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Synthesis of flexible silica aerogels using methyltrimethoxysilane (MTMS) precursor

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Abstract

The experimental results on the synthesis of flexible and superhydrophobic silica aerogels using methyltrimethoxysilane (MTMS) precursor by a two-step (acid–base) sol–gel process followed by the supercritical drying, are reported. The effects of various sol–gel parameters on the flexibility of the aerogels have been investigated. The aerogels of different densities were obtained by varying the molar ratio of MeOH/MTMS (S) from 14 to 35, with lower densities for larger S values. It has been observed that the Young's modulus (Y) decreased from 14.11×10^4 to $3.43 \times 10^4\ N/m^2$ with the decrease in the density of the aerogels from 100 to 40 kg/m^3. Simultaneously, the aerogels are superhydrophobic with a contact angle as high as 164°. The superhydrophobic aerogels are thermally stable up to a temperature of 530 K, above which they become hydrophilic. The aerogels have been characterized by bulk density, percentage volume shrinkage, and porosity measurements. The microstructures of the aerogels have been studied using the transmission electron microscopy (TEM). The Young's modulus of the aerogels has been determined by an uniaxial compression test. The variation of physical properties of the aerogels has been explained by taking into consideration the hydrolysis, condensation reactions, the resulting colloidal clusters and their network formation.

Keywords: Silica aerogels; Elastic properties; TEM; Superhydrophobicity; Flexible aerogels

1. Introduction

Silica aerogels are sol–gel-derived materials consisting of interconnected nano-particle building blocks, which form an open and highly porous three-dimensional silica network. Typical silica aerogels have high surface area ($\sim 1000\ m^2/g$), high optical transmission (∼93%), low density (40 kg/m^3) and low thermal conductivity (0.02 W/mK) [1–4]. These features have led the aerogels for various applications such as super thermal insulation [5,6], acoustic insulation [7], in Cerenkov radiation detectors [8,9], low dielectric constant aerogel films in ultra large scale integrated circuits [10,11], superhydrophobic aerogels for oil-spill cleanup [12], in catalysis [13], and inertial confinement fusion (ICF) targets in thermonuclear fusion reactions [14].

Despite having these fascinating properties, the aerogels have major drawbacks that they are fragile, brittle and moisture sensitive, which limit their applications in various fields. Due to the fragility and the brittleness, aerogels easily break and become into pieces and powder with the application of a small stress. Therefore, in the present studies, attempts have been made to synthesize highly flexible and superhydrophobic silica aerogels using methyltrimethoxysilane (MTMS) precursor by a two-step acid–base sol–gel process [15]. The aerogels consist of cross-linked network of silica polymer chains extended in three dimensions as can be seen from Fig. 1. Due to the presence of non-polar alkyl groups (i.e. methyl) attached to the silica polymer chains, the inter-chain cohesion is minimized resulting in the elastic and flexible three-dimensional network. Also, the higher dilution of the MTMS precursor with methanol solvent yielded silica network with a low degree of polymeriza-

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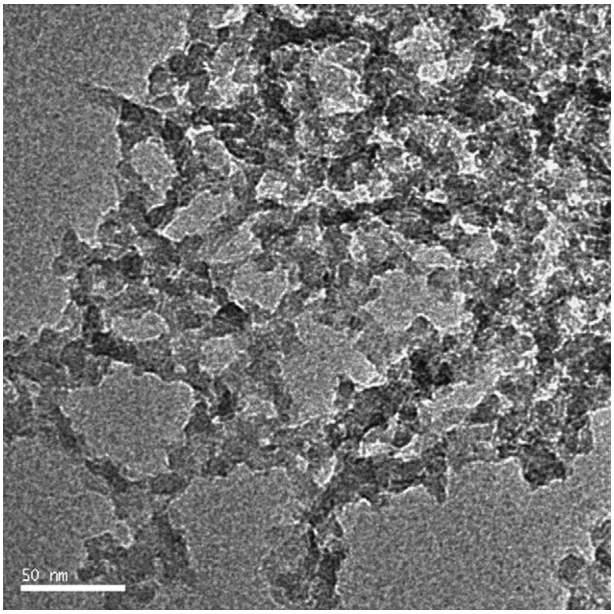

Fig. 1. Transmission electron micrograph of silica aerogel showing three-dimensional cross-linked network of silica chains.

tion exhibiting higher flexibility. Whereas, for lower dilution of the MTMS precursor, an extensive polymerization resulted in dense and rigid structures. Because of the new property, i.e. flexibility in the aerogel, it can be bent to any shape and acts as a good shock absorber as well.

2. Experimental procedures

2.1. Sample preparation

Silica aerogels were produced by a two-step, acid–base, catalyzed sol–gel process followed by the supercritical drying. The chemicals used were: methyltrimethoxysilane (MTMS, H_3C–Si–$(OCH_3)_3$) and ammonium hydroxide (NH_4OH) of purum grades (from Fluka Company, Switzerland), methanol (MeOH, CH_3OH) and oxalic acid ($C_2H_2O_4$) of ExcelR and SQ grades, respectively (from Qualigens Company, India). Double distilled water was used to prepare both the acidic and basic catalysts.

Silica alcosols were prepared in a 150-ml beaker in two steps (acidic and basic): (i) by mixing and stirring the methyltrimethoxysilane (MTMS), methanol (MeOH) and water (half of the total amount) in the form of oxalic acid catalyst, for 30 min, and (ii) after 24 h, the base catalyst (NH_4OH) in the form of H_2O (the remaining half amount) was added drop by drop while stirring for 30 min. The total molar ratio of H_2O/MTMS was kept constant at 8. The molar ratio of MeOH/MTMS (S) was varied from 14 to 35. The oxalic acid catalyst and NH_4OH catalyst concentrations were varied from 0.0005 to 0.1 M and 6 to 13.36 M, respectively. The sols were transferred to Pyrex test tubes of 15 mm outer diameter and 125 mm height. The test tubes were made air-tight using wooden corks and kept for gelation at 300 K. After the sols were set, methanol was added over the gels in order to prevent shrinkage and cracks. The alcogels were aged for two days at 300 K. Silica aerogels were obtained by the supercritical drying of the alcogels (at 538 K and 10 MPa) in an autoclave of 600 ml capacity (Parr Instrument Company, Moline, IL, USA). An excess amount of methanol (MeOH) was added into the autoclave (total filling of the autoclave with MeOH is 25% by the volume including in the gels). After reaching the temperature and pressure well above the critical points of methanol solvent ($T_c \sim 516$ K and $P_c \sim 7.9$ MPa), the methanol vapors were released from the autoclave and finally flushed with 0.3 MPa dry nitrogen. The autoclave was then cooled to an ambient temperature and the aerogels were taken out for characterization.

2.2. Methods of characterization

The bulk densities of the aerogels were calculated by their mass to volume ratios. The percentage of porosity (P %) of the aerogels was calculated using the equation:

$$P\ \% = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100, \tag{1}$$

where ρ_b is the bulk density and ρ_s is the skeletal density of the aerogels which was measured using helium pycnometry and its value was found to be 1900 kg/m^3. The percentage of volume shrinkage (V_s %) was determined from the change in the volumes of the alcogel and the aerogel using the equation:

$$V_s\ \% = \left(1 - \frac{V}{V^1}\right) \times 100, \tag{2}$$

where V is the volume of the aerogel and V^1 is the volume of the alcogel.

To quantify the degree of hydrophobicity, the contact angle (θ) of a water droplet placed on the hydrophobic aerogel surface, was calculated using the equation [16]:

$$\tan(\theta/2) = (2h/W), \tag{3}$$

where the base contact length W and height h of the droplet were measured using a traveling microscope. Also, the contact angle (θ) was measured by contact angle meter (Tantec Company, USA). Good agreement has been observed by both the methods in the measurement of θ.

The microstructure of the aerogels was studied using the transmission electron microscope (TEM, Philips, Tecnai F20 model). The thermal stability of the hydrophobic aerogels was investigated by heating them in a furnace at various temperatures ranging from 320 to 773 K. Here, the term thermal stability refers to the threshold temperature up to which the aerogel retains its hydrophobic property, and above which it becomes hydrophilic.

The elastic constant called the Young's modulus (Y) or modulus of elasticity, is a measure of hardness, stiffness, rigidity (or softness, flexibility, or pliability) of the solid. It is also defined as the resistance to any deformation in the solids. It means that the lesser the value of Y, the more flexible is the solid. The Young's modulus (Y) of the aerogels has been determined by an uniaxial compression test as shown in Fig. 2. In this test, the aerogel sample under the testing was kept in a glass tube fixed with a rigid support and having a little bigger diameter than that of the aerogel sample. Various loads (e.g., 0.01, 0.02, 0.03 kg,