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Physicochemical properties of bamboo leaf aerogels synthesized via different modes of gelation

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ABSTRACT

Aerogels with ultralow silica concentration (3.5 %) was synthesized using bamboo leaf. The synthesis of aerogel was carried out in different pH to study the effect of gelation mechanisms on the properties of aerogel. Aerogel synthesized at acidic pH has generally exhibits more attractive properties, i.e. low shrinkage (24.3%), large specific surface area (547.2 $m^2 g^{-1}$), large pore volume (2.72 $cm^3 g^{-1}$) and low thermal conductivity (0.024 $W m^{-1} K^{-1}$). As comparison, the aerogel synthesized at basic condition has different properties, in which it has small pore volume (0.287 $cm^3 g^{-1}$) and pore size (11.44 nm), large primary particles (6.69 nm), small specific surface area (247.7 $m^2 g^{-1}$), low degree of fractality (6.69), strong absorption of water and relatively high thermal conductivity (0.0415 $W m^{-1} K^{-1}$). Properties of aerogels synthesized were also compared with aerogels synthesized using conventional TEOS precursor. The difference in the gelation mechanisms was discussed in detailed.

Introduction

Silica aerogel exhibits many attractive properties such as extremely low density (0.003–0.35 $g cm^{-3}$) [1], high porosity (80–99.8%) [1,2], low thermal conductivity (0.005–0.164 $W m^{-1} K^{-1}$) [3–5], high specific surface area (500–1200 $m^2 g^{-1}$) [6], ultra-low dielectric constant (k = 1.0–2.0) [7] and low refractive index (1–1.08) [1,8]. Conventionally, silica aerogel is synthesized by following methods:

(i) Hydrolysis and condensation of alkoxides such as tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) as below:

Hydrolysis

$$\equiv Si - OR + H_2O \leftrightarrow \equiv Si - OH + ROH \quad (1)$$

Condensation

$$\equiv Si - OH + HO - Si \equiv \rightarrow \equiv Si - O - Si \equiv + H_2O \quad (2)$$

where –R is alkyl groups, i.e. methyl and ethyl in TMOS and TEOS, respectively.

Acidification of water glass (sodium silicate, $Na_2O \cdot nSiO_2$):

$$Na_2O \cdot nSiO_2 + H_2O + H^+ \rightarrow Si(OH)_4 + 2Na^+ \quad (3)$$

In previous work, water glass has been successfully produced from bamboo leaf [9] and thus can be a potential source to produce silica aerogel. Hence, in this continual study, it is aimed to synthesize silica aerogel using water glass produced from bamboo leaf. Synthesis of silica hydrogel from water glass is commonly accomplished by either acidifying water glass to pH near 7 [2,10–16], or to substitute Na^+ in water glass by H^+ using ion exchange column [3,17–26]. Both of this yield silicic acid which can then condensed to form siloxane bond (Si–O–Si) in between monomers as shown in Eq. (2). Though ion-exchange method can produce aerogel with better properties, it requires frequent regeneration of ion resins. The regeneration of ion resins involves time consuming process and uses large amount of acid [12]. Alternatively, similar ion exchange also can be achieved by *water glass-into-acid* approach. In water glass-into-acid method, water glass is added into excessive acid causes its pH decreased rapidly to <7. This is different from direct acidification method in which water glass is added with acid gradually from basic condition to pH ≈ 7. The silicic acid formed in water glass-into-acid method then condensed to produce hydrogel. The hydrogel formed contains larger amount of salt as compared with those obtained in ion exchange method.

Due to the very different gelation mechanisms which depends on pH value, hydrogel gelled at pH ≤ 7 is called *silica-gel* whereas

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other formed at pH ≈ 8–10 is termed *precipitated-silica*. As their name implies, silica-gel is more gel-like and rigid, whereas precipitated-silica is soft and flaky as common precipitate [27]. Since the synthesis of aerogel involves supercritical fluid or ambient pressure drying, silica-gel is less brittle when subject to many subsequent processing steps. On the other hand, precipitated-silica exhibits weak mechanical characteristics. It may experience severe shrinkage in drying process and thus has not been used to synthesize aerogel. However, this can be improved if precipitated-silica is modified by silylating agents prior to drying. Silylation is commonly applied to change the surface of aerogel from hydrophilic to hydrophobic [28–30]. It also reduces the capillary force in pores that can cause the hydrogel to collapse during drying [29–31]. Hence, the use of silylating agent in precipitated-silica may prevent it from collapse in drying process.

Aerogels produced by these methods may exhibit different properties but has not been discussed in literature up till now. Hence, this work is aimed to synthesize silica aerogel by using water glass obtained from bamboo leaf. In addition, effect of modes of gelation (i.e. water glass-into-acid, ion exchange column and precipitated-silica) to the properties of aerogels was investigated. The properties of bamboo leaf aerogels was also compared with aerogels synthesized with TEOS.

Methods

Materials

Water glass solution (1.1 g cm^{-3}, 3.5 wt% of SiO_2) was synthesized from bamboo leaf (*Bambusa heterostachya*) as described in previous work [9]. Hydrochloric acid (HCl, 2N), nitric acid (HNO_3, 2N), sodium hydroxide (NaOH, 2N) and absolute ethanol (99.8%) were purchased from R&M Chemicals (Malaysia). Tetra-orthosilicate (TEOS, 98%) and acidic cation-exchange resin (Amberlite IR-120H) were purchased from Sigma-Aldrich (Malaysia). Silylation agent hexa-methyldisilazane (HMDZ for synthesis) and n-hexane (EMSURE® ACS) were purchased from Merck chemicals (Malaysia).

Experimental procedure

Fig. 1 shows synthesis scheme of silica aerogels from bamboo leaf water glass.

The synthesis of aerogels began with the gelation of water glass. In order to study the effect of modes of gelation, water glass was gelled in the following conditions:

(i) *ion exchange column* (sample ID: BLG 3.5E)–water glass was flow into Amberlite resin column (length ≈60 cm, inner diameter 10.7 mm). The resulted silicic acid had pH 4.5, and it was let to gel at ambient condition;
(ii) *precipitated silica* (sample ID: BLG 3.5B)–HCl was added drop-by-drop to water glass (HCl: water glass = 1:2 v/v) until precipitate formed at pH ≈ 9.5;
(iii) *water glass-into acid* (sample ID: BLG 3.5N)–excessive acid (2 ml) was added into water glass (6 ml) in single step. The resulted silicic acid had pH 4.5. The pH was then adjusted again to 7 by adding 0.025 ml of NaOH, and mixture formed was let to gel at ambient condition.

As the hydrogel formed contains salts, it was soaked in deionized water to remove salts. Deionized water was replaced for every 4 h. The degree of salt removal was determined as sodium percentage in remained dried gel using Energy Dispersive X-Ray analysis (EDX, INCA Energy 400). The salt-free gel was then aged in ethanol. It was observed in the preliminary study that the gel shrunk severely in absolute ethanol. Therefore, hydrogel was aged in TEOS-ethanol mixture (15 vol% TEOS) for 24 h [12,20,32] to reduce shrinkage during aging. The alcogel formed was then silylated with HMDZ-hexane mixture (15 vol% HMDZ) for 12 hours [19]. Silylated gels can normally be dried under ambient pressure because silica concentration in precursors is high (8–25 wt%) [2,12,13,15,17,19,21–23,33–35]. However, water glass used in this study has ultralow silica content (3.5 wt%), and the preliminary studies had shown aerogel collapsed under ambient drying. Hence, the silylated alcogel was dried in supercritical carbon dioxide to prevent aerogel from collapsing. Supercritical drying was performed by using supercritical drying unit (*Thar*, SFE 5000F2) as shown in Fig. 2. Silylated alcogel was initially pressurized with liquid CO_2 to 100 bar. Drying vessel was flushed with liquid CO_2 (25 g min^{-1}) by maintaining the pressure at 100 bar using Automatic Back Pressure Regulator (APBR). The gel was then soaked in liquid CO_2 (100 bar) for solvent exchange. After 24 h, gel was dried in supercritical CO_2 at 25 g min^{-1} (100 bar, 45 °C) for 4 h. The vessel was finally depressurized at 2 bar min^{-1} to ambient pressure; while maintaining the temperature above 40 °C. The aerogels synthesized was then characterized.

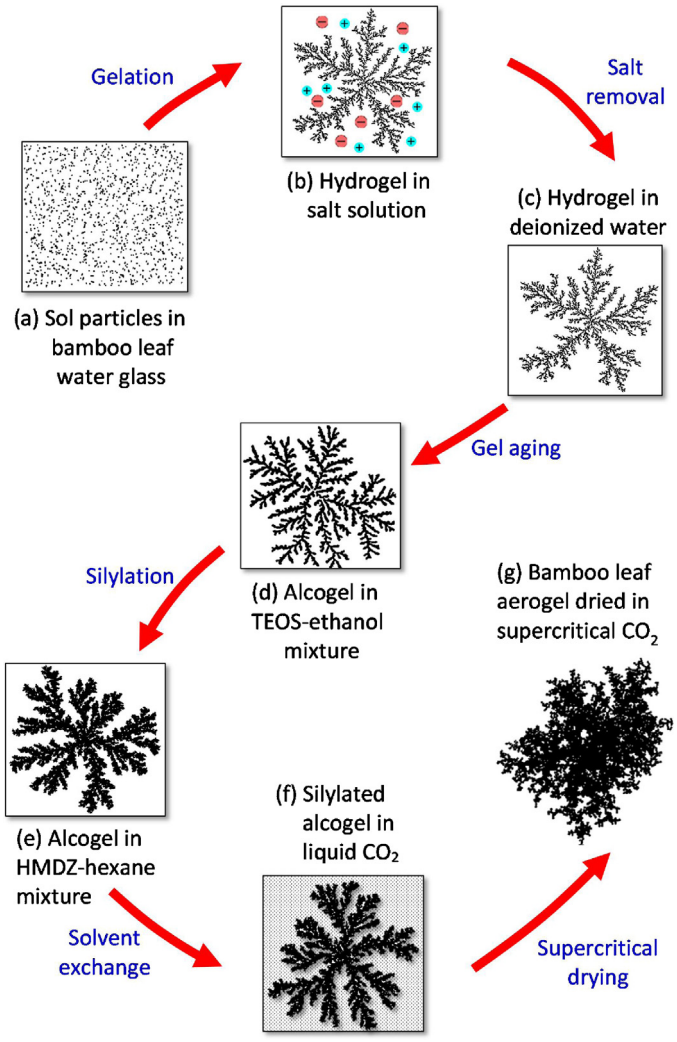

Fig. 1. Synthesis scheme of silica aerogels from bamboo leaf.