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Boron Nitride Aerogels with Super-Flexibility Ranging from Liquid Nitrogen Temperature to 1000 °C

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Abstract

Aerogels with extraordinary mechanical properties attract a lot of interest for their wide spread applications. However, the required flexibility is yet to be satisfied, especially under extreme conditions. Herein, a boron nitride nanoribbon aerogel with excellent temperature-invariant super-flexibility is developed by high temperature amination of a melamine diborate precursor formed by hydrogen bonding assembly. The unique structure of the aerogel provides it with outstanding compressing/bending/twisting elasticity, cutting resistance, and recoverable properties. Furthermore, the excellent mechanical super-flexibility is maintained over a wide temperature range, from liquid nitrogen temperature (−196 °C) to higher than 1000 °C, which extends their possible applications to harsh environments.

1 Introduction

Aerogels are ultralight solids with a 3D interconnected porous network, high porosity, and large specific surface area, exhibiting outstanding performance in applications such as thermal/acoustic/electrical insulation, as catalyst supports, drug carriers, cosmic dust collectors, energy conversion, storage materials, sensors, etc.¹ So far, many kinds of aerogels based on silicone,¹ silica,¹ silicon carbide,² metal/metal oxide,³ polymer,⁴ supramolecules,⁵ carbon/nanocarbon (carbon nanotube and graphene),¹ and boron nitride (BN)⁶ have been developed. However, due to mechanical brittleness and weak elasticity, most aerogels suffer from a structural collapse and performance damping when external shocks (e.g., compression, bending, twisting, or stretching) are applied, hindering their use in many practical applications.

To overcome the above-mentioned flaws, many strategies have been developed, such as directional freeze-casting of the sol precursors,⁷ conformal growth of the incipient networks,⁴ cross-linking of aerogels with organic polymers,⁸ chemical vapor deposition (CVD) growth within a template,⁹ etc. Recently, an improved multidirectional freezing strategy was developed in order to construct multioriented-microladder arrays in aerogels. The resulting aerogel can bear an iterative and multidirectional cutting pressure with a

complete recovery of its original shape.⁷ In addition, the double-cross-linked aerogels exhibited super-flexibility with excellent toleration of the compressing, bending or twisting stress.⁸ However, aerogels with a remarkable mechanical flexibility are still rarely reported, without mentioning whether those could maintain their flexibility over a broader temperature range.

Herein, we report on a temperature-invariant super-flexibility of BN aerogels constructed by intertwined BN nanoribbons derived from high temperature amination of the hydrogen-bond directed assemblies of melamine and boric acid. These BN nanoribbon aerogels can bear compressing, bending, twisting, or cutting forces over a wide temperature range from liquid nitrogen temperature ($-196\text{ }^{\circ}\text{C}$) to more than $1000\text{ }^{\circ}\text{C}$. To be specific, these BN nanoribbon aerogels can adsorb and squeeze out liquid nitrogen repeatedly, as well as bear flame burning in ambient air while maintaining the flexibility very well. Such a temperature-invariant super-flexibility of BN nanoribbon aerogels holds bright promises for applications in harsh environments.

2 Results and Discussion

The synthesis of BN nanoribbon aerogels involved four simple steps (**Scheme 1** and Figure S1, Supporting Information): 1) mixing the boric acid (B) and melamine (M) in the hot distilled water/tertiary butanol (TBA) co-solvent; 2) cooling the solution during ultrasonication to ambient condition ($25\text{ }^{\circ}\text{C}$) for gelation and with the subsequent obtaining of the M·2B hydrogel; 3) freeze-drying of the M·2B hydrogel obtaining the aerogel-like M·2B precursor; 4) pyrolysis of the M·2B at $1200\text{ }^{\circ}\text{C}$ in NH_3 atmosphere (serving as the reducing agent to etch the precursor M·2B¹⁰) for 3 h, which finally yielded the ultralight (with the density of $\approx 15.5\text{ mg cm}^{-3}$), thermal-insulating (with the conductivity of $0.0346 \pm 0.0015\text{ W m}^{-1}\text{ K}^{-1}$), hydrophobic BN nanoribbon aerogel monolith (insets in **Figure 1a,b**). The water/TBA co-solvent provides optimal crystallization conditions for the formation of M·2B nanoribbons with a large-aspect ratio. Under high-temperatures and NH_3 atmosphere, the M·2B nanoribbons can be converted to BN nanoribbons, accompanied by the further interweaving/intertwining of the nanoribbons, resulting in a robust porous-nanoribbon network.

Scheme 1
Schematic synthesis of BN nanoribbon aerogels.

Figure 1
The structural characterization of BN nanoribbon aerogels. *a, b*) SEM images, *c–e*) TEM images, and *f*) an AFM image of BN nanoribbon aerogel, *g*) STEM and element mappings of single BN nanoribbon, *h*) Nitrogen adsorption-desorption isotherms of BN nanoribbon aerogels. Inset in (*a*), a BN nanoribbon aerogel monolith was placed on a flower. Inset in (*b*),

the contact angle of BN aerogel. Insert in (d), the corresponding electron diffraction pattern. Inset in (h), the corresponding pore size distribution curve.

The morphology of the BN nanoribbon aerogels was investigated by scanning electron microscope (SEM). As shown in Figure 1a,b and Figures S2–S4 (Supporting Information), BN nanoribbons intertwine/interweave and contact with each other to form an isotropic porous open-cell network, resembling aerogel-like M·2B precursors (Figure S5, Supporting Information). The individual BN nanoribbons exhibit different states in this porous network, such as flat, bended, twisted, etc., as shown in Figure 1b and further confirmed by transmission electron microscope (TEM) (Figure 1c,d and Figure S6, Supporting Information) and atomic force microscope (AFM) images (Figure 1f), indicating the flexibility of the individual BN nanoribbons. These BN nanoribbons have average widths of 0.6–1.8 μm (Figure S7, Supporting Information), a very thin thickness of ≈ 3.2 nm (Figure 1f), and lengths of a few hundred micrometers, all exhibiting a high-aspect ratio. The TEM images also reveal the porous structure of the individual nanoribbon (Figure 1d). High-resolution TEM images and the corresponding selected area electron diffraction patterns show the polycrystalline character of the stacked h-BN layers (Figure 1e). The calculated interplane distance of the BN layers (0.36 nm) is slightly larger than that of bulk h-BN (0.34 nm), revealing a turbostratic BN phase of the nanoribbon. This is also consistent with the X-ray diffraction (XRD) analysis (≈ 0.357 nm) (Figure S8, Supporting Information).^{6, 10} Spatially resolved elemental mapping is shown in Figure 1g, individual B and N species are uniformly distributed along and across the nanoribbons, and further confirmed by X-ray photoelectron spectroscopy (XPS) spectra (Figure S9, Supporting Information).

The nitrogen sorption spectra were performed to study the specific surface area and pore size distribution of the BN nanoribbon aerogel. As shown in Figure 1h and Figure S10 and Table S1 (Supporting Information), the isotherm exhibits the combined features of type I and type IV curves, with a rapid increase in the low-pressure range ($P/P_0 < 0.02$) and a hysteresis loop characterizing the existence of both micro- and meso-pores. This hierarchically porous feature was further confirmed by a Barrett–Joyner–Halenda (BJH) analysis, where a multimodal distribution with the main characteristic pore sizes of ≈ 0.6 –1.2, 1.7–3.8, 7.8–10.3, and 11.8–44.9 nm was displayed. The specific surface area is unraveled by Brunauer–Emmett–Teller (BET) to be ≈ 920 m^2 g^{-1} , hence higher than that of the M·2B derived BN microfiber foams (773 m^2 g^{-1}),⁶ nanotubular BN architectures (166 m^2 g^{-1}),⁶ highly crystalline BN aerogels (431 m^2 g^{-1}),⁶ and h-BN nanosheet/PVA foams (30.7–124.4 m^2 g^{-1}).⁶

To investigate the formation mechanism of the resulting aerogels, a variety of M·2B precursors were prepared in water/TBA co-solvent with the volume ratios of water to TBA 5:0, 5:3, 5:5, 5:7, 5:9, and 5:11, respectively (the ratio of 0:5 was not investigated as the raw materials could not be dissolved completely under the same conditions). According to the SEM images (Figures S11 and S12, Supporting Information), the M·2B precursors exhibited a nanoribbon morphology when the TBA volume percentage reached above 50%, while the M·2B were microfibers when the TBA volume percentage was below 50% (in pure water or $V_{\text{Water}}: V_{\text{TBA}} = 5:3$). In addition, the precursor concentration (Figure S13, Supporting Information) and sonication conditions (Figure S14, Supporting Information) had only a slight effect on the formation of the nanoribbon morphology, but showed a significant effect on the thickness of the resulting ribbon. Furthermore, M·2B nanoribbons could also be obtained from other co-solvents (Figures S15 and S16, Supporting Information).

To understand the formation mechanism of the solvent-determined morphology of the M·2B precursors, molecular dynamics (MD) simulations were performed in the canonical ensemble by using the LAMMPS (large-scale atomic/molecular massively parallel simulator) code.¹¹ A simulation model of a M·2B layer¹² (**Figure 2a**) sandwiched between solvent slabs was initially built, which is illustrated in **Figure 2b**. After the equilibration procedures of a single layer M·2B in several kinds of pure solvents for 100 ps, the M·2B exhibit different structure geometries (**Figure S17**, Supporting Information). The M·2B keeps its original structure when in TBA, isopropanol (IPA), methyl alcohol (MA) or ethyl alcohol (EA) solution, while ethylene glycol (EG) or water molecules disturb the M·2B hydrogen-bonded networks in varying degrees. Although the M·2B sheet in pure water turns into several small hydrogen-bonded oligomers, the M·2B can unexpectedly preserve its complete topology if the hydrogen-bond interaction between the H₂O and M·2B molecules is eliminated by purpose (**Figure S18**, Supporting Information). The same phenomena were also found in MA and EG, strongly indicating that the hydrogen-bonded interaction between M·2B and solvent molecules can be related to the varying morphologies of the M·2B precursors in different solvents (**Figures S11–S16**, Supporting Information). Further analyses reveal that the density of hydroxyl (number of hydroxyl per volume) in the solvent is a key factor in assembling the M·2B networks. The snapshots (**Figure S19**, Supporting Information) indicate that a higher hydroxyl density results in smaller oligomer sizes, which could also be quantitatively proven from the hydrogen-bond number variations of M·2B oligomers in TBA, MA, EG, and water (**Figure S20**, Supporting Information), respectively.

Figure 2

a) The atomic structure of a M·2B cell in top (left) and side (right) view. The hydrogen bonds are presented with dashed lines. b) Simulation setups of a single layer of M·2B embedded in solvent (left), snapshots of M·2B after equilibration in pure TBA (top) and pure water (bottom) (right). c) Simulation of two crossed M·2B layers. d) The side view of two crossed M·2B layers, and linked to each other via the H-bond at the edge of the layer. e) Simulated illustration of the H-bond converted to a B–N bond at the edge of the layer.

The M·2B expands its planar size by connecting the oligomers during its precipitation from the solvent, and the expansions should be oriented rather than homogeneous, due to the different binding energies when connecting the M·2B units together along its different in-plane lattice vectors. The binding strength along *a* is about 34.97 kcal mol⁻¹ per unit, thus, higher than that along *b* (28.03 kcal mol⁻¹ per unit), resulting in a preferred anisotropic expansion of the M·2B (Figure 2a and Figure S21, Supporting Information). Moreover, the existence of solvent molecules increases the interlayer distance between the M·2B sheets, leading to a drastically decreased interlayer binding energy. For example, a layer of TBA separates two M·2B sheets from 0.35 to 0.81 nm, and decreases the stacking energy almost 13 times from 10.12 to 0.73 kcal mol⁻¹ nm⁻² (Figure S22, Supporting Information). These simulation results strongly suggest that the M·2B in low hydroxyl density solvents, such as TBA, IPA, and EA, has the tendency to form orientationally-expanded thin segments. The M·2B will easily grow into long and wide ribbons (Figures S12–S16, Supporting Information) since the formed hydrogen-bonded M·2B networks are hardly destroyed by the solvent molecules. The entanglements and crosses among long nanoribbons effectively prevent their aggregation and rather assemble into porous 3D M·2B structures. On the contrary, high hydroxyl density solvents, like water and EG, let the M·2B exist in short narrow ribbons or even small oligomers, which will easily aggregate together to assemble into rods (Figure S11, Supporting Information). As a result, it is possible to control the M·2B precursors such that ribbons or rods shapes evolve by changing the density of hydroxyl through mixing organic solvents with water in different ratios.

The boron nitride is obtained via a high temperature treatment of the M·2B precursors in a NH₃ atmosphere. The proposed formation mechanism is the attachment of boron atoms to the edges of the melamine,¹² which could be considered as the substitutions of covalent chemical bonds for the hydrogen bonds between the melamine and the boric acid in M·2B. It is worth noticing that the hydrogen bonds exist not only within the single M·2B nanoribbons, but also between the two adjacent ribbons at their edges (Figure 2c–e). Although the angles of the crossed nanoribbons are random, the interlayer hydrogen-bonds always existed (Figure 2d). The presence of interlayer hydrogen-bonds enables the adjacent nanoribbons to be chemically connected to each other in the cross region during the high temperature treatment (Figure 2e), endowing the nanoribbon assemblies with their outstanding super-flexibility.

The mechanical properties of the BN aerogel are studied first by a compression test (Figure 3a and Figures S23–S30, Supporting Information). All BN aerogels derived from water/TBA with different ratios are compressed to 90% without fracture, rapidly recovering their original sizes after force removal (Figure 3a,d), while the BN aerogel derived from the pure water-M·2B system displayed fracture (Figure S24, Supporting Information). For the first compression cycle (Figure 3a), three deformation regimes can be observed: an initial Hookean region at strain $\varepsilon < 13\%$ with a Young's modulus of ≈ 28.5 kPa for BN-53 ($V_{\text{Water}}:V_{\text{TBA}} = X:Y$, BN-XY), 78.4 kPa for BN-55, a plateau, and the final densification regime.¹³ The deformation in the Hookean region is nearly linear elastic, corresponding to the bending of the nanoribbons. The relatively flat plateau is attributed to the postbuckling

deformation of nanoribbons, and the rapid stress increase region is due to the densification of the cells. It should be noted that BN-55 exhibits a higher modulus than the other BN aerogels derived from other solvent compositions, and the stress plateau (ϵ , 13–45%) became narrower as compared to BN-53 (ϵ , 13–50%). Furthermore, the stress plateau is nearly invisible for BN-57, a nearly linear elastic region from 0–60% strain could be observed, indicating the elastic formation of BN nanoribbons over a wide range of strain. The BN-59 and BN-511 exhibited weaker mechanical strength compared to other BN aerogels (for more details see Table S1, Supporting Information).

Figure 3

The flexibility of BN nanoribbon aerogels at ambient conditions: a) The strain–stress curves of BN aerogels derived from water/TBA mixed solutions with different volume ratios. b) The loading–unloading cycles and strain–stress curves of BN-57 with subsequent increasing of the strain from 5% to 75%. c) The strain–stress curves of the compression test during 50 loading–unloading cycles. d) Photographs of BN nanoribbon aerogel compressed and recovered to its original shape. e–g) Photograph and SEM images of BN aerogel in the bending state (e), twisting state (f) and cutting–shearing state (g).

To investigate the degree of recovery of the BN nanoribbon aerogels, BN-57 with a density of $\approx 15.5 \text{ mg cm}^{-3}$ underwent first a compression–recovery treatment for about 10 cycles. As shown in Figure 3b, six-cycles compressive strain–stress curves (with increasing strain from 5% to 75%) of the BN aerogel exhibit a continuous trend, demonstrating a perfect shape recovery.⁶ Furthermore, 50 cycles of consecutive loading–unloading (Figure 3c, $\epsilon = 40\%$) exhibited similar features as other superelastic materials, such as graphene foams,⁹ CNT aerogels,¹⁴ and silicone aerogels.^{1, 8} For the recovery process, unrecoverable residual deformations of about $\epsilon = 2.8\%$, $\epsilon = 7.6\%$ remained after 10- and 50-cycles at 40% strain, respectively (for more details see Figure S31, Supporting Information)¹⁵ due to the appearance of nanoribbon slippage and fractured junction nodes during the loading–unloading cycles (Figure S28, Supporting Information). The unrecoverable residual deformation is smaller than that of BN microfiber foam⁶ and comparable to that of superelastic BN nanotubular cellular-network architectures.⁶

The BN aerogel also exhibited excellent resistance to bending, cutting, and twisting. As shown in Figure 3e–g, the BN aerogel could be bent into a large deflection, bidirectionally-uniaxially compressed into a “dumbbell” shape and slightly twisted with helical buckling without any fracture. When the external loading was removed, all the deformed BN aerogels recovered to their original shape. Furthermore, SEM observations revealed the intact micromorphology of the BN aerogels under external loading. A clear “V”-like shape and a “U”-like shape with smooth curves were observed (Figure 3e,g), corresponding to the bended BN aerogel and cutting-pressed BN aerogel, respectively. The intertwined BN nanoribbon porous network was maintained well in the bending region and the deformed wrinkles surrounded the blade in the cutting-pressure region of the BN aerogel, indicating the nanoribbons network of the BN aerogel was maintained intact without any cracking or tearing.

We further explored the flexibility of BN nanoribbon aerogels over a wide temperature. The BN aerogel was first immersed into liquid N₂ (−196 °C). When in liquid N₂, the BN aerogel could adsorb liquid N₂, but it did not become hardened. It could be compressed about 80% strain without fracture. After the loading was removed, the BN aerogel recovered to its original shape (Figure 4a–a3). The liquid N₂ in the BN aerogel was squeezed out as water from a sponge. When the BN aerogel was taken out from the liquid N₂, the swollen aerogel could be compressed with the liquid N₂ dripping out (Figure 4b). After removing the force, the aerogel recovered partially to its original shape (Figure 4c1). However, pouring again liquid N₂ onto the aerogel surface, the deformed aerogel rapidly recovered to its original shape (Figure 4c2), indicating a large flexibility, good resilience, and recyclability in the low temperature environment. Moreover, even in high-temperature air, the BN aerogel also exhibited excellent stability (Figure 4f) and flexibility. Placing a BN aerogel in a flame (Figure 4d,e) or in a tube furnace with a temperature of 1018–1020 °C (Figure 4f and Figures S32 and S33, Supporting Information). The BN aerogel was compressed by external shocks, and it recovered its original shape without combustion or fracture. Although the specific surface areas decreased to different degrees, the intertwining nanoribbon network, the degree of crystallinity as well as the loading–unloading behavior remained almost unaltered (for more details see Figures S34–S39, Supporting Information). These results reveal that the BN nanoribbon aerogels have excellent flexibility over a wide range of temperatures, comparable with entangled carbon nanotube architectures (nonaerogel) synthesized by the “super-growth” method,^{1, 16} and the temperature range is wider than that of the aerogels reported elsewhere, such as the marshmallow-like porous aerogel based on methyltrimethoxysilane–dimethyldimethoxysilane co-polymers (from liquid nitrogen temperature to 335 °C).¹

Figure 4

The flexibility of the BN nanoribbon aerogel in liquid N₂ and in a flame: a–a3) the BN aerogel was immersed into liquid N₂ with subsequent compression and release. b) Squeezing out liquid nitrogen with a sharp nipper. c–c2) Squeezing out liquid nitrogen and pouring liquid nitrogen onto the BN aerogel. d,e) The BN aerogel was placed in a flame testing again the compression and release via surface-loading d–d3) and linear-loading e–e2). f) The TGA curve of the BN nanoribbon aerogel in air atmosphere. Insets in (f) are photographs of the BN nanoribbon aerogel in 1018–1020 °C tube furnace with air atmosphere.

3 Conclusion

In summary, BN nanoribbon aerogels with excellent temperature-invariant super-flexibility was obtained based on the synthesis and pyrolysis process of H-bond assemblies (M·2B precursors). The water/TBA mixed solvent provided an optimal crystallization condition to form the nanoribbon precursor with regular shape and high-aspect ratio. After pyrolysis, this uniform intertwined-interwoven nanoribbon network could be transformed in the BN aerogel. This unique structure provides outstanding compressing/bending/twisting elasticity, excellent cutting resistance and it is recoverable to a large extent. Furthermore, the flexibility is maintained over a wide temperature range, from –196 °C up to more than 1000 °C, which extends their possible applications to harsh environments.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aerogel, boron nitride, nanoribbon, super-flexibility

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