



Fabrication of elastic silica-bacterial cellulose composite aerogels with nanoscale interpenetrating network by ultrafast evaporative drying

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ABSTRACT

A nanoscale interpenetrating network (IPN) structure comprised of silica gel and bacterial cellulose gel is designed and surface-modified, to enable the fabrication of intact composite aerogels via direct heating to a relatively high temperature (110 °C). Compared to currently employed supercritical drying, freeze drying and ambient pressure drying, this process shortens the drying time of the aerogels from more than a few hours to less than 10 min. Although wet silica gels and bacterial cellulose gels seriously crack and shrink, respectively, when they exist individually, synergic effects between the fragile silica gel skeleton and soft bacterial cellulose gel skeleton ensure structural integrity of the composite gels during ultrafast evaporative drying. In particular, these synergic effects endow the composite aerogels with excellent elasticity so that they could recover their initial shapes even after undergoing 60% deformation. Hence, in addition to their low density (less than 0.12 g cm⁻³), high specific surface area (823 m² g⁻¹) and low thermal conductivity (0.032 W m⁻¹ K⁻¹) are well preserved, these synergic effects also aid to overcome some limitations with respect to practical applications of the fragile silica aerogels and soft bacterial cellulose aerogels, particularly when they are used as effective kinetic energy absorbers and recyclable oil absorbents.

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1. Introduction

Aerogels, commonly referred as frozen smoke, are intriguing porous materials that are generally created through a special drying process to replace the liquid component of the wet gel by air, while preventing the shrinkage of the gel skeleton [1]. Although the gel skeleton sometimes transformed into another state through a post treatment process (e.g., carbonization of organic aerogels to form carbon aerogels), this special drying process is always a prerequisite. The unique microstructure of aerogels endows them with impressive properties such as high specific surface, high porosity, low density and low thermal conductivity [2,3]. However, the low solid content associated with the presence of nanopores not only results in poor mechanical properties but also requires the drying process to be conducted at a very slow rate to maintain the structural integrity of these nanoporous materials, which otherwise is

lost by the ubiquitous capillary tension, irrespective of the type of gel, viz., traditional aerogels (e.g., inorganic oxide aerogels [4] and resorcinol-formaldehyde aerogels [5]) with fragile pearl-necklace-like network or new types of aerogels (e.g., cellulose aerogels [6] and graphene aerogels [7]) with nanoscale soft building blocks. The restrictions widely encountered in current drying method for aerogel preparation are (i) the very slow rate of release of the high pressure in supercritical drying (SCD) [8], (ii) strictly limited evaporation rate of liquid in ambient pressure drying (APD) [9], (iii) and limitation imposed over the sublimation rate in freeze drying (FD) by the inherent phase transition [10]. Precious time is seriously wasted in the drying process, which obviously restricts the production efficiency of aerogels. Moreover, their poor mechanical properties also severely restrict the practical application of aerogels.

Until now, drying processes and the mechanical properties of aerogels were optimized by tailoring the microstructure of the gel skeleton to enable them to withstand the capillary force. For example, endowing a gel skeleton with flexibility by employing a suitable precursor [11–15], strengthening it by adding individual dispersed fibers into the gel skeleton [16–18], or conformally

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coating the gel skeleton with a polymer [19–21] have been used to streamline the drying process and improve the mechanical properties of silica-based aerogels, the typical and most widely studied inorganic oxide aerogels. These excellent studies rendered the silica gel skeleton strong enough to sustain the impact of capillary tension more effectively. Consequently, the drying condition required is rendered less harsh, such that the process could be completed in more than a few hours in lab scale. However, further shortening of the drying time remains a formidable challenge because it is difficult to improve the strength of the gel skeleton further. Therefore, we wondered that whether there are alternatives routes to enhance the drying rate to a much higher level to obtain intact and robust aerogels?

During rapid solvent evaporation process, it is difficult for a fragile inorganic oxide (e.g., SiO_2) gel skeleton to endure the huge non-uniform capillary tension and therefore, it gets divided into different regions, thereby resulting in the severe crumbling of aerogels. In case of wet gels constructed from nanoscale soft building blocks (i.e., ultra-fine nanofibers), the gel skeleton is squeezed together by the capillary tension, and the porous gel structure is altogether lost, instead of cracking. In view of this, we consider that if a fragile as well as rigid silica gel skeleton could be constructed and confined in a soft gel skeleton to avoid the separation of different regions, and revived back after drying, both the fragile gel skeleton and soft gel skeleton in the composite aerogels will be well preserved. As a result, the strength of aerogels could be improved and the drying rate will also no longer be restricted by the necessity to maintain the integrity of the aerogels. Moreover, the drying of the gel could be conveniently carried out by direct heating without the need for special and expensive equipment. Hence, a nanoscale interpenetrating network (IPN) structure composed of a silica gel skeleton and a robust nanofibrous gel skeleton that could freely deform along with the silica gel skeleton is designed.

In order to verify this hypothesis, bacterial cellulose aerogels (BCAs) comprised of a flexible and robust ultrafine nanofiber network are selected as the biopolymer matrices. Classical and simple tetraethoxysilane rather than molecular with complex structure (e.g., the molecular with flexible bridging groups) [11,15]

is utilized as the precursor to generate the silica gel skeleton to obtain wet composite gels with IPN structure (Fig. 1a and e). Then, the wet gels are hydrophobized (Fig. 1f) followed by direct heating and drying (Fig. 1b ~ d and g ~ i). The obtained aerogels not only fully preserve the high specific surface, low density, large porosity and low thermal conductivity, but also exhibit superhydrophobicity and remarkable elasticity, which may extend the practical applications areas of aerogels.

2. Experimental section

2.1. Materials

The food product *nata-de-coco* (i.e., bacterial cellulose hydrogel, BC hydrogel) was procured from Kuangquan Food Co., Ltd. (Tangshan, China). Tetraethoxysilane (TEOS, 28% SiO_2) was purchased from Modern Orient Technology Development Co. Ltd (Beijing, China). Trimethylchlorosilane (TMCS, $\geq 98\%$) and triethylamine (TEA, $\geq 99\%$) were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH), hydrochloric acid (HCl), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$), ethanol ($\geq 99.7\%$), dichloromethane (CH_2Cl_2 , $\geq 99.5\%$), *n*-hexane ($\geq 95\%$), and ethyl acetate ($\geq 99.5\%$) were purchased from Beijing Chemical Reagents Co. (Beijing, China). *tert*-Butanol was supplied by Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). All chemicals were used as received without further purification.

2.2. Preparation of the primitive biopolymer matrix (PBM, i.e., BCAs without hydrophobization)

PBM was prepared from BC hydrogel via freeze drying, following a procedure previously published by our group [22].

2.3. Preparation of the wet silica gels

Different amounts (Table S1) of TEOS, deionized water (4 mL), ethanol (20 mL), and the acid catalyst (1% w/w HCl, 0.4 mL) were mixed in a beaker followed by stirring for 1 h. Dilute ammonia (0.1 mol L^{-1} , 2 mL) was added to this system to form silica alcosols.

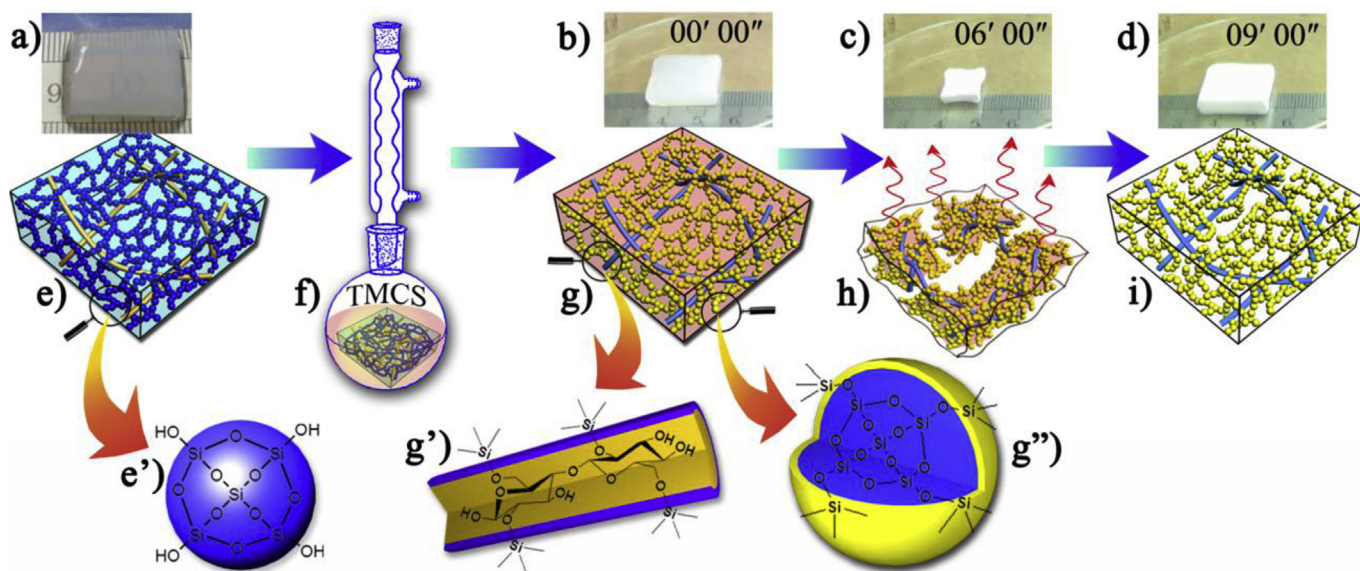


Fig. 1. Photographs and schematics illustrating the ultrafast evaporative drying (UFED) process. a, e) Wet composite gels before hydrophobization. b ~ d, g ~ i) The hydrophobized composite gels in the drying process at different periods. f) The hydrophobization of wet composite gels. Schematic images of e') silica nanoparticles before hydrophobization, g') BC nanofiber and g'') silica nanoparticle after hydrophobization.

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