Synthesis of mesoporous silica materials with ascorbic acid as template via sol-gel process

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Mesoporous silica materials with pore diameters of 2—5 nm have been prepared using ascorbic acid as a nonsurfactant template or pore-forming agent in HCl-catalyzed sol-gel reactions of tetraethylorthosilicate, followed by removing the ascorbic acid compound by extraction with ethanol. Characterization results from nitrogen sorption isotherm, powder X-ray diffraction and transmission electron microscopy indicate that the materials have large specific surface areas (e. g. 1000 m^2/g) and pore volumes (e. g. 0.8 cm^3/g). The mesoporosity is arisen from interconnecting disordered wormlike channels and pores with relatively broad size distributions. As the ascorbic acid concentration is increased, the pore diameters and pore volumes of the materials increase.

Keywords   Mesoporous silica material, ascorbic acid, nonsurfactant template, sol-gel process

Introduction

Since the discovery of ordered mesoporous M41S materials by Kresge et al.,[1] it has attracted researchers much attention[2-12] because of the potential use of these materials in catalysis,[13,14] chemical separation technology[15,16] and polymerization.[17,18] In most of the studies, ionic[3-8] and neutral[9-12] surfactants have been employed as templates, which direct the mesophase formation based on the electrostatic and hydrogen bonding interactions, respectively.

In 1998, Wei et al.[19] reported a versatile nonsurfactant templating route for synthesis of mesoporous materials via the sol-gel process, in which nonsurfactant organic compounds, such as D-glucose, D-maltose, dibenzoyl-L-tartaric acid, etc., were employed as the templates or pore-forming agents. Mesoporous materials with large specific surface areas of ca. 1000 m^2/g, pore volumes of ca. 1.0 cm^3/g as well as narrow pore size distributions can be obtained upon the removal of the nonsurfactant molecules by solvent extraction. The pore diameter and pore volume can be controlled by varying the template concentration. The mesoporous silica materials obtained can be used in enzyme immobilization.[20] So far, this nonsurfactant pathway has been used to synthesize mesoporous silica,[21,22] alumina[23] and titania[24] materials. Unlike the M41S but very similar to the MSU-19 silica, the materials exhibit largely disordered channel or pore arrangements and good thermal stability. The interconnected channel arrangements might be advantageous[12] in catalysis and separation technology over ordered but parallel-packed channels. D-Glucosamine hydrochloride[25] was also found to direct the formation of mesoporous zinc phosphate crystalline phases.

In order to expand the kinds of organic compounds that can act as templates or pore-forming agents, herein we report the preparation of mesoporous silica materials using ascorbic acid, a nontoxic and low-cost organic compound as a nonsurfactant template. The hydroxyl and carbonyl groups in ascorbic acid molecules may lead to hydrogen bonding interactions between the template compounds and the inorganic species, which might play important roles in directing the mesophase formation.[9,19,21] The syn-

thesis was achieved by HCl-catalyzed hydrolysis and poly-condensation ($i. e.$ the sol-gel reactions) of tetraethyl orthosilicate (TEOS) in the presence of ascorbic acid, followed by removal of the ascorbic acid compound through solvent extraction.

Experimental

Synthesis of mesoporous materials

The synthetic procedures were taken according to our previous literatures.[19,22] In a typical synthetic procedure, 25 cm^3 of tetraethyl orthosilicate (TEOS, Acros Organics, 98%) was prehydrolyzed with deionized H$_2$O in ethanol using HCl as catalyst (at TEOS:HCl:H$_2$O:EtOH molar ratios of 1:0.01:4:3) at about 75 ℃ for 5 h. Upon being cooled to room temperature, the prehydrolyzed solution was equally divided into 5 beakers. Then a designed amount ($e. g.$ 4.5 cm^3 for sample AA-50) of 0.3 g/cm^3 aqueous solution of ascorbic acid (China Medical Co., AR) was added into one of the beakers under stirring to afford homogeneous solution. The beakers were then sealed with a cellophane film containing several pinholes to allow for slow evaporation of the solvent and reaction by-products. The brown monoliths or small pieces of silica/ascorbic acid composites were obtained after being gelled and dried for about two months at room temperature. Then the silica composites were ground into fine powders and extracted with ethanol for 3 days in a Soxhlet apparatus under ambient pressure. Upon being dried in a vacuum oven at about 80 ℃ for ca. 3 h, the porous silica materials were obtained. The removal of the ascorbic acid was monitored by FT-IR analysis, based on the disappearance of the characteristic absorption band of ascorbic acid C = O stretching vibration at about 1755 cm^{-1}. A control sample was also prepared under identical conditions except for the absence of ascorbic acid.

Characterization of mesoporous materials

The FT-IR spectra of the samples before and after solvent extraction were measured in the form of KBr powder-pressed pellets on a Bruker Vector 22 FT-IR spectrometer. The surface area, pore volume, pore diameter and pore size distribution of the silica samples after the solvent extraction were determined by nitrogen adsorption-desorption isotherms at 77 K on a Micromeritics AS-

AP2010 analyzer. Before each measurement, the sample was degassed at 473 K and below 1.33 Pa for more than 3 h. The powder X-ray diffraction (XRD) pattern was recorded on a Rigaku DMAX2400 instrument using Cu K$_\alpha$ radiation (λ = 0.15418 nm, 40 kV, 100 mA) at scanning rates of 1°/min in the 2θ range of 0.6—10° and of 8°/min in the ranges of 10—40°. Morphologies of the mesoporous samples were examined on a Hitachi H-9000NAR HREM transmission electron microscope (TEM) operated at an accelerating voltage of 300 kV. The samples for TEM were prepared by dipping an ethanol suspension of finely ground sample powders onto a Cu grid coated with a holey C film.

Results and discussion

The silica/ascorbic acid composites were achieved via HCl-catalyzed sol-gel process of TEOS in the presence of ascorbic acid. The appearance of brown color of the composites was due to the oxidation reaction of ascorbic acid during the sol-gel process. Upon removal of the ascorbic acid compounds by extraction with ethanol, the porous silica matrices were obtained. The Brunauer-Emmett-Teller (BET) surface area and pore parameters of the porous silica materials after the removal of ascorbic acid are summarized in Table 1, along with the control sample (SiO$_2$-gel). It can be seen that the total pore volume and average pore diameter of the silica matrices generally rise with the increase of ascorbic acid contents in the silica/ascorbic acid composites, which is similar to the reported results in the literatures.[19,22] From the t-plot analysis with Harkins-Jura equation, we can estimate the negligible contributions of micropores to the measured surface areas and pore volumes at ascorbic acid contents higher than 40wt%. However, the control sample (SiO$_2$-gel) prepared without ascorbic acid is basically microporous.

The N$_2$ adsorption-desorption isotherms were determined at various relative pressure (P/P_0) on the silica samples after the solvent extraction. Fig. 1 shows the isotherms of the samples prepared with or without ascorbic acid. The silica (SiO$_2$-gel) prepared without ascorbic acid shows a completely reversible type I isotherm[26] with the N$_2$ volume adsorbed less than 100 cm^3/g, which is typical of the xerogels with microporous structures. The volume adsorbed for the sample AA-20 prepared with 20wt% of ascorbic acid is about 250 cm^3/g, greater than that of SiO$_2$-gel, but the isotherm still remains as a reversible

Table 1   Physicochemical properties of the porous silica materials obtained upon removal of the template ascorbic acid (AA) by extraction with ethanol

| Sample code	Template content^a (wt%)	BET surface area (m²/g)	Total pore volume (cm³/g)	Average pore diameter		Micropore^b	
				by BET (nm)	by BJH (nm)	Surface area (m²/g)	Volume (cm³/g)
SiO₂-gel^c	0	336	0.164	1.9	—	289	0.134
AA-20	20	819	0.425	2.1	2.6	169	0.070
AA-40	40	1002	0.633	2.5	2.8	—	—
AA-50	50	1077	0.883	3.3	3.3	—	—
AA-60	60	967	1.344	5.5	4.8	18	—

^{a} Designed ascorbic acid content in the silica/ascorbic acid composites, as calculated from the feed composition with the assumption that TEOS transformed into SiO₂ completely. ^{b} The surface area and pore volume of micropores were obtained by the t-plot analysis with Harkins-Jura equation using the software from Micromeritics Corporation. ^{c} Control sample: sol-gel SiO₂ prepared in the absence of ascorbic acid.
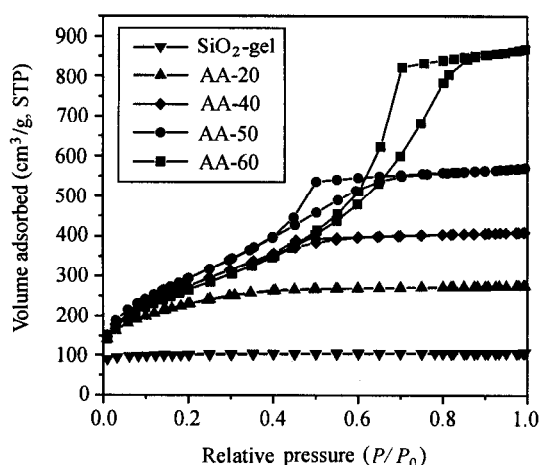
Fig. 1   N₂ adsorption-desorption isotherms for the porous silica materials prepared in the presence of ascorbic acid at concentrations of 0, 20, 40, 50, and 60wt%.

type I form. As the ascorbic acid concentration is increased to 50wt%, the samples exhibit type IV-like isotherms with weak H2 hysteresis loops.[26] The weak capillary condensation taking place in mesopores[26] might be due to the irregular pore sizes. Similar N₂ adsorption-desorption isotherms were also reported for mesoporous silica materials by nonionic surfactant pathway.[12] The initial part of the isotherm at low relative pressure ($P/P_0 < 0.4$) is mainly attributed to the monolayer-multilayer adsorption of the mesopores.[26] As the ascorbic acid concentration is increased, the final volume adsorbed increases significantly, indicating the increase of the pore volume. The Barrett-Joyner-Halenda (BJH) pore size distributions of the porous silica samples after extraction with ethanol is shown in Fig. 2. The pure silica gel prepared without ascorbic

acid has few mesopores, which is consistent with the result from t-plot analysis. The samples prepared with 40 or higher of ascorbic acid show mesoporosity, and the peak pore diameters rise with the increase of template content in the silica/ascorbic acid composites. However, it can be seen that the pore diameters of the samples AA-40 and AA-60 are not very regular.
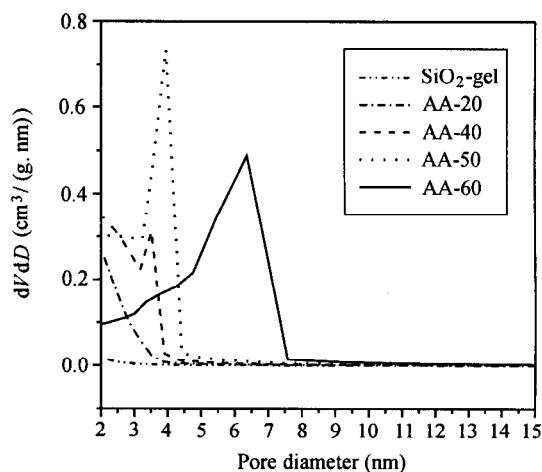
Fig. 2   BJH pore size distributions of the porous silica materials prepared in the presence of ascorbic acid at concentrations of 0, 20, 40, 50, and 60wt%.

A typical XRD pattern of the ethanol-extracted mesoporous silica materials is shown in Fig. 3, for sample, AA-50 prepared with 50wt% of ascorbic acid. The pattern appears to consist of a single broad diffraction peak centered at the 2θ value of 1.34°, which corresponds to a d-spacing of 6.6 nm calculated from the Bragg equation. From the difference in the d-spacing and the average pore diameter ($e.g.$ 3.3 nm), it can be estimated that the

mesoporous material might have thick pore wall.[11] The broadness of the single peak and the absence of additional higher degree peaks suggest that these samples lack long range ordering of the structure,[9] as well as relatively irregular pore diameters. The analogous XRD patterns were also reported for some mesoporous materials by neutral surfactant templating route.[9] There is a typical amorphous halo around the 2θ value of $23.2°$, indicating the amorphous nature of the sol-gel silica matrix.[19]
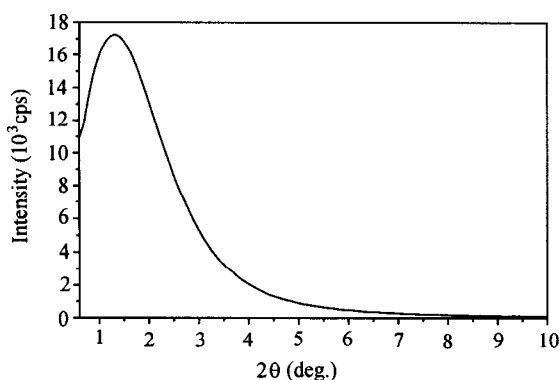

Fig. 3 Powder XRD pattern of the sample AA-50 after the ascorbic acid removal by ethanol extraction.

Fig. 4 shows the TEM image of the mesoporous sample AA-60 after ethanol extraction. The TEM image shows numerous wormlike interconnected channels or pores that are disordered in arrangements. The framework-confined mesoporosity is clearly revealed. The pore diameters are
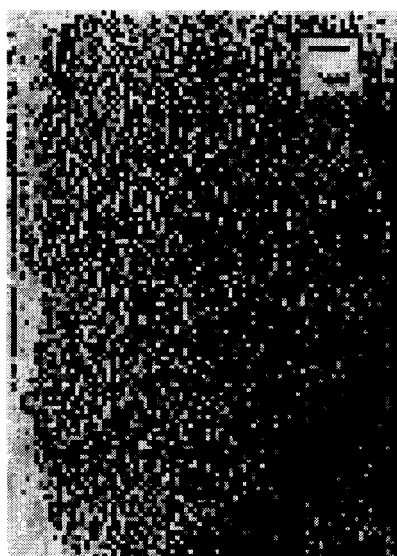

Fig. 4 Representative transmission electron micrographs (TEM) of the sample AA-60 prepared with 60wt% ascorbic acid.

mostly about 5 nm, which are comparable to the average pore diameter obtained from nitrogen sorption measurements.

Conclusion

Ascorbic acid has been utilized as the template or pore-forming agent to prepare mesoporous silica sol-gel materials with large specific surface areas ($e. g.$ 1000 m^2/g) and pore volumes ($e. g.$ 0.8 cm^3/g). The pore size can be changed simply by varying the ascorbic acid contents in the HCl-catalyzed sol-gel reactions of TEOS. The mesoporosity is arisen from interconnecting disordered wormlike channels and pores.

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