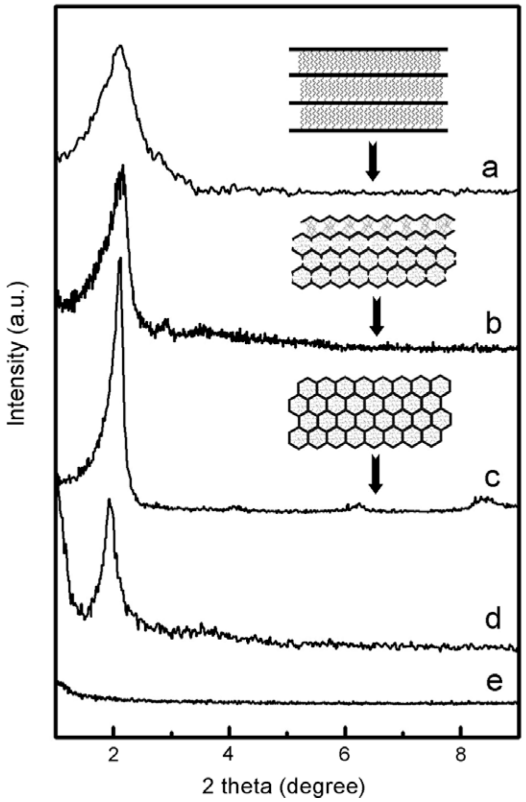

Fig. 2. XRD patterns of (a) lamellar POSS-surfactant hybrid; (b) 2-day sample; (c) 10-day sample; (d) 10-day sample after TGA test; and (e) Octa(sulfonic phenyl) POSS (Osp-POSS).