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Na_2EDTA: Trifunctional controller for formation of tubular mesoporous silica at circumneutral pH and low temperature

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Abstract

Using organic salt Na_2EDTA as trifunctional controller, hollow silica tubes with mesoporous wall were synthesized at circumneutral pH and low temperature. XRD, N_2 sorption measurements, FTIR, TG-DTA, ^{29}Si MAS NMR, SEM and TEM were performed to characterize the topology and morphology of mesoporous silica. The material exhibits disordered wormlike mesoporous structure with thick pore wall (estimated to be about 3 nm). The diameter of silica tubes ranges from 1 to 5 μm with the wall thickness of about 100–200 nm. Na_2EDTA plays ternary roles in the synthesis: (1) as catalyst for hydrolysis and condensation of TEOS at circumneutral pH and low temperature; (2) to co-assemble with micelles of CTAB to give rise to wormlike mesoporous structure and (3) the incipient crystallization of Na_2EDTA as template to induce formation of tubular morphology. The addition of ethanol to the synthesis system benefits the formation of silica tubules.

Keywords: Mesoporous silica; Tube; Na_2EDTA; TEOS; Mild condition

1. Introduction

Significant advances have been made in the past decades to fabricate mesoporous silica with versatile structures and morphologies [1–3]. Hollow mesoporous fibers or tubes attracted great attention due to their wide prospective applications in nanotechnology, catalysis and separation technology, biomaterials engineering and fabrication of nanodevices [4–6]. Mou's group firstly reported mesoporous silica with a hollow tubules-within-a-tubule hierarchical structure, which was synthesized in a high alkaline solution [7]. In a static two-phase acidic system, mesoporous silica tubules, together with mesoporous silica fibers were also prepared [8]. With organic gel fibers [9] or organic salt [10] as templates, silica tubes were fabricated at acidic or basic pH, respectively. However, the tube wall was non-porous. Afterwards, nanoporous aluminum oxide membrane was used as hard template to prepare mesoporous silica nano-tubal arrays in HCl–ethanol system at 100 °C [11]. Recently, Lu et al. fabricated mesoporous silica microtubules through the self-assembly of β-cyclodextrin and Triton X-100 in an acidic aqueous solution [12]. Summarizing the above methods, although silica tubes have been obtained with ease, the synthesis was performed under either *basic* or *acidic* conditions. Thus some applications of mesoporous silica such as in situ immobilization/encapsulation of bioactive enzymes will be limited [13,14]. So synthesis of mesoporous silica with specific morphology such as tubes under mild conditions would be an attractive subject.

The hydrolysis and condensation of organic silicane will not occur in the absence of catalyst (typically OH^-, H^+ and

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F^-). To find proper catalysts for hydrolysis of alkoxysilane at neutral pH, people investigated the silicification of some proteins such as silaffin and silicatein extracted from diatoms [15,16]. Inspired by the finding of residues in silicatein, Roth et al. found cysteamine can catalyze hydrolysis and condensation of alkoxysilane at neutral pH [14]. Amines were also found to have the ability to catalyze the biomimetic hydrolysis and condensation of organosilicate at mildly acidic pH [17].

In fact electrolytes (such as salts) have been found to be able to modify the rate and extent of silicon alkoxide hydrolysis and condensation [18]. The presence of salts in the synthesis of non-ionically templated MSU-X mesoporous silica was reported to have significant influence on both the conformation of PEO surfactant and the rate of hydrolysis and condensation of TEOS [19,20]. Based on the above results, it would be possible to utilize a salt to catalyze the hydrolysis and condensation of TEOS. Simultaneously it is expected that this salt can interact with the micelles of the cationic surfactant to produce mesoporous structure under mild conditions.

Just recently, we have demonstrated the function of Na_2EDTA for the synthesis of mesoporous silica under mild conditions of circumneutral pH and room temperature [21]. In this work, Na_2EDTA is investigated as a trifunctional controller for the formation of tubular mesoporous silica with cationic surfactant CTAB, at circumneutral pH and low temperature. Na_2EDTA plays ternary roles in the synthesis: (1) as catalyst for hydrolysis and condensation of TEOS; (2) to form co-assembly with micelles of CTAB to give rise to the mesoporous structure. Na_2EDTA, as a frequently used chelating agent, can have a strong interaction with polyelectrolyte, for instance, poly (L-lysine), to form polymer aggregates [22]. In the case of cationic surfactant CTAB, EDTA can be a good candidate to interact with CTAB micelles through electrostatic interaction to form supramolecular co-assembly, which could be applied as templates for mesoporous silica. (3) in situ crystal of Na_2EDTA would act as template to induce the formation of tubular morphology. At near neutral pH and low temperature, the obtained silica exhibits tubular morphology with wormlike mesoporous silica tube wall. To our best knowledge, it is the first time to report the formation of tubular mesoporous silica under near neutral pH and low temperature. This Na_2EDTA inspired method might widen the synthesis field of mesoporous materials by extending other cationic polyelectrolyte as templates under mild conditions.

2. Experimental

2.1. Materials

Tetraethoxysilcane (TEOS, A.R.) and ethylenediaminetetraacetic acid disodium salt (Na_2EDTA, A.R.) were purchased from Rgent Chemical Reagent Co., Tianjin, China. Cetyltrimethylammonium bromide (CTAB, A.R.) was purchased from Amresco Co., USA. All materials were used as received without further purification.

2.2. Synthesis

In a typical synthesis procedure, 0.73 g of CTAB and 1.86 g of Na_2EDTA were added into 18.0 g of deionized water under stirring to make a transparent solution. Then 2.08 g of TEOS was added dropwise. The final reactant composition in molar ratio was 0.2CTAB/1TEOS/$0.5Na_2EDTA/100H_2O$. The pH of this reactant mixture was about 5. After stirring for a day, the mixture was left static in a sealed conical flask at given temperature for 4 days and gradually a white gel formed. The obtained white gel was filtered, washed with deionized water and dried at 323 K for overnight. Then the fleecy white product was obtained, referred as CTE.

For the case with addition of ethanol, the synthesis procedure is: 0.73 g of CTAB and 1.86 g of Na_2EDTA were added into 18.0 g deionized water under stirring to make a transparent solution. Then a mixed solution of 2.08 g of TEOS and 5 g of ethanol was added dropwise. The reactant composition in molar ratio was 0.2CTAB/0.5TEOS/$0.5Na_2EDTA/100H_2O$/5.43 ethanol. After stirring for 10 min, the mixture was left static in a sealed conical flask at 293 K for 6 days.

2.3. Removing template

The as-synthesized sample was firstly treated with 0.28 mol/L of $ZnSO_4$ solution at 298 K for 3 h twice to remove the EDTA. Then the product was calcined in an air–atmosphere muffle furnace at a heating rate of 2.5 K/min from room temperature to 573 K and held for 90 min, then raised to 813 K at a heating rate of 1.5 K/min. Another mode of removing template is by mixing 1 g of the air-dried CTE with 150 mL ethanol and refluxing for 2 h and the process was repeated twice.

2.4. Characterizations

X-ray powder diffraction (XRD) data were collected with a Rigaku D/max 2500 diffractometer, equipped with a graphite monochromator and using CuKα radiation (at 40 kV and 100 mA, $\lambda = 0.154$ nm) with step width of 0.01°. N_2 adsorption measurements were performed at 77 K using a Micromeritics TriStar 3000 analyzer. Before measurements, the sample was outgassed at 523 K for 4 h. The specific surface area was calculated by Multi-BET from 8 points in the range of relative pressure 0.1–0.3. The pore size distribution (PSD) was calculated by BJH method from adsorption branch. SEM observations were carried out on a Hitachi X-650 and a Shimadzu SS-550 scanning electron microscope. The powder sample was stuck onto the observation platform and sprayed with gold vapor under high vacuum for 20 s. TEM observations were carried out on a Philips Tecnai F20 transmission