Boron nitride colloidal solutions, ultralight aerogels and freestanding membranes through one-step exfoliation and functionalization

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Manufacturing of aerogels and membranes from hexagonal boron nitride (h-BN) is much more difficult than from graphene or graphene oxides because of the poor dispersibility of h-BN in water, which limits its exfoliation and preparation of colloidal solutions. Here, a simple, one-step mechano-chemical process to exfoliate and functionalize h-BN into highly water-dispersible, few-layer h-BN containing amino groups is presented. The colloidal solutions of few-layer h-BN can have unprecedentedly high concentrations, up to 30 mg ml⁻¹, and are stable for up to several months. They can be used to produce ultralight aerogels with a density of 1.4 mg cm⁻³, which is ~1,500 times less than bulk h-BN, and freestanding membranes simply by cryodrying and filtration, respectively. The material shows strong blue light emission under ultraviolet excitation, in both dispersed and dry state.
wo-dimensional boron nitride (BN) nanosheets, also called ‘white graphene’ or ‘non-carbon graphene’, consist of a few layers of alternating boron and nitrogen atoms in a hexagonal arrangement. Their mechanical, thermal and electronic properties are attractive for applications in polymer matrix composites, hydrogen storage, field emitters, electrocatalysts and sorbents. In addition, it has been demonstrated that BN single crystals, unlike carbon materials, have strong luminescence in the ultraviolet range, which makes BN attractive for blue light and ultraviolet emission.

In recent times, significant efforts have been focused on the isolation and functionalization of BN nanosheets to achieve better dispersion, which would enable applications in optical devices, biological systems and composites. Organic solvents such as N,N-dimethylformamide have been employed for exfoliation and stabilization of disperse BN nanosheets, through polar–polar interactions between the functional groups and the hexagonal BN (h-BN) surface, using a sonication–centrifugation technique. Lin et al. have reported that ball-milled h-BN with an increased number of defects can be functionalized with a long alkyl chain amine via Lewis acid–base interactions to produce water-soluble sheet-like particles. They also reported that water dispersion of h-BN nanosheets can be achieved directly by using water as the exfoliating molecule through edge functionalization. In recent times, Sainsbury et al. obtained hydroxyl-terminated BN nanosheets by the oxidation of exfoliated h-BN nanosheets using a two-step functionalization procedure. However, the concentration of the h-BN dispersions was typically below 2 mg ml$^{-1}$, even after long periods of intense ultrasonication. The low concentration may present an especially severe limitation for the aqueous suspensions preferred in many applications. Therefore, the development of a practical high-yield process to achieve highly water-soluble BN nanomaterials remains a challenge.

Graphene oxide and graphene, in the form of aerogels and membranes, have been used as efficient adsorbents for the separation of organic pollutants and oils from water, for gas separation and for molecular and ion selective devices. There is potential for h-BN, which is more oxidation and intercalation resistant than sp$^2$ carbon, to be used to produce similar structures. The h-BN-based materials represent a great advantage for high-temperature applications and extreme environments. However, it is very difficult to achieve aqueous dispersion of h-BN using conventional routes. In recent times, BN foams assembled from nanosheets showed excellent thermal stability, super-elasticity and very low electrical permittivity, but the assembly process required the use of templates, high temperature and vacuum, hazardous and toxic chemicals, and sophisticated fabrication techniques.

Here we present a simple and efficient one-step method for the preparation and functionalization of few-layer BN by solid-state ball milling of commercially available h-BN and urea powder. This ambient temperature method has several advantages, including scalability for mass production, low cost, high yield and does not require the use of organic solvents, catalysts, substrates or vacuum systems. The as-produced few-layer BN shows unprecedented high dispersibility in water, yielding stable colloidal solutions with concentrations up to 30 mg ml$^{-1}$. A urea-assisted exfoliation and functionalization mechanism is proposed to explain the formation of the water-soluble few-layer BN. Ultralight BN aerogels can be produced by cryodrying and thin freestanding membranes fabricated by filtration of the two-dimensional few-layer BN dispersions. Both colloidal solutions and freestanding membranes show strong ultraviolet and blue light luminescence.

**Results**

**Synthesis and characterization.** We have developed a one-step method for the preparation and functionalization of few-layer BN based on urea-assisted solid exfoliation of commercially available h-BN (Fig. 1a). After ball milling and washing with water to remove urea, few-layer BN can be readily dispersed in water without sonication, to form stable colloidal solutions at different concentrations (Fig. 1b and Supplementary Fig. 1). The concentration of the suspensions can reach up to 30 mg ml$^{-1}$ (Fig. 1b), the highest ever value reported for BN water suspensions. The suspensions with a high concentration up to 30 mg ml$^{-1}$ exhibited a milky and light yellow appearance compared with the low-concentration suspensions, possibly due to a relatively high concentration of amino groups. The yield of the exfoliated BN sheets in the proposed urea-assisted, high-energy ball mill processing was as high as 85%. The path of a red laser beam can be clearly seen through all the dispersions due to light scattering by the few-layer BN colloid (Tyndall effect), as shown in Fig. 1b. The aqueous BN dispersion with the highest

![Figure 1](https://example.com/figure1.png)  
**Figure 1** | **Schematic illustration of the exfoliation and dispersion process.** (a) Schematic illustration of the exfoliation. (b) Photos of as-prepared colloidal solutions of few-layer BN with concentrations of 0.5, 2.0, 6.0 and 30 mg ml$^{-1}$, respectively, and demonstration of the Tyndall effect and stability of the colloidal solutions.
corresponding line-scan profile of few-layer BN. (Fig. 2g, two main characteristic diffraction peaks can be observed to six monolayers). The structure of few-layer BN was further suggests that the thickness of the few-layer BN is about 2 nm (five lateral size. The nanometre-scale thickness of few-layered BN was distributions were statistically evaluated by HRTEM measure-
transform images in Fig. 2d, the structure of the few-layer BN parallel fringes corresponding to three and six stacked layers in (Fig. 2a inset). The selected area electron diffraction image has a slightly pronounced hexagonal pattern, due to the few-layer stacking of h-BN. The high-resolution TEM (HRTEM; Fig. 2b,c) images at the edges of few-layered BN clearly show three and six parallel fringes corresponding to three and six stacked layers in the samples. As seen in the HRTEM and the fast Fourier transform images in Fig. 2d, the structure of the few-layer BN remains ordered after ball milling. The thickness and lateral size distributions were statistically evaluated by HRTEM measurements on 100 sheets (Supplementary Fig. 3). Eighty-three per cent of the BN sheets were < 2.5 nm thick and around 100 nm in lateral size. The nanometre-scale thickness of few-layered BN was further confirmed by atomic force microscopy (Fig. 2e). Figure 2f suggests that the thickness of the few-layer BN is about 2 nm (five to six monolayers). The structure of few-layer BN was further investigated by X-ray diffraction (XRD) analysis. As shown in Fig. 2g, two main characteristic diffraction peaks can be observed at 26.2° and 42.8°, arising from (002) and (100) planes of few-layer BN, respectively. Compared with the pristine h-BN, the (002) and (100) peaks of few-layer BN show a remarkably reduced intensity and dramatically broadened width, indicating the presence of thin BN sheets and much less extended/ordered stacking in the c direction.

The Fourier transform infrared (FTIR) spectrum shows an additional peak at 3,240 cm⁻¹ due to the N–H stretching vibration, whereas pristine h-BN exhibits only the characteristic peaks of in-plane B–N stretching vibrations at ~1,364 cm⁻¹ and out-of-plane B–N–B bending vibrations at ~1,746 cm⁻¹ (Supplementary Fig. 4). The shoulder at 3,411 cm⁻¹ can be ascribed to O–H stretching vibrations due to the washing in water after ball milling. The appearance of N–H stretching vibrations indicates that functionalization has occurred. Functional groups such as NH₂ from urea have been created and bonded to the defect sites and edges of few-layer BN. In addition, the strong pungent smell and the readings of an ammonia sensor on opening the milling jar further demonstrate that ammonia gas and/or low-molecular-weight amines were formed as intermediates in the mechano-chemical process. Although the recently reported hydroxyl functionalized BN nanosheets prepared via NaOH-assisted ball milling had very low dispersibility in water with highest achievable concentrations < 1 mg ml⁻¹, the functionalized few-layer BN reported here forms aqueous colloidal solutions with concentration up to 30 mg ml⁻¹.

Dispersions of the pristine BN and few-layered BN were investigated using zeta potential measurements. Both of them exhibit highly negative potential values, −44 ± 3 and −34 ± 4 mV, respectively, consistent with the reported values for BN materials due to the B–O–H and N–O–H generated on h-BN in water. It has been reported that the hydrophilicity, shape, size distribution and zeta potential of particles are all important factors governing their dispersibility in water and stability of formed dispersion. The excellent hydrophilicity and narrow size distribution are essential to the good dispersibility, whereas high zeta potential helps to stabilize the dispersion. Although zeta potential of pristine BN is −44 ± 3 mV, it cannot disperse in water well due to its

Figure 2 | Exfoliated few-layer BN. (a) TEM image of few-layer BN, with the selected-area electron diffraction pattern (inset) indicating a layered BN structure. Scale bar, 50 nm. (b,c) HRTEM images of the edge folding of two few-layer BN sheets with three and six BN layers, respectively. Scale bars, 2 nm (b) and 5 nm (c). (d) HRTEM and the fast Fourier transform images of a few-layer BN sheet. Scale bar, 2 nm. (e,f) Atomic force microscopy image and corresponding line-scan profile of few-layer BN. (g) XRD patterns of few-layer BN and pristine h-BN.
Thus, NH2 species produced from urea and attached to BN has an average contact angle of 115° resulting in a high dispersibility in water, whereas the pristine BN hydrophilic, with an average observed contact angle of 43° of urea-induced N–H-containing groups render the few-layer BN (B2O3) or boric acid are typically used as a precursor. It is possible synthesis process of h-BN, oxygen-containing boron trioxide B–O bonds may originate from the pristine h-BN. In the exposure of the few-layered BN to ambient environment and the (Fig. 2 and Supplementary Fig. 5b). The high-resolution B 1s and N 1s X-ray photoelectron spectroscopy (XPS) results are shown in Supplementary Fig. 6. In Supplementary Fig. 6a, the component at 190.4 eV corresponds to B–N bonds in h-BN and the shoulder (191.5 eV) should be attributed to the B atoms in B–O bonds formed due to the exposure of the few-layered BN to ambient environment and the hydroxyl groups attached to defects along the edges of h-BN during washing in water after ball milling14,37. In addition, the B–O bonds may originate from the pristine h-BN. In the synthesis process of h-BN, oxygen-containing boron trioxide (B2O3) or boric acid are typically used as a precursor. It is possible that the h-BN particles used in the present study contained small amounts of oxygen. In Supplementary Fig. 6b, the main peak with a binding energy of 398.2 eV in the N 1s spectrum corresponds to N–B bonds in h-BN; a shoulder can be deconvoluted at 399.6 eV corresponding to N–H bonds, which is another evidence of the presence of amino group37. The amount of the attached NH2 groups was evaluated from the thermogravimetric analysis (TGA), which suggests ~1.3 wt% content of NH2 groups in the functionalized h-BN sheets (Supplementary Fig. 7). The presence of urea-induced N–H-containing groups render the few-layer BN hydrophilic, with an average observed contact angle of 43 ± 1° resulting in a high dispersibility in water, whereas the pristine BN has an average contact angle of 115 ± 4° (Supplementary Fig. 5). Thus, NH2 species produced from urea and attached to BN during ball milling are strongly beneficial to the colloidal properties of the few-layer BN, providing stable aqueous dispersions. To confirm this, the pristine h-BN was milled with NaCl, which has previously been used to de-agglomerate nanodiamond38, under the same milling conditions. Compared with the sample milled with urea, there was no apparent water solubility of h-BN after milling with NaCl (Supplementary Fig. 8). This shows the importance of the presence of urea in the mechano-chemical process of exfoliation and functionalization of BN, yielding hydrophilic few-layer BN readily dispersible in water.

Theoretical simulations. Interactions of amino groups with an h-BN monolayer were studied by density functional theory (DFT) calculations. The following sites for the adsorption of NH2 on the h-BN single layer were considered: (1) N atoms at the zigzag edge of BN (Fig. 3a), (2) B atoms at the edge of BN (Fig. 3b), (3) basal-plane N atoms (Fig. 3c) and (4) basal-plane B atoms (Fig. 3d). The corresponding bond lengths and angles, as well as final enthalpy values for the most stable structures of each configuration produced by geometry optimization, are listed in Supplementary Table 1. As expected, due to the dangling bond saturation, the structures where an NH2 group is attached to the zigzag edge of h-BN (Fig. 3a,b) are more stable than the structures where the NH2 is attached to the atoms in the base plane (Fig. 3e). For NH2 attached to an edge N atom (Fig. 3a), there is evidence of additional interactions between H atoms of the amino group and the nearby N atoms, potentially hydrogen bonding, indicated by dashed lines in Fig. 3a. This is supported by an unusually short N–N distance between the N atom of the NH2 and the edge N atom of h-BN, as well as a large H–N–H valence angle of NH2 (Supplementary Table 1). These interactions additionally stabilize the structure. Still, bonding of NH2 to B terminating the edge resulted in the most stable and preferred configuration of the four considered, as shown by the enthalpy of reaction (Fig. 3e).

For both structures with basal attachment of NH2 (Fig. 3c,d), by contrast, the formed bonds are longer (Supplementary Table 1), an indication of steric hindrance to NH2 bonding. The basal B atom bonded to NH2 comes slightly off the BN plane, signifying its transition from planar to tetrahedral bonding. The configuration with NH2 attached to a basal N atom of h-BN is the least energetically stable (Supplementary Table 1) and its formation is unfavourable, as indicated by a positive ΔHf value (Fig. 3e). The H–N–H angle of NH2 in this configuration (Fig. 3c) is close to unbonded NH2 (Supplementary Table 1) and the HNH plane is oriented more in parallel to the h-BN plane in contrast to its nearly perpendicular orientation in another basal configuration (Fig. 3d). These are indicators that NH2 adsorption, not covalent bonding, may be the most probable mechanism in this case. In fact, we observed that in several simulations when the

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![Figure 3](https://example.com/f3.png)

**Figure 3 | Optimized configurations of BN–amine interaction.** (a) An NH2 at the nitrogen edge atom, (b) an NH2 at the boron zigzag edge atom, (c) an NH2 on a basal-plane N atom and (d) an NH2 on a basal-plane B atom. (e) Reaction enthalpies for the different optimized geometries of the configurations (a–d).
NH₂ group was not precisely positioned above the basal N atom, it moved and formed covalent bond with a neighbouring B atom, ending up in a configuration similar to Fig. 3d. Thus, DFT modelling confirms that NH₂ groups can be adsorbed and chemically bonded to h-BN. Most preferred sites for chemical bonding are the edge B and N atoms, with covalent bonding to the edge B atom being the most favourable. On the basal BN plane NH₂ bonding to a B atom is possible, whereas the reaction of NH₂ with a basal N atom is not energetically favourable.

Mechanism of exfoliation and functionalization of h-BN. Based on the above structural characteristics and analysis, as well as DFT calculations, we propose the following mechanism for the one-step exfoliation and functionalization of few-layer BN. The exfoliation process involves two stages.

At the beginning of ball milling, the sizes of pristine h-BN and urea particles are reduced due to the high shear forces and high-energy collisions with the stainless steel balls. In this process, BN and urea particles are thoroughly mixed together and some small urea particles adsorb on the BN surface. The layered BN structure is wedged by the small urea particles, resulting in a slight increase of the interlayer spacing (Supplementary Fig. 9). Some urea molecules may intercalate into the BN structure from the edges of BN layers during high-energy ball impacts. Size reduction and exfoliation were confirmed by the XRD patterns of the products after 20h milling (Supplementary Fig. 9) without washing with water, which show dramatically broadened and less intense (002) diffraction. An excess of urea over BN ensured sufficient exfoliation were confirmed by the XRD patterns of the products after 20h milling (Supplementary Fig. 9) without washing with water.

Mechano-chemical processes powered by the energy of colliding balls lead to decomposition of urea and chemical bonding of NH₂ groups to few-layer BN⁴². This results in the attachment of NH₂ to BN edges and defects, as confirmed by FTIR and XPS spectra and TGA (Supplementary Figs 4, 6 and 7), and prevents restacking of BN sheets. The DFT calculations demonstrate that the NH₂ groups can be adsorbed on the B sites of the BN surface and easily form bonds with the edge B and N sites, rendering few-layer BN hydrophilic and assisting in its stabilization in aqueous dispersions.

BN aerogels and membranes. Functional aerogels and transparent thin membranes¹⁶–¹⁸ have been extensively developed, to exploit the properties of nanomaterials over a wide range of applications. Ultralight BN aerogels and freestanding membranes can be produced by cryo-drying and filtration of few-layer BN suspensions, respectively. A BN aerogel can be easily prepared by a one-step cryo-desiccation of the BN aqueous dispersion (Fig. 4).

The ultralow density of the aerogel was demonstrated by placing it on the delicate spike of a plant (Fig. 4a), as well as adhering to a nearly vertical beaker wall by electrostatic attraction (Fig. 4b). The density of the aerogel was estimated, including the density of the air occupying the pores, to be in the range from 1.4 to 20 mg cm⁻³, depending on the concentration of few-layer BN in the aqueous dispersion. The 1.4 mg cm⁻³ BN aerogel is the lightest reported among BN-based materials and much lighter than many carbon and other aerogels⁴³–⁴⁷. In addition, the Brunauer–Emmett–Teller analysis of low-temperature nitrogen adsorption isotherms shows that the BN aerogel has a high specific surface area of 273 m² g⁻¹ (Supplementary Fig. 10). Barret–Johnner–Halenda calculations give a broad pore size distribution in the range of 2–50 nm. Larger pores were probably present, but they could not be measured by gas adsorption. The heavier sample, with a density of 20 mg cm⁻³, distorted the seed spike more (Fig. 4c). The corresponding SEM investigations revealed that the BN low-density aerogel has a loose 3D structure of pores connected by thin walls, whereas the BN aerogel has larger ‘sheet-like’ structure of thicker connecting walls (Fig. 4d,e). The ultralow weight together with low electrical conductivity and high thermal and chemical stability of BN enable potential applications of these gels in insulation, dielectrics and ultralight materials²⁴.

BN membranes were directly fabricated using vacuum-assisted filtration of the few-layer BN dispersion. The membrane can be readily peeled off from the filter and retains its mechanical properties.

**Figure 4 | BN aerogel.** (a) Photo of an aerogel with a low density (1.4 mg cm⁻³) placed on the spike of a plant. (b) Photo of an aerogel adhering to a beaker wall. (c) Photo of an aerogel of a higher density (20 mg cm⁻³) pressing the spine of a plant. (d,e) SEM images of aerogels with densities of 1.4 and 20 mg cm⁻³, respectively. Scale bars, 2 μm (d,e).
integrity, while being flexible in the freestanding state (Fig. 5a).
This ultrathin membrane is nearly transparent to visible light as shown in Fig. 5b. The optical transparency of the membrane can be attributed to its thickness and the inherently low extinction coefficient of BN in the visible range—in striking contrast to graphene. Furthermore, the thickness of the membrane can be tuned in the range of 0.2–100 μm by filtering the desired quantity of few-layer BN dispersion with a fixed concentration. The optical transmittance of a freestanding membrane (~10 μm thick according to SEM) was measured by ultraviolet–visible–near infrared spectrometer and is shown in Fig. 5b. The membrane completely absorbs ultraviolet light, while retaining high optical transmittance in the visible range above 500 nm and up to 95% transmittance in the near-infrared range. The oscillations in the transmittance in the near-infrared region are a result of the interference of light reflected at the air–membrane and membrane–substrate interfaces. The pronounced and clean interference pattern indicates a relatively smooth surface and uniform thickness of the membrane. These optical properties indicate potential applications of BN membranes for ultraviolet shielding/protection. Moreover, the BN membrane is also fire-resistant and does not burn in the flame of a gas lighter in ambient air (Fig. 5c). BN membranes are much more thermally stable and have a higher resistance to oxidation than any carbon-based material. Figure 5d,e show the top surface and cross-sectional SEM images of the BN membrane. The cross-sectional image, as shown in Fig. 5e, reveals a compact stacking of few-layer BN with uniform thickness (~10 μm).

Photoluminescence spectra. Figure 6 shows the photoluminescence (PL) spectra of a few-layer BN dispersion in water and of a freestanding membrane recorded with an excitation wavelength of 200 nm. As shown in Fig. 6, a strong ultraviolet PL emission peak at 275 nm can be seen in both samples, attributed to deep levels in the band gap from intrinsic B or N defects, which is similar to previously reported results for BN nanosheets, bamboo-like multiwall nanotubes and nanohorns containing bent BN layers. There is a weak peak at ~385 nm, appearing as a shoulder to the main PL peak. This peak may be assigned to impurities (possibly oxygen) or to generic structural defects. The digital photographs (Fig. 6 insets) of the aqueous dispersions and freestanding membranes under 365 nm ultraviolet light further confirm the blue light emission. The strong ultraviolet and blue light emission indicates that few-layer BN dispersions and freestanding membranes may have potential applications in bioimaging, ultraviolet laser emitters and optoelectronic devices.

Discussion
A simple and high-yield process has been developed to fabricate few-layer h-BN with a thickness around 2.5 nm and lateral dimensions mostly below 100 nm. The procedure involves urea-assisted mechanical exfoliation during which mechano-chemical reactions take place at atmospheric pressure and room temperature. The residual urea can be washed away, resulting in a high concentration of well-dispersed few-layer BN in water without
any posttreatment. Ultragraft and freestanding aerogels can be produced by cryodrying of the few-layer dispersions, whereas filtration gives thin, high-quality membranes of controllable thickness. Importantly, the as-obtained few-layer BN dispersions and membranes show strong light emission when excited with an ultraviolet source. The stable colloidal aqueous dispersions of few-layer BN, ultragraft aerogels and freestanding membranes produced in this study may be highly beneficial for a wide range of applications.

Methods

Synthesis. In a typical synthesis, h-BN (Momentive Performance Materials Inc.) and urea (Sigma–Aldrich) were mixed together at the weight ratio 160:1 inside a steel mill using a planetary ball mill (atomixet 7, Frisch) at a rotation speed of 700 r.p.m. for 20 h at room temperature under nitrogen atmosphere. The high rotation speed provides high power and effective exfoliation of h-BN on a large scale. The urea not only assists the exfoliation but also protects the BN from excessive mechanical damage, preventing an extensive formation of lattice defects. The variations in weight ratio (1:20 and 1:100) and milling time (10 and 30 h) were also investigated. The size and thickness of the few-layer BN particles were reduced at lower h-BN:urea weight ratio or longer milling time. The results are shown in Supplementary Table S2. In this study, the weight ratio of h-BN:urea and milling time were fixed at 1:60 and 20 h, correspondingly, to get BN sheets with suitable size and quality. The following preparation of aerogel and membrane. After ball milling, the obtained powders were dissolved in water. The resulting few-layer BN aqueous dispersion was dialysed for 1 week (membrane cutoff: 3,500 kDa) in de-ionized water, to remove the urea. Stable aqueous dispersions were then obtained. For milling of pristine h-BN with NaCl, the same milling conditions were used. XRD and FTIR spectra were recorded to confirm the absence of any traces of urea and NaCl in the few-layer BN. The as-prepared hydrogel was directly dehydrated via a freeze-drying process to maintain the 3D monolith architecture. The BN membrane can be readily fabricated by vacuum filtration of a stable few-layer BN in water suspension through an Anodisc membrane filter (47 mm diameter, 0.22 μm size, Whatman), followed by drying in air and peeling the membrane off the filter.

Materials characterization. XRD measurements were performed on a Panalytical X’Pert PRO apparatus with Cu Kα radiation. SEM analysis was performed on a Zeiss Supra 55 VP SEM instrument. The BN samples were sputtered with carbon before imaging. TEM and HRTEM imaging was performed on a JEOL 2100F microscope operated at 200-kV. Samples were prepared by evaporating a drop of diluted aqueous suspension on a carbon-coated copper grid. The atomic force microscopy measurements were performed on a Cypher atomic force microscope. The FTIR and optical transmittance spectra were recorded using a Nicolet 7199 spectrometer and Cary 5000 spectrophotometer, respectively. XPS was performed using an ESCALAB 250 instrument equipped with a monochromatic Mg-Kα X-ray source for the following preparation of aerogel and membrane. After ball milling, the obtained powders were dissolved in water. The resulting few-layer BN aqueous dispersion was dialysed for 1 week (membrane cutoff: 3,500 kDa) in de-ionized water, to remove the urea. Stable aqueous dispersions were then obtained. For milling of pristine h-BN with NaCl, the same milling conditions were used. XRD and FTIR spectra were recorded to confirm the absence of any traces of urea and NaCl in the few-layer BN. The as-prepared hydrogel was directly dehydrated via a freeze-drying process to maintain the 3D monolith architecture. The BN membrane can be readily fabricated by vacuum filtration of a stable few-layer BN in water suspension through an Anodisc membrane filter (47 mm diameter, 0.22 μm size, Whatman), followed by drying in air and peeling the membrane off the filter.

Theoretical simulations. The analysis of the different geometries was carried out using a pseudopotential plane-wave method within the DFT framework by Accelrys Materials Studio package. The DFT calculations were performed for the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional implemented in CASTEP module of Accelrys Materials Studio. The BN nanoribbon infinite in one direction (labelled c) was constructed using Materials Studio Visualizer. First, a 5,5 BN periodic single wall nanotube was created and the lattice parameters were fixed at 1:60 and 20 h, correspondingly, to get BN sheets with suitable thickness and size. N atoms were exposed on the edge and basal B and N atoms, as well as a cell with just one NH2 group in the center, were constructed. Geometry of all systems was optimized using same settings in CASTEP (no cell optimization, energy cut-off 250 eV, 1 x 1 x 2 k-points on Monkhorst–Pack grid) with convergence tolerance 1.0 x 10−3 eV per atom (energy), 0.03 eV Å−1 (force), 0.05 GPa (stress) and 0.001 Å (displacement). The final energy calculated by CASTEP was used as a measure of the stability of the optimized structures. The enthalpy of reaction of an NH2-BN nanosheet with BN was calculated as ΔH = ΔH_products − ΔH_reagents = ΔH_NH2 − NH2_BN − ΔH2_NH2, where ΔH_NH2 − NH2_BN = the final enthalpy of an h-BN−NH2 structure, ΔH_NH2 and ΔH2_NH2 are enthalpies of h-BN nanoribbon and NH2 group placed in a periodic box of same dimensions and calculated using same settings, respectively.

References

1. Wang, X., Zhi, C., Weng, Q., Bando, Y. & Golberg, D. Boron nitride nanosheets: novel syntheses and applications in polymeric composites. J. Phys. Chem. Lett. 4, 7140–7144 (2013).
2. Liu, D. et al. Multifunctional polymer/porous boron nitride nanosheet membranes for superior trapping emulsified oils and organic molecules. Adv. Mater. Interfaces 2, 1500228 (2015).
3. Wei, L. et al. Oxygen-doped boron nitride nanosheets with excellent performance in hydrogen storage. Nano Energy 6, 219–224 (2014).
4. Chen, Z.-G. & Zou, J. Field emission from ultrathin BN nanosheets proruced from BN fibers. J. Mater. Chem. B 1, 1191–1195 (2013).
5. Uosaki, K. et al. Boron nitride nanosheet on gold as an electrocatalyst for oxygen reduction reaction: Theoretical suggestion and experimental proof. J. Am. Chem. Soc. 136, 6542–6545 (2014).
6. Wei, L., Portehault, D., Liu, D., Qin, S. & Chen, Y. Porous boron nitride nanosheets for effective water cleaning. Nat. Commun. 4, 1777 (2013).
7. Liu, D., Le, W., Qin, S. & Chen, Y. Template-free synthesis of functional 3D BN architecture for removal of dyes from water. Sci. Rep. 4, 4453 (2014).
8. Watanabe, K., Taniguchi, T. & Kanda, H. Direct-bandgap properties and direct-gap band alignment of h-BN. Phys. Rev. B 77, 195421 (2008).
9. Marsh, K. L., Soulman, M. & Kaner, R. B. Co-solvent exfoliation and suspension of hexagonal boron nitride. Chem. Commun. 51, 187–190 (2015).
10. Weng, Q. et al. Highly water-soluble, porous, and biocompatible boron nitride for anticancer drug delivery. ACS Nano 8, 6123–6130 (2014).
11. Liu, D. et al. Scalable exfoliation process for highly soluble boron nitride nanoplatelets by hydroxide-assisted ball milling. Nano Lett. 15, 1238–1244 (2015).
12. Zhi, C., Bando, Y., Tang, C., Kuwahara, H. & Golberg, D. Large-scale fabrication of boron nitride nanosheets and their utilization in polymeric composites with improved thermal and mechanical properties. Adv. Mater. 21, 2889–2893 (2009).
13. Lin, Y., Williams, T. V., Cao, W., Elsayed-Ali, H. E. & Connell, J. W. Defect functionalization of hexagonal boron nanosheets. J. Phys. Chem. C 114, 17434–17439 (2010).
14. Lin, Y. et al. Aqueous dispersions of few-layered and monolayered hexagonal boron nitride nanosheets from sonication-assisted hydrolysis: critical role of water. J. Phys. Chem. C 117, 20298–20305 (2013).
15. Sainsbury, T. et al. Oxygen radical functionalization of boron nitride nanosheets. J. Am. Chem. Soc. 134, 18758–18771 (2012).
16. Hu, H., Zhao, Z., Wu, W., Gogotsi, Y. & Qiu, J. Compressible carbon nanotube–graphene hybrid aerogels with superhydrophobicity and superoleophilicity for oil sorption. Environ. Sci. Technol. Lett. 1, 214–220 (2014).
17. Hu, H., Zhao, Z., Wu, W., Gogotsi, Y. & Qiu, J. Ultralight and highly compressible graphene aerogels. Adv. Mater. 25, 2219–2223 (2013).
18. Weng, Q., Zhao, Z., Degennaro, Y. & Qiu, J. Highly controllable and green reduction of graphene oxide to flexible graphene film with high strength. Mater. Res. Bull. 48, 4797–4803 (2013).
19. Liu, X. F. & Antonietti, M. Mollen salt activation for synthesis of porous carbon nanostuctures and carbon sheets. Carbon 69, 460–466 (2014).
20. Zhang, M., Huang, L., Chen, J., Li, C. & Shi, G. Ultrathin, ultrastrong, and highly conductive graphene films with arbitrary sizes. Adv. Mater. 26, 7588–7592 (2014).
21. Kim, H. W. et al. Selective gas transport through few-layered graphene and oxygen-functionalized graphene oxide membranes. Adv. Mater. 25, 431–435 (2013).
22. Joshi, R. K. et al. Precise and ultrafast molecular sieving through graphene oxide membranes. Science 343, 752–754 (2014).
23. Sun, P. et al. Selective ion penetration of graphene oxide membranes. ACS Nano 7, 428–437 (2012).
24. Zeng, X. et al. Artificial nacre-like papers based on noncovalent functionalized boron nitride nanosheets with excellent mechanical and thermally conductive properties. Nanoscale 7, 6774–6781 (2015).
25. Zeng, X., Ye, L., Sun, R., Xu, J. & Wong, C. Observation of viscoelasticity in boron nitride nanosheet aerogel. Phys. Chem. Chem. Phys. 17, 16709–16714 (2015).
26. Zeng, X. et al. Facile preparation of superelastic and ultralow dielectric boron nitride nanosheet aerogels via freeze-casting process. Chem. Mater. 27, 5849–5855 (2015).
27. Yin, J., Li, X., Zhou, J. & Guo, W. Ultralight three-dimensional boron nitride foam with ultralow permittivity and superelasticity. Nat. Nano. Lett. 13, 3232–3236 (2013).
28. Rousseas, M. et al. Synthesis of highly crystalline sp²-bonded boron nitride aerogels. ACS Nano 7, 8540–8546 (2013).
29. Wang, Y., Shi, Z. & Yin, J. Boron nitride nanosheets: large-scale exfoliation in methanesulfonic acid and their composites with polybenzimidazole. J. Mater. Chem. 21, 11371–11377 (2011).
30. Xie, S.-Y. et al. Solubilization of boron nitride nanotubes. Chem. Commun. 3670–3672 (2005).
31. Jung, S. M., Jung, H. Y., Dresselhaus, M. S., Jung, Y. J. & Kong, J. A facile route for 3D aerogels from nanstructured 1D and 2D materials. Sci. Rep. 2, 849 (2012).
32. Kim, K. S. et al. Hydrogen-catalyzed, pilot-scale production of small-diameter boron nitride nanotubes and their macroscopic assemblies. ACS Nano 8, 6211–6220 (2014).
33. Lei, W., Portehault, D., Dimova, R. & Antonietti, M. Boron carbon nitride nanostructures from salt melts: tunable water-soluble phosphors. J. Am. Chem. Soc. 133, 7121–7127 (2011).
34. Peng, H. et al. Urea-assisted aqueous exfoliation of graphite for high-quality graphene. Chem. Commun. 51, 4651–4654 (2015).
35. Crimp, M. J. D., Oppermann, A. & Krehbiel, K. Suspension properties of hexagonal BN powders: effect of pH and oxygen content. J. Mater. Sci. 34, 2621–2625 (1999).
36. Joni, I. M., Balgis, R., Ogi, T., Iwaki, T. & Okuyama, K. Surface functionalization for dispersing and stabilizing hexagonal boron nitride nanoparticle by bead milling. Colloids Surf. A Physicochem. Eng. Aspects 388, 49–58 (2011).
37. Sainsbury, T. et al. Self-assembly of gold nanoparticles at the surface of amine- and thiol-functionalized boron nitride nanotubes. J. Phys. Chem. C 111, 12992–12999 (2007).
38. Pentecost, A., Gour, S., Mochalin, V., Knose, I. & Gogotsi, Y. Deaggregation of nanodiamond powders using salt- and sugar-assisted milling. ACS Appl. Mater. Interfaces 2, 3289–3294 (2010).
39. Liu, D., Lei, W. & Chen, Y. Scalable production of wrinkled and few-layered graphene sheets and their use for oil and organic solvents absorption. Phys. Chem. Chem. Phys. 17, 6913–6918 (2015).
40. Liu, D., Lei, W., Portehault, D., Qin, S. & Chen, Y. High N-content holey few-layered graphene electrocatalysts: scalable solvent-less production. J. Mater. Chem. A 3, 1682–1687 (2015).
41. Lei, W., Liu, D. & Chen, Y. Highly crumpled boron nitride nanosheets as adsorbents: scalable solvent-less production. J. Mater. Chem. A 3, 1682–1687 (2015).
42. Sun, J. F., Wang, M. Z., Zhao, Y. C., Li, X. P. & Liang, B. Y. Synthesis of titanium nitride powders by reactive ball milling of titanium and urea. J. Alloys Compd. 482, L29–L31 (2009).
43. Li, J. et al. Ultra-light, compressible and fire-resistant graphene aerogel as a highly efficient and recyclable absorbent for organic liquids. J. Mater. Chem. A 2, 2934–2941 (2014).
44. Ji, H. et al. Ultrathin graphite foam: a three-dimensional conductive network for battery electrodes. Nano Lett. 12, 2446–2451 (2012).
45. Chen, Z. et al. Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. Nat. Mater. 10, 424–428 (2011).
46. Worsley, M. A. et al. Mechanically robust 3D graphene macroassembly with high surface area. Chem. Commun. 48, 8428–8430 (2012).
47. Sui, Z., Meng, Q., Zhang, X., Ma, R. & Cao, B. Green synthesis of carbon nanotube–graphene hybrid aerogels and their use as versatile agents for water purification. J. Mater. Chem. 22, 8767–8771 (2012).
48. Wang, Y., Shi, Z. X. & Yin, J. Boron nitride nanosheets: large-scale exfoliation in methanesulfonic acid and their composites with polybenzimidazole. J. Mater. Chem. 21, 11371–11377 (2011).
49. Gu, B. & Wang, H. -T. in Ferroelectrics—Physical Effects. (ed. Lallart, M.) 507–526 (InTech, 2011).
50. Gao, R. et al. High-yield synthesis of boron nitride nanosheets with strong ultraviolet cathodoluminescence emission. J. Phys. Chem. C 113, 15160–15165 (2009).
51. Chen, H. et al. Eu- doped boron nitride nanotubes as a nanometer-sized visible-light source. Adv. Mater. 19, 1845–1848 (2007).
52. Zhu, C. et al. Large-scale fabrication of boron nitride nanohorn. Appl. Phys. Lett. 87, 063107 (2005).
53. Tang, C., Bando, Y., Zhi, C. & Golberg, D. Boron–oxygen luminescence centres in boron–nitrogen systems. Chem. Commun. 4599–4601 (2007).
54. Su, C. -Y. et al. Large-scale synthesis of boron nitride nanotubes with iron-supported catalysts. J. Phys. Chem. C 113, 14732–14738 (2009).
55. Silly, M. G. et al. Luminescence properties of hexagonal boron nitride: cathodoluminescence and photoluminescence spectroscopy measurements. Phys. Rev. B 75, 085205 (2007).
56. Zhong, B. et al. Hollow BN micropherses constructed by nanoplates: synthesis, growth mechanism and cathodoluminescence property. Cryst. Eng. Commun. 13, 819–826 (2011).

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Author contributions

W.W.L. and D.L. conceived the project. W.W.L., D.L. and S.Q. carried out materials synthesis and performed materials characterization. V.M. carried out experiments. W.W.L., D.L. and S.Q. carried out materials synthesis and performed materials characterization. V.M. carried out ab initio simulations. W.W.L., V.M., Y.G. and Y.C. wrote the manuscript. All authors contributed to analysis of the data and discussions of results.

Additional information

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