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Synthesis and Characterization of Nanoporous Silica Using Dendrimer Molecules

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A water soluble porogen, e.g., poly(amido amine) dendrimer, has been used as a structure-directing agent to introduce porosity of nanometer scale in silica-based nanocomposite materials. Hydrothermal synthesis was carried out at different elevated temperatures (343–413 K) in a closed teflon-lined stainless steel autoclave under autogenerated pressure. The synthesis time varied from 2 to 6 days, depending upon pH, synthesis temperature, concentration of porogen, etc. X-ray diffraction, transmission and scanning electron microscopic analyses, as well as infrared absorption spectroscopic measurements, were carried out to characterize these materials. Mostly disordered mesostructures were observed. The porous silica particles with sphere-like morphology varied from 30 to 200 nm in size were prepared depending upon the conditions of preparation. The structure and nanoporosity were preserved after the removal of structure-directing porogen through calcination at 823 K. The pore size was in the range of the dendrimer molecule as a template, indicating the structure-directing role of the terminal amino groups in the dendrimer molecule for the synthesis of nanoporous silica, since the nanoporous silica could be prepared by the hydrogen bonding or electrostatic interaction of dendrimer amino groups and tetraethyl orthosilicate.

Keywords: Nanoporous Silica, Template, Porogen, Poly(amido amine) Dendrimer, Nanocomposite, Transmission Electron Microscopy.

1. INTRODUCTION

It is predicted that within a few years, 100-nm nodes would be realized in the semiconductor industry.[1] For these purposes, interlayers with extremely low dielectric constants (low-k) are imperative to reduce cross-talk and to increase processor speed. Then, it is estimated that inter-level metal insulators with bulk dielectric constants $k = 2.2$ or below[1, 2] would be required, which is significantly less than the current industrial standard of silica-based insulators ($k = 4.3$). Significant advancement has been made in materials science in recent years to innovate the alternate systems capable of meeting the desired level of $k = 2.2$. Decreasing the polarizability and density could reduce the dielectric constant of a material. However, the most powerful synthetic method involves the introduction of porosity. A variety of pore generation methods have been utilized to date, using organic templates or structure-directing agents.[3, 4] The most common criteria emerge for developing low-*k* dielectric material to introduce nano-scale porosity in a controlled manner to further reduce *k*.

Porous silicas with ultra low-*k* dielectric constant can have high mechanical and thermal stability and low thermal conductivity, and are very suitable for size-specific applications in catalysis, adsorption and separation. Mesoporous materials are usually obtained by micelle-templating processes and are expected to display higher mechanical strengths because of their engineered periodic structure.[4] These mesoporous silicas with exceptionally high surface areas and tunable pore diameters of 2–50 nm could be prepared using assemblies of ionic or non-ionic surfactants under mild acidic or alkaline conditions.[5, 6] Different synthesis parameters[7, 8] guide the electrostatic and hydrogen bonding interactions between the surfactants and hydrolyzed silica precursors for the formation of mesostructure.

In this context, one can expect that organic molecules having a large number of suitable functional groups in the periphery can be effectively used as a single molecule template for the synthesis of nanoporous materials with defined pore sizes. One group of such interesting molecules, dendrimer, is a nearly perfect monodisperse macromolecule with a regular and highly branched three-dimensional structure of a few nanometer size.[9–13] The water-soluble

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Table I. Synthesis parameters for dendrimer/silica nanocomposites.

Sample no.	TEOS: Dendrimer (molar ratio)	pH (NaOH/NH_3/HCl)	Synthesis temp. (K)	Time (day)
1	1000	10, NaOH	373	2
2	1000	7.5, HCl	373	4
3	400	10, NH_3	298	4
4	300	9, without addition	298	6
5	300	10, NH_3	343	6
6	300	12, NH_3	343	4

poly(amido amine) (PAMAM) dendrimer of fourth generation, containing terminal amino groups with an individual size of 4 ~ 5 nm, could be a suitable single molecule template for the syntheses of nanocomposite materials with well-defined nanopores.[14, 15] Since few attempts of synthesis of mesoporous silica using dendrimer as a template have been reported in literature,[14, 15] there is a need for further investigation of synthesis in other conditions. Such studies are always useful to improve the quality of materials.

Here, we report the use of a PAMAM dendrimer as a template for the hydrothermal synthesis of silica nanocomposite materials. The dendrimer molecules could be easily removed by calcination at high temperature (823 K) and the resultant solid can generate nanometer scale porosities, which could be useful for adsorption, low-k dielectric materials, ion exchange and catalytic applications.

2. EXPERIMENTAL DETAILS

For the synthesis of nanoporous silica, tetraethyl orthosilicate (TEOS) (TCI, Japan) was used as the silica source in all syntheses. Hydrothermal synthesis was carried out at different dendrimer concentrations, solution pHs and hydrothermal treatment temperatures. In a typical synthesis, the initially desired amount of TEOS was first allowed to mix with a commercial methanol solution of fourth generation PAMAM dendrimer (Aldrich, USA) under constant stirring. A white precipitate appeared within 30 min and the rate of precipitation was dependent on the concentration of dendrimer in the solution. Then, the required amount of NaOH or ammonia (taken in water) was added to the aged silica gel. Dilute aqueous HCl solution was added in the case where the synthesis was done at pH 7.5. The final mixture was vigorously stirred for 1 hr and then autoclaved at an elevated temperature for 2–6 days. The molar ratio of various solvents and TEOS in the hydrothermal gels was

$$\text{TEOS} : \text{MeOH} : \text{EtOH} : H_2O = 2 : 25 : 6 : 83$$

After the hydrothermal treatment, the solid products were filtered, washed with water and dried in air. The dendrimer was removed from the solid as-synthesized products by heating under airflow at 823 K for 8 h.

The samples were characterized by powder X-ray diffraction (XRD) patterns, which were measured on an X-ray diffractometer (RIGAKU, RINT2500) using CuK_α (λ = 1.54 Å) radiation. Morphology and particle sizes of different samples were analyzed using a Hitachi H-7000 transmission electron microscope (TEM). The accelerating voltage was 100 kV. Prior to the TEM measurements, a small amount of sample was sonicated in methanol/ethanol for 10 min, and then a drop of the dispersed liquid was dropped onto the holey carbon grid, followed by drying at room temperature. The scanning electron microscopic (SEM) observations were performed with a JEOL JSM-6330 electron microscope operating at 12 KV. Fourier-transform infrared (FT-IR) absorption spectra in the region of 4000–700 cm^{-1} were recorded on a Bio-Rad FTS 575C FT-IR instrument using KBr discs. All measurements were carried out at ambient room temperature.

3. RESULTS AND DISCUSSION

The synthesis parameters for different dendrimer/silica nanocomposites are given in Table I. A typical XRD pattern of sample 3 is shown in Fig. 1. A single broad low-angle peak with no distinctive higher order peaks was observed. This indicates that the products may be classified as disordered mesophases. For sample 1, synthesized at pH = 10, the existence of pores and their disordered

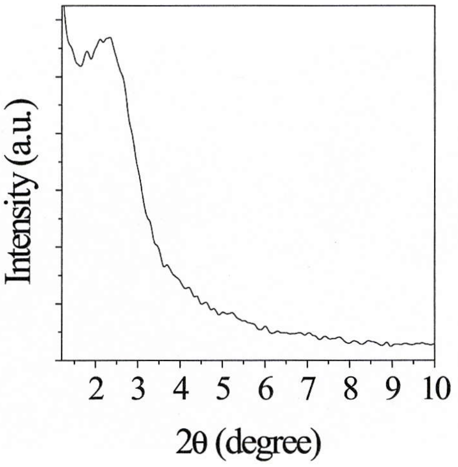

Fig. 1. X-ray diffraction pattern of sample 3 after calcination.

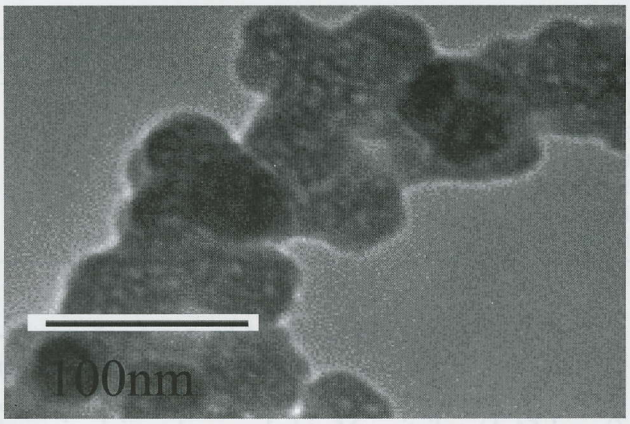

Fig. 2. TEM image of sample 1 after calcination.

arrangement were displayed in the TEM image (Fig. 2). Although it was not possible to calculate the exact pore size from the TEM image due to the low resolution of TEM technique, the approximate diameter of the pores was comparable with that of the individual dendrimer molecule. This suggests that the pores are generated through the imprinting of the individual dendrimer molecule in the silica matrix.

In Fig. 3, a TEM image of a sample 2 is shown. Nanopores with disordered arrangements could be seen, as well as a case of a sample 1, although whole size was larger. It was revealed from various TEM images (figures not shown) of other uncalcinated and calcinated samples from different batches (1–6 in Table I) that dendrimer concentration, solution pH and hydrothermal treatment temperature have little effect on the appearance of pores with disordered distribution, but affect sizes of the silica particles. SEM images of nanoporous dendrimer/silica composite materials are shown in Fig. 4. Although uniform sphere-like particles were observed both for sample 1 and 2, their sizes vary from 50 nm (sample 1) to 200 nm (sample 2). This could be due to the change in pH of the synthesis gel.

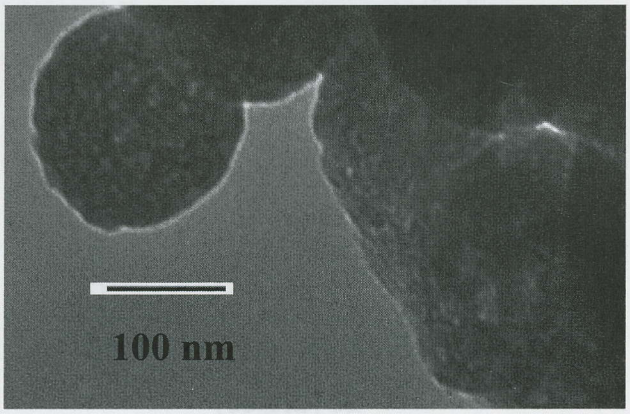

Fig. 3. TEM image of sample 2 after calcination.

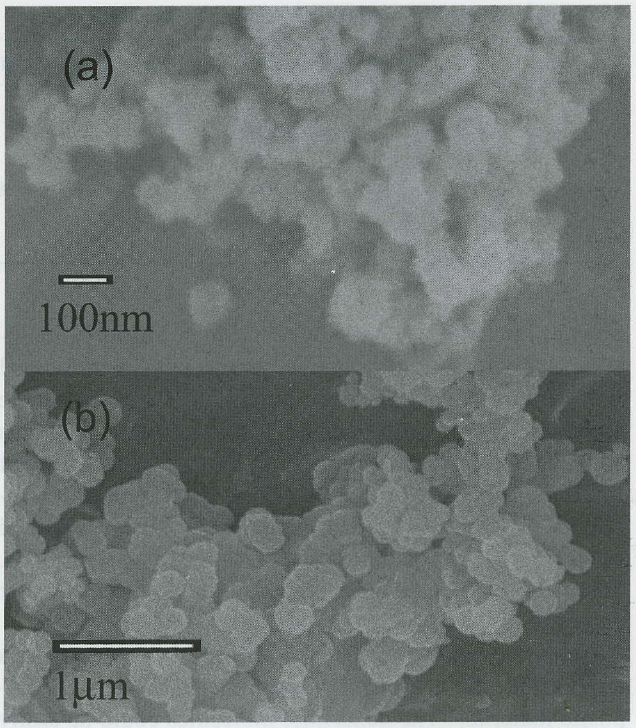

Fig. 4. SEM images of samples ((a) sample 1, (b) sample 2) after calcination.

In Fig. 5, FT-IR spectra of different nanoporous silica samples are shown. Broad bands were observed in the hydroxyl region at 3400 cm^{-1}. These correspond to OH stretching vibration bands of the residual water and Si-OH. The C=O stretching and N-H bending vibrations were observed at 1651 cm^{-1} (amide I) and 1551 cm^{-1} (amide II) in the uncalcinated samples, indicating the presence of dendrimers in the composite materials. These bands disappeared for the calcined nanoporous sample, supporting the complete removal of templates during calcination.

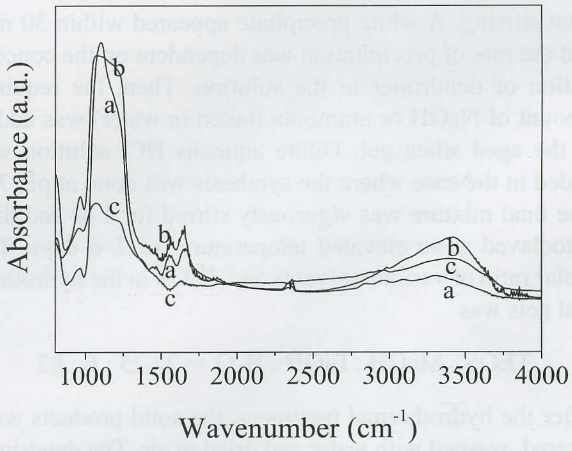

Fig. 5. FT-IR spectra of samples ((a) sample 1, (b) sample 3) before calcination and a sample ((c) sample 3) after calcinations.

4. CONCLUSIONS

From experimental observations, we can conclude that a water-soluble PAMAM dendrimer was found to be a useful porogen for the hydrothermal synthesis of nanoporous silica. The interaction between the terminal amino group of dendrimer and Si-OH possibly occurs through the hydrogen bonding at pH 10 or 12. The importance of the hydrogen bonding interaction in the preparation of mesoporous silica was suggested by Tanev and Pinnavaia.[16] At pH 7.5, in which all the terminal amino groups are positively charged,[17] the electrostatic interaction force also plays a crucial role besides the hydrogen bonding. TEM images of nanoporous silica materials indicated the disordered mesostructures of the silica-dendrimer nanocomposites with a pore diameter close to the porogen size. SEM images showed sphere-like structures of these silica nanocomposite materials. After the removal of dendrimer, nanopores can be maintained in the silica matrix suitable for applications in absorption, catalysis and low-k dielctric materials.

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