Recent Progress on Nanocellulose Aerogels: Preparation, Modification, Composite Fabrication, Applications

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The rapid development of modern industry and excessive consumption of petroleum-based polymers have triggered a double crisis presenting a shortage of nonrenewable resources and environmental pollution. However, this has provided an opportunity to stimulate researchers to harness native biobased materials for novel advanced materials and applications. Nanocellulose-based aerogels, using abundant and sustainable cellulose as raw material, present a third-generation of aerogels that combine traditional aerogels with high porosity and large specific surface area, as well as the excellent properties of cellulose itself. Currently, nanocellulose aerogels provide a highly attention-catching platform for a wide range of functional applications in various fields, e.g., adsorption, separation, energy storage, thermal insulation, electromagnetic interference shielding, and biomedical applications. Here, the preparation methods, modification strategies, composite fabrications, and further applications of nanocellulose aerogels are summarized, with additional discussions regarding the prospects and potential challenges in future development.

1. Introduction

Cellulose is one of the most abundant polysaccharides in nature, mainly composed of β-d-glucose monomers linked by 1,4-β-glycosidic bonds. As numerous free active hydroxyl groups exist on the surface at the C2, C3, and C6 positions, there are strong hydrogen bonds between the linear cellulose molecular chains (Figure 1a).[1] Nanocellulose is defined as having at least one dimension of 1–100 nm, which can be isolated from natural cellulose fibrils, and is mainly divided into three categories according to sources (Figure 1b–d): cellulose nanocrystals (CNCs), cellulose nanofibers (CNFs), and bacterial nanocellulose (BNC).[2] CNFs, also called elementary fibrils, are the smallest structural unit of the cellulose fiber (diameters of 20–50 μm and lengths of 1–4 mm) after chemical treatment (e.g., carboxymethylation and carboxylation),[3] mechanical separation,[4] or a combination of the two. Owing to different sources, elementary fibrils have a high aspect ratio (diameter: 2–20 nm; length: >1 μm), distributed with crystalline and amorphous segments.[5] CNCs are rod-like nanoparticles, which can be obtained by concentrated acid hydrolysis of amorphous regions in elementary fibrils with a lower aspect ratio.[6] BNC (<100 nm in diameter), originating from bacteria, is often used in some special fields, e.g., food and medical packaging materials, because of its high elastic modulus, good mechanical stability, and biocompatibility.[7] Owing to inherent features and their nature, including high surface activity and crystallinity, excellent hydrophilicity and biocompatibility, and superior strength, nanocelluloses have a wide range of applications when compounded with other materials in recent years, mainly concentrated in reinforced polymer composites,[8] functional fibers,[9] nanopapers and membranes,[10] hydrogels,[11] and aerogels/sponges.[12]

Aerogel is a special class of material with gas as a dispersion medium and a continuous 3D porous network, first prepared successfully by Kistler in 1931.[13] In contrast, nanocellulose-based aerogels are a combination of excellent properties, including green reproducibility, good biocompatibility, and easy degradation,[14] along with advantages of previous inorganic aerogels and polymer aerogels (low density, large porosity, and specific surface area (SSA)),[15] making them of interest for a broad range of functional applications, e.g., efficient...
adsorption,[18] thermal insulation,[7c,19] and energy storage[20] (Figure 2). Conversely, nanocellulose-based aerogels can also compensate for the shortcomings of brittleness and complex equipment of traditional aerogel materials such as silica (SiO$_2$), carbon, and tin dioxide,[21] which have been favored by several researchers as inexpensive and environmentally friendly alternatives for aerogel synthesis.

Based on several reports regarding nanocellulose aerogels, with accumulating evidence regarding “polymer aerogel” in recent years (Figure 3), this article provides a review regarding functional nanocellulose-based composite aerogels. In Section 2, a general introduction to the preparation of nanocellulose aerogels is presented, including the steps involved in the synthesis of the nanocellulose aerogel precursor and the classification of drying technology. Section 3 introduces some basic characteristics of nanocellulose aerogels. Section 4 discusses functional composite aerogels fabricated by compounding nanocellulose and different functional materials (e.g., metal or metal compounds, carbon materials, inorganic materials, and polymers). Section 5 describes the status quo of functional applications of nanocellulose aerogels in the fields of adsorption, energy storage, thermal insulation, sensors, electromagnetic interference (EMI) shielding, and biomedicine. Finally, in Section 6, we consider the applications of nanocellulose-based aerogels in the area of functional composites, as well as challenges and prospects that will be encountered in the future.

2. Preparation of Nanocellulose Aerogels

Different cellulose sources and fabrication methods can endow nanocellulose aerogels with different microstructures and performances. Generally, nanocellulose-based aerogels are prepared in three steps: i) dispersion of nanocellulose; ii) gelation of nanocellulose; iii) gel drying process.

2.1. Dispersion and Gelation of Nanocellulose

Owing to a large number of active hydroxyl groups on the nanocellulose surface, it is liable to form intermolecular and intramolecular hydrogen bonds,[22] along with self-aggregation and entanglement of nanocrystals or nanofibrils. Some negatively charged groups (e.g., carboxyl, carboxymethyl, or sulfonic)[23] can be introduced onto the nanocellulose surface to form a stable and uniform aqueous nanocellulose dispersion owing to electrostatic repulsions between the negatively charged nanocellulose,[24] e.g., 2,2,6,6-tetramethylpiperidine-1-oxylradical (TEMPO)-oxidized CNFs and sulfonated CNCs. When CNFs are dispersed in water, a 3D network can be formed by hydrogen bonding and entanglement of the long fibrils. As a network backbone, these nanofibrils can increase the strength and
modulus of the shaped gel. Therefore, the gel does not shrink significantly during the subsequent drying process. This helps the fabricated aerogel to maintain structural integrity even at a low solid nanocellulose content. However, these modified nanocelluloses cannot be well dispersed in organic solvents with low-polarity (e.g., tert-butyl alcohol (TBA) or ethanol) frequently used during the aerogel drying process.[25] Interestingly, adding a small amount of TBA to the aqueous CNF dispersion can evenly disperse nanofibrils in the mixed system and increase the SSA (>300 m² g⁻¹) of the nanocellulose aerogel prepared by subsequent freeze drying.[25–26]

After obtaining the precursor dispersion, many nanocellulose aerogels usually need to undergo a gelation process, which helps maintain and enhance the 3D network inside aerogels.[27] The gelation behavior of the nanocellulose is generally sorted into two major categories according to the nature of the gel: chemical crosslinking[28] and physical crosslinking[29] (Figure 4).

Chemical crosslinking refers to the addition of specific crosslinking agents (multifunctional monomers) to the solution such as citric acid or glutaraldehyde,[30] which can react with the nanocellulose and form irreversible covalent bonds between the cellulose chains. To fabricate a mechanically robust aerogel at an extremely low concentration of 0.3 wt% of nanocellulose, Chen et al. employed 1,2,3,4-butanetetracarboxylic acid (BTCA) as a chemical crosslinker to assist the TEMPO-oxidized CNFs form a crosslinking network structure.[31] Chemical-crosslinking was achieved by esterification reactions between the hydroxyl and carboxylic acid groups of CNFs and BTCA, respectively (Figure 5a). The physical gel is crosslinked by weak physical interactions between polymer chains through appropriate interactions, e.g., van der Waals forces, hydrogen bonds, electrostatic interactions, and ionic interactions.[32] Furthermore, some inorganic salts (e.g., CaCl₂, CaSO₄) can be added to the nanocellulose dispersion to form reversible crosslinks.[33] For example, carboxylic CNFs can undergo chelation with some multivalent metal ions (e.g., Zn²⁺, Cu²⁺, Co³⁺) via ionic gelation to form a hydrogel.[34] After adding appropriate ligand precursors, the combined metal ions can promote the formation of metal–organic framework (MOF) crystals within the CNF network through H-bonding and physical entanglements (Figure 5b). The stable and fibrous CNF/MOF hydrogels can survive the subsequent drying process for aerogels. In general, the chemical method can better control the porosity and SSA of the gel than the physical method, but has additional costs and requires a longer processing time.

2.2. Gel Drying

After dispersion and gelation of nanocellulose to form a stable 3D network structure, it is necessary to replace the liquid solvent filled in the structure with gas, while maintaining the original structure, thereby obtaining an aerogel. The most critical step in the preparation of the nanocellulose aerogel is to select a suitable drying technique. Different drying techniques have been developed to fabricate a porous aerogel network during solvent removal.

2.2.1. Atmospheric Pressure Drying

Generally, the solvent in the network gel structure is mainly water, with relatively large surface tension. Accordingly, collapse and destruction of the pore structure occur owing to the large capillary pressure (P₁, P₂, F₁, and F₂) and resultant forces (F₁', F₂', F₁', F₂') acting on pore walls in the horizontal direction between gas–liquid interfaces during solvent evaporation (Figure 6a).[35] The capillary pressure (P) is calculated depending on the Young–Laplace equation[35b]

$$p = -\frac{2y\cos\theta}{r}$$  \hspace{1cm} (1)

where γ, r, and θ are surface tension, radius of pores, and contact angle between solvent and pore walls, respectively. Therefore, several strategies can be employed to reduce the capillary pressure: i) decrease the γ of the solvent; ii) increase the pore size r to reduce the θ; iii) regulate the uniformity of the pore size to balance the pressure on pore walls; iv) strengthen mechanical performances of pore walls.[36]

For the simple and easy-to-operate atmospheric pressure drying, it is generally possible to replace water or alcohol in
the nanocellulose gel with a solvent presenting low surface tension or incorporate some oil-soluble surfactants to lower the surface tension, thereby reducing the internal capillary pressure. Li et al. pretreated the CNF gel by freezing and solvent exchanging water with 2-propanol that had a much lower surface tension, followed by drying under ambient pressure to obtain an aerogel without collapse and noticeable shrinkage (Figure 6b), similar to the preparation process of the traditional Chinese food, tofu.[37] The obtained nanocellulose aerogel was economical and environmentally friendly, presenting large porosity and low density of >98% and 18 mg cm\(^{-3}\), respectively. Similarly, Toivonen et al. presented an atmospheric-pressure-dried CNF aerogel membrane obtained through vacuum filtration and solvent exchanging using 2-propanol and then octane (Figure 6c).[38] A transparent CNF aerogel membrane with a thickness of \(\approx 25 \mu\text{m}\) (Figure 6d, left) was obtained.

Figure 5. a) The mechanism of the gel formation by chemical crosslinking between CNFs and BTCA. Reproduced with permission.[31] Copyright 2019, American Chemical Society. b) The gelation process of nanocellulose with physical crosslinking. Reproduced with permission.[34] Copyright 2018, American Chemical Society.
by slow drying of the CNF gel in octane, compared with the ≈12 µm transparent and compacted CNF film (Figure 6d, right) by rewetting the CNF aerogel membrane using water and then drying. This difference was attributed to the high capillary pressure from water that induced the compaction of the aerogel membrane after rewetting with water.

Additionally, pore network enhancement can reduce or eliminate aerogel collapse during atmospheric pressure drying. Li et al. used glycidoxypropyltrimethoxysilane (GPTMS) and branched polyethyleneimine (b-PEI) to enhance mechanical performance inside CNF gels, and replace the water in gels with acetone to reduce the solvent surface tension. On the CNF surface, covalent crosslinking occurred between silicon hydroxyl groups of hydrolyzed GPTMS and hydroxyl groups. Simultaneously, the crosslink density of the gel network increased owing to strong interactions between epoxide groups of GPTMS and amine groups of b-PEI (Figure 6e). This improved crosslinked 3D network helped the gel pore walls to resist the stress from the capillary pressure during the drying process. After atmospheric pressure drying, the fabricated CNF aerogel possessed a larger (4.3 times) SSA than that by freeze drying, demonstrating an enormous potential technique with ease-to-operate, as well as low energy consumption and cost for mass production, for functional nanocellulose aerogels.

2.2.2. Supercritical Drying

Supercritical drying involves the replacement of the solvent in the nanocellulose gel with supercritical fluids based on their special solubility, diffusivity, and lower surface tension. As with a drying kettle, the suitable temperature and pressure are controlled to allow the solvent to reach its critical point, followed by slowly relieving pressure and cooling down. The solvent is discharged from liquid phases to gas phases by supercritical transformation, obtaining a structurally complete aerogel. As the solvent presents no apparent surface tension during this process, the wet gel can be converted into an aerogel while maintaining its skeleton structure. Carbon dioxide (CO2) and ethanol are often suitable supercritical fluids for nanocellulose gels under supercritical drying. However, the critical temperature of ethanol is above 200 °C, which presents the dangers of using ethanol as a supercritical fluid, along with challenges in mass production.

For CO2, the critical temperature is only 31.3 °C, a little higher than room temperature and is more stable. Therefore, it is much safer and used more frequently. Zu et al. fabricated a nanocellulose aerogel by exchanging the precursor gel with ethanol and supercritical CO2 drying. Gas–liquid conversion, a process of two-way mass transfer between the solvent in gels and the fluid, occurred when the gel liquid and CO2 reached the supercritical state (31.3 °C and 72.9 atm). This replacement did not induce liquid surface tension, thus avoiding a collapsed gel structure during the drying process. Additionally, they observed that the obtained nanocellulose aerogel exhibited an interconnected 3D network nanostructure with more homogenous pores and less shrinkage, and a larger SSA of 299 m² g⁻¹ than that presented by the freeze-dried sample (103 m² g⁻¹), confirming that using supercritical CO2 drying to preserve the nanocellulose gel structure is a more effective method than...
freeze drying. However, the development of supercritical drying is limited and only applied to high-quality products owing to the cumbersome process, longer production cycle, and higher cost of solvent replacement.

### 2.2.3. Freeze Drying

Freeze drying is the most common method employed to remove the solvent in the nanocellulose gel and control the network structure inside the aerogel to prevent collapse. Moreover, compared with the above two methods, freeze drying possesses advantages of environmental protection, high efficiency, and low cost, attracting widespread attention for nanocellulose aerogels.\[7c,12d,46\] Freeze drying is essentially a process of sublimation drying: i) freezing the nanocellulose wet gel to a solid-state; ii) at a certain low pressure and temperature, the frozen solvent (mainly water) in the internal gel is directly sublimated from the solid-state to the gaseous state; iii) as the solvent is discharged, several pores are maintained to form a porous aerogel. This process avoids contact with the gas–liquid phases. Thus, it can effectively hinder the capillary pressure formed during the drying process, preserving the integrity of the skeleton structure.\[45\]

In general, most nanocellulose aerogels formed by freeze drying involve immersing the precursor dispersion/gel directly into liquid nitrogen or refrigeration. The ultralow liquid nitrogen (−196 °C) causes the water solvent to quickly form ice crystals, leaving dense and tiny pores in the aerogel after sublimation. Notably, additional time is required to form larger pores on using a cold source with a higher temperature owing to the slower freezing rate, which has been confirmed by Mueller et al.\[46\] Their resultant nanocellulose aerogels showed different pore sizes, with 20 μm at −196 °C for 5 min and 200 μm at −26 °C for 24 h. However, this traditional freezing method also presents limitations, mainly that the microporous structure of the aerogel is usually isotropic. The disordered structure prevents the aerogel from achieving a directional mass transfer, heat transfer, electrical conductivity, and other functions. Owing to its long and tortuous transmission path, the applications of this material are also restricted. Moreover, compared with the 3D ordered structure, the disordered nanocellulose aerogel is uncontrollable.

For functional structural materials to exert their functionalities, they greatly rely on the effective regulation and assembly of the micro/nanoscale structure. Directional freeze drying, mainly including unidirectional freeze drying and bidirectional freeze drying, has been developed based on the traditional freeze drying approach for effectively controlling the pore structure of materials employing ice crystals.\[47\] It is known to exhibit several advantages such as simplicity, flexibility, and a wide range of applications when compared with traditional methods for preparing porous materials (e.g., particle leaching, foaming, and phase separation).\[48\] The predominant difference is that the temperature gradient is applied in only one/two directions of the material during the freezing process instead of isotropic freezing. For unidirectional freeze drying (Figure 7a), after applying a bottom-up temperature gradient, the ice crystals of the solvent grow in this direction. During this process, the solute (CNFs) in the solution is extruded to interfaces between ice crystals to realize a solid–liquid separation, followed by sublimation and drying using a dryer to obtain a CNF aerogel after complete freezing.\[49\] The structural anisotropy is reflected in hexagonal honeycomb pores along the transverse direction (Figure 7b) and aligned ordered directional tunnels along the longitudinal direction (Figure 7c).\[50\] Furthermore, tilting the bottom of the container containing the precursor to a certain angle (≈20°) allows the formation of two temperature gradients along the Y-axis and Z-axis owing to contact with the cold source liquid nitrogen, resulting in a bidirectional anisotropic aerogel after drying (Figure 7d). The special aerogels showed good thermal insulation and mechanical properties over the isotropic and unidirectional aerogel owing to their well-aligned lamellar structures.\[51\]

Using this simple and flexible directional freeze drying technique, the selective adjustment of the aerogel structure can be realized by employing an appropriate cold source (liquid nitrogen at −196 °C or milder cold ethanol with adjustable temperatures) and temperature gradients,\[48\] and has been promoted in numerous fields of nanocellulose aerogel applications, including selective absorption,\[52\] gas capture,\[53\] solar steam generation,\[12d\] EMI shielding,\[54\] energy storage,\[55\] strain sensor,\[56\] and others.\[31,55\]

Recently, nanocellulose aerogels with precisely controlled 3D structures and inner pore architecture have been printed by using a 3D printing technique in a customizable manner. Utilization of the 3D printing technique can compensate for shortcomings of the above methods that fail to quickly manufacture aerogels with complex shapes, expanding the applicability of nanocellulose aerogels to meet the specific needs for various applications, especially tissue engineering.\[57\] For example, Li et al. printed high-pressure homogeneous TEMPO-oxidized CNFs using direct ink writing (DIW) to customize gels with various 3D structures, obtaining nanocellulose aerogels with high deformability and shape recovery by freeze drying (Figure 8a).\[58\] Qian et al. employed an all-printing method to construct a 3D hierarchically porous structure, with different tilt angles of the CNF-based aerogel assembled into a triboelectric nanogenerator (TENG) (Figure 8b).\[59\] The printed micro/nanostructures effectively increased the surface roughness, contact area, and mechanical elasticity of the TENG, which is beneficial to enhance corresponding triboelectric performances.

### 3. Properties of Nanocellulose Aerogels

The pristine nanocellulose aerogel exhibits excellent performance in several aspects, e.g., density, porosity, SSA, morphology, and mechanical and thermal properties, which are greatly affected by some major parameters, including the content of the nanocellulose precursor, drying methods, and freezing temperatures (Table 1).

#### 3.1. Density and Porosity

The bulk density (\(\rho\)) measured by dividing the weight (\(m\), mg) by the volume (\(v\), cm\(^3\)), of lightweight and porous nanocellulose aerogels usually fluctuates between 1 and 100 mg cm\(^{-3}\)
The porosity \( P \) of the aerogel can be calculated as follows, where \( \rho_n \) is the cellulose density (1.6 g cm\(^{-3}\))[12b]

\[
P(\%) = \left(1 - \frac{\rho}{\rho_n}\right) \times 100
\] (2)

After drying, the solvent is removed, leaving numerous pores inside the aerogel with a low density. Generally, the density of the aerogel can be increased by increasing the nanocellulose precursor content (Figure 9a). When the content of CNFs is only 0.05 wt\%, the density of the aerogel is as low as 0.98 mg cm\(^{-3}\). This aerogel is extremely weak and fragile and can be adsorbed via electrostatic forces (Figure 9b). On reaching 0.5 wt\%, the aerogel becomes stable and complete, but its density remains markedly low such that the aerogel can stand on a grass well (Figure 9c).[48] The rationale for the low density of aerogel has been attributed to a large amount of air within the aerogel, resulting in an extremely high porosity of >99%. As the nanocellulose content increases, the pores inside the aerogel are occupied by increasing solid cellulose, resulting in a gradual decrease in porosity (Figure 9a). A trend of a negative correlation between density and porosity can also be obtained from formula (2). In addition, the porosity and density of the aerogel can be adjusted through modification. For example, the nanocellulose carbon aerogel (CA) fabricated by the carbonization treatment will become lighter and increasingly porous owing to the thermal weight loss of cellulose.[59] The modified CNF aerogel obtained by chemical vapor deposition (CVD) of hexadecyltrimethoxysilane (HDTMS) showed a slightly higher density and lower porosity than the unmodified aerogel, owing to the thermal stress applied during the modification process and the HDTMS-induced condensation between CNF chains.[60]

### 3.2. Specific Surface Area

The SSA of the nanocellulose aerogel has a profound influence on its adsorption, heat transfer, catalysis, and other capabilities.[43] The freeze-dried CNF aerogel at –196 °C presents...
an SSA of $\approx 42 \text{ m}^2\text{ g}^{-1}$ at a low 0.5 wt% content, higher than at $-20 ^\circ\text{C} (\approx 30 \text{ m}^2\text{ g}^{-1})$ with similar content. At the same freezing temperature, as the CNF content increases, the aerogel SSA is gradually decreased due to reduced porosity. During the freezing of water as the main solvent in the traditional freeze drying, ice crystals can nucleate, grow, and concentrate CNFs in the interstitial area between the crystals, thereby forming “nanopaper” pore walls of the significantly aggregated CNFs during the sublimation process. This leads to a limitation in the aerogel SSA. Replacing water with a solvent such as TBA is an effective method to increase the aerogel SSA as TBA demonstrates a lower extent of surface tension effects, thus avoiding pore closure during the drying process. Sehaqui et al. solvent-exchanged the CNF aqueous dispersions from wood pulp using TBA, followed by TBA freeze drying. The fibril structure of the aerogel was well preserved, and hence, the obtained SSA was up to 284 m$^2$ g$^{-1}$, which was markedly higher than that obtained by the traditional freeze drying.

Kobayashi et al. observed that supercritical drying could maintain constant contact areas between nanofibrils, even if the content of the dispersion was altered, resulting in a high SSA liquid-crystalline nanocellulose aerogel with 500–600 m$^2$ g$^{-1}$. Later, Sakai et al. also confirmed that the SSA ($\approx 300 \text{ m}^2\text{ g}^{-1}$) of the supercritical-dried aerogel was higher than the traditional freeze-dried ($\approx 20 \text{ m}^2\text{ g}^{-1}$) or the TBA freeze-dried ($\approx 160 \text{ m}^2\text{ g}^{-1}$).

Notably, aerogels composed of only CNCs exhibited a higher SSA when compared with those composed of only CNFs, e.g., the high concentration supercritical-dried CNC aerogel with an SSA of $\approx 605 \text{ m}^2\text{ g}^{-1}$, the ethanol solvent-exchanged freeze-dried CNC aerogel with an SSA of $\approx 250 \text{ m}^2\text{ g}^{-1}$. Further, Zu et al. performed carbonization treatment based on freeze-dried ($\approx 103 \text{ m}^2\text{ g}^{-1}$) and supercritical-dried CNC ($\approx 299 \text{ m}^2\text{ g}^{-1}$) aerogels, obtaining a greatly improved SSA of $\approx 418$ and $\approx 892 \text{ m}^2\text{ g}^{-1}$, respectively.

3.3. Morphology and Structure

Fluffy, high porosity nanocellulose aerogels with numerous openings are rich in porous network structures. An open 3D porous fibrillar network of continuous self-assembled nanofibrils appears inside the aerogel with a low CNF content (e.g., 0.1 or 0.2 wt%) owing to the high SSA of the CNFs and strong hydrogen bonds between nanofibrils in the freeze-drying process. As the content increases, the porous structure becomes denser. Once the content exceeds 0.5 wt%, the increased nanofibrils will shorten the distance between the fibrils, and the displacement and growth of ice crystals will further promote physical entanglement and self-aggregation of CNFs, leading to a transformation from porous 3D web-like structures to 2D sheet-like structures.
The pore size of the freeze-dried CNF aerogel is closely related to the freezing temperatures, e.g., −18, −30, and −196 °C, causing decreasing pore sizes of ≈150, ≈50, and ≈15 µm, respectively (Figure 10a–c). This has been attributed to ice crystals growing slowly at a higher freezing temperature, leaving numerous large pores after drying and sublimation. Furthermore, liquid nitrogen as a cold source will freeze the ice crystals quickly without growing time, resulting in denser and smaller pores. Yang and Cranston compared the effects of different CNC contents on solute interaction induced mesopores and macropores formed by ice crystals of the aerogel. All of the CNC aerogels presented a similar porous structure, with <50 nm smaller pores and >1 µm bigger pores, respectively. With increasing CNC contents, the macropore structure of the aerogel became tighter and its pore size tended to be smaller (Figure 10d–g). This was because a larger number of CNCs

| Material | Content [wt%] | Density [mg cm⁻³] | Porosity [%] | Specific surface area [m² g⁻¹] | Drying | Stress [kPa, 70%] | Thermal conductivity [mW m⁻¹ K⁻¹] | Refs. |
|----------|---------------|-------------------|--------------|-------------------------------|--------|-----------------|----------------------------------|-------|
| CNF      | 0.7           | –                 | –            | 300.0                         | FD (−20 °C) | –               | –                                | [25]  |
| CNF      | 1.0           | 10.0              | 99.3         | –                             | FD (−196 °C) | –               | –                                | [59]  |
| Carbonized CNF | 1.0 | 8.8              | 99.5         | 249.9                         |        |                 |                                  |       |
| CNF      | 0.6           | 8.0              | 99.5         | –                             | FD (−196 °C) | –               | –                                | [60]  |
|          | 0.9           | 10.3             | 99.3         |                               |        |                 |                                  |       |
|          | 1.2           | 13.8             | 99.1         | 300.0                         |        |                 |                                  |       |
| Modified CNF | 1.2   | 17.5             | 98.8         | 261.9                         |        | 30.0            |                                  |       |
| CNF      | 1.0           | 14.0             | 99.0         | 284.0                         | FD (−196 °C) | 3.2             | –                                | [61]  |
|          | 2.0           | 29.0             | 98.0         |                               |        | 24.4            |                                  |       |
|          |              | 50.0             | 96.6         | 234.0                         |        | 69.0            |                                  |       |
|          |              | 105.0            | 92.8         |                               |        | 238.0           |                                  |       |
| CNF      | 2.0           | 20.0             | 98.0         | 66.0                          | FD (−180 °C) | 203.0           | –                                | [62]  |
| CNF      | 0.1           | 1.7              | 99.9         | –                             | FD (−20 °C) | –               | –                                | [18b] |
|          | 0.2           | 2.7              | 99.8         | 10.9                          |        | ≈5.0            |                                  |       |
| CNC      | 0.5           | 5.6              | 99.6         | –                             | FD     | 8.0             | –                                | [13]  |
|          | 2.0           | 21.7             | 98.6         | 230.0                         |        | 11.0            |                                  |       |
| CNF      | 0.5           | 4.0              | 99.8         | 42.0                          | FD (−196 °C) | –               | –                                | [63]  |
|          | 1.0           | 8.0              | 99.5         | 16.0                          |        |                 |                                  |       |
|          | 1.5           | 11.0             | 99.3         | 14.0                          |        |                 |                                  |       |
|          | 2.0           | 14.0             | 99.1         | 11.0                          |        |                 |                                  |       |
| CNF      | 0.6           | 8.0              | 99.5         | 30.0                          | FD (−20 °C) | –               | –                                | [64]  |
| CNF      | 1.3           | 20.0             | 98.6         | –                             | FD     | –               | –                                | [65]  |
| CNF      | 1.5           | 18.0             | 98.9         | >30.0                         | AD (70 °C) | 29.0            | –                                | [37]  |
|          | 2.0           | 23.0             | 98.5         |                               |        | 54.0            |                                  |       |
|          | 2.5           | 27.0             | 98.3         |                               |        | 82.0            |                                  |       |
|          | 3.0           | 32.0             | 98.0         |                               |        | 133.0           |                                  |       |
| CNC      | –             | –                | –            | 103.0                         | FD (−50 °C) | –               | –                                | [42]  |
|          |              |                  |              |                               |        | 299.0           | SD                               |       |
| Carbonized CNC |         | 418.0            |              |                               |        | 892.0           | SD                               |       |
| CNF      | 0.1           | 1.3              | 99.9         | –                             | FD (−18 °C) | –               | –                                | [66]  |
|          | 1.5           | 17.0             | 98.9         |                               |        |                 |                                  |       |
| CNF      | 0.5           | 5.0              | >99.0        | –                             | FD (−18 °C) | –               | <16                              | [67]  |
| CNF      | 1.3 vol%      | ≈99.0            | ≈20.0        | FD (−196 °C)                 | –     | ≈19              |                                  | [68]  |
| CNF      | 0.6 vol%      | 10.0             | ≈300.0       | SD                            |        | ≈22              |                                  |       |
| CNF      | 0.3 vol%      | 4.0              | ≈160.0       | FD (−196 °C)                 | –     | ≈18              |                                  |       |
| CNF      | 2.0           | 23.0             | ≈99.0        | ≈90.0                         | FD (−80 °C) | 160.0           | 18                               | [69]  |

*AD, atmospheric pressure drying; CNC, cellulose nanocrystal; CNF, cellulose nanofibril; SD, supercritical drying; FD, freeze drying; a)Solvent exchange.

Yang and Cranston compared the effects of different CNC contents on solute interaction induced mesopores and macropores formed by ice crystals of the aerogel. All of the CNC aerogels presented a similar porous structure, with <50 nm smaller pores and >1 µm bigger pores, respectively. With increasing CNC contents, the macropore structure of the aerogel became tighter and its pore size tended to be smaller (Figure 10d–g). This was because a larger number of CNCs...
would occupy more space and hinder the growth of ice nuclei, resulting in smaller ice crystals, which would leave smaller pores after removal. However, the mesopore structure was not significantly altered (Figure 10d–g′), suggesting that aerogel mesopores might not be considerably dependent on the CNC content.

Supercritical CO2 drying has been utilized to generate highly homogenous and denser structures of the CNC aerogel without clear aggregation (Figure 10i, i′) when compared with freeze-dried aerogels exhibiting randomly interconnected networks with sheet-like aggregated larger pores (Figure 10h, h′). Zu et al. confirmed that supercritical drying was a more suitable and efficacious strategy than freeze drying to maintain the integrity and uniformity of the aerogel structure.[42] Accordingly, they further observed that the high-temperature heat treatment could reduce the pore size of the aerogel with a compact structure, owing to the structural shrinkage during the carbonization process. Additionally, the CVD hydrophobic modification treatment or solvent exchange both reduced the pore size of the nanocellulose aerogel to a certain degree.[60,68]

3.4. Mechanical and Thermal Properties

Nanocellulose aerogels often exhibit good mechanical performances under an external force, including compressive strength, Young’s modulus, and flexibility, better than the traditional brittle SiO2 aerogels that are usually broken easily under pressure, owing to the high strength of nanocellulose and the stable porous structure of the formed aerogel. Three typical stages of the compressive process are generally applied to the nanocellulose aerogel: i) a linear elastic region at low strain ($\varepsilon$<10%); ii) a nonlinear plastic deformation plateau at moderate strain; iii) a plastic stiffening effect at high strain.[18b,71] A 0.0117 g aerogel was effectively regulated by directional freeze drying, which greatly improved the compressive strength in the oriented direction.[48] A 0.0117 g aerogel could withstand a weight more than 4000 times of itself with no deformation because of the ordered arrangement of aerogel pore walls, composed of intertwined nanofibrils in the longitudinal direction. Qi et al. extracted CNF suspensions from cotton, followed by freeze drying to construct a soft aerogel.[72] The cotton-derived long CNFs with a high aspect ratio as building blocks formed strong web-like entangled structures inside the aerogel, which endowed the aerogel with high flexibility and bending resistance without structural damage or destruction. In addition, some crosslinking agents, polymers, or reinforcing fillers (e.g., diisocyanate,[28a] poly(vinyl alcohol) (PVA)[53c] and graphene[73]) can be introduced to further improve the mechanical performance of nanocellulose aerogels.

High-porosity solid materials are thermally insulating with low thermal conductivities, and aerogels are no exception. Nanocellulose aerogels show a low thermal conductivity below air (≈25 mW m$^{-1}$ K$^{-1}$) because of its high porosity and low density.[67] To further lower the aerogel thermal conductivity, thermal solid conduction and thermal gas convection can be employed. By reducing the CNF content to lower the aerogel bulk density, the solid conduction contribution can be decreased owing to the reduced solid nanofibril contact.[68] By constructing a CNF aerogel ultraporous structure that is mainly mesoporous, smaller than the gas mean free path (≈70 nm),
the gas convection contribution can be effectively lowered by confining air molecules within the aerogel. These excellent thermal properties ensure that nanocellulose aerogels show great potentials in the field of thermal insulation, as discussed in a later section.

4. Modification of Nanocellulose Aerogels and Composite Fabrication

4.1. Modification

The lyophilized nanocellulose aerogels reportedly form sponge-like porous networks, but often need to be further modified to improve some specific properties, including hydrophobicity, conductivity, and mechanical strength. Common methods such as dipping or coating,[74] heat treatment,[52] surface modification,[75] and crosslinking treatment[76] are beneficial to enrich aerogel properties and lay a foundation for subsequent applications by introducing functional materials.

For aerogels, the most frequently used methods include surface coating with hydrophobic agents[30c,51b,77] or carbonization treatment,[18a,78] to modify hydrophobicity and lipophilicity, mainly for effective oil–water separation. For instance, the high-temperature carbonization process can remove numerous oxygen-containing hydrophilic functional groups on the surface of CNF aerogels,[49] and also obtain some special features, including excellent thermal stability, a high-water contact angle (≈140°), ultralow density (≈6 mg cm⁻³), and stable and enhanced oil adsorption capacity (>200 g g⁻¹).

Furthermore, some special materials (e.g., conductive polymers or hydrophobic agents) can be introduced into aerogels...
by impregnation or surface spraying, providing aerogels with further support. Previously, Ikkala and co-workers soaked the highly compressible cellulose I nanofibril aerogel directly into a polyaniline (PANI)–toluene solution, obtaining a relatively high conductivity \( (1 \times 10^{-2} \text{ S cm}^{-1}) \).\(^{[62]} \) After solvent evaporation, the aerogel maintained a stable hierarchical morphology with minimal shrinkage and good flexibility, which enhanced the functional applications of nanocellulose aerogels. Zhang et al. deposited methyltrimethoxysilane (MTMS) on the surface of the CNF aerogel using the CVD method to obtain a high hydrophobic surface with a 142° water contact angle.\(^{[51b]} \) The experimental results confirmed that hydrophobic groups were strongly adsorbed on the surface and inside the aerogel, thus exhibiting an efficient selective absorption for different oils or organic solvents. Furthermore, this provided a simpler strategy for oil–water separation and sewage treatment.

4.2. Materials as Various Composites

The versatile functions of nanocellulose composite aerogels are attributed to new groups or components generated in the aerogel system. There are mainly three different methods for the incorporation of other functional materials into matrices: i) direct addition or formation of guest materials in nanocellulose dispersions. ii) Guest materials constructed in the bulk structure of aerogels. iii) Coating guest materials on nanocellulose surfaces to form composite materials.\(^{[79]} \)

4.2.1. Composites with Metal or Metal Compounds

Metals (e.g., silver, aluminum, copper, and iron), as well as their several types of compounds, show excellent electrical, thermal, and magnetic effects. However, the high price, high density, and difficulties in processing limit their scope of application. Therefore, researchers have introduced these metal materials as functional fillers into nanocellulose aerogels to enrich their uses.\(^{[18d, 44a, 53b, 80]} \)

Henry et al. utilized the nanofibrillated cellulose aerogel as a biological matrix and template to directly mineralize TiCl\(_4\) on the surface of CNFs, resulting in TiO\(_2@\)nanocellulose composites with a novel nanothorn morphology (Figure 12a).\(^{[81]} \) In this case, the CNF aerogel provided a high SSA and stable

Figure 12. a) The formation of TiO\(_2\) in the nanocellulose aerogel by mineralization. Reproduced with permission.\(^{[81]} \) Copyright 2015, American Chemical Society. b) The schematic illustration of the process for nanocellulose/silver composite aerogel. Reproduced with permission.\(^{[83]} \) Copyright 2017, Elsevier Ltd.
intertwined network between nanofibrils, which was beneficial to the formation and loading of TiO$_2$. Additionally, the TiO$_2$@C nanocomposite with hollow nanostructures was prepared upon pyrolysis after mineralization, showing superior potential applications in photocatalysis or electrochemistry. Similarly, the BNC aerogel was used as a template and soaked with precursor solutions (FeCl$_3$·6H$_2$O and CoCl$_2$·6H$_2$O). After coprecipitation, the CoFe$_2$O$_4$ nanotubes, presenting a diameter exceeding 200 nm, were formed in the aerogel with a 3D structure, exhibiting magnetic behavior at room temperature. In the field of adsorption, magnetic Fe$_3$O$_4$ was embedded in the BNC carbon aerogel by Leamviteevenich et al. By applying an external magnetic field, the aerogel was easily manipulated and collected repeatedly during the oil absorption process, which helped avoid direct contact with possible hazardous solvents.

Directly mixing CNFs and [Ag(NH$_3$)$_2$]$^+$ solutions, followed by the hydrothermal treatment and conventional freeze drying allowed the preparation of a self-supporting and flexible nanocellulose/silver composite aerogel (Figure 12b). Strong hydrogen bonding of nanofibrils and highly conductive spherical silver nanoparticles (AgNPs) presented the aerogel with excellent structural stability, as well as electrical and mechanical properties. Even after 100 cycles of compression tests, the aerogel structure recovered quickly without collapsing. Uddin et al. added silver nitrate (AgNO$_3$) into the CNF dispersion, lyophilized, and reduced it to AgNPs using ultraviolet (UV) irradiation. The presence of well-distributed AgNPs generated aerogels effective against Escherichia coli. Increasing the Ag content enhanced the inhibitory effect of aerogels against E. coli. By utilizing the antibacterial property of silver, Matsuyama et al. fabricated CNF aerogels loaded with AgNPs, which demonstrated similar superior bacterial and fungal inhibitory effects (e.g., E. coli and Aspergillus niger). These nanocellulose aerogels are expected to be developed as antibacterial materials to play new roles in the field of biomedicine.

4.2.2. Composites with Carbon Nanomaterials

Carbon nanomaterials refer to carbon materials containing at least one dimension at the nanometer scale, including 0D fullerenes, 1D carbon fibers or carbon nanotubes (CNTs), 2D graphene, and 3D facies formed by the low-dimensional accumulation. They have provided several novel features to nanocellulose aerogels based on their excellent virtues, including large SSA, excellent electrical conductivity and heat conduction, and supermechanical strength. Compressible CNTs or graphene present great advantages such as excellent mechanical compression and thermal stability, high electrical conductivity, and sensitivity. However, the brittleness of the structural stability of carbon itself limits its development in the field of flexible wearable devices. Accordingly, Peng et al. utilized the synergism of CNFs, CNTs, and graphene oxide (GO) to fabricate ultralight composite carbon aerogels by directional freeze drying. Among them, nanocellulose allowed the formation of an interwoven network and a stable structure. CNTs enhanced the mechanical properties of the whole aerogel, rendering the structure difficult to collapse. Even if compressed to more than 90% strain, the carbon aerogel could almost recover to its original height, indicating outstanding mechanical compressibility and elasticity (Figure 13b). Coincidentally, Wang et al. also employed the directional freeze technology to regulate an anisotropic CNF/CNT aerogel sensor reinforced by polydimethylsiloxane (PDMS). The oriented growth of ice crystals created the anisotropic structure of aerogels in the directional direction.

![Figure 13](image-url)

**Figure 13.** a) The fabrication of the CNF/CNT/graphene composite carbon aerogel. b) The compression and recovery ability of the carbon aerogel. a,b) Reproduced with permission. Copyright 2018, The Royal Society of Chemistry. c) The morphology of the CNF/CNT aerogel in the microchannel direction (c) and orthogonal direction (d). e) The relationship between sensitivity ratios and directions of the aerogel. c–e) Reproduced with permission. Copyright 2019, Wiley-VCH.
(Figure 13c) and vertical direction (Figure 13d). Furthermore, this structure resulted in diverse sensitivity ratios to external forces in different directions, with large gaps in electrical conductivity and Young’s modulus (Figure 13e).

Moreover, nanocellulose can be utilized as a matrix or dispersant to achieve a homogeneous nanocellulose/graphene aerogel system for multifunctional uses. Fu and co-workers formulated a CNF-based hybrid aerogel by cation-induced network crosslinking and chemical reduction of GO. This hydrophobic aerogel with an ultralow density of ≈6 mg cm\(^{-3}\) exhibited superior performance in aspects such as multiple compression and resilience, an absorption capacity higher than 150 times its own weight for chloroform, and stable pressure-responsive capability.

In follow-up investigations, researchers have undertaken several in-depth studies to improve the microstructure, adsorption capacity, mechanical cycle stability, electric or magnetic applications, and other aspects, which are beneficial to further the development of nanocellulose/carbon composite aerogels.

### 4.2.3. Composites with Polymers

In recent years, biomass hybrid aerogels with high performances have been generated by the combination of nanocellulose and various polymers (e.g., PVA, polyurethane (PU), polypyrrole, polyethylenimine (PEI), and polydopamine (PDA)). Pollution-free nanocellulose with strong hydrogen bond forces can be directly blended, or as a base by in situ polymerization of functional polymers to form the composite materials, which provide good carriers for enhanced composite aerogels.

In general, the compatibility between nanocellulose and polymers is a critical point that must be considered during aerogel preparation. PVA can form intermolecular interactions with CNFs owing to its hydrophilicity. A hydrophobic aerogel was fabricated by directional freeze drying of the CNF/PVA mixture, followed by treatment with hydrolyzed MTMS sol, thus possessing advantages such as high oil absorption ratio and good compressive recovery (Figure 14a). To improve the mechanical strength and structural stability, some crosslinkers are often used to accelerate the formation of the porous networks of aerogels to further consolidate interface bonding and compatibility by chemical crosslinking. Liu et al. investigated the effects of glutaraldehyde or borax as crosslinkers on the structural and mechanical performance of ternary aerogels based on montmorillonite, PVA, and CNFs (Figure 14b). They observed that the aerogel pore size with glutaraldehyde crosslinking (Figure 14c) was considerably larger and looser than with borax (Figure 14d), bound with different kinetics of crosslinking reactions. Furthermore, these compact and regular pores were more conducive for enhancing the mechanical strength of composite aerogels, owing to the instantaneous crosslinking process of borax when
compared with glutaraldehyde for a few hours of gelation or no crosslinking.

As a biocompatible synthetic adhesion protein, PDA is obtained by the self-polymerization of dopamine (DA) under alkaline conditions.[93] There are several kinds of active groups on the PDA surface available as ideal substrates for surface modification, which can theoretically adhere to almost all materials.[94] Accordingly, one end of PDA can be linked to the surface of nanocellulose, while the other end can adhere to various substances to generate a bridge. Gao et al. introduced PDA between CNFs and octadecylamine (ODA) to establish an ODA–PDA@CNF aerogel, presenting superhydrophobicity with a \( \approx 152.5^\circ \) contact angle (Figure 14e),[70b] with amine moieties of ODA reacting with PDA for polymerization by a Schiff base reaction.[95] Notably, CNF and PEI can also be firmly combined to form composite aerogels via the oxidation of catechol groups and amalgamation of amine functionalization of PDA.[96] This bioinspired strategy helps promote interface consistency and improves the stability of the composite aerogels under a high deformation.

4.2.4. Composites with Inorganic Materials

Inorganic materials (e.g., clay, SiO\(_2\), zeolite, and montmorillonite) exhibit low thermal conductivity and fire-retardant behavior, and are also prepared as first-generation aerogels. However, the neat inorganic aerogels suffer from a high production cost, low compressive yield strength, and are brittle and prone to cracking during the freezing process, hindering their widespread application.[100,97] Therefore, some researchers combine polymer nanocellulose and inorganic materials to prepare composite aerogels by compensating for individual shortcomings, exerting their greatest advantages.

Conversely, nanocellulose can assist in the dispersion of inorganic nanofillers that are easily agglomerated, while providing stable 3D network skeletons and preventing aerogel cracking.[98] Zeng et al. utilized the TEMPO-oxidized CNFs with a high aspect ratio to stabilize the large MXene monolayers because of electrostatic repulsions of abundantly available negatively charged carboxyl groups (Figure 15a).[99] The uniform MXene/CNF aqueous dispersions could be obtained (Figure 15b) because of noncovalent interactions formed between the CNFs and MXene nanosheets with similar hydrophilicity and surface hydroxyl-containing groups (Figure 15c), facilitating the subsequent assembly of the intact pore wall of the aerogel. Liu et al. dispersed boron nitride nanosheets (BNNSs) with CNFs and utilized a silane modification to obtain a hydrophobic CNF/BNNS composite aerogel.[100] Owing to the inherent amphiphilic structure of CNFs, the addition of CNFs rendered BNNSs in water more homogeneous, and the lightweight aerogel was considerably stable and intact. After modification with MTMS, the silylated aerogel could float on the water surface, indicating high hydrophobicity. Fu et al. selected tetraethyl orthosilicate (TEOS), HCl, and NH\(_4\)OH as the precursor, acid catalyst, and base catalyst, respectively, to grow SiO\(_2\) nanoparticles by the sol–gel process inside the CNF aerogel.[101] Unlike the cracked SiO\(_2\) aerogel (Figure 15d), the CNF/SiO\(_2\) composite aerogel presented a complete white cuboid structure, similar to the neat CNF aerogel (Figure 15e,f). The spherical SiO\(_2\) nanoparticles were evenly distributed on the surface of the nanofibrils, and these CNFs entangled with each other to form an interconnected 3D network (Figure 15g), implying that nanocellulose could be used as a structurally stable carrier template for SiO\(_2\).

In contrast, inorganic materials can improve the thermal properties and mechanical strength of the nanocellulose aerogel.[100,102] It is difficult to avoid the formation of macropores inside freeze-dried nanocellulose aerogels as growing ice
crystals persistently results in large spaces after the sublimation process, limiting further improvement in the thermal insulation properties.\textsuperscript{[103]} SiO\textsubscript{2} nanoparticles can provide numerous mesoporous aerogels based on the original structure of the nanocellulose aerogel by increasing the SSA and surface roughness of the aerogel.\textsuperscript{[104]} to limit collision between air molecules, thus reducing the gas thermal conductivity of the composite aerogel as a superinsulator based on the Knudsen effect.\textsuperscript{[102a]} The CNF/SiO\textsubscript{2} composite aerogel can withstand the long-term high-temperature test, indicating its excellent thermal insulation performance.\textsuperscript{[101]}

In addition to effective thermal management, nanocellulose/inorganic composite aerogels have emerged in some additional areas (e.g., bone tissue engineering,\textsuperscript{[105]} CO\textsubscript{2} adsorption,\textsuperscript{[27b]} self-cleaning,\textsuperscript{[106]} and oil–water separation\textsuperscript{[7b,107]}) with expectations that they will be further explored in the future.

5. Applications of Nanocellulose Aerogels

As ultralight 3D porous materials, many nanocellulose-based functional aerogels have been reported as adsorbents\textsuperscript{[18,49,76a]} insulators,\textsuperscript{[102c,108]} supercapacitors (SCs),\textsuperscript{[200–d,109]} sensors,\textsuperscript{[300,54,73,75b,110]} and scaffolds.\textsuperscript{[71,111]} Conversely, surface modification can be undertaken to introduce different functional groups on the cellulose surface, thereby imparting special applied properties to the aerogel, including hydrophobicity, electricity, thermal performance, and magnetism. In contrast, adding, coating, or applying other substances in the precursor of nanocellulose are also commonly used methods for preparing composite aerogels for multifunctional applications.

5.1. Adsorption and Environment Protection

5.1.1. Adsorption and Filter of Oil and Organic Solvents

In nanocellulose-based aerogels, a crucial element of the pore structure is its unique openness and interconnectivity. In this open system, a gas or liquid can easily flow from one pore to another and eventually fill the entire material. Coupled with the advantages of high porosity and large SSA, it ensures the strong adsorption capacity of nanocellulose aerogels as superior materials in the field of adsorption, separation, and sewage treatment.\textsuperscript{[290,57,112]} Owing to underwater hydrophilic and oleophobic characteristics of the nanocellulose with abundant hydroxyl groups, the nanocellulose aerogel can be exploited as a filter material for separating the oil–water mixture or emulsion. A nanocellulose aerogel filter with hydrophilicity and underwater superoleophobicity was obtained by crosslinking CNFs with polyamidamine-epichlorohydrin (PAE). The filter presented a superior separation efficiency of 100% for the oil–water mixture after 10 repeated tests, as well as an emulsion with 98.6% separation efficiency.\textsuperscript{[113]} However, the natural hydrophilic properties of nanocellulose aerogels are not conducive to the selective adsorption of oil, and hence, hydrophobic and lipophilic modifications remain extremely crucial.

There are two main types of nanocellulose aerogels as adsorbent materials for oil or organic solvents. The first is the hydrophobic treatment on the surface of the nanocellulose aerogel using silane coupling agents such as trimethylchlorosilane (TMCS) and MTMS,\textsuperscript{[10c,60,63,70a,114]} or various hydrophobic agents.\textsuperscript{[24,70b,115]} Laitinen et al. silanized CNF suspensions by mixing the silane solutions consisting of MTMS and HDTMS, to impart the resultant aerogel with hydrophobicity.\textsuperscript{[27]} Its ultrahigh adsorption capacity for the marine diesel oil reached 142.9 g g\textsuperscript{-1}, superior to commercial absorbent materials. Zhou et al. relied on a directional freeze drying technique to combine CNFs, PVA, and GO to obtain the three-phase composite aerogel, which was then hydrophobically modified with TMCS by a simple CVD method.\textsuperscript{[116]} The results revealed that the aerogel demonstrated good hydrophobicity with a static water contact angle of 142°, and good adsorption for different oils or organic liquids (Figure 16a). Simultaneously, the aerogel presented excellent compressive strength and was surprisingly capable of withstanding more than 20 000 times of its weight with no collapse (Figure 16b). Furthermore, Korhonen et al. demonstrated the uniform deposition of a hydrophobic but oleophilic layer of TiO\textsubscript{2} with a 7 nm thickness on the framework of the nanocellulose aerogel by vacuum freeze drying, successfully resulting in a hydrophobic aerogel material with a core–shell structure (Figure 16c).\textsuperscript{[44a]} This material rapidly adsorbed organic contaminants in water within 3 s, which could be reused with a stable structure and adsorption capacity after washing (Figure 16d,e).

Another strategy to achieve hydrophobic modification of the nanocellulose aerogel is by high-temperature carbonization.\textsuperscript{[5c,80b,102]} Chen et al. reported a full cellulose carbon aerogel derived from CNFs through the process of timber milling, purification, nanofibrillation, freeze drying, as well as pyrolyzation at 850 °C (Figure 17a).\textsuperscript{[18a]} After pyrolysis, the carbon aerogel with a low density of 78 mg cm\textsuperscript{-3} was rendered hydrophobic and oleophilic (Figure 17b) owing to the breakage of the CNF crystalline structure and formation of amorphous carbon, which could be employed for the adsorption of different organic solvents or oils with increasing weights from 7422% to 22 356%. However, using only CNFs as the precursor carbon source, the carbon aerogel shrinks easily and is unstable, and its mechanical strength is also limited owing to the evaporation of the volatile components, which is not conducive for practical applications during the adsorption process. Zhou and Xu fabricated an ultralight carbonized CNF/PVA/reduced graphene oxide (rGO) composite aerogel with an anisotropic lamellar structure by unidirectional freeze drying (Figure 17c).\textsuperscript{[49]} PVA, as a water-soluble polyhydroxy polymer, formed strong interactions with CNFs by hydrogen bonds. Graphene provided a carbon skeleton and well-maintained the stable structure of the carbon aerogel, with less shrinkage after high-temperature carbonization. In turn, CNFs helped the dispersion of graphene to prevent its agglomeration and stacking. Taking advantage of synergism between these three features, the composite aerogel exhibited excellent compressive recovery owing to the directional freeze-dried ordered structure and stable tough internal carbon skeleton (Figure 17d). Furthermore, the carbonization treatment provided the aerogel with good hydrophobicity, and the aerogel could withstand multiple flame burn tests with minimal reduction in the adsorption capacity (Figure 17e), showing good
flame retardancy and structural stability. Long et al. introduced glucose and kaolin as carbon precursors into the system of CNFs and GO to further improve the mechanical performance of the aerogel composite, which was fabricated using unidirectional freeze drying and carbonization at 700 °C.[78] The composite aerogel possessed mechanical stability with good nonlinear elastic behavior under compaction. Even after 100 compressive cycles, the aerogel could still recover its original height by nearly 100% (Figure 17f), showing excellent fatigue resistance and structural robustness as a result of the timely and effective release of stress by the strong skeletal network. Its supercompressibility and elasticity could be attributed to the construction of the well-designed hierarchical wave-shaped architecture, with enhancement effects of CNF, rGO, glucose, and kaolin (Figure 17g), which were beneficial in hindering the collapse of the carbon aerogel structure during the oil–water separation process, prolonging the utilization period of the material.

Overall, hydrophobic modification using the silane coupling agent remains a mainstream method to impart hydrophobic properties to the nanocellulose aerogels for adsorption and filtration applications. However, the cost of the hydrophobic agents is high accompanied by certain toxicity. Furthermore, for high-temperature carbonization, time cost and energy consumption need to be considered. More importantly, how to stabilize the structure of the aerogel without being destroyed, especially during recycling, is still an important task that needs to be undertaken in the field of adsorption and filtration of oil and organic solvents in the future.

5.1.2. Adsorption of Heavy Metal Ions

Heavy metal ions are another important water contaminant, known to cause serious harm to humans and other living organisms. Common heavy metal ions in water usually include plumbum Pb(II), stannum Sn(II), chromium Cr(VI), hydrargyrum Hg(II), and copper Cu(II). In contrast to other methods such as biological treatment, ion exchange, and chemical precipitation, adsorption has become the most widely used owing to its easy preparation procedure and environmental friendliness.[118] Different kinds of absorption materials, including metal oxides, carbon-based materials, and conduction polymer composites have been widely investigated. Researchers have attempted to construct 3D porous materials/composites to attain the required criteria such as high porosity, low density, and large surface area. Furthermore, the high cost and difficult separation processes have rendered current absorption materials less attractive for practical applications. In recent studies, it has been observed that nanocellulose-based hybrid aerogel materials are the most promising class of high-capacity absorbers, as they not only meet important criteria, but also possess additional advantages allowing the absorption of the heavy metal ions, including a large absorption capacity, superior structural and chemical stability, strong selectivity, high efficiency, good recyclability, and sustainability/renewability.[2b,18d,e,29a,119]

Typically, there are two different nanocellulose aerogel-based composites for the adsorption of heavy metal ions; one is to introduce some functional groups on cellulose that could bind with heavy metal ions, and the other is to combine with
magnetic nanofillers that could remove ions and recover the aerogel under magnetic conditions in an efficient and controllable manner.

By surface modification, functional groups can be introduced to the outer surface of nanocellulose, which can significantly improve the adsorption capacity.[120] Several research groups have comprehensively utilized the ability to tackle different functional groups including hydroxyl, aldehyde, and carboxyl, with their corresponding heavy metal ions, as listed in Table 2.

According to a previous study regarding strong affinities toward Hg(II) ions by thiol groups, Geng et al. first demonstrated a directly freeze-dried and mercaptosilylated TEMPO-oxidized CNF aerogel with a high content of −SH groups on surfaces (Figure 18a).[121] The 3D scaffold demonstrated improved structural durability, as well as increased adsorption capacity toward Hg(II) ions. The achieved maximal uptake capacity up to 718.5 mg g⁻¹ was almost the highest value among cellulose-based adsorbents for Hg(II) ions. Mo et al. synthesized nitrogen-containing biologically active compounds to react with carboxyl groups and obtain amino ester bonds by employing trimethylpropane-tris-(2-methyl-1-aziridine) propionate (TMPTAP) as an important intermediate at room temperature (Figure 18b).[28b] The synthesized CNF/TMPTAP/PEI aerogel exhibited a multiwall perforated 3D porous structure containing...
abundant amino- and oxygen-containing groups, achieving an ultrahigh adsorption capacity of Cu(II) ion (485.44 mg g⁻¹). Tang et al. proposed a bioinspired coating method where PDA was first introduced on the CNF surface and then crosslinked with PEI to obtain the aerogels.[96] This aerogel exhibited a highly porous structure, which was lightweight (25 mg cm⁻³), had high porosity (98.5%), as well as shape reversibility in air and water. The achieved maximum adsorption capacities for Cu(II) and methyl orange (MO) were 103.5 and 265.9 mg g⁻¹, respectively.

In addition, composites containing magnetic nanofillers have demonstrated efficient removal properties for heavy metal ions, owing to their unique properties, including large surface area, easy binding with chemicals, easy separation by the extracting magnetic field, and reusability.[129] Wei et al. directly blended nanocellulose and ferroferric oxide nanoparticles to develop a hybrid aerogel for the highly efficient adsorption of heavy metal chromium ions.[130] The results revealed that the ferroferric oxide nanoparticles were physically joined onto the nanocellulose surface, retaining their original structure and composition. The resulting aerogel exhibited a high saturation magnetization of 53.69 emu g⁻¹, beneficial to effectively and controllably recover the aerogel under magnetic conditions.

In summary, diverse strategies for adsorption or removal of different contaminants have been systematically discussed in this section. Nanocellulose aerogels have shown great potential for the removal of heavy metal ions owing to the presence of different surface functional groups and other introduced functional materials. However, several challenges remain unresolved, including complex and time-consuming fabrication, low adsorption or removal efficiency, and challenges in large industrial-scale production. To resolve these limitations, efforts are being made to seek novel approaches capable of improving the existing process, as well as the efficiency of the adsorption process.

5.2. Energy Storage

5.2.1. Supercapacitors

SCs, as high-capacity energy storage devices, have attracted extensive attention owing to their high-power density, superior rate capability, long cycle life, and fast charge/discharge processes.[131] SCs can be generally divided into electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. The performance of EDLCs mainly depends on surface properties of electrode materials and electrostatically accumulated charges between the electrode/electrolyte interfaces, whereas pseudocapacitor properties are strongly influenced by the redox reaction rate and electrode conductivity.[132] From both aspects, materials or composites with a large SSA such as nanostructured carbon materials and conducting polymers have been intensively investigated to provide additional adsorption sites for electrolyte ions and improve energy storage.[133] However, the agglomeration phenomena in carbon-based materials is a critical issue, which limits the cycle performance of SCs. Hence, porous

### Table 2. Comparison of maximum adsorption capacities for various nanocellulose aerogels.

| Aerogel composites[4] | Physical properties | Adsorption performances | Refs. |
|----------------------|---------------------|-------------------------|-------|
|                      | Density [mg cm⁻³]   | Specific surface [m² g⁻¹] | Porosity [%] | Metal ion | Capacity [mg g⁻¹] | Efficiency [%] | pH |
| CNF-MAA-MA           | 65                  | 65                      | 9        | Pb²⁺     | 165               | >70           | 5   |
|                      |                     |                         |          | Cd²⁺     | 135               |               |     |
|                      |                     |                         |          | Zn²⁺     | 138               |               |     |
|                      |                     |                         |          | Ni²⁺     | 117               |               |     |
| PAMAM-g-CNFs         | 10                  | –                       | 99.3     | Cr⁶⁺     | 377.4             | >80           | 2   |
| CNFs/PEI             | –                   | –                       | –        | Cu²⁺     | 52.3              | –             | 5   |
| PVA/CNFs             | 13                  | 172                     | 99.0     | Hg²⁺     | 157.5             | –             |     |
|                      |                     |                         |          | Pb²⁺     | 110.6             |               |     |
|                      |                     |                         |          | Cu²⁺     | 151.3             |               |     |
|                      |                     |                         |          | Ag⁺      | 114.3             |               |     |
| CNFs/PVA/AA          | –                   | –                       | –        | Cu²⁺     | 30.0              | 89            | 6   |
|                      |                     |                         |          | Pb²⁺     | 131.5             | 88            | 5   |
| Carboxylated CNFs    | 20.3                | –                       | 98.4     | Cu²⁺     | 45.1              | 90            | –   |
|                      |                     |                         |          | Cu²⁺     | 175.4             | –             | 5   |
|                      |                     |                         |          | Pb²⁺     | 357.4             |               |     |
| PDA/CNFs/PEI         | 25                  | –                       | 98.5     | Cu²⁺     | 103.5             | 91            | 5   |
| CNFs/TMPTAP/PEI      | –                   | –                       | –        | Cu²⁺     | 485.4             | –             | 5.5 |
| CNF-Si-SH            | 11.4                | 43.6                    | 99.1     | Hg²⁺     | 718.5             | 97.8          | 7   |

[4] AA, acrylic acid; CNFs, cellulose nanofibrils; CNF-MAA-MA, poly(methacrylic acid-co-maleic acid) grafted CNFs; PAMAM-g-CNFs, poly(amidoamine)-grafted CNFs; PEI, polyethylenimine; PVA, poly(vinyl alcohol); TMPTAP, trimethylolpropane-tris-(2-methyl-1-aziridine) propionate.
carbon materials, especially CAs, have been widely investigated as electrode materials. The special structure of CAs can provide i) efficient diffusion/mass transfer channels for electrolyte ion/electron migration and ii) several active sites for the electrostatic attraction, leading to excellent electrochemical performance for SCs. In recent investigations, it is found that there are still some disadvantages of CAs in supercapacitors, including the expensive and harmful precursors and complex preparation process. Therefore, researchers have attempted to determine an easy, simple, and environmentally approach to synthesize CAs.

Nanocellulose aerogels are among the most promising candidates for CAs owing to their eco-friendly and sustainable source, outstanding mechanical strength, large SSA, and impressive flexibility. For designing SCs, nanocellulose aerogels can be used as electrode materials, electrolytes, and separators. From the separator aspect, nanocellulose aerogels can build 3D interconnected networks using blocks and crosslinkers, presenting robust mechanical properties. From the electrode aspect, nanocellulose aerogels contain highly reactive –OH groups, which allow easy modification of the surface, and bond with conductive fillers via covalent or hydrogen bonds as high-performance electrodes. Additionally, the porous structure helps the loading and uniform distribution of carbon conductive materials, enabling the fabrication of stable electrode materials. Collectively, these advantages result in CAs, derived from nanocellulose by freeze drying and carbonization, to possess several excellent properties for SCs, including large SSA, high specific capacitance, good cycling stability, as well as improved energy and power density. SCs were fabricated using the selected nanocellulose aerogels, and their energy storage performances are listed in Table 3. For example, Zu et al. first synthesized carbon aerogels with a high surface area through the carbonization of nanocellulose aerogels by supercritical CO₂ drying, resulting in 3D nanostructured CAs with high SSAs (1837 m² g⁻¹) and a large pore volume (2.65 cm³ g⁻¹). To further improve electrolyte ion and electron transportation, N-doped porous CNF aerogels have been proposed by some investigators. Compared with CAs, the N-doped CAs exhibited a larger mass volume, enhanced wettability, as well as superior conductivity, which resulted in a 152% higher specific capacitance than CAs, and good cycling stability (94.5% capacitance retention, 10 000 cycles), owing to the hierarchically porous nanostructure and N-doping.

Figure 18. a) Schematic illustration of the adsorption mechanism of the cellulose nanofibril/silicon/thiol (CNF-Si-SH) aerogel for the Hg(II) ions. Reproduced with permission. Copyright 2017, American Chemical Society. b) Schematic illustration and formation mechanism of the CNF/TMPTAP/PEI aerogel. Reproduced with permission. Copyright 2019, Elsevier B.V.
With the development of CA-based SCs, researchers have established an effective approach for achieving excellent electrochemical properties by combining CAs with electroactive materials, including transition metal oxides or hydroxides, metal oxides, rGO, and conducting polymers. Owing to the synergistic effect of porous nanostructures and conductive frameworks from CAs and the high capacitive property provided by electroactive nanomaterials, resulting hybrid aerogels presented superior electrochemical properties. Inorganic materials with high theoretical specific capacity have been widely selected in composites such as nickel sulfide (NiS), mixed-valent manganese oxide (MnO$_x$)$_{y}$, tin (IV) oxide (SnO$_2$), and metal oxynitride (MO$_x$N$_y$)$_{z}$ for example, Zheng et al. reported a highly flexible manganese oxynitride (MnO$_{x}$)$_{y}$N$_{z}$/rGO–CNF as a high areal mass loading electrode toward SC application. Introducing oxygen vacancies and N-doping to MnO$_2$ was achieved by hydrazine vapor treatment, resulting in a considerable improvement in electrochemical performances, with high capacitance (455.8 F g$^{-1}$) and excellent rate capability. Furthermore, as shown in Figure 19a–c, investigators achieved all-solid asymmetric SCs (ASCs), which assembled MnO$_x$N$_y$/rGO/CNF, MoO$_x$N$_y$/rGO/CNF aerogel,

Table 3. Comparison of selected supercapacitor electrodes with nanocellulose aerogels.

| Aerogel composites | Preparation | SSA [m$^2$ g$^{-1}$] | Specific capacitance [F g$^{-1}$] | Cycle Retention [%] | Specific energy [Wh kg$^{-1}$] | Power density [W kg$^{-1}$] | Refs. |
|--------------------|-------------|------------------------|----------------------------------|---------------------|-------------------------------|-----------------------------|-------|
| Cas                | Freeze drying and CO$_2$ activation | 1873 | 302 F g$^{-1}$ at 0.5 A g$^{-1}$ | 4000 | 92 | – | – | [42] |
| N-CNFs             | Freeze drying and ultrasonication | 2290 | 278.0 F g$^{-1}$ at 1.0 A g$^{-1}$ | 10 000 | 92.4 | – | – | [135a] |
| N-Cas              | Freeze drying and carbonization | – | 253.7 F g$^{-1}$ at 1.0 A g$^{-1}$ | 10 000 | 94.5 | 9.53 | 250 | [135b] |
| N-CNFs/melamine/GO| Freeze drying and carbonization | 487 | 225.0 F g$^{-1}$ at 0.25 A g$^{-1}$ | – | – | 31.25 | 12 900 | [135c] |
| CAs/Ni:S           | Freeze drying and solvothermal reaction | 367.5 | 1606 F g$^{-1}$ at 1.0 A g$^{-1}$ | 10 000 | 92.1 | 21.5 | 700 | [136] |
| CNFs/MnO$_x$       | Freeze drying and carbonization | 219.3 | 269.7 F g$^{-1}$ at 0.5 A g$^{-1}$ | 1000 | 80 | 37.5 | 2750 | [137] |
| CNFs/SnO$_2$/rGO   | Freeze drying and solvothermal reaction | – | 4.31 F cm$^{-2}$ at 1 mA cm$^{-2}$ | 2000 | 60.5 | – | – | [138] |
| CNFs/MnO$_x$/N$_y$/rGO | Freeze drying | 208 | 455.8 F g$^{-1}$ at 1.08 A g$^{-1}$ | 10 000 | 94 | 49.0 | 953.7 | [20c] |
| CNFs/MoO$_x$N$_y$/rGO | Freeze drying and hydrazine reduction | 186.3 | 680 F g$^{-1}$ at 1.0 A g$^{-1}$ | 2000 | 89 | 114 | – | [89b] |
| CNFs/rGO          | Freeze drying and thermal reduction | – | 270 F g$^{-1}$ at 1.0 A g$^{-1}$ | 100 | 97 | – | – | [141] |
| CNFs/rGO/CNTs     | Freeze drying and thermal reduction | – | 252 F g$^{-1}$ at 0.5 A g$^{-1}$ | 1000 | 99.5 | 8.1 | 2700 | [142] |
| CNFs/rGO/PPy      | Oxidation and HCl vapor treatment | – | 405.0 F g$^{-1}$ at 0.25 A cm$^{-2}$ | 2000 | 95 | – | – | [139] |
| CAs/PPy           | Oxidative polymerization | – | 268.5 F g$^{-1}$ at 0.5 A g$^{-1}$ | 10 000 | 88 | 23.8 | 450.4 | [143] |
| CAs/Ag/PANI       | Freeze drying and carbonization | 576.5 | 223.2 F g$^{-1}$ at 0.5 A g$^{-1}$ | 5000 | 92.4 | 4.5 | 1750 | [144] |
| CAs/MWCNTs/PPy    | Freeze drying and chemical polymerization | – | 232.7 F g$^{-1}$ at 0.5 A g$^{-1}$ | 5000 | 93.3 | – | – | [87b] |
| CAs/MWCNTs/rGO/Fe$_3$O$_4$ | Freeze drying and solvothermal reaction | – | 357 F g$^{-1}$ at 0.5 A g$^{-1}$ | 2000 | 83 | 34 | 459 | [145] |
| CNFs/rGO          | Freeze drying and carbonization | 514.5 | 398.5 F g$^{-1}$ at 0.5 A g$^{-1}$ | 10 000 | 99.8 | – | – | [89a] |
| Lignin/CNFs       | Freeze drying and carbonization | 806 | 124.0 F g$^{-1}$ at 0.2 A g$^{-1}$ | 3000 | 92 | 2.8 | 2500 | [52] |
| Alkali lignin/CNFs | Freeze drying and carbonization | 950.4 | 260.0 F g$^{-1}$ at 0.5 A g$^{-1}$ | 5000 | 88.5 | 8.6 | 250 | [110] |

BTCA, 1,2,3,4-butanetetracarboxylic acid; CAs, carbon aerogels; CNCs, cellulose nanocrystals; CNFs, cellulose nanofibrils; CNTs, carbon nanotubes; GO, graphene oxide; MnO$_x$, manganese oxide; MnO$_x$N$_y$, manganese oxynitride; MWCNTs, multiwalled CNTs; PANI, polyaniline; PPy, polypyrrole; rGO, reduced GO; SnO$_2$, tin (IV) oxide; SSA, specific surface area.

With the development of CA-based SCs, researchers have established an effective approach for achieving excellent electrochemical properties by combining CAs with electroactive materials, including transition metal oxides or hydroxides, metal oxides, rGO, and conducting polymers. Owing to the synergistic effect of porous nanostructures and conductive frameworks from CAs and the high capacitive property provided by electroactive nanomaterials, resulting hybrid aerogels presented superior electrochemical properties. Inorganic materials with high theoretical specific capacity have been widely selected in composites such as nickel sulfide (NiS), mixed-valent manganese oxide (MnO$_x$)$_{y}$, tin (IV) oxide (SnO$_2$), and metal oxynitride (MO$_x$N$_y$)$_{z}$. For example, Zheng et al. reported a highly flexible manganese oxynitride (MnO$_{x}$)$_{y}$N$_{z}$/rGO–CNF as a high areal mass loading electrode toward SC application. Introducing oxygen vacancies and N-doping to MnO$_2$ was achieved by hydrazine vapor treatment, resulting in a considerable improvement in electrochemical performances, with high capacitance (455.8 F g$^{-1}$) and excellent rate capability. Furthermore, as shown in Figure 19a–c, investigators achieved all-solid asymmetric SCs (ASCs), which assembled MnO$_x$N$_y$/rGO/CNF, MoO$_x$N$_y$/rGO/CNF aerogel,
and PVA/Na$_2$SO$_4$ gel as a positive electrode, negative electrode, and electrolyte and separator, respectively. The highly porous structure of the aerogel benefited the gel, which could easily and directly be in contact with the active materials and decreased the ion diffusion distance. A high capacitance ($104.1 \text{ F g}^{-1}$) could be obtained in this solid-state asymmetric SC at a current density of $1.09 \text{ A g}^{-1}$. Meanwhile, it was able to maintain a $71\%$ capacitance with increasing current density ($1.09$ to $16.35 \text{ A g}^{-1}$), and $94\%$ capacitance after $10$ 000 cycles. The outstanding properties might be attributed to two reasons: i) the formation of interpenetrating structures between the electrodes and electrolytes, and ii) the increased conductivity by the N-doped metal oxide and oxygen-defects.

Furthermore, compared with the poor cycling stability of conducting polymers (i.e., PPy and PANI) as electrodes, the investigators determined that the combination of conducting polymers with carbon nanomaterials (i.e., rGO) could overcome this disadvantage, significantly improving the charge storage and cycling performances. With the homogeneous distribution of PPy/rGO on CAs, the contact surface area, electrical conductivity, as well as ion diffusion rates were enhanced. In some reports, more than three phases with different dimensions were prepared to achieve better performance. Xia et al. proposed a strategy to design and fabricate flexible ASCs using CNF/multiwalled CNTs (MWCNTs)/rGO/Fe$_3$O$_4$ as a negative electrode, as shown in Figure 19d–f. The 1D MWCNTs and 2D rGO were uniformly distributed on the 3D porous structure, providing a 3D network channel for the introduction of 0D Fe$_3$O$_4$ nanoparticles. The ASC device possessed an improved volumetric capacity and energy density with increasing operating voltage ($1.0$ to $1.8 \text{ V}$), as well as outstanding cycle stability ($94.7\%$ of the initial capacitance, $5 \text{ mA cm}^{-2}$ current density, 5000 cycles).

More recently, researchers have proposed a novel TEMPO-oxidized CNF with a smaller width ($>3 \text{ nm}$), high aspect ratio ($>200$), and abundant carboxylate groups on the surface, which was extremely beneficial to a high-performance electrode. Yang et al. reported a highly scalable 3D aerogel as the SC electrode material, which combined carbonized CNFs with GO. The obtained CNF/GO aerogels exhibited improved conductivity and enhanced electrochemical performance with a high specific capacitance ($398.47 \text{ F g}^{-1}$ at $0.5 \text{ A g}^{-1}$) and outstanding cycling stability ($99.77\%$, 10 000 cycles). Furthermore, additional simple methods have been proposed for fabricating nanocellulose-derived CAs. Lignin, another key component derived from plants, has been employed to produce CAs. Geng et al. reported an anisotropic hierarchical CA from lignin/CNF precursors by freeze drying and carbonization. Lignin/CNF-derived CAs (LCAs) with a discernible structure could be obtained. The LCA SC showed energy densities of $4.3 \text{ Wh kg}^{-1}$ at $100 \text{ W kg}^{-1}$ and $2.8 \text{ Wh kg}^{-1}$ at $2500 \text{ W kg}^{-1}$, indicating a superior electrochemical performance comparable with other porous carbonaceous electrodes. All LCA SCs exhibited a stable cycle behavior with $92\%$ capacitance retention even after 3000 cycles. Another example is the incorporation of lignin to wood-derived CNFs, which can reduce the thermal degradation of the aerogel network and provide a highly stable structure, enabling a flexible and free-standing all-solid-state symmetric SC with improved electrochemical performance and mechanical flexibility.

In summary, it is environmentally sustainable to develop porous carbon materials from renewable carbon resources, with a controllable structure and excellent performance. The combination of CAs derived from nanocellulose aerogels with multiple electroactive nanomaterials has become a widely used strategy to achieve improved electrochemical performance for SCs, as well as for other relevant applications.
5.2.2. Lithium-Ion Batteries (LIBs)

In the last two decades, LIBs have been considered the main power sources for portable electronic devices when compared with other energy storage electronics owing to their appreciable lifespan, high energy density, lowest reduction potential, large voltage output, and environmentally benign operation.[1b,146] LIBs are generally composed of cathodes, anodes, electrolytes, and separators, in which the migration of \( \text{Li}^+ \) between the anode and cathode in the electrolyte is critical to generate power.[147] In the recent decade, cellulose-based materials have been successfully utilized in commercial LIBs owing to their superior mechanical performances, biodegradability, renewability, and high porosity. Compared with cellulose fibers, nanocellulose aerogels possesses several advantages, including: i) contact enhancement between electrolytes and electrodes, ii) increased diffusion channels for ions, iii) reduced pore size distribution, and iv) effectively shortened ion transport distances, meaningful for the performance in many parts of LIBs.[148] Additionally, to overcome the weak mechanical property and poor flexibility of nanocellulose-based CAs, other conductive fillers such as metal oxides, transition metal complexes, carbon materials, and conducting polymers have been incorporated to form composite aerogels. Although nanocellulose has been widely used in different parts of LIBs, most of recent work about aerogel-based composites have been mainly used for electrodes. In this section, we discussed nanocellulose aerogels integrated with other active materials or nanocellulose aerogel derived carbon materials as electrodes for LIBs.

In LIBs, the anode electrode usually includes metal oxides with a tunneled or layered structure, whereas the cathode generally consists of layered graphitic carbon.[149] Similar to the role in SCs, nanocellulose-derived CAs with a porous nanostructure and high SSA can be good candidates as LIB electrodes to improve performance using the following advantages: i) increasing the electrode–electrolyte contact area, ii) decreasing the diffusion length of \( \text{Li}^+ \), iii) reducing the ion diffusion resistance, and iv) generating solid and continuous pathways for electron transport.[150] Nanocellulose aerogels with active materials can be employed as binder materials or flexible substrates to prepare electrodes for LIBs.[150] Metal or metal oxides have been widely used as the filler in hybrid aerogels.[81] Wang et al. fabricated 3D porous and conductive CNF scaffolds to support anode nanomaterials for LIBs, as shown in Figure 20a–d.[151] By incorporating SnO2 and Ge nanoparticles, improved electrochemical performances were achieved owing to the efficient electron conduction pathways and interconnected voids provided by the whole electrode scale for the diffusion of lithium.

**Figure 20.** a) In situ assembly of active nanoparticles into pyrolyzed bacterial cellulose (PBC) nanofibrils as LIB electrode. b) SEM image showing the morphology and structure of PBC-Ge. c) Comparison of cycling performances of PBC-Ge and aggregated Ge nanoparticles over 100 cycles at 100 mA g\(^{-1}\). d) Specific capacities at various current densities as marked. a–d) Reproduced with permission.[151] Copyright 2013, Wiley-VCH. e) The preparation process of Fe3O4–BC-CNFs. f) Discharge/charge profiles of Fe3O4–BC-CNF-10. g) Charge and discharge capacities with Coulombic efficiency as a function of cycle number of Fe3O4–BC-CNF-10. e–g) Reproduced with permission.[153] Copyright 2015, The Royal Society of Chemistry. h) Transport pathway of Li ions and electrons in the hierarchical porous N-ACNF-50. i) Specific capacity comparisons of N-ACNF-10, N-ACNF-50, and N-ACNF-200 aerogels at different current densities. h,i) Reproduced with permission.[154] Copyright 2017, The Royal Society of Chemistry.
ions. A remarkably high specific capacity (967 mAh g\(^{-1}\)) and a reasonable rate capability (230 mAh g\(^{-1}\) under fast discharge/charge cycling) were achieved. Compared with SnO\(_2\), iron oxides (Fe\(_2\)O\(_3\) or Fe\(_3\)O\(_4\)) exhibited a higher theoretical capacity (1005 mAh g\(^{-1}\) for Fe\(_2\)O\(_3\) and 930 mAh g\(^{-1}\) for Fe\(_3\)O\(_4\)) and were more cost-effective as promising electrode materials.\(^{[352]}\) A flexible 3D aerogel with carbon-supported iron oxides was fabricated as an anode for advanced LIBs. The hierarchically porous structure could help reduce the volume changes and enhance electrolyte penetration and Li\(^+\) diffusion, while the amorphous Fe\(_2\)O\(_3\) could improve the discharge capacity. Furthermore, nanosized Fe\(_3\)O\(_4\) particles have been decorated on the 3D CNF aerogel by the eco-friendly approach of hydrothermal processing and carbonization.\(^{[153]}\) As shown in Figure 20e–g, the bacterial cellulose (BC) aerogel was first to adsorb Fe\(_{3+}\) onto the nanofiber surfaces by –OH groups by chem- and electroadsorption, followed by treatment with hydrothermal processing and carbonization to obtain Fe\(_2\)O\(_3–BC\)-CNFs. Thus, the uniform distribution of Fe\(_{3+}\) was determined by the intrinsic uniform dispersion of –OH on the BC nanofibers. In addition to the excellent flexibility without structural failure, the Fe\(_3\)O\(_4–carbon\) hybrid aerogels as electrodes showed extremely improved electrochemical performance (754 mAh g\(^{-1}\), 100 mA g\(^{-1}\), 100 cycles). In another example, similar Fe\(_3\)O\(_4–carbon\) hybrid aerogels were fabricated via an easy ion-crosslinking method followed by pyrolysis.\(^{[34]}\) Comparing the rate performance with that of a Fe\(_2\)O\(_3/C\)-based anode, the 3D network of Fe\(_3\)O\(_4/CNF\) aerogels not only improved the ion transportation but also prevented aggregation and volume swelling of Fe\(_3\)O\(_4\) during Li insertion. The composite aerogel presented an excellent reversible capacity (1635 mAh g\(^{-1}\), 100 cycles, 1 A g\(^{-1}\)) and a superior rate performance (1025 mAh g\(^{-1}\), 4 A g\(^{-1}\))

Besides inorganic nanofillers, carbon-based active materials or other elements were also introduced with nanocellulose to fabricate composites for electrodes. Hu et al. fabricated flexible and conductive nanopaper aerogels by depositing a thin layer of silicon nanoparticles on the CNF/CNT nanopaper aerogels using the plasma-enhanced CVD method.\(^{[155]}\) Advanced energy storage performances with specific capacities (800 mAh g\(^{-1}\)) and good cycling stability were achieved because of electrolyte accessibility to the silicon surface through open aerogel channels. The aerogels as anodes exhibited a stable capacity (1200 mAh g\(^{-1}\), 100 cycles, half-cells). Ye et al. fabricated highly N-doped CNF aerogels via carbonization of bamboo cellulose, as shown in Figure 20h,i.\(^{[156]}\) For LIBS, the N-doped porous carbon nanofiber (N-ACNF) anode showed high capacity, supercycling stability, as well as good rate performance. For example, the N-ACNF-50 aerogel showed the highest capacity (630.7 mAh g\(^{-1}\), 1 A g\(^{-1}\)), the best rate capability (289 mAh g\(^{-1}\), 20 A g\(^{-1}\)), and cycling performance (651 mAh g\(^{-1}\), 1 A g\(^{-1}\), 1000 cycles).

In summary, the advanced performance by unique porous 3D CAs with other active nanomaterials can be attributed to several features: i) enhanced conductivity and efficient ion transport owing to the 3D interconnected carbon scaffolds for transport paths, ii) extra redox-sites and ultrashort ion diffusion owing to interconnected pores with high surface area, and iii) the increased active sites because of the uniformly dispersed active nanomaterials.

### 5.3. Sensors

Sensors are devices that can react with an external stimulus, transforming them into electrical signals and information for further processing and understanding, and include gas, solvent, sound, light, heat, force, and temperature. The sensing materials are key components as they will directly react and sense the external stimulus, and produce communicable data in a rapid, effective, and efficient manner.\(^{[113a,157]}\) In recent years, considerable progress and encouraging accomplishments have been achieved in terms of aerogel-based sensing materials, owing to their highly porous, continuous, and homogeneous structure.\(^{[158]}\) Nanocellulose aerogels, as a kind of important polymeric aerogel, have revealed advantages such as biocompatibility, degradability, and renewability for sensing application needs.\(^{[100,110,140,159]}\) Based on functions, the main categories of sensors using nanocellulose include strain and pressure sensors, chemical sensors, and biosensors. Currently, nanocellulose aerogels are most widely utilized as sensing materials in strain and pressure sensors owing to their porous structures.

Strain and pressure sensors have gained momentum owing to their extensive and potential applications in artificial electronic skins (e-skins) and health diagnosis/monitoring.\(^{[160]}\) The sensing materials determine major performance criteria, including sensitivity, stretchability, strain linearity, and long-time stability. As strain and pressure sensors are usually related to the resistance change under external mechanical loading, aerogels containing conductive nanomaterials (i.e., metal, CNTs, graphene, and conducting polymers) have been considered promising materials with both superior mechanical properties and high conductivity.\(^{[74a,83,161]}\) Aerogels with carbon-based fillers have been investigated by several research groups because of their high electrical conductivity, as well as thermal and chemical stability.\(^{[78,88a,90,162]}\) Peng et al. fabricated a high-performance CNT/rGO/CNF lightweight carbon aerogel by utilizing CNFs as bridges between rGO and CNTs.\(^{[73]}\) Ultrahigh compressibility at 95% strain, superior elasticity (94.6%, 50 000 cycles), and high sensitivity with an ultralow detection limit (0.875 Pa) were achieved (Figure 21a,b), indicating their potential as an excellent candidate for biosignal detection. Furthermore, Wang et al. prepared a composite aerogel combining GO with TEMPO-oxidized CNFs,\(^{[163]}\) achieving a low density (3.26 mg cm\(^{-3}\)), high electrical conductivity (0.32 S m\(^{-1}\)), and high fatigue resistance (8.2% plastic deformation, 50% strain, 10 000 cycles). As discussed in Section 4.2.2, Wang et al. described an anisotropic microhoneycomb hybrid aerogel as a strain sensor by combining CNFs with CNTs (MCCA) with unidirectional freeze drying.\(^{[54]}\) The MCCA in PDMS exhibited anisotropic electrical and mechanical properties. It was observed that in the parallel direction, Young’s modulus and electrical conductivity were both approximately twice that in the perpendicular direction. This investigation provided a simple method to prepare anisotropic nanocellulose aerogels for multiple sensing applications.

In addition to carbon-based materials, conducting polymers are widely used as fillers to form a 3D sensor,\(^{[164]}\) because nanostructured conducting polymers demonstrate controllable electrical conductivity, easy production process, good mechanical stability, low density, and low cost.\(^{[165]}\) Zhou and Hsieh fabricated highly conductive strong aerogels from CNFs protonated...
with poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS). A favorable electron conductive planar quinoid structure was obtained with PEDOT by interactions between PSS and carboxylate/carboxyl groups of CNFs. The aerogel with 70% of CNFs exhibited a markedly high gauge factor (14.8, 95% strain) and high linearity (0.98, from 0% to 95% strain), which was five times higher than the value of PDMS-infused PEDOT/PSS aerogels and seven times the value in conventional metal gauges. Huang et al. reported a piezoresistive sensor using a novel porous polyaniline/bacterial cellulose/chitosan (PANI/BC/CH) aerogel fabricated by freeze drying (Figure 21c). This piezoresistive sensor with a 1:1 BC/CH weight ratio exhibited an extremely high sensitivity of 1.41 kPa⁻¹ and a low-pressure detection of 32 Pa, indicating promising potential in applications of health monitoring and motion distinguishing in real-time (Figure 21d). Recently, Han et al. proposed a single-sensor
Table 4. Thermal insulation properties of the nanocellulose aerogels.

| Materials                        | Porosity [%] | Pore size [nm] | Thermal conductivity [mW m⁻¹ K⁻¹] | Refs. |
|----------------------------------|--------------|----------------|-----------------------------------|-------|
| CNFs/zeolites                    | –            | 1–100          | 18                                | [102a]|
| Liquid-crystalline nanocellulose | 99.7         | ≈30            | 18                                | [12b] |
| CNFs                             | 98–99        | 10–100         | 18                                | [174] |
| CNFs/MDPA/BTCA                   | 99.5         | 2–20           | 33                                | [172] |
| CNFs                             | 99.4         | 2–50           | 26                                | [173] |
| CNFs/PVA                         | –            | –              | 40                                | [174] |
| Cotton CNFs                      | 98.5         | –              | 44                                | [72]  |
| CNFs                             | >99          | –              | 32                                | [175] |
| CNFs/CNCs                        | >93          | 5–13           | 23                                | [176] |
| CNFs/SiO₂                        | >93          | 40–70          | 20                                | [97a] |

4) BTCA, 1,2,3,4-butanetetracarboxylic acid; CNCs, cellulose nanocrystals; CNFs, cellulose nanofibrils; SiO₂, silica; PVA, poly(vinyl alcohol).

for multiparameter detection that could simultaneously or consecutively measure pressure–temperature–humidity (P–T–H) without crosstalk in the sensing functionality. The resistance of the sensor decreased from 68 to 26 Ω on applying increasing pressure (0 to 300 Pa). The relationship between P–T–H was also investigated under different conditions. This work could provide a new pathway on multifunctional electronic sensing devices for wearable and biomedical applications.

In this section, strain and pressure sensors have been mainly introduced and discussed, as the porous structure of nanocellulose aerogels is more suitable and sensitive to detect tiny shape alterations. In future investigations, from the fabrication aspect, it is necessary to prepare novel composites with unique 3D structures that can exhibit a wider detection range, higher sensing property, and ultralow detection limit. From the applications aspect, substantially detailed studies regarding biomedical and healthcare applications are needed. Multifunctional performances, including a high sensing sensitivity, excellent thermal stability, and outstanding stability, will provide great potential for a human behavior monitoring sensor, as well as for sensing under certain extreme conditions.

5.4. Thermal Insulation

For the lightweight materials required in the aerospace industry, it is desirable to achieve excellent thermal insulation performance by utilizing characteristics of the nanocellulose aerogel, including their lightweight feature, high porosity, and low thermal conductivity (Table 4). The thermal transfer of solid material is mainly divided into thermal conduction, thermal convection, and thermal radiation. When the pore size is larger than the average free path of the gas (70 nm), according to the Knudsen effect, the thermal conductivity of the nanocellulose aerogel will be affected as the porous structure can no longer restrict gas movement. Accordingly, it is necessary to adjust the pore size of the aerogel based on actual demands. Several strategies have been employed to achieve effective thermal insulation properties:

1) Nanocellulose only: Kobayashi et al. explored a novel type of aerogel from liquid-crystalline nanocellulose (LC-NCCell) with higher-order frameworks (Figure 22a). They studied the relationship between aerogel density and thermal conductivity, and reported that when the aerogel density was 17 mg cm⁻³ (pore size of ≈30 nm), the lowest thermal conductivity (18 mW m⁻¹ K⁻¹) could be achieved (Figure 22b). For the CNF aerogel with surface C₆-carboxylate groups, the thermal conductivity remained 18 mW m⁻¹ K⁻¹ even on increasing the density and reducing the porosity by compression, when compared with the uncompressed aerogel with 14 mW m⁻¹ K⁻¹, showing an excellent thermal insulation property. To determine the thermal insulation effect of the cotton CNF aerogel more intuitively, Qi et al. placed the aerogel on a hot plate and a cold plate with temperatures of ≈70 and ≈0 °C, respectively (Figure 22c). The heat effectively stopped and diffused inside the aerogel network, allowing the aerogel to resist effects from different external environments without any obvious changes in shape and structure.

2) Introducing inorganic additives: SiO₂ aerogel is a traditional super thermal insulation material, but its poor mechanical strength hinders further development. Zhao et al. first synthesized the methylylated nanocellulose aerogel scaffold by freeze drying, followed by mixing with SiO₂, with a very low solid thermal conductivity, to obtain a hierarchical porous composite aerogel with meso/macropores. This ensured the superior thermal insulation properties of the aerogel (λ ≤ 20 mW m⁻¹ K⁻¹) and compensated for the brittleness of the pristine SiO₂ aerogel. Further, Bendahou et al. controlled the pore size of the nanocellulose/SiO₂ aerogel by regulating the charge, aspect ratio, and concentration of particles. Owing to the presence of SiO₂, additional mesopores were created to effectively reduce thermal conductivity (Figure 22d). Furthermore, they introduced nanozeolites into nanocellulose, reducing the aerogel pore size below 100 nm through their synergistic effects. The thermal conductivity was as low as 18 mW m⁻¹ K⁻¹ when compared with other porous materials, which far exceeded the thermal insulation capability of air (≈25 mW m⁻¹ K⁻¹).

3) Introducing carbon materials: Although the introduction of inorganic additives can enhance the thermal insulation performance of nanocellulose aerogels, it is difficult to withstand long-term manipulation at high-temperature conditions because the thermal resistance temperature of cellulose is not high (≈200 °C), thus limiting aerogel application as a thermal insulation material in harsh environments. Wang et al. reported that the incorporation of zirconium phosphate/rGO nanosheets into CNFs could improve the thermal stability with higher decomposition temperatures and additional char residues than those of the neat CNF aerogel, thus providing the composite aerogel a superior flame resistance property.

4) Introducing thermally stable polymer: Zhang et al. fabricated an aerogel with excellent thermal insulation properties by combining CNFs with thermally stable polyimide (PI). Both at cold (−40 °C) and hot (160 °C) temperatures, the
BC/PI composite aerogel exhibited superior thermal insulation when compared with other thermal resistance materials (Figure 22e), indicating that the aerogel could effectively block heat transfer in a fairly large temperature range.

Recently, several studies regarding superinsulating and lightweight nanocellulose aerogel-based composites have been reported, indicating the extensive potential to utilize these composites for sustainable and thermal insulating applications. In this section, strategies to achieve effective thermal insulation were described and discussed. For further investigations, controlling the pore size, as well as pore distribution, are both critical to analyze the influence of pore structure on heat transfer properties. The wide size distribution and network connections should be improved, and systematic investigation on heat transport with structural features is warranted.

5.5. EMI Shielding

With the development of miniaturized and multifunctional electronic packaging, EMI has become an increasingly critical and intractable task to avoid undesirable EM energy generated by electronic components. Generally, the EMI shielding performance will be gradually enhanced with increasing electrical conductivity. However, high electrical conductivity is not the only criterion for EMI. For mobile charge carriers to interact with the incoming EM field and for the porous structure to promote the multiple reflections, adsorption of EM waves plays an important role. Compared with other 1D or 2D conducting composites, nanocellulose composite aerogels exhibited promising properties for EMI shielding by introducing novel conductive fillers (e.g., silver nanowires (AgNWs), MXene), as they can combine advantages of nanocellulose, conductive fillers, and aerogels including i) biocompatibility, biodegradability, and chemical stability, ii) excellent electrical conductivity, and iii) ultralow density, large open pores, and ultrahigh SSA.

Recently, Zeng et al. assembled 1D AgNWs with a higher aspect ratio and electrical conductivity into CNF dispersions, forming ultralight and highly flexible CNF/AgNW composite aerogels via unidirectional freeze drying (Figure 23a). The lamellar, honeycomb-like porous structures, and effective conductive networks provided by the AgNWs, and strong hydrogen bond interactions between CNFs and polyvinylpyrrolidone adsorbed on the AgNW surfaces endowed aerogels with a markedly high EMI shielding effectiveness (SE) of >70 dB (Figure 23b). Fei et al. loaded zeolitic imidazolate framework-67 (ZIF-67) into the continuous porous network of CNF aerogels and then annealed it to obtain the Co/C@CNF aerogels. The electrically conductive and magnetic aerogels exhibited excellent EMI SE owing to the enhanced magnetic loss and dielectric loss ability. Moreover, the interface impedance mismatch of aerogels has been improved, which was beneficial to reduce reflection loss and alleviate the undesired secondary pollution of EMI waves.
Overall, reports regarding nanocellulose aerogels in the field of EMI shielding remain relatively rare. To meet the needs for EMI shields, including lightweight, flexibility, wide frequency band, and high shielding performances, it is necessary to consider multidirectional features of structural control, shielding mechanism, as well as filler selection and dispersion in the matrix based on the advantages of nanocellulose aerogels. In the future, we believe that novel conducting materials with homogeneous dispersion in nanocellulose aerogels and a unique microstructure for scattering and trapping electromagnetic waves will be potential candidates for EMI shielding.

5.6. Biomedical Applications

As a natural polymer material, nanocellulose has numerous advantages such as degradability, nontoxicity, and biocompatibility when compared with traditional synthetic polymers. These features further highlight the superiority of nanocellulose aerogels for use as drug carriers and bioscaffolds in biomedical applications. Nanocellulose aerogels grafted with PEI (CNFs–PEI) have been manufactured as a new drug carrier by freeze drying.[182] The drug loading and release properties of aerogels were investigated using a drug model of water-soluble sodium salicylate (NaSA). The aerogels revealed an effective drug load capacity ($287.39 \text{ mg g}^{-1}$) (Figure 24a). The drug adsorption process was in agreement with the Langmuir isotherm adsorption and pseudosecond-order kinetic models. In addition, controlled sustained release of sodium salicylate in the aerogel could be achieved by regulating the pH and temperature conditions during release, which was expected to be a new generation drug carrier (Figure 24b,c).

Cell culture scaffolds are usually composed of a 3D porous network that can facilitate cell fusion, nutrient transport, and cellular waste metabolism.[43] Cai et al. designed a honeycomb aerogel microsphere using CNFs covalently crosslinked with the epichlorohydrin resin without toxic solvents by spray freeze drying (Figure 24d).[111a] This unique ultralight aerogel presented an open porous structure with a low density ($1.8 \text{ mg cm}^{-3}$) and a high water uptake capacity ($\approx 100 \text{ g g}^{-1}$). Furthermore, it proved to be an excellent culture scaffold for 3T3 NIH cells even in a critical environment, owing to the openness of pores and enhanced mechanical properties provided by covalent crosslinking. Similarly, Zhang et al. also confirmed the good seeding, attachment, and propagation of 3T3 NIH cells on the surface and inside the crosslinked CNF/PVA composite aerogel microspheres, presenting cell culture scaffolds with good biocompatibility and chemical stability, as promising candidates for cell cultures in the tissue engineering field.[183]

In summary, nanocellulose aerogels with an effective design can be widely used to develop sustainable biomaterials for wound dressing, scaffolds for tissue culture, and drug delivery systems.[185] In contrast to other applications, biocompatibility and noncytotoxicity are highly critical parameters for biomedical applications. However, there exist several limitations to be improved in future research. First, the current study on in vivo and biocompatible tests between aerogels and tissues/organs have not been widely and systematically investigated. Additional composites based on nanocellulose aerogels, as well as...
an increased number of animals or microorganisms, need to be employed in these experiments. Second, lab-scale toxicity experiments and animal model studies on nanocellulose aerogels need to be performed to confirm safety issues on different organisms. Third, the current technologies for nanocellulose aerogel preparation fail to effectively allow large-scale industrial production and avoid pollution. Furthermore, the high production cost may restrict their biomedical applications.

6. Conclusions and Prospects

As a third-generation biomass polymer material, nanocellulose-based aerogels not only present typical characteristics of low thermal conductivity, large SSA, high porosity, lightweight, and low dielectric constant similar to traditional inorganic aerogel material, but also incorporate their inherent excellent properties such as good biocompatibility, degradability, and high mechanical strength. The composite functionalized nanocellulose-based aerogels, obtained by physical blending or chemical modification, can be imparted with additional special features, including antibacterial properties, transparency, superhydrophobicity, as well as electrical and magnetic properties. Therefore, it has great application prospects as adsorbent materials, drug loading, thermal insulation materials, and electrical and magnetic materials. However, the practical application of nanocellulose-based functional composite aerogels is not without obstacles, and there are still several hurdles to overcome as listed below:

i) Complex fabrication process. The process of preparing a nanocellulose gel precursor is complicated and time-consuming. In particular, the process consumes a large amount of alcohol (mainly ethanol) as a replacement solvent during the process of solvent exchange performed repeatedly. Determination of a suitable replacement method to rapidly replace the water inside the gel will help shorten the fabrication cycle of the aerogel, reduce production costs, and pave the way for industrialization.

ii) Time and energy consumption. Aerogel drying mainly relies on freeze drying or supercritical CO₂ drying, which usually requires 24–96 h, high pressure, and continuous CO₂ incorporation, increasing the risks and energy consumption. The development of a novel and simple drying method, which can maintain the structure without collapse and unchanged performance of the aerogel to achieve large-scale production, is a key issue that needs to be addressed in future research.

iii) Bottleneck of functionalization. The further functionalization of nanocellulose aerogels has encountered several challenges such as undesirable dispersion of fillers, designable structures, modification of functional groups, and the smooth transition from a laboratory to industrialization.

Therefore, all the above issues need to be addressed in future research. Moreover, we need to comprehensively consider subjective initiation, combined with the advantages of cellulose itself, to further explore potential applications, as well as the development of nanocellulose-based functional composite aerogels.

i) Anisotropic functions. It is well-known that the structure determines performance. Some functional fillers can be incorporated to endow the structurally anisotropic nanocellulose aerogel by directional freeze drying with anisotropic functions (heat, electricity, and magnetism), thereby broadening their application fields, including the directional flow of media and anisotropic functions in materials.

ii) Mechanical strength. Currently, the ultralight feature of nanocellulose aerogels has gained momentum; however, a relatively low compressive strength significantly limits its practical application. Inspired by our group’s previous research in the field of porous materials, from an opposing perspective, it can be interesting to develop nanocellulose aerogels with high strength and toughness, along with high density and thermal resistance for building materials.
iii) Long-range orientation. The existing directional freeze-drying technology is only suitable for short-range orientation control (<5 cm) of nanocellulose aerogel structures. On preparing a long-oriented structure, the insufficient driving force of growing ice crystals can cause uneveness of the upper and lower structures. Therefore, actualizing the construction of an ultralong aerogel with a uniform directional structure will significantly promote the development of nanocellulose aerogels in the field of rapid liquid adsorption and intelligent detection.

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Conflict of Interest

The authors declare no conflict of interest.

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