VIP Aerogels Very Important Paper

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An Easy Way To Prepare Monolithic Inorganic Oxide Aerogels**

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Abstract: *Inorganic oxide aerogels have unique thermal, optical, electrical, magnetic, and chemical properties, which result in them potentially having a broad range of applications. However, their preparation is commonly based on a supercritical drying method, which greatly limits real applications of aerogels and their commercialization. Here we demonstrate a general method for drying wet gels to form aerogels that is based on the sublimation of organic solvent. The organic solvent must have a low surface tension, undergo sublimation easily, and have a high freezing point to allow the rapid synthesis of monolithic inorganic oxide aerogels under vacuum conditions. This cost-effective process will facilitate application of aerogel materials. This approach may also be used for the preparation of other porous materials, whose theoretical and practical applications should be investigated.*

An aerogel, commonly named frozen smoke, is a porous material prepared by using air to replace the liquid component of the wet gel.[1–3] During recent decades, aerogels have attracted great interest in a broad range of both commercial and fundamental scientific applications because of their large pore volumes, high specific surface areas, low bulk densities, and low thermal conductivities.[4–8] Nevertheless, the practical application of aerogels has been constrained because of their fragility and the laborious drying methods.[7] In particular, it is very hard to keep inorganic oxide aerogels intact during the drying process because of the large capillary forces that exist during drying as a consequence of the surface tension at the liquid–vapor interface.[3,6] Most aerogels are formed by extracting the liquid of a gel by critical point drying (CPD) to avoid the damaging effects of surface tension.[6] However, CPD is difficult to carry out, time-consuming, expensive, and dangerous.[9] The replacement of CPD by techniques such as freeze drying (FD) and ambient-pressure drying (APD) has been investigated.[6,10,11–15] However, aerogels prepared by non-supercritical drying usually tend to break into fragments during the drying process.[6] Thus, the development of a new drying technique to shorten the aerogel production time and reduce its production costs would be valuable.

The first stage in the preparation of an inorganic aerogel is to create a wet gel. Drying the wet gel then results in the formation of an aerogel with a complex network structure. This is the most important step, and the original spatial configuration should be maintained during the drying process.[16] We have developed a new organic solvent sublimation drying (OSSD) method for forming monolithic inorganic oxide aerogels. Here, the organic solvents must have a low surface tension, undergo sublimation easily, and have a high freezing point to enable the rapid synthesis of monolithic inorganic oxide aerogels under vacuum conditions. Acetonitrile (freezing temperature: −45 °C) and *tert*-butanol (freezing temperature: 25.5 °C) are fully in line with our requirements, and their solid forms could be removed easily by sublimation under a low vacuum. We have successfully prepared SiO_2, Al_2O_3, Fe_2O_3, and NiO aerogels by the OSSD method.

Figure 1 a is a schematic view of the entire drying process. First, the liquid that impregnated the wet gels is exchanged with acetonitrile or *tert*-butanol (Figure 1 b). The aerogels with high specific surface area (see Table S1 in the Supporting Information) are then synthesized by drying the wet gels under vacuum conditions (Figure 1 c). For comparison, wet alumina gel without exchanged solvent and the frozen alumina gel exchanged with acetonitrile were also dried (see Figure S1 in the Supporting Information). Both samples broke into pieces when prepared by the above method. This result shows that OSSD is an optimal drying method for preparing monolithic porous materials (Figure S2 in the Supporting Information shows that the prepared alumina aerogel strongly absorbs ink, which indicates the aerogel has a highly porous structure). The SEM and TEM images of SiO_2, Al_2O_3, Fe_2O_3, and NiO in Figure 2 reveal the distinct textures and indicate that the main channels of the aerogels (ranging from a few tens to a few hundred nanometers) are formed by the random accumulation of colloidal particles.

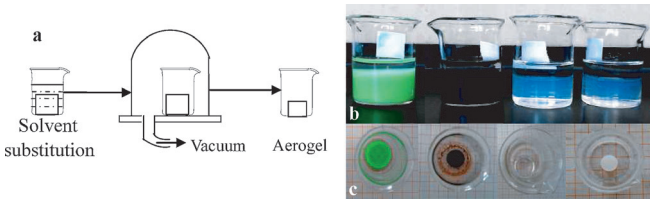

Figure 1. a) A schematic representation of the OSSD process. b) Photograph of the solvent-exchange process. c) Photograph of the aerogels propared by OSSD. From left to right: NiO, Fe_2O_3, SiO_2, and Al_2O_3.

The pore structure distribution and N_2 adsorption–desorption isotherms for the alumina aerogel were determined (see Figure S3 in the Supporting Information). The isotherms are type IV with H1 hysteresis loops characteristic of mesoporous materials. The size of the pores were

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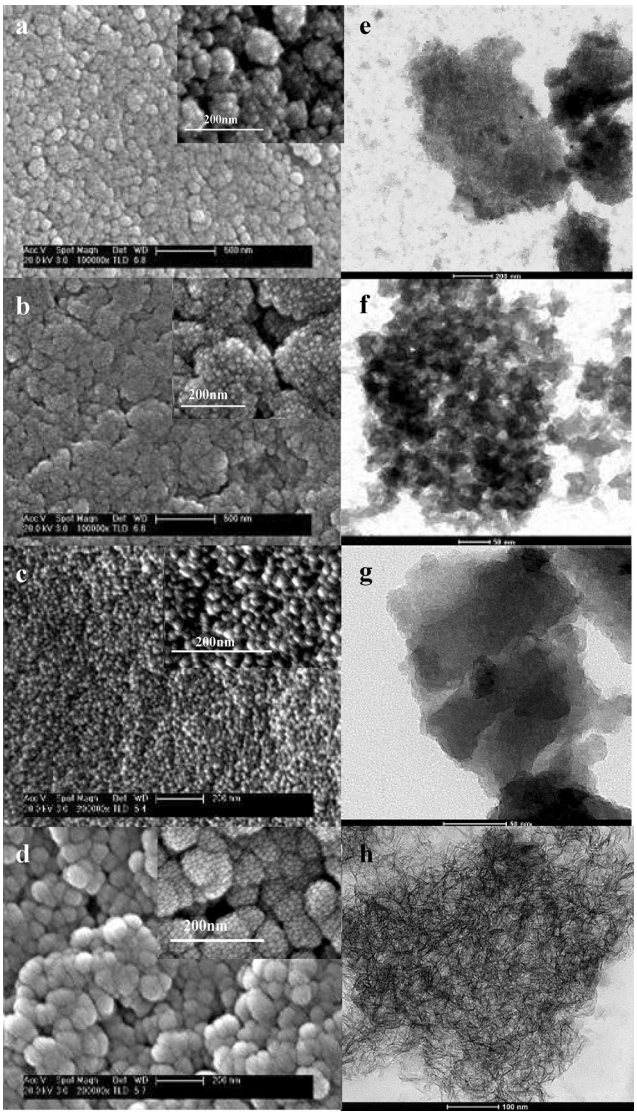

Figure 2. SEM (a–d) and TEM (e–h) images of different inorganic oxide aerogels prepared by OSSD: a,e) SiO_2; b,f) NiO; c,g) Fe_2O_3; and d,h) Al_2O_3.

predominantly about 10 nm. The electron microscopy images show that secondary particles with diameters of a few tens of nanometers are actually aggregations of small nanoparticles and consist of large mesoporous voids.

We propose the following mechanism, based on the characteristics (easy sublimation and high freezing point) of the organic solvents, to explain the formation of aerogels by OSSD (Figure 3). The M-O-M bridges forming through interaction with the inner surface hydroxy group in the wet gel allow its network structure to be maintained in a certain elastic range.[3,6] As drying proceeds, by increasing the vacuum, the organic solvent at the outer surface begins to evaporation first. Endothermic evaporation of the solvent leads to the internal temperature of the gel instantly decreasing, which results in a portion of the solvent becoming solid. Solidified solvent is very easy to sublimate to gas. Endothermic sublimation further leads to more solvent becoming solid. Thus, instantaneous changes in the three-phase liquid-gas-solid system continuously occur during the OSSD process, which not only avoids the influence of surface tension that occurs during the gas–liquid conversion in conventional drying processes, but also avoids the destruction of the pore structure through the formation of ice crystals during freeze-drying. To investigate the drying process, we chose a glass vacuum dryer to prepare the alumina aerogel. We recorded the whole process from the wet alumina gel to the alumina aerogel as a function of time (see Figure S4 in the Supporting Information). The surface structure of the aerogel remains intact and no cracks appear during the entire drying process, while the volume of the gel gradually reduces. Thus, the results are in accord with the proposed mechanism.

Figure 4 a,b show the different inorganic aerogels prepared by OSSD. The inorganic aerogels remained intact and cracks were not observed, irrespective of whether acetonitrile or *tert*-butanol was used as the substitute solvents. Figure 4 c–f shows the FTIR spectra of these inorganic aerogels. The characteristic bands of acetonitrile and *tert*-butanol are not evident in all the IR spectra, as during the drying process, the solvents are substantially removed by the sublimation. Compared with traditional supercritical drying, OSSD is extremely convenient and time-saving, and can be performed on a large-scale without the need for special high-pressure instruments.

In conclusion, the strategy developed herein to prepare aerogels can be applied to the drying of many porous materials. Compared with supercritical drying, OSSD has great practical value because of the short synthesis time and low production costs. In principle, any type of porous materials can be prepared by this method and it can be anticipated that aerogels will very shortly find commercial applications.

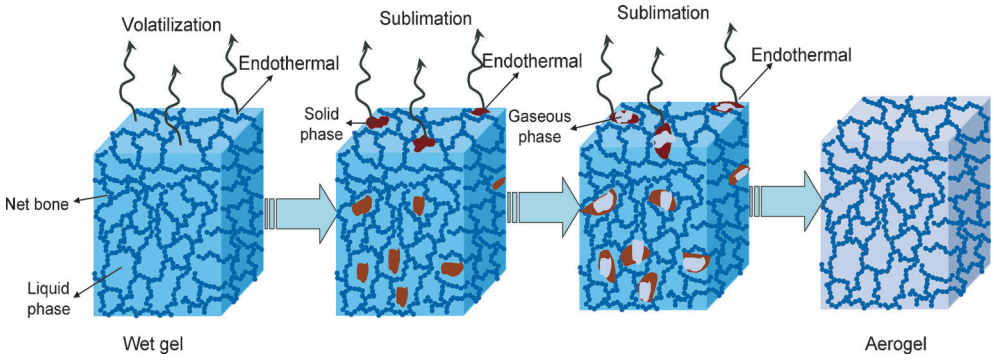

Figure 3. Proposed mechanism of the formation of aerogels by OSSD.

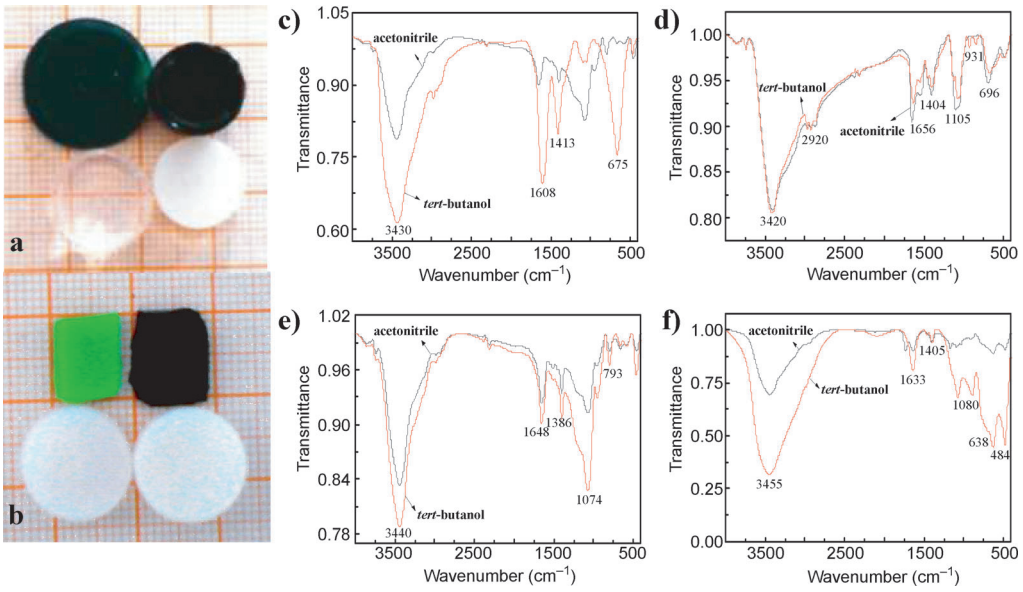

Figure 4. Aerogel samples prepared by OSSD and their FTIR spectra. a) Acetonitrile as the substitute solvent. b) *tert*-Butanol as the substitute solvents. From left to right: NiO, Fe_2O_3, SiO_2, and Al_2O_3. FTIR spectra of: c) NiO, d) Fe_2O_3, e) SiO_2, and f) Al_2O_3.

Experimental Section

Materials: The wet gels were prepared by stirring a mixture of the metallic salt (Aladdin, AR), deionized water, and ethanol (C_2H_5OH, Aladdin, AR) in the desired molar ratio, with stirring maintained under normal pressure at room temperature until the inorganic metal salt had dissolved completely. The calculated amount of propylene oxide (C_3H_6O, Aladdin, 99%) was added and the mixture stirred vigorously for ten minutes at room temperature. The weight ratio of mixture to propylene oxide was 1:8. The sample was then sealed for about 0.5–3 h until gelation occurred. The obtained wet gel was washed in 50%, 80%, 100% exchanging solvent (acetonitrile or *tert*-butanol)/EtOH (v/v) for 24 h at 50 °C before being aged in EtOH for 48 h at 50 °C. The wet gel was then stored in a beaker and dried at 50 °C under 80–100 KPa. The trapped solvent in the pores of the wet gel was easily removed under the low vacuum to afford the aerogel.

Characterization: Transmission electron micrographs and scanning electron micrographs of the aerogel samples were recorded. The surface areas and pore volumes were determined by the Brunauer-Emmett-Teller (BET) method on a ASAP 2010 Micromeritics apparatus. FTIR spectroscopy (Nicolet740, America) between 400 and 4000 cm^{-1} was used to confirm the chemical structure of the surface of the aerogels.

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