

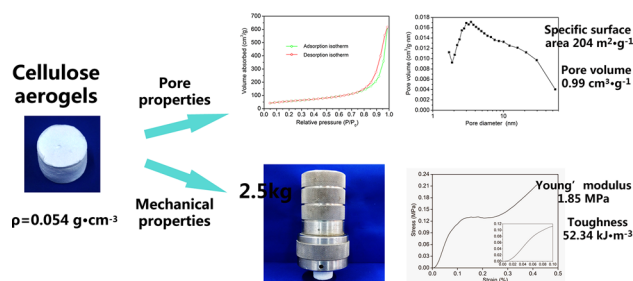
# Preparation of mechanically strong and lightweight cellulose aerogels from cellulose-NaOH/PEG solution

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**Abstract** Novel mechanically strong and lightweight cellulose aerogels were successfully prepared by the procedures in four steps: (1) dissolving bamboo fiber in a mild NaOH/PEG solution; (2) freeze–thaw treatment; (3) regeneration; (4) freeze drying. The aerogels with dense interconnected and hierarchical pore structures had high specific surface area of  $204 \text{ m}^2 \text{ g}^{-1}$ , large pore volume of  $0.99 \text{ cm}^3 \text{ g}^{-1}$ , high porosity as high as 97 % and low density of  $0.054 \text{ g cm}^{-3}$ , and showed cellulose II crystal structure. Moreover, the aerogels exhibited strong resistance to compression load with high Young's modulus of 1.85 MPa, yield stress of 83.57 kPa, and toughness of  $52.34 \text{ kJ m}^{-3}$ .

## Graphical Abstract



**Keywords** Cellulose aerogels · Freeze drying · Mechanical properties · Porous materials · Polymers

## 1 Introduction

Aerogels with their large specific surface area, high porosity and low density have been extensively considered as potential candidates for multifarious advanced applications [1]. However, some drawbacks including fragility, hydrophilicity, and demand of supercritical drying in production hamper commercialization of aerogels [2, 3], especially for fragility. The last two issues could be conceivably dealt with by some special modification and alternative means, nevertheless, the inherent fragility problems widely occurring in some inorganic and thermoset polymer aerogels impose severe restrictions on the handling and long-term use. Recently, green cellulose aerogels combined traditional good qualities with some new properties from cellulose such as biocompatibility have attracted increasing attention [4, 5]. Meanwhile, native cellulose aerogels are not found to significantly suffer from the

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fragility problems, and usually show excellent flexibility according to some literatures [6–8]. Notwithstanding some hybrid cellulose aerogels incorporated with reinforcing agents exhibit improved mechanical properties [9, 10], the reports aiming at mechanically strong pure cellulose aerogels are not abundant. Therefore, in this paper, a kind of mechanically strong and lightweight native cellulose aerogels had been successfully prepared by dissolving cellulose in a green cellulose solvent named NaOH/PEG solution, followed by freeze–thaw treatment, regeneration and freeze drying. The micromorphology, structure and properties of the products were characterized by scanning electron microscope (SEM), nitrogen adsorption measurements, X-ray diffraction (XRD), and universal testing machine.

## 2 Experimental

### 2.1 Materials

Bamboo fiber was supplied by Beijing Murun Technology Development Co. Ltd. and further completely cleaned and dried at 60 °C for 24 h. All chemicals were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. and used as received.

### 2.2 Preparation of cellulose aerogel

Dried bamboo fiber was added to 10 % aqueous solution of NaOH/PEG-4000 (9:1 wt/wt) with magnetic stirring at room temperature for 6 h to form 2 wt% homogeneous cellulose solution. Then, the cellulose solution was frozen at –15 °C for 12 h, and subsequently thawed at room temperature with vigorous stirring for 30 min. After being frozen again at –15 °C for 5 h, the frozen cake was successively regenerated in 1 % HCl solution, distilled water and tertiary butanol until the formation of an amber-like hydrogel. Finally, the cellulose aerogel was successfully prepared after the 48 h of freeze drying at –30 °C of the hydrogel.

### 2.3 Characterizations

SEM observations of cellulose aerogels morphology were performed using a FEI, Quanta 200 SEM at the acceleration voltage of 10–15 kV. Nitrogen adsorption measurements were carried out at –196 °C by an accelerated surface area and porosimetry system (3H-2000PS2 unit, Beishide Instrument S & T Co. Ltd.). All of the samples were outgassed at 90 °C for 10 h to remove any moisture or adsorbed contaminants prior to the measurements. Besides, the cellulose aerogels were tested in triplicate to ensure reproducibility. Specific surface area and pore characteristic parameters were calculated by the Brunauer–

Emmett–Teller and Barrett–Joyner–Halenda methods. Crystalline structures were identified by XRD (Rigaku, D/MAX 2200) operating with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a scan rate ( $2\theta$ ) of  $4^\circ \text{ min}^{-1}$  and the accelerating voltage of 40 kV and the applied current of 30 mA ranging from  $5^\circ$  to  $40^\circ$ . Compression tests were performed in a universal testing machine (Suns, UTM4304X) with a compressing velocity of  $2 \text{ mm min}^{-1}$ .

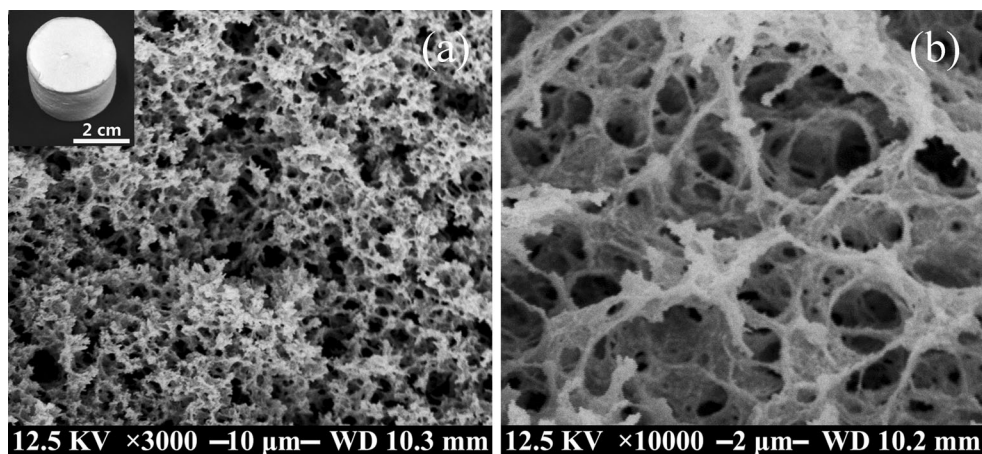
## 3 Results and discussion

Figure 1 showed the SEM images of the cellulose aerogels. As can be seen in the image at a low magnification (Fig. 1a), the aerogels exhibited homogeneous three-dimensional (3D) network structure. Moreover, the higher magnification image (Fig. 1b) showed dense interconnected and hierarchical pore structures with pores of different sizes from micro- to nano-scale. The inset in Fig. 1a showed the macrograph of the aerogels, and the aerogels sample maintained well-defined form without significant collapse, indicating the superior molding ability. The bulk density of the aerogels was calculated by dividing the weight by the sample volume measured with a micrometer, and the value was low (ca.  $0.054 \text{ g cm}^{-3}$ ).

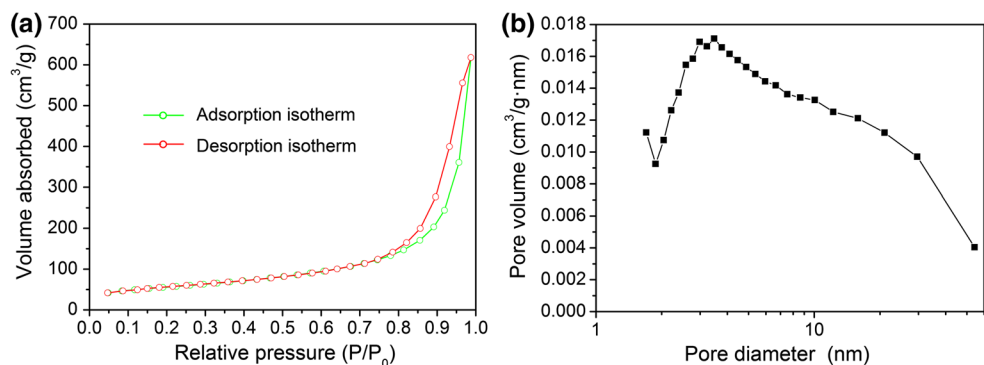
Figure 2 presented N<sub>2</sub> adsorption–desorption isotherms and pore diameter distribution of the cellulose aerogels. As shown in Fig. 2a, the typical IV adsorption isotherm could be identified according to the IUPAC classification, involving adsorption on mesoporous adsorbents with strong adsorbate–adsorbent interaction [11]. Furthermore, the as-prepared aerogels had high specific surface area of  $204 \text{ m}^2 \text{ g}^{-1}$  and large pore volume of  $0.99 \text{ cm}^3 \text{ g}^{-1}$  with porosity as high as 97 %, which was comparable to some porous cellulose aerogels from other approaches [12, 13], and high values were desirable for applications like catalyst carrier, supercapacitor, fuel cell and drug release. In Fig. 2b, the aerogels were mainly made up of micropores (<2 nm) and mesopores (2–50 nm).

The XRD patterns of the cellulose aerogels and the bamboo fiber were shown in Fig. 3. The bamboo fiber exhibited peaks at around  $14.9^\circ$ ,  $16.4^\circ$ ,  $22.1^\circ$  and  $34.7^\circ$ , corresponding to the (101), (10 $\bar{1}$ ), (002) and (040) planes of cellulose I crystal structure. For the aerogels, the existence of diffraction peaks at around  $12.0^\circ$ ,  $20.0^\circ$  and  $21.6^\circ$  revealed the transformation of cellulose I–cellulose II [14].

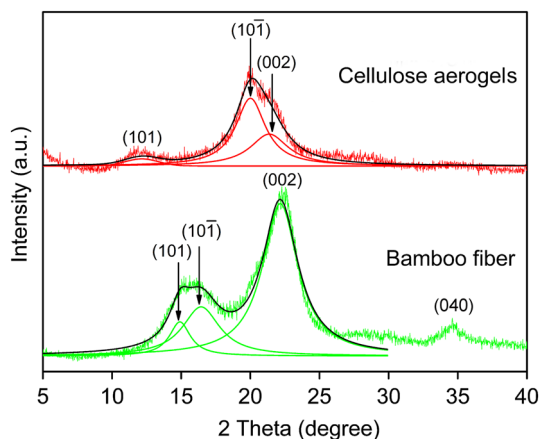
The compression mechanical properties of the aerogels were investigated by universal testing machine, and the tests were performed in triplicate and were done at least two different times to ensure reproducibility. Figure 4 showed the compression stress–strain curve and the digital photograph of the aerogels. It was observed that the aerogels sample could bear 2.5 kg load without obvious



**Fig. 1** **a** Low-magnification and **b** high-magnification SEM images of the cellulose aerogels. *Inset* showed the digital photograph of the dried cellulose aerogels sample

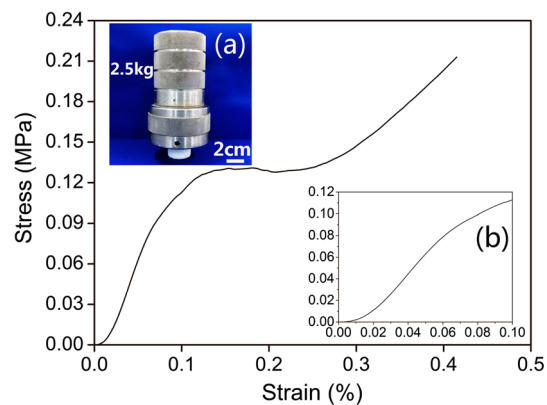


**Fig. 2** **a**  $N_2$  adsorption–desorption isotherms and **b** pore diameter distribution of the cellulose aerogels



**Fig. 3** XRD patterns of the cellulose aerogels and the bamboo fiber

collapse and deformation (inset a in Fig. 4), indicating promising compression resistance. Moreover, the compression stress–strain curve could be divided into four stages [15]. First, the linear elastic behavior in nature (inset b in Fig. 4) attributed to elastic cell wall bending occurred



**Fig. 4** Compression stress–strain curve of the cellulose aerogels. *Inset a* the aerogels sample with a load bearing of 2.5 kg. *Inset b*: expanded low-strain range

in low strain ( $<6\%$ ); second, the curve gradually transformed from linear to non-linear in higher strain, and the material would collapse in this region; third, a horizontal plateau region appeared after reaching yield stress, and the

resulting plastic hinges would result in cell collapse; final, the loose porous 3D network structure started to touch leading to considerable stiffening. The aerogels had high Young' modulus of 1.85 MPa, yield stress of 83.57 kPa, and toughness of  $52.34 \text{ kJ m}^{-3}$ , which were calculated based on the curve. Especially, the cross-linked and hierarchical micro-nano pore structures could effectively resist compression load and relieve deformation.

#### 4 Conclusions

In conclusion, we successfully fabricated a class of mechanically strong and lightweight nanoporous cellulose aerogels with cellulose II crystal structure via dissolution in a mild NaOH/PEG solution, freeze–thaw treatment, regeneration and freeze drying. The aerogels with hierarchical pore structures had high specific surface area ( $204 \text{ m}^2 \text{ g}^{-1}$ ), pore volume ( $0.99 \text{ cm}^3 \text{ g}^{-1}$ ), and porosity (97 %) as well as low density ( $0.054 \text{ g cm}^{-3}$ ); meanwhile, the material also exhibited strong resistant to compression deformation.

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