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Controllable Synthesis Borophene Directly from h-BN layers for High Performance Li-Ion Batteries and Devices

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ABSTRACT: Two dimensional materials and borophene aerogels (BoA) are synthesized by converting hexagonal boron nitride aerogels (hBNAGs). In this approach, borophene grows between h-BN layers utilizing boron-boron (B-B) bridges as a nucleation site. Thus, borophene forms monolayers mixed with sp²-sp³ hybridization. The process is highly generic and suitable for large-scale material processing. Batteries made with the resultant aerogel exhibit superior capacity and fast charging capability. In the future, this technique can be used to engineer superior anode materials with properties.

Electrochemical cells, especially Lithium-ion batteries (LIBs), have revolutionized energy storage and enabled a new era of electronic devices. However, current battery performance cannot sustain the increasing energy and power demands. Its progress predominantly relies on advanced material development of the anode and cathode. Especially, since the development of the anode is progressing very slowly and thereby limiting batteries true potential to achieve high energy and power densities. A new type of two-dimensional (2D) layered material, the 2D boron polymorph (that is, borophene) has merged and is considered a promising anode material.1-2 Borophene is an exceptional anode material due to its high absorption energy of atoms (e.g., the absorption of energy of Li atom on borophene is −1.12 eV)3 and low barrier for ion diffusion (approximately 2.6 meV for Li ion)4, especially, for Li, Na, Mg, and Al. Thus, it can achieve higher specific capacity, energy density and conductivity than any other 2D material. The maximum theoretical storage capacity for the monolayer h-borophene based LIBs is 5268 mAh·g⁻¹, 14 times larger than commercially used graphite-based LIBs (372 mAh·g⁻¹). A similar trend is observed in sodium ion batteries (NIBs) with borophene based NIBs (1860 mAh·g⁻¹) having a three times higher storage capacity than that of graphite-based NIBs (35 mAh·g⁻¹).5,6 Borophene also has a highly anisotropic metallic behavior with high electronic and thermal conductivity. Most borophene polymorphs (2-Pmnn, b12, c3 and honeycomb) are synthesized on noble metal substrates (i.e. Ag (111), Ir (111), etc.) using mainly Chemical Vapor Deposition (CVD) or Molecular Beam Epitaxy (MBE) at high temperatures (above 500 °C).2,7 These growth techniques often yield nanometer-sized domains of a mixture of different polymorphs resulting in undesirable altered electronic and material structures with stability problems for energy storage applications.

Here, we demonstrate a simple conversion method to grow stable borophene aerogels (BoA) using hexagonal boron nitride aerogels (hBNAGs) as a template. To obtain a nucleation site for boron, nitrogen defects (N-defect) were chemically induced to hBNAGs, then converted to boron-boron (B-B) bridges under the high-pressure boron vapor. The process is very generic and an effective way to produce a high-performance anode utilizing borophene/h-BN hybrid aerogels. N-deficient double layer h-BN is also used to grow borophene to produce 2D borophene/h-BN based device geometries.

Figure 1 Sequential images of the Borophene/h-BN aerogels (BoBN) fabrication process
The fabrication process of the borophene aerogels is illustrated in Fig.1. BoA were synthesized starting from precursors of hBNAGs which were prepared similarly to our previous methods.\textsuperscript{8-10} Sol-gel chemistry was used to crosslink graphene oxide, followed by hydrothermal reduction at 900°C to form monolithic reduced graphene oxide (rGO). This way the bonding scheme can be altered to have more stacking, cross-linking, and gelation. Then, samples were subjected to supercritical drying and carbonization under argon and nitrogen, at 1050°C. This way oxygen functional groups were eliminated, and material aromaticity increased. The resulted aerogel was then placed inside an induction furnace under boron oxide (B_2O_3) and nitrogen vapor at 1800°C. During this process, C-C bonds were replaced with B-N with a 1 to 1 ratio and formed hBNAG. Afterwards, hBNAG was submerged into potassium hydroxide (KOH) and urea propanol solution (1:1, v:v) at 600°C. Then the precursors were dried in a vacuum at room temperature. Then, annealed at 600°C for 2h under an Ar environment to form N-defect (Fig 2a). Finally, N-defect hBNAG was merged into a boric acid solution and vacuum dried at 80°C. This sample was then transferred to an induction furnace with boron source (Sigma-Aldrich 99.7% crystalline) and annealed at 1400°C for 4h to form Borophene/h-BN aerogels (BoBN). Borophene only grew on N-defected hBNAG samples, which indicated N-defects create some kind of boron-boron (B-B) bridges as a nucleation site for borophene (Fig. 2b).\textsuperscript{14,15} Thus, borophene can grow between two h-BN sheets in a self-limiting manner and form borophene/h-BN monolayers mixed with sp^2-sp^3 hybridization (Fig. 2c and 2d). We believe volume expansion seen in Figure 1 can be correlated with this nucleation growth, but mechanism is still puzzling. Borophene/h-BN aerogels then turn into powder by selectively grinding and pure sulfur powder is added (aerial mass loading: 2-10mg/cm^2) to the mixture. From this mixture, we used two different techniques, slurry and free-standing, to prepare the electrode materials. The slurry was prepared with conventional methods by mixing 80 wt% of sulfur added Borophene/h-BN aerogels, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The mixed slurry was coated on electropolished Al foil (15μm, Sigma Aldrich) and dried at 60°C overnight. The free-standing binder free electrodes were prepared by adding sulfur added Borophene/h-BN aerogels in DI water and ammonium hydroxide (20 mg to 1mL DI+10% ammonium hydroxide). The solution was then sonicated at room temperature to make sure surface wetting, followed with annealing at 60°C for 48 hours. The resulted mix was further freeze-dried at -50°C at around 2 x 10^4 Torr, to achieve a free-standing BoBN (F-BoBN) aerogel form again (Fig. S1). Coin cells were prepared using standard CR2032 housing with a Celgard 2320 separator soaked in a Li^+ conducting typical electrolyte and Lithium discs ribbons (99.9% Sigma Aldrich, 10mm diameter) as a counter electrode.

The electrochemical behaviors, specific capacity, and cycling performance, of commercial sulfur electrode and BoBN composites were extensively investigated using Biologic BSC-810 and confirmation done by Gamry Reference 3000 potentiostat–galvanostat at the frequency range of 0.1Hz-1000kHz. Figure 3a shows long term cycling performances of the typical electrochemical measurements. It can be clearly shown that BoBN(5:2) cells (Borophene/h-BN, 5:2) with 4 mg/cm^2 sulfur aerial mass loading have better performance than

![Figure 2](image)

**Figure 2** Characterization of BoBN a) PL properties of N-deficient h-BN layers. b) Raman spectroscopy measurements c) XRD patterns, and d) schematic illustration of borophene nucleation and metal-ion intercalation.

![Figure 3](image)

**Figure 3** Electro chemical performances of BoBN with differen borophene to h-BN ratio a) Long-term cycling, b) impedance spectra, c) Rate capabilities
commercial sulfur electrode (CSE), other BOBN, and F-BoBN cells. Long term cycling performance at 0.1C, 500 cycles, shows initial discharge 1398 mAh g\(^{-1}\), 1193 mAh g\(^{-1}\), 1045 mAh g\(^{-1}\), 912 mAh g\(^{-1}\) and 810 mAh g\(^{-1}\) for BoBN(5:2), BoBN(5:1), BoBN(5:3), F-BoBN, and CSE. This implies two things: Borophene based electrodes drastically improve performance of the cell while retain 85% of its initial capacity after 500 cycles and its performance strongly relies on the Borophene/h-BN conversion ratio. The impedance spectra measurement also provides a clear indication of the importance of BoBN reinforcement on cell performances (Fig. 3b). BoBN modified cells, as expected, exhibit better performance. A semicircle and tail were observed in the high- and low- frequency ranges that can be correlated with ionic conductivity and the ion diffusion-controlled process. Medium frequencies can be associated with charge transfer efficiency between electrodes. As it can be clearly seen in Fig. 3b, the cells with BoBN modification exhibit lower impedance and higher ionic conductivity than the cells without any modification. Especially, cells with BoBN(5:2) modification exhibits the best performance with better ionic diffusion and ohmic resistance, as expected. Fig. 3c shows rate performance with and without BoBN modification from 0.1C to 10C. BoBN(5:2), while Fig. S1 shows CV profiles and charge discharge curves at various cycles, providing a clear demonstration of the importance of BoBN modification on cell performance.

After the encouraging battery performance results, we developed 2D borophene/h-BN/graphene based device geometries. The prototype was fabricated by partially converting graphene into hexagonal boron nitrate (h-BN) with high voltage, high power, and short electric pulses (25-50 kV, 20 ns) in Boron and Nitrogen vapor (B\(_2\)O\(_3\)+N\(_2\)) at 900°C (Fig. 4a).

In this conversion, graphene is masked as a trapezoid shape pattern to achieve ballistic transport properties of the graphene, while keeping feature size smaller than the electron mean free path. In the final stage, another h-BN layer is transferred on top of the structure using a high vacuum stamping technique utilizing anodic alumina oxide (Fig. S2). The sample was then annealed in high boron-contained vapor through chemical vapor deposition. Thus, boron atoms interstitially (vertically/diagonally) bonded on top of the h-BN layer, hence, borophene growth can be fostered through these interstitial defect sites by using electrical pulses for conversion in boron and Ar vapor. We believe borophene growth can occur similarly to how BoBN forms from B-B bridges. With this device architecture, we were able to have a small solid-state electrochemical device.

This device architecture works below 268K and exhibits two interesting phenomena: coulomb blockage and expected ballistic transport. We believe coulomb blockage is a key feature that prevents electron tunneling, however, it requires low temperatures to prevent thermal fluctuations and keep tunneling resistance higher than quantum resistance. To measure the electro chemical performance an ionic quid is dropped on top of the device. It can be seen from I-V characteristics that electron tunneling is not permanent up to 268K, afterwards, the coulomb blockage threshold lowers, and subthreshold current occurs (Fig. 4b). Coulomb diamonds with respect to difference conductance can be seen in Fig. S3. Fourier transport measurements are also indicated for ballistic transport that can be seen with positive to negative resistance transition, diffusive to ballistic, which is in line with the literature (Fig. 4c). Also, four-probe resistivity measurements carried out to determine mobility, \(\mu = 1/\rho \cdot \sigma\). 205,000 cm\(^2\) V\(^{-1}\) s\(^{-1}\) is achieved as a peak mobility at 270K (Fig. S4). Also, temperature dependence of ballistic negative diffraction resistance can be seen in Fig. S5.

In summary, we demonstrated a new method to grow borophene aerogels utilizing hexagonal boron nitride as a template. We successfully implemented BoA material to the battery cell framework to enhance the specific capacity of Li-S.
batteries. The cells with the BoBN modification display higher performance (1406 mAh g⁻¹) up to allowing for better specific capacity and better ionic diffusion, as predicted in the literature. However, this improvement critically depends on the loading ratio of BoBN in the electrode structure. In addition to 3D structures, 2D borophene/h-BN based device geometries are developed by inducing coulomb blockade and ballistic transport. We believe these two-quantum phenomenon can lead battery operation distances to sub-nanometer level. We believe, this technology may be one of the key elements to implement borophene into battery production to achieve superior batteries in the future.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website as PDF, includes detailed information about the additional synthesis and electrical characterization. The Supporting Information is available free of charge on the ACS Publications website.

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ABBREVIATIONS
OE, electrical measurements and design

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