

Rapid Communication

SYNTHESIS OF MESOPOROUS POLY(STYRENE-*co*-MALEIC ANHYDRIDE)/
SILICA HYBRID MATERIALS VIA A NONSURFACTANT-TEMPLATED
SOL-GEL PROCESS*

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Abstract Mesoporous poly(styrene-*co*-maleic anhydride)/silica hybrid materials have been prepared. The synthesis was achieved by the HCl-catalyzed sol-gel reactions of tetraethyl orthosilicate (TEOS) and styrene-maleic anhydride copolymer in the presence of 3-aminopropyl triethoxysilane (APTES) as a coupling agent and citric acid as a nonsurfactant template or pore-forming agent, followed by ethanol extraction. Characterization results from nitrogen sorption isotherms and powder X-ray diffraction indicate that polymer-modified mesoporous materials with large specific surface areas (e.g. 900 m²/g) and pore volumes (e.g. 0.6 cm³/g) could be prepared. As the citric acid concentration is increased, the specific surface areas, pore volumes and pore diameters of the hybrid materials increase.

Keywords Mesoporous hybrid material, Poly(styrene-*co*-maleic anhydride)/silica, Citric acid, Nonsurfactant template, Sol-gel process

INTRODUCTION

The synthesis and application of mesoporous materials have attracted much attention since 1992^[1, 2]. Recently, the synthesis of organo-modified hybrid mesoporous materials has been reported^[3-9]. The functional groups include phenyl^[3, 9], amino^[4, 5, 9], cyano^[4], thiol^[5, 9], allyl^[5, 9], and so on. These materials could have important uses in optical applications^[7], catalysis, metal-ion extraction^[8] and adsorption processes. However, merely one paper^[10] on the synthesis of polymer-modified mesoporous hybrid materials has appeared. These new kind of mesoporous hybrid materials might have special properties which could be advantageous in application, due to the introduction of organic polymer into the framework.

Here, the preparation of mesoporous poly(styrene-*co*-maleic anhydride)/silica hybrid materials via the nonsurfactant-templated sol-gel process^[11-14] is reported. This process combines the nonsurfactant-templated^[11-14] pathway to mesoporous silica materials with the preparation of poly(styrene-*co*-maleic anhydride)/silica^[15, 16] hybrid materials. The synthesis was achieved by HCl-catalyzed sol-gel reactions of tetraethyl orthosilicate (TEOS) and styrene-maleic anhydride copolymer in the presence of 3-aminopropyl triethoxysilane (APTES) as a coupling agent and citric acid as a nonsurfactant template or pore-forming agent, followed by ethanol extraction.

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EXPERIMENTAL

Materials

Poly(styrene-*co*-maleic anhydride) [P(St-*co*-MAN)] having a M_n of 1.1×10^5 and MWD of 4.4 with 12 mol% of maleic anhydride unit was received from Shanghai Research Institute of Petrochemical Technology^[15, 16]. 3-Aminopropyl triethoxysilane (APTES, 99%) and tetraethyl orthosilicate (TEOS, 98%) were purchased from Acros Company and citric acid (CA, CP) was supplied by Beijing Chemical Plant. All chemicals were used as received. The solvent tetrahydrofuran (THF, AR) was purified by distillation from CaH_2 .

Synthesis of Mesoporous Materials

In a typical procedure of preparing the mesoporous hybrid sample HM-20-50, 1.4 mL of APTES/THF(1/9 *V/V*) mixture was added dropwise to 5 mL P(St-*co*-MAN)/THF(0.1 g/mL) solution under stirring for about 20 min (at APTES: maleic anhydride unit molar ratio of 1:1), then 14.8 mL TEOS/THF (1/1 *V/V*) solution was added to the mixture obtained above under stirring for about 5 min. Finally, 10 mL CA/THF (0.25 g/mL) solution was added to the reacted system, followed by 2.4 mL 0.14 mol/L HCl as catalyst. The transparent or translucent monoliths of CA/P(St-*co*-MAN)/silica composites were obtained upon gelling and drying at room temperature for about 3 months. Then the products were ground into fine powders, followed by Soxhlet extraction with ethanol for 3 days to remove the remaining CA and vacuum drying at about 80°C for ca. 3 h to afford the mesoporous hybrid materials.

Characterization of Mesoporous Materials

The removal of the citric acid was monitored by FT-IR analysis, based on the disappearance of the characteristic C=O stretching vibration of citric acid at about 1741 cm^{-1} . The FT-IR spectra of the samples before and after ethanol 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 hybrid samples after the solvent extraction were determined by nitrogen adsorption-desorption isotherms at 77 K on a Micromeritics ASAP2010 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 $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm, 40 kV, 100 mA) at the scanning rates of 1°/min in the 2θ range of 0.6–8° and of 8°/min in the ranges of 8–40°. Thermogravimetric analysis (TGA) were carried out on a Thermal Analysis SDT2960 simultaneous TGA-DTA instrument with a heating rate of 10 K/min and under a dry N_2 atmosphere with a flow rate of 100 cm^3/min .

RESULTS AND DISCUSSION

The CA/P(St-*co*-MAN)/silica composites were prepared from the sol-gel process of TEOS and P(St-*co*-MAN) in the presence of APTES as the coupling agent^[15, 16] and CA as the nonsurfactant template or pore-forming agent^[14]. Upon removal of the CA by extraction with ethanol, the porous hybrid materials were obtained. From FT-IR and TGA analyses^[15], we affirm that polymer-modified porous materials were obtained after complete removal of the template by extraction with ethanol. The Brunauer-Emmett-Teller (BET) surface area and pore parameters of the porous hybrid materials after the removal of CA as well as the control sample (HM-20-0) prepared without CA are summarized in Table 1. The samples HM-10-50 and HM-20-50 exhibit large specific surface areas (~ 900 m^2/g), pore volumes (~ 0.6 cm^3/g) and 2.4 nm average pore diameters, which designate the mesoporosity of the samples. We also found that the treatment temperature (e.g. 473 K or 358 K) for BET measurement has little effect on the pore parameters of the porous hybrid materials. It can be seen that the specific surface area, total pore volume and average pore diameter of the hybrid matrices with 20 wt % of P(St-*co*-MAN) generally rise with increasing CA contents, which is similar to the reported results in the literature^[13, 14]. From the t -plot analysis with the Harkins-Jura equation, we can estimate the contributions of micropores to the measured surface areas and pore volumes decrease with increasing CA contents. The control sample (HM-20-0) prepared without CA is basically microporous.

Table 1 Physicochemical properties of the porous P(St-co-MAN)/silica hybrid materials obtained after the removal of CA by extraction with ethanol

Sample Code ^a	Polymer/SiO ₂ ^a (wt/wt)	CA content ^a (wt%)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	BET average pore diameter (nm)	Micropore ^b	
						Surface area (m ² /g)	Volume (cm ³ /g)
HM-10-50	10/90	50	1153	0.688	2.4	–	–
HM-20-0 ^c	20/80	0	285	0.138	1.9	229	0.106
HM-20-20	20/80	20	621	0.308	2.0	418	0.190
HM-20-40	20/80	40	871	0.464	2.1	60	0.015
HM-20-50	20/80	50	947	0.578	2.4	–	–
HM-20-50 ^d	20/80	50	942	0.570	2.4	–	–

^a In the sample codes, the first numerical figure denotes the polymer content (wt%) in the hybrid matrices after the removal of CA, the second numerical figure denotes the designed CA content (wt%) in the CA/P(St-co-MAN)/silica composites before the removal of CA. All the numerical figures are calculated from the feed composition with the assumption that TEOS transformed into SiO₂ completely

^b The surface area and pore volume of micropores (< 2.0 nm) were obtained by the *t*-plot analysis with the Harkins-Jura equation using the software from Micromeritics Corporation

^c Control sample: P(St-co-MAN)/silica hybrid was prepared in the absence of CA

^d Degassed at 358 K before BET measurement

The N₂ adsorption-desorption isotherms were determined at various relative pressures (P/P_0) on the hybrid samples after solvent extraction. From Fig. 1, we can see that the hybrid sample (HM-20-0) prepared without CA shows a completely reversible Type I isotherm^[17] with the N₂ volume adsorbed less than 100 cm³/g, which is typical of the xerogels with microporous structures. As the CA concentration is increased, the final volume adsorbed increases significantly, indicating the increase of the pore volume. The N₂ sorption isotherms for HM-20-50 exhibit Type IV-like isotherms with very weak H₂ hysteresis loops^[17], which indicates the formation of mesopores. The Barrett-Joyner-Halenda (BJH) pore size distributions of the porous P(St-co-MAN)/silica hybrid materials after ethanol extraction is shown in Fig. 2. With the CA content less than 20 wt%, the pore sizes falls mainly in micropore range. As the content of CA is increased further to 40 wt%, 50 wt%, the mesopores become identifiable with pore diameters of 2.0–3.5 nm. However, the pore diameter is smaller than those of pure silica mesoporous materials at the same content of CA^[14]. Further experimental studies are in progress in our laboratories to increase the pore diameter of the hybrid materials.

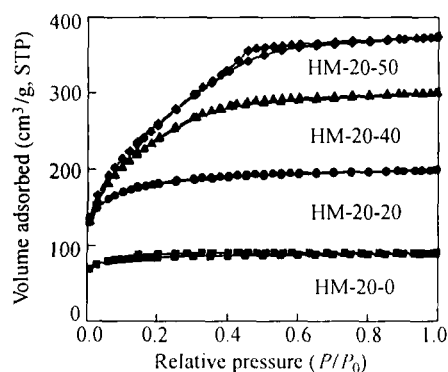


Fig. 1 N₂ adsorption-desorption isotherms for the porous P(St-co-MAN)/silica hybrid materials prepared with 0, 20, 40 and 50 wt % of CA

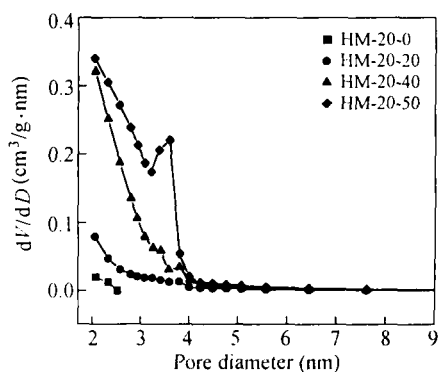


Fig. 2 BJH pore size distributions of the porous P(St-co-MAN)/silica hybrid materials prepared with 0, 20, 40 and 50 wt % of CA

The XRD pattern of the ethanol-extracted hybrid materials is shown in Fig. 3. The hybrid sample HM-20-0 prepared without CA exhibits no diffraction peak in the low-angle range, while the XRD pattern of the sample prepared with 20 wt % of CA shows a very weak and broad diffraction peak. As the content of CA increases, the

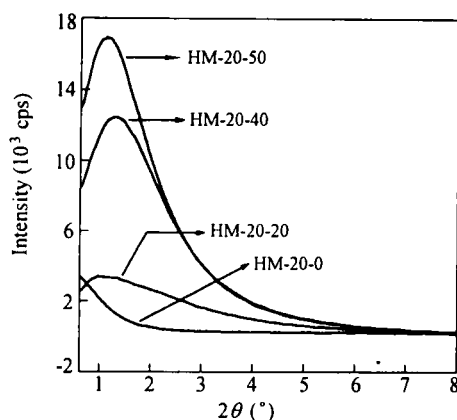


Fig. 3 Powder XRD pattern of the ethanol extracted hybrid samples prepared with 0, 20, 40 and 50 wt % of CA

intensity of the diffraction peaks increases while their broadness decreases, which indicates the formation of mesopores^[11]. The pattern for sample HM-20-50 appears to consist of a single diffraction peak centered at the 2θ value of 1.14° , which corresponds to a d -spacing of 7.7 nm calculated from the Bragg equation. There is a typical amorphous halo around the 2θ value of 22.2° , indicating the amorphous nature of the sol-gel silica matrix^[11].

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