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Unidirectional freeze casting of compressible metallic aerogel composed of freeze-dried cellulose nanofibers and silver nanowires

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Abstract

Metallic aerogels have attracted tremendous interest because of their superior properties, such as low density, high electrical conductivity, and large specific surface area. However, extremely brittle connections in their 3D networks remain a challenge. In this study, compressible aerogels with microporous fiber-like structure consisting of freeze-dried cellulose nanofibers (CNFs) and silver nanowires (AgNWs) were fabricated by unidirectional freeze-casting process. To improve the robustness, elasticity, and deformability of the aerogel, freeze-dried microfiber-structured CNFs assembled with AgNWs were used. The freeze-dried CNF/AgNW-based aerogels exhibited a low density (8.51–13.5 mg/cm^3) and high porosity (up to 98.2%). Furthermore, these aerogels demonstrated impressive mechanical properties with high compressive strength (up to 4.85 kPa at 70% strain), elastic modulus (up to 16.3 kPa), and yield strength (up to 2 kPa). Additionally, the aerogels exhibited reversible deformability up to a 10% strain and maintained their durability over 200 cycles of compressive strain at 10%. The fabricated aerogels also showed a low electrical resistivity (< 8.65 mΩ·m) in addition to robust and compressible mechanical properties. These aerogels are expected to be useful in a wide range of applications that require characteristics such as light weight, high compressive strength, high elasticity, and low electrical resistivity.

Keywords Metallic aerogel, Silver nanowires, Cellulose nanofibers, Robustness, Elasticity, Electrical resistivity

Introduction

Metallic aerogels or metal-based porous structures have received substantial attention owing to their remarkable characteristics, such as low density, high specific surface area, high electrical conductivity, and catalytic activity. Conventional manufacturing methods for metallic aerogels include self-propagating high-temperature synthesis (SHS) [1, 2] and dealloying [3, 4]. SHS is a rapid and simple method for producing metallic aerogels via exothermic combustion. However, aerogels fabricated using SHS typically exhibit low compressive strength and inherent brittleness. On the other hand, dealloying enables the fabrication of nanoporous structures by selectively etching an element in metal alloys. However, aerogels produced by dealloying often exhibit poor flexibility and compressive deformability [5, 6]. In addition, both methods commonly encounter limitations in material selection.

Freeze casting has emerged as a useful technique for fabricating deformable and robust metallic aerogels [7–11]. The freeze casting process involves controlled solidification of the solution or suspension, followed by sublimation of the solvent. Freeze casting offers several advantages, including a diverse array of material options, the ability to combine different materials, and the flexibility to make alterations to create aerogels with desirable macro/microporous structures. Based on these advantages of the freeze casting

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process, robust and deformable aerogels can be fabricated using cellulose nanofibers (CNFs) and silver nanowires (AgNWs). Especially, AgNWs are promising candidates for metallic aerogels owing to their excellent characteristics, such as low electrical resistivity, high flexibility, and percolative network formation due to their high aspect ratio [12]. Furthermore, CNFs, which are earth-abundant biopolymers, possess a high aspect ratio, a large specific surface area, and various surface functional groups [13, 14]. The overall hydrophilicity of the abundant functional groups facilitates adequate chemical interactions, making it easy to disperse within deionized (DI) water and form stable assemblies of AgNWs and CNFs in aerogels.

Notably, aerogels fabricated through the freeze-casting process using normal CNFs tend to exhibit microporous wall-like structures because of the strong binding between CNFs expelled from the grown ice crystals [15–17]. However, these microporous wall-like structures may not be suitable for improving the elasticity and deformability of aerogels. To address this issue, microfiber-structured CNFs were used to construct elastic aerogels by freezing the CNF suspension at extremely low temperatures and then freeze-drying it prior to the freeze casting process [18]. The process was guided by the power-law relationship between the temperature and the size of ice crystals [19, 20]. Owing to their strong binding properties, these freeze-dried CNFs can withstand subsequent dispersion processes without easy decomposition. Although the development of such highly elastic CNF-based aerogels has already been carried out, incorporating electrical conductivity into these materials is yet to be achieved.

In this work, compressible metallic aerogels with microporous fiber-like structures fabricated by freeze-casting are proposed based on a combination of freeze-dried CNFs and AgNWs. The freeze-dried CNFs/AgNWs-based aerogels exhibited excellent robustness and elasticity. Notably, these metallic aerogels exhibit high compressive strength (> 4.85 kPa at 70% strain), elastic modulus (> 16.3 kPa), and yield strength (> 2 kPa) while maintaining reversible deformability at a 10% strain and mechanical durability over 200 cycles. Furthermore, these aerogels exhibit extremely low electrical resistivity, measuring no more than 8.65 mΩ/m. The freeze-dried CNFs/AgNWs-based robust and elastic aerogels described in this study have the potential for enhancing performance in various applications that require attributes such as light weight, high compressive strength, high elasticity, and excellent electrical properties.

Results and discussion

The fabrication process for the freeze-dried CNFs/AgNWs-based flexible aerogel using freeze-casting is shown in Fig. 1. Initially, 2 g of CNFs was dispersed in 100 g of DI water using a paste mixer at 2000 rpm for 5 min. The mixture was centrifuged at 2000 rpm for 10 min, and the resulting well-dispersed CNF suspension was separated from the precipitate. The prepared CNF suspensions were frozen in liquid nitrogen (LN2). The extremely low temperature (− 196 ℃) led to the formation of tiny ice crystals. The sublimation of these ice crystals after freeze-drying led to the formation of microfiber-structured CNFs [19, 20]. These freeze-dried microporous fiber-like CNFs are not easily separated from each other because of the strong binding properties of cellulose.

To prepare the freeze-dried CNF/AgNW-based suspension, 28 mg of freeze-dried CNFs were mixed with 10 g of DI water. Additionally, either 14 mg (0.14% concentration) or 28 mg (0.28% concentration) of AgNWs, synthesized using a modified polyol synthesis method [21], was added to the mixture. The resulting suspension was poured into a polytetrafluoroethylene (PTFE) mold with a Cu plate blocking the bottom. Due to the low temperature (− 70 ℃) of the Cu plate, ice crystals nucleated on the bottom surface and grew along the temperature gradient during freezing. Simultaneously, owing to the sufficiently high interfacial energy between ice and nanomaterials, the nanomaterials were expelled from the growing ice crystals and agglomerated [22]. Subsequently, freeze-drying removed the ice crystals through sublimation, leaving behind robust and elastic structures of the assembled freeze-dried CNFs/AgNWs. Two different compositions of freeze-dried CNFs/AgNWs-based aerogels were prepared: one with a weight ratio of 66.6 wt% CNF/33.3 wt% AgNW and another with a weight ratio of 50 wt% CNF/50 wt% AgNW. Additionally, for comparison, CNFs-based aerogels without adding AgNWs and normal CNFs/AgNWs-based aerogels were also fabricated. It is noted that the normal CNFs indicate the suspension that is not freeze-dried.

Scanning electron microscopy (SEM) images of the normal and freeze-dried CNF/AgNW-based aerogels are shown in Fig. 2. Both aerogels exhibited highly porous structures (Fig. 2a, c), with anisotropic pores aligned parallel to the direction of ice crystal growth (Fig. 2b, d). Notably, the aerogel composed of freeze-dried CNFs and AgNWs exhibited a three-dimensional network characterized by microporous fiber-like structures (Fig. 2c, d), unlike a wall-like structure in normal CNFs/AgNWs-based aerogel. Furthermore, densities and porosities of freeze-dried CNFs/AgNWs-based aerogels were measured using a mercury porosimeter (PM33GT,

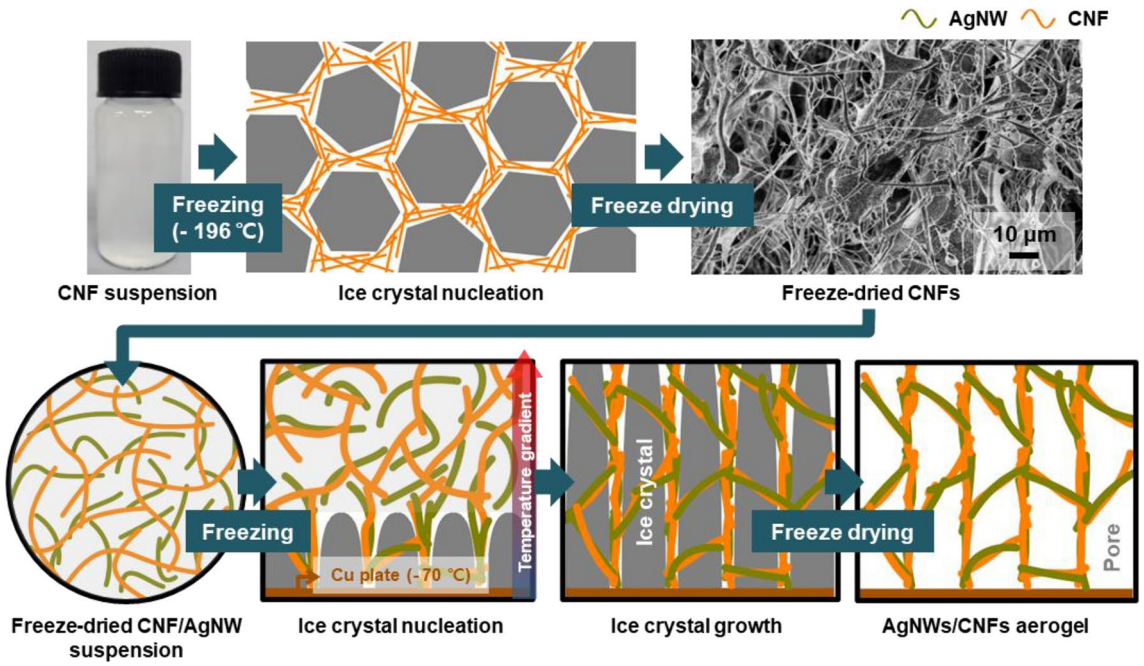

Fig. 1 Schematic of the fabrication process for the freeze-dried CNFs/AgNWs-based aerogel. The CNF suspension was directly frozen by LN2 and freeze-dried. Then, the freeze-dried CNF/AgNW suspension was frozen, and ice crystals grew along the temperature gradient within the suspension. Once the freezing process was complete, the frozen suspension was subjected to freeze-drying. As a result, the freeze-dried CNFs/AgNWs-based aerogel with uniform distribution and assembly of microfiber-structured CNFs and AgNWs within the aerogel matrix is obtained

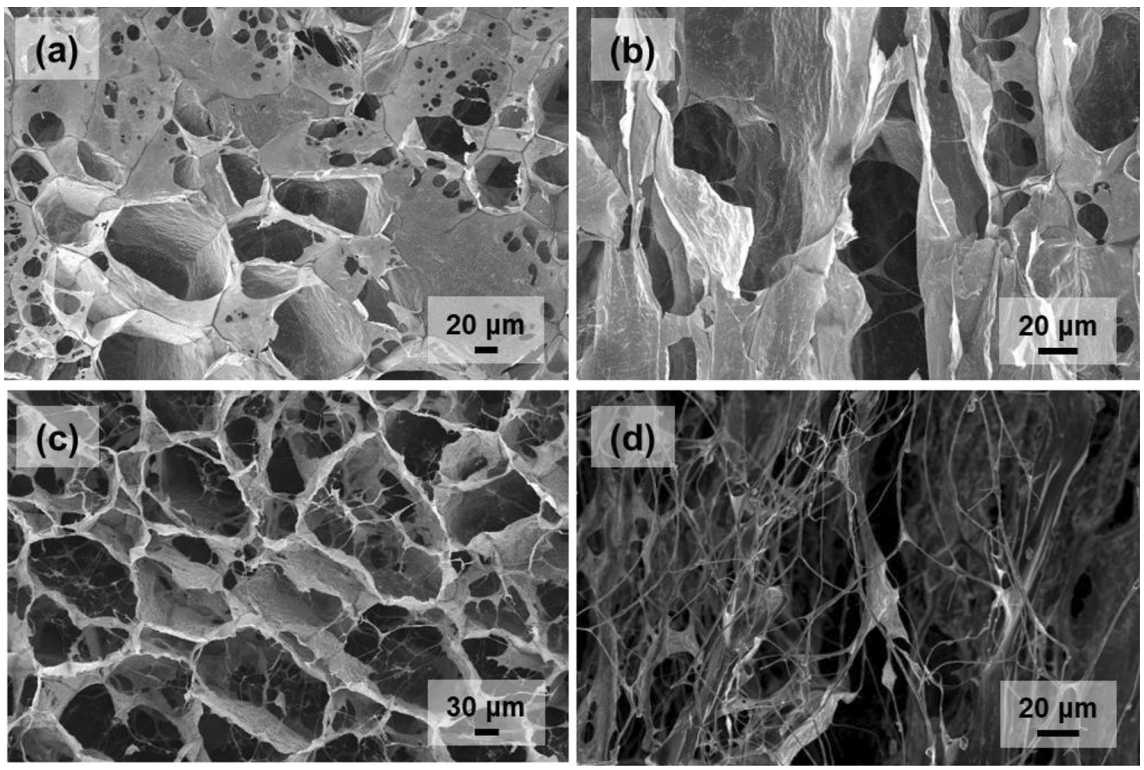

Fig. 2 SEM images of **a** the top view and **b** the side view for the normal CNF/AgNW-based aerogel. SEM images of **c** the top view and **d** the side view for the freeze-dried CNF/AgNW-based aerogel

Quantachrome). Consequently, both aerogels with 66.6 wt% CNF/33.3 wt% AgNW and 50 wt% CNF/50 wt% AgNW showed low densities and high porosities of 8.5 mg/cm^3 (with a porosity of 98.2%) and 13.5 mg/cm^3 (with a porosity of 97.8%), respectively.

The compressive stress–strain curves of the aerogels with and without AgNWs are shown in Fig. 3a. The compressive strength increases with the addition of AgNWs. Both 66.6 wt% CNF/33.3 wt% AgNW aerogel and 50 wt% CNF/50 wt% AgNW aerogel exhibited higher compressive stress (2.92 kPa and 4.85 kPa, respectively) than that of the CNF-based aerogel (1.34 kPa) at 70% strain. This improvement in compressive strength was due to the strong binding properties of the CNFs with AgNWs. Based on these results, the elastic moduli and yield strengths of the aerogels were characterized (Fig. 3b). Both properties also increased with the AgNW content, particularly in the case of the 50 wt% CNF/50 wt% AgNW aerogel, where both properties sharply increased by 443.8% and 344.4%, respectively, compared to the only CNFs-based aerogel. Furthermore, the cyclic compressive test for the 50 wt% CNF/50 wt% AgNW aerogel exhibited a good capability to recover over 200 cycles with a 10% strain (Fig. 3c). The impressive durability of the freeze-dried CNFs/AgNWs-based aerogel was attributed to its microporous fiber-like structure.

Owing to the formation of a well-connected percolative network and the excellent electrical conductivity of AgNWs, freeze-dried CNFs/AgNWs-based aerogels exhibited linear I–V characteristics with low electrical resistance (Fig. 4a). As shown in Fig. 4b, 66.6 wt% CNF/33.3 wt% AgNW and 50 wt% CNF/50 wt% AgNW aerogels exhibited extremely low resistivity of 9.17 and 8.65 mΩ·m, respectively. This exceptional electrical conductivity presents novel prospects for the application of

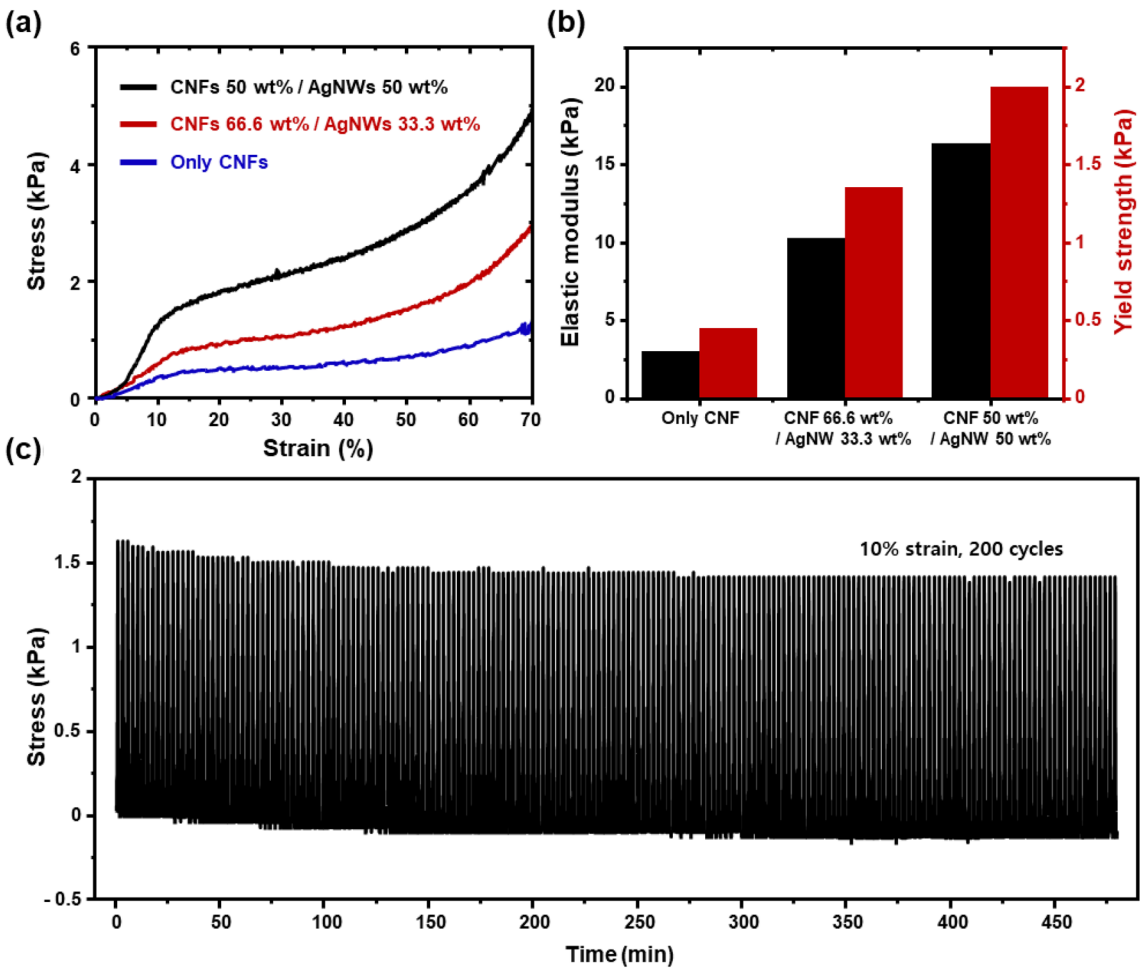

Fig. 3 Compressive mechanical properties of freeze-dried CNF-based aerogels. **a** Stress–strain curves of freeze-dried CNF-based aerogels with and without the addition of AgNWs. **b** Compressive elastic moduli and yield strengths of aerogels. Both mechanical properties are considerably increased when AgNW content increases. **c** Cyclic compressive test for 200 cycles of 10% strain for 50 wt% CNF/50 wt% AgNW aerogel

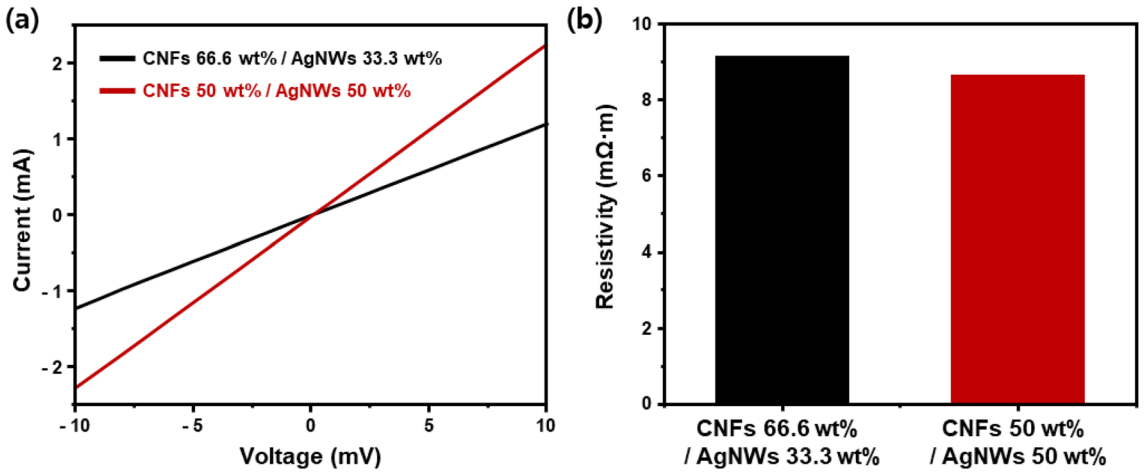

Fig. 4 Electrical properties of freeze-dried CNFs/AgNWs-based aerogels. **a** Linear I–V curves of metallic aerogels. **b** Electrical resistivity of aerogels with different compositions

these aerogels to various electronic devices as well as piezoresistive pressure sensors.

Conclusion

Freeze-dried CNFs/AgNWs-based metallic aerogels with microporous fiber-like structures were manufactured by freeze-casting process. Because of the extremely low-temperature freezing and freeze-drying of the CNF suspension, microfiber-structured CNFs were successfully prepared. Furthermore, the strong binding properties of cellulose led to stable microporous 3D networks assembled with freeze-dried CNFs and AgNWs, which improved the mechanical and electrical properties of the aerogels. The freeze-dried CNFs/AgNWs-based aerogels exhibited high compressive strength (>4.85 kPa at 70% strain), elastic modulus (>16.3 kPa), and yield strength (>2 kPa) while maintaining a reversible deformability of 10% strain and durability over 200 cycles. The proposed aerogels exhibit extremely low electrical resistivity (<8.65 mΩ·m) along with remarkable and stable electrical properties. Our approach could be useful for a broad spectrum of applications that demand low electrical resistivity, high compressive strength, high elasticity, and light weight.

Abbreviations

3D	Three-dimensional
AgNW	Silver nanowire
CNF	Cellulose nanofiber
LN2	Liquid nitrogen
PTFE	Polytetrafluoroethylene
Cu	Copper

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Not applicable.

Author contributions

All authors contributed to writing and editing the manuscript and approved the final manuscript.

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Availability of data and materials

Not applicable.

Declarations

Competing interests

The authors declare that they have no competing interests.

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