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Synthesis of length controllable mesoporous SBA-15 rods

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ABSTRACT

Monodispersed SBA-15 rods with different lengths (from hexagonal platelets to short rods, and to longer rods) have been synthesized by using triblock copolymer P123 as a structure-directing agent and glycerol as a cosolvent. Our studies showed that glycerol is indispensable for tuning the length of SBA-15 rods. And, in the presence of glycerol, the length of these SBA-15 rods was reversely proportional to the concentration of the acid (HCl) in the synthetic mixture. Based on our characterizations (XRD, SEM, TEM, N_2-sorption, and dynamic light scattering (DLS) analyses) and the literature results, a possible glycerol-induced growth mechanism was proposed for the formation of these SBA-15 rods. Furthermore, an adsorption of lysozyme on these SBA-15 materials was investigated and the results showed that they all exhibited rapid lysozyme immobilization and high adsorption capacity (the highest up to 907 mg g^{-1} for capsulelike SBA-15 synthesized at M_{HCl} = 2.0 M).

1. Introduction

Ordered mesoporous silicas synthesized from the surfactant-template method have attracted much attention due to their wide potential applications in catalysis, separation, adsorption, sensors, drug delivery and nanotechnology. Recent studies showed that the external morphology of mesoporous silicate materials was one of the major factors to influence their practical applications [1–3]. For instance, mesoporous silica spheres used as matrix materials for chromatographic separations showed a superior separating ability than commercial porous silica [1] and the hollow mesoporous silicate spheres with a 3D pore-network showed excellent store and release properties of drug (e.g. aspirin) [2]. Recently, Zhao's group reported the synthesis of the highly ordered rodlike (1–2 μm long) hexagonal mesoporous SBA-15 materials in the presence of inorganic salts (KCl), which possessed much better immobilization behaviors for enzymes than the conventional SBA-15 materials [3,4]. Meanwhile, this kind of mesoporous silica can further be employed as the templates to synthesize rodlike mesoporous carbon [5].

Among these mesoporous materials, SBA-15 has been studied extensively because of its larger pore sizes and better chemical and physical stabilities. Typically, this material was synthesized by the self-assembly of silica-surfactant (commonly used P123) in which inorganic species simultaneously condense, giving rise to mesoscopically ordered composites formation. The most common morphology of mesoporous SBA-15 synthesized by conventional method is fiberlike, several tens of micrometers in length aggregated by coupling short rodlike particles [6]. However, for a variety of practical applications, the fabrication of desired morphologies is important as well as the control in composition, structure, porosity, etc. Recent reports in the literature have demonstrated that the morphology and the textural properties of SBA-15 materials may be affected by kinds of synthetic parameters, such as stirring, acidity, reaction ratio, salt, reaction duration, cosolvent, cosurfactant, and so on [7–10]. Mesoporous SBA-15 materials in the form of rod, sphere, fiber, platelet, gyroid, discoid, sausage and doughnut shapes have been obtained by various synthetic strategies [7,10–12]. Zhao et al. [7] have described the synthesis of micrometer-sized mesoporous silica SBA-15 with various morphologies through the cosolvent, cosurfactant, and inorganic electrolyte approaches. Liu et al. [9] synthesized SBA-15-type mesoporous silicas with various structures and morphologies through adjusting the TMP/P123 ratio, these materials also showed good adsorption capacity for enzyme. Kubo and Kosuge [10] reported the synthesis of long, homogeneous fiberlike SBA-15 particles with the addition of salt, which exhibited an effective performance on toluene adsorption.

Although some studies have reported the preparation of rodlike SBA-15 materials [5,11], there has been no report on the successful synthesis of length controllable rodlike SBA-15 so far. It is expected that the smaller size of SBA-15 may be promising for better biological applications [4]. So considering the difference in size among the ordered mesoporous SBA-15 rods, the comparison of the bio-adsorption behavior among different length of materials with similar mesostructure and textural properties would be

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very meaningful for further studying the driving force in bio-adsorptions.

Here, we report the successful synthesis of highly ordered SBA-15 rods with controllable length by using P123 as a template and glycerol as a cosolvent. The effects of glycerol on the morphologies and pore structure of mesoporous silica were studied, and a possible formation mechanism of nanorods was discussed briefly on the basis of our results and previous study. Furthermore, the adsorption isotherms and adsorption amounts of lysozyme on these SBA-15 rods are presented and compared. The highest lysozyme adsorption capacity of 900 mg g^{-1} was obtained on the capsulelike SBA-15 rods.

2. Experimental

2.1. Synthesis

Rodlike mesoporous SBA-15 silicas were synthesized using triblock copolymer, Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as the template and tetraethylorthosilicate (TEOS) as the silicate source at different acidic conditions in the presence of glycerol. All commercial chemicals were used without further purification. In a typical synthesis, 1.8 g of P123 and equal mount (1.8 g) of glycerol were dissolved in 69 g aqueous acidic solution with different HCl concentration (M_{HCl} = 2.5, 2.0, 1.0, 0.5 M), which was stirred at 35 °C for 6–10 h to get a transparent solution. Then, 3.87 g of TEOS was added to the above solution under vigorous stirring. After stirring for 5 min, the mixture was kept in static conditions at the same temperature for 24 h, followed by aging at 100 °C for 24 h. The solid products were collected by filtration, washed with water, and dried at 80 °C overnight in air. The resulting powders were calcined at 550 °C for 5 h to remove surfactant.

2.2. Characterization

Small angle X-ray diffraction (SXRD) patterns were recorded on a Rigaku D/MAX-2550VB/PC diffractometer (CuKα_1 radiation, λ = 1.5406 Å), operated at 40 kV and 200 mA (scanning step: 0.02° s^{-1}). The nitrogen sorption experiments were performed at 77 K on a NOVA 4200e surface area and pore size analyser. Before the measurements, the samples were outgassed at 300 °C in vacuum for 6 h. The Brumauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. The total pore volume (V_p) was estimated at a relative pressure of 0.975. TEM images were obtained with FEI Tecnai 20 S-TWIN. SEM was performed on a JEOL JSM-6360 scanning electron microscope operating at an acceleration voltage of 20–30 kV. Dynamic light scattering (DLS) measurement was carried out using a Malvern instrument with a He–Ne laser (633 nm) as a light source to investigate the size distribution of P123 micelles in different concentration of HCl solution at the temperature of 35 °C. Zeta-potential was measured by POWEREACH JS94 micro-electrophoresis apparatus. The samples were dispersed in buffer solution (pH 6.86) and sonicated for 2 h before measurement.

2.3. Enzyme adsorption

For lysozyme adsorption, about 20 mg of mesoporous silica was added to 5 mL of lysozyme solution with a concentration of 4.0 mg mL^{-1} (25 mM; potassium phosphate buffer at pH 6.86) in a vessel. The resulting mixture was stirred at room temperature for 72 h to reach adsorption equilibrium. The suspension was centrifuged at 4500 rpm for 5 min, and the supernatant was analyzed by UV absorbance at 280 nm to determine the adsorbed amount of lysozyme according to the following equation:

$$q = \frac{V_0(C_0 - C)}{W} \quad (1)$$

where q is the equilibrium adsorbed amount in SBA-15 rods, C_0 and C are the enzyme concentrations at initial and equilibrium solution, respectively, V_0 is the volume of the initial enzyme solution, and W is the weight of adsorbent. For the kinetic experiments, 20 mg of mesoporous silica was suspended in 4 mL of

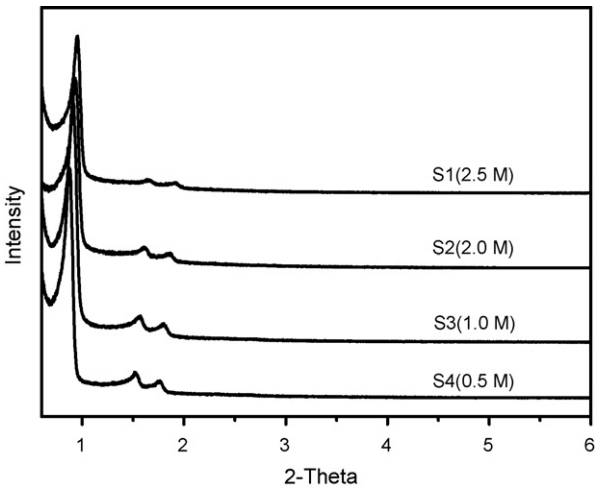

Fig. 1. Small angle XRD patterns of four samples synthesized at different concentrations of HCl.

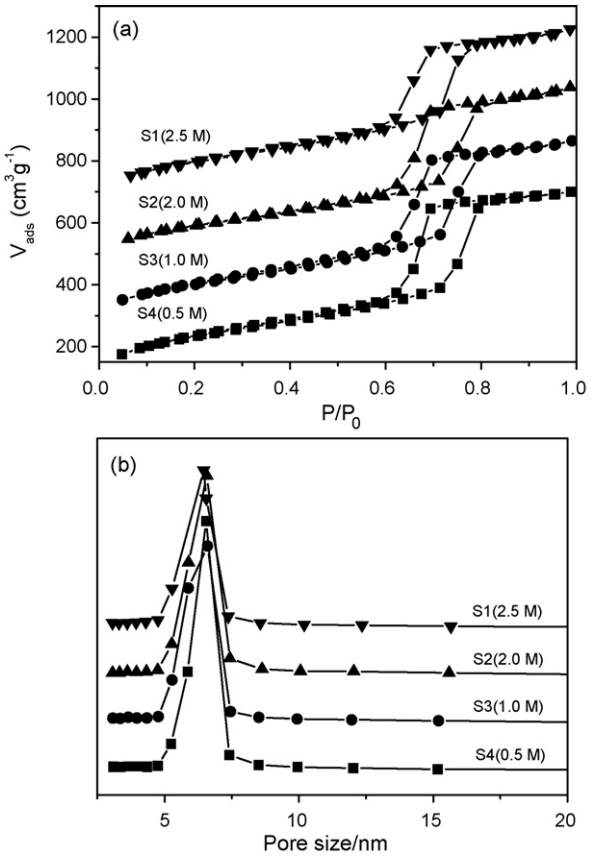

Fig. 2. N_2 sorption isotherms of four mesoporous SBA-15 rods (a) and their pore size distribution curves (b).

Table 1
Textural properties of four SBA-15 rods and their lysozyme adsorption capacities.

Samples	HCl (M)	a_0 (nm)	S_{BET} (m^2 g^{-1})	D_P (nm)	V_t (cm^3 g^{-1})	Wall thickness (nm)	Length (μm)	Lysozyme capacity (mg g^{-1})
S1	2.5	10.86	701.7	6.5	0.968	4.4	0.3	746.6
S2	2.0	10.95	677.8	6.6	0.987	4.4	0.8	907.0
S3	1.0	11.22	716.0	6.6	1.029	4.6	2.5	852.0
S4	0.5	11.56	692.0	6.5	0.958	5.1	4.0	494.5

S_{BET}: specific surface area; V_t: the total pore volume at relative pressures 0.95; D_P: the pore diameter calculated from the desorption branch of the isotherm using the BJH method; a_0: unit cell parameter equal to $2d_{100}/3^{1/2}$; the wall thickness $h_w = a_0 - D_p$.