Low-temperature Liquid Exfoliation of Milligram-scale Single Crystalline Few-layer $\beta_{12}$-Borophene Sheets as Efficient Electrocatalysts for Lithium–Sulfur Batteries

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Article

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Abstract

Two-dimensional (2D) borophene is predicted as an ideal electrode material for lithium sulfur (Li-S) batteries because of low-density, metallic conductivity, high Li-ion surface mobility and strong interface bonding energy to polysulfide. But until now, 2D borophene-based Li-S batteries have not yet been achieved due to the absence of massive synthesis method. Herein, we developed a novel low-temperature liquid exfoliation (LTLE) method for scalable synthesis of single crystalline 2D few-layer $\beta_{12}$-borophene sheets with a $\text{C}_{\text{12}}$ symmetry. The as-synthesized 2D sheets were used as the polysulfide immobilizers and electrocatalysts of Li-S batteries for the first time. The resulting Li-S cells employing borophene sheets delivered a strikingly high areal capacity of 5.2 mAh cm$^{-2}$ at a high sulfur loading of 7.8 mg cm$^{-2}$ with an ultralow capacity fading rate (0.039 % per cycle) in 1000 cycles, outperforming most of the Li-S batteries employing other 2D materials. Under the help of few-layer $\beta_{12}$-borophene, their high-activity behaviors should be attributed to the significant enhancement of both the Li-ion’s surface migration and the adsorption energy for Li$_2$S$_n$ clusters based on density functional theory (DFT) models. Our research reveals great potential of 2D $\beta_{12}$-borophene sheets in future high-performance Li-S batteries.

Introduction

The rapid development of electrochemical energy storage devices in the fields of electric vehicles, portable electronic devices and large-scale smart power grids continuously drive the researchers to explore lower cost, higher energy density, and better safety batteries than current lithium-ion batteries$^{1-4}$. Among many candidates, lithium sulfur (Li-S) batteries have been gaining the global attention due to their overwhelming energy density (2600 Wh kg$^{-1}$), natural abundance and environment-friendly of sulfur feedstock$^{5-9}$. However, the existence of internal polysulfide shuttling, large volume expansion of sulfur and sluggish redox kinetics inevitably lead to the sharp deterioration of the electrochemical performances of Li-S batteries$^{10-12}$.

Considering the irreversible loss and inefficient utilization of sulfur cathodes, much effort has been devoted to the design of advanced materials for immobilizing and activating sulfur materials, such as transitional-metal oxides$^{13,14}$, sulfides$^{15-17}$, carbides$^{18-20}$, metal nitrides$^{21-23}$ and heterostructures$^{24-26}$. Recently, two-dimensional (2D) materials with strong in-plane covalent bonds and weak interlayered van der Waals (vdW) forces have been intensively studied because of their superior advantages over traditional bulk materials for Li-S cell applications$^{27,28}$. 2D materials such as siloxane$^{29}$, black phosphorene$^{30,31}$, BN$^{32,33}$, C$_3$N$_4$ $^{34,35}$, and MXene$^{36,37}$, were found to exhibit excellent catalytic activities towards polysulfides because of their extraordinary surface properties. However, most of these 2D material-based Li-S cells still have some disadvantages, such as low capacity$^{38}$, slow charge-discharge rate$^{39,40}$, structure instability$^{38,41}$, and poor cyclic stability$^{32}$. Hence, the design and development of novel 2D materials are highly demanded towards high-performance Li-S batteries with large catalytic activity, high-efficient adsorption, fast conversion of polysulfides and long-term durability.
As a typical 2D Dirac material consisted of the lightest solid element, 2D borophene with unique surface configuration and complex multicenter-two electron bonds has been earlier predicted as an ideal electrode material for Li-S batteries due to its native metallic conductivity\(^42\), large elastic modulus\(^43\), heavy anisotropy\(^44\), high Fermi velocity (\(6.6\times10^5\) m/s)\(^45\), excellent thermal and chemical stability\(^46\), large Li-ion surface mobility as well as strong bonding energy to polysulfide clusters\(^47\). However, borophene-based Li-S cells have not yet been achieved for practical use so far owing to the absence of a facile route for the scalable production of 2D borophene nanomaterials.

In this work, we developed a low-temperature liquid exfoliation (LTLE) strategy for scalable production of single crystalline borophene sheets as efficient polysulfide electrocatalyst for Li-S batteries. Few-layer 2D borophene sheets with \(\beta_{12}\)-phase were thus identified with an average flake size of \(\sim3\) \(\mu\)m and an ultrathin thickness less than 10 atomic layers. The \(\beta_{12}\)-borophene sheets exhibited extraordinary performances as efficient immobilizer and electrocatalyst for advanced Li-S batteries, showing excellent rate performance of 721 mAh g\(^{-1}\) at 8 C (1 C = 1675 mAh g\(^{-1}\)) and an ultralow decay rate of less than 0.039 % in 1000 continuous cycling measurements. More impressively, the areal capacity can arrive as high as 5.2 mAh cm\(^{-2}\) at a large sulfur loading of 7.8 mg cm\(^{-1}\) in lean electrolyte with a ratio of electrolyte to sulfur (E/S) ratio of 6.8 ml g\(^{-1}\). Our work suggests that single crystalline few-layer borophene sheets hold great potential for high-efficiency Li-S batteries.

**Results And Discussions**

The LTLE synthesis process of few-layer borophene sheets is schematically illustrated in Fig. 1a. By optimizing the sonication power and solvent concentration, massive production of 2D borophene sheets has been successfully achieved. N-methyl pyrrolidone (NMP) was found to be the most effective among a series of solvents adopted in our experiment, as seen in Supplementary Figs. 1 and 2. The color of the product solution is dark-brown or dark-black in Fig. 1b, varying with the sheet concentration. Moreover, the mass of 2D sheets reaches as high as 10 mg and their yield is over 20 %, evidently increased compared with previous reports (\(\leq10\) %\(^{48,49}\)). The low-temperature approach is thus believed to improve the exfoliation efficiency of non-layered bulk materials, because of which significantly enhances the anisotropy discrepancy between the in-plane and out-of-plane covalence bonds\(^50\). Scanning electron microscope (SEM) and atomic force microscope (AFM) images of the as-grown products are respectively in Fig. 1c, d, where ultrathin 2D borophene sheets are observed to have an edge length of 2 ~ 5 \(\mu\)m and exhibit uniform and smooth appearance. The thickness of 2D sheet is observed to be only 1.32 ~ 2.32 nm, suggesting its ultra-thin nature.

X-ray diffraction (XRD) pattern of 2D borophene sheets (Supplementary Fig. 3) shows the same characteristic diffraction pattern as that of the theoretically calculated \(\beta_{12}\)-borophene using density functional theory (DFT), clearly different from that of the bulk \(\beta\)-rhombohedral boron powder (JCPDS No. 00-031-0207). As seen in Fig. 1e, the X-ray photoelectron spectrum (XPS) of B 1s core level is consisted of two characteristic components, attributed to the B-B species at 187.5 eV\(^51\) and the B-O species at 189.1
eV\(^{52}\), respectively. And the molar ratio of the B-B to B-O species is estimated to be more than 94 %, suggesting a majority of pure boron composition in 2D borophene sheets. The minor B-O species are supposed to originate from the edge oxidation of borophene sheets during the short exposure to the air after being taken out for XPS measurements (Supplementary Fig. 4)\(^{52}\).

Raman spectroscopy was employed to better differentiate the 2D borophene sheets from the bulk boron powders\(^{53,54}\). Four Raman peaks of 2D borophene sheets are clearly identified (Fig. 1f) as the fingerprints of \(\beta_{12}\) phase\(^{55}\), differing from those of bulk boron with \(\beta\)-rhombohedral phase. Accordingly, the strong peak at ~ 268 cm\(^{-1}\) is ascribed to the out-of-plane bending vibration mode of \(\beta_{12}\) phase\(^{55}\). And the other peaks at ~ 423, ~901 and ~1017 cm\(^{-1}\) are respectively indexed as the , and modes, resulting from the in-plane stretching modes of \(\beta_{12}\) phase\(^{55}\).

Transmission electron microscopy (TEM) was performed to determine the surface configuration of 2D borophene sheets. A typical TEM image in Fig. 2a exhibits a similar planar morphology in line with the aforementioned SEM and AFM results (Fig. 1c, d). Close examination (Fig. 2a inset) reveals an ultrathin thickness of only 6 atomic layers with an adjacent planar distance of 5.1 Å. The high-resolution TEM (HRTEM) image further verifies high-quality single crystal nature of 2D borophene sheets. As shown in Fig. 2b, the 2D borophene sheets are found to have a hexagonal honeycomb lattice with a perfect planar periodicity of \(a = b \approx 2.76\) Å and the intersection angle \(\theta\) of about 120° in the unit cell. Based on the DFT calculations, we thus propose a novel allotrope with symmetry (referred to as \(\beta_{12}\)-B\(_5\)) for few-layer \(\beta_{12}\)-borophene sheets, where there are 5 boron atoms in a unit cell (Fig. 2c). In this model, both of the lattice constants \((a\) and \(b\)) of few-layer borophene are 2.83 Å and the angle \(\theta\) between \(a\) and \(b\) vectors is equal to 120°, which are in good agreement with the HRTEM results (Fig. 2b). Based on the theoretical model, the bright contrasts in the HRTEM image (Fig. 2b) thus correspond to the six-member rings of the boron honeycomb lattice (Fig. 2c). Besides, the layer distance of adjacent (001) planes is theoretically calculated to be about 5.0 Å for \(\beta_{12}\)-B\(_5\) borophene, nearly identical to the experimental results (5.1 Å) measured by TEM. Statistically, the thickness of most of the 2D sheets is less than 5 nm. (Supplementary Fig. 5a). Therefore, the atomic layer numbers of the as-synthesized borophene sheets should be less than 10, unveiling the ultrathin nature of few-layer borophene. In addition, the 2D \(\beta_{12}\)-borophene sheets are thermodynamically stable as evidenced by the absence of any negative frequency in the entire Brillouin zone (Fig. 2d) according to the density functional perturbation theory (DFPT). Similar calculations are carried out on the (104) plane (Supplementary Fig. 5), which are also in good agreement with our experimental results. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX) mapping (Fig. 2e-h) images also reveal a uniform distribution of boron element across the 2D sheet with a pure boron content over 98 %, which is in good consistent with the electron energy loss spectrum (EELS) (Supplementary Fig. 5b).

Based on all characterizations mentioned above, we can thus conclude that single crystalline few-layer borophene sheets with \(\beta_{12}\)-B\(_5\) phase were successfully synthesized using LTLE. In comparison with other
synthetic methods summarized in Supplementary Table 1, our route is thus low-cost, facile and high-efficient for scalable production of single crystalline $\beta_{12}$-borophene sheets towards practical applications such as Li-S battery.

To demonstrate the catalytic activity of few-layer $\beta_{12}$-borophene sheets for Li-S battery, the potentiostatic experiments were carried out to monitor the liquid-solid conversion in the nucleation and growth of Li$_2$S from polysulfides. The galvanostatic discharge was respectively performed on CNT/$\beta_{12}$-borophene (CNT/B) and bare CNT hosts at 2.05 V, in which 0.01 V overpotential was used to induce the generation of Li$_2$S. All the cells reached the highest potentiostatic current after about 1000 s, but the nucleation abilities of Li$_2$S were found to be completely different, causing a capacity of 193 mAh g$^{-1}$ and 72 mAh g$^{-1}$ for CNT/B and CNT electrodes, respectively (Fig. 3a). Besides, the dissolution ability of solid Li$_2$S was also remarkably promoted by the implantation of few-layer $\beta_{12}$-borophene. After the fully conversion of sulfurs into Li$_2$S, the Li$_2$S dissolution was kinetically evaluated by using a potentiostatic charge process. Clearly, a larger oxidation current was detected on CNT/B (0.13 mA cm$^{-2}$) enabled cell in comparison with bare CNT electrode (0.11 mA cm$^{-2}$), unveiling the excellent electrocatalysis behaviors of 2D $\beta_{12}$-borophene in enhancing the dissolution of Li$_2$S (Fig. 3b).

To gain insight into the enhancement effect of $\beta_{12}$-borophene sheets on the liquid-liquid conversion process (Li$_2$S$_y$ to Li$_2$S$_x$, $8 \geq x \geq 2$, $8 \geq y \geq 2$), Li$_2$S$_8$ symmetric cells were employed for the cyclic voltammetry (CV) measurements. The CNT/B-based cell yielded a higher redox current than the bare CNT-based cell, suggesting enhanced reactivity of the polysulfide on $\beta_{12}$-borophene interface (Fig. 3c). The kinetic-regulating role of $\beta_{12}$-borophene was subsequently demonstrated in actual Li-S batteries. The CV curves of the as-assembled Li-S batteries exhibited two typical redox peaks, corresponding to the formation of soluble polysulfides (2.2–2.4 V) and solid Li$_2$S (2.0–2.1 V), respectively. And the two overlapped anodic peaks (2.4–2.6 V) were attributed to the sequential oxidation of Li$_2$S and polysulfides$^{29}$. In contrast with the Li-S battery using non-undecorated CNT electrode, the Li-S battery using CNT/B electrode possessed higher current density (Fig. 3d). As shown in Fig. 3e, the Tafel plots of the first oxidation process of the cells using CNT and CNT/B were respectively 57 and 29 mV dec$^{-1}$, where the smaller Tafel slope of the CNT/B-based cell suggests that the $\beta_{12}$-borophene induces higher surface reaction rates. In addition, the simulated interfacial impedance of the Li-S cells sharply decreased from 41.2 $\Omega$ to 24.9 $\Omega$ when the electrodes changed from CNT to CNT/B (Fig. 3f), reflecting the $\beta_{12}$-borophene was more favorable for the interface electrochemical reactions$^8$.

Considering the distinguished electrocatalytic reactivity and polysulfide interactions of the CNT/B-based Li-S battery in the sulfur redox reactions, their actual working performances were further evaluated by regarding the bare CNT-based Li-S battery as a reference. In our experiments, the same amount of polysulfide (Li$_2$S$_8$) solution was added as active material (Supplementary Fig. 6). As seen in Fig. 4a, the CV profiles of CNT/B-based battery overlap each other and exhibit excellent reversibility in the redox process, revealing the high-efficiency utilization of sulfur. The galvanostatic charge/discharge profiles are
shown in Fig. 4b. The high reversible specific capacities of 1329, 1236, 1159, 1057, 993, and 919 mAh g\(^{-1}\) were obtained at 0.3, 0.5, 1, 2, 3, and 5 C rates (1 C = 1675 mAh g\(^{-1}\)), respectively. Even if the current density increased to 8 C, the CNT/B-based Li-S battery still remained an ultrahigh capacity of 721 mAh g\(^{-1}\). More significantly, after returning current density back to 0.3 C, a reversible capacity of 1216 mAh g\(^{-1}\) recovered immediately with a columbic efficiency of nearly 100% (Fig. 4c). By contrast, the battery using bare CNT electrode exhibited inferior rate performances, such as a lower initial capacity of 981 mAh g\(^{-1}\) at 0.3 C and a rapider degradation into 394 mAh g\(^{-1}\) with the increase of capacity to 8 C as well as unsatisfactory capacity restoration after high-rate test (Fig. 4c). As shown in Fig. 4d, the CNT/B-based battery possessed a much lower polarization voltage of 188 mV than the CNT-based battery (217 mV), further revealing the outstanding catalytic property of \(\beta_{12}\)-borophene sheets for polysulfide conversion. The CNT/B cathode also exhibited excellent cycling stability at current density of 0.5 C, as found in Fig. 4e. The capacity fading rate was only 0.003% per cycle and kept nearly unvaried after 300 cycles when the initial capacity of the CNT/B-based Li-S battery was 1110 mAh g\(^{-1}\). Moreover, the CNT/B-based cell maintained a high coulombic efficiency of \(~100\%\) in continuous 300 cycle measurements. On the contrary, the bare CNT-based cell delivered a low capacity of 918 mAh g\(^{-1}\) and sharply decreased to 394 mAh g\(^{-1}\) after 300 cycles, resulting in a fast-fading rate of 0.2% per cycle (Fig. 4e and Supplementary Fig. 7). In addition, both of the high- and low-plateau capacities of CNT/B electrode were much better than bare CNT electrode, demonstrating few-layer \(\beta_{12}\)-borophene sheets can effectively suppress the polysulfide diffusion and improve the polysulfide immobilization (Supplementary Fig. 9). Moreover, high areal sulfur loadings of 5.3 mg cm\(^{-2}\) and 7.8 mg cm\(^{-2}\) with low E/S ratios of 9.8 and 6.8 ml g\(^{-1}\) were respectively performed on the Li-S batteries to test the high-energy density behaviors. It was noted that the areal capacities of the CNT/B-based Li-S cells can reach up to 4.6 and 5.2 mAh cm\(^{-2}\) when the capacities respectively adopted 871 and 661 mAh g\(^{-1}\) (Fig. 4f), which were much higher than those of 4.0 mAh cm\(^{-2}\) for commercial Li-ion batteries\(^{57}\). Impressively, the CNT/B-based battery could preserve an enough high reversible capacity of 572 mAh g\(^{-1}\) with an extremely-low capacity decay rate of 0.039% per cycle after 1000 long-term cycles, reflecting excellent cycling stability (Fig. 4g and Supplementary Fig. 8). Notably, the ultralow decay rate and ultrahigh rate performance of 2D \(\beta_{12}\)-borophene sheets are superior to most of other 2D material-based Li-S batteries (Supplementary Table 2), such as phosphorene (785 mAh g\(^{-1}\) at 3 C, decay rate of 0.053% for 1000 cycles)\(^{30}\), C\(_3\)N\(_4\) (340 mAh g\(^{-1}\) at 4 C, decay rate of 0.5% for 200 cycles)\(^{58}\), and graphene (700 mAh g\(^{-1}\) at 2 C, decay rate of 0.5% for 70 cycles)\(^{59}\).

Finally, we calculated the adsorption energy of soluble polysulfides on a monolayer \(\beta_{12}\)-borophene using DFT calculation to comprehend the improvement mechanism of \(\beta_{12}\)-borophene sheets on Li-S batteries, as observed in Supplementary Fig. 10. Figure 5a gives the optimized configurations of S\(_8\) and Li\(_2\)S\(_n\) on monolayer \(\beta_{12}\)-borophene sheet. Based on the DFT calculations, S\(_8\) has the weakest adsorption energy on borophene of only 1.23 eV among all configurations, and the adsorption energy gradually increases with the progression of the polysulfides’ lithiation and eventually arrives at 3.8 eV for the fully-lithiated Li\(_2\)S.
The adsorption energy of polysulphides on \( \beta_{12}\)-borophene is far higher than that on CNT (below 1 eV), unveiling that \( \beta_{12}\)-borophene can anchor polysulphide and inhibit the shuttle of lithium polysulphide more effectively than CNT. Figure 5c shows the typical partial density of states (PDOS) of \( \text{Li}_2\text{S}_4 \) on monolayer \( \beta_{12}\)-borophene, and more details can be seen in Supplementary Fig. 11. The 2p orbital electrons of \( \text{Li}_2\text{S}_4 \) and \( \beta_{12}\)-borophene were found to overlap near the Fermi level, suggesting the formation of a strong chemical bonding between \( \beta_{12}\)-borophene and \( \text{Li}_2\text{S}_4 \) cluster. This is probably originated from a strong charge transfer of 0.22 e from \( \beta_{12}\)-borophene to \( \text{Li}_2\text{S}_4 \) cluster (Fig. 5d) based on the charge density difference and Bader charge analysis. The strong chemical interaction between \( \beta_{12}\)-borophene and \( \text{Li}_2\text{S}_4 \) cluster can be also ascertained because the dark-yellow color of \( \text{Li}_2\text{S}_4 \) solution will gradually attenuate with the increase of the mixing time with \( \beta_{12}\)-borophene (Supplementary Fig. 12).

Furthermore, the diffusion barrier of \( \text{Li}^+ \) on \( \beta_{12}\)-borophene was deduced to be only 0.10 eV (Fig. 5e), much lower than that (0.28 eV) on CNT (Supplementary Fig. 13). The enhanced surface migration of \( \text{Li}^+ \) on borophene would further accelerate the nucleation and decomposition of \( \text{Li}_2\text{S}_n \) and thus improves the capacity and charge-discharge rate of Li-S battery.

In summary, we have developed a novel, facile and high-yield LTLE strategy to produce single crystalline few-layer \( \beta_{12}\)-borophene sheets. As promising 2D electrode materials, the \( \beta_{12}\)-borophene sheets were firstly used as efficient polysulphide-conversion electrocatalysts for Li-S batteries. Due to the usage of few-layer \( \beta_{12}\)-borophene sheets, the CNT/B-based Li-S batteries exhibited a high areal sulfur loading of 5.2 mgh cm\(^{-2}\) at 7.8 mg cm\(^{-2}\) under a low E/S ratio of 6.8 ml g\(^{-1}\) at 0.3 C. Compared with the CNT-based Li-S cell, the CNT/B-based Li-S cell exhibited a better rate performance of as high as 721 mAh g\(^{-1}\) at 8 C and a much lower decay rate of only 0.039 % in 1000 cycles. By DFT calculations, \( \beta_{12}\)-borophene had a lower surface diffusion barrier of Li ion and a stronger adsorption for \( \text{Li}_2\text{S}_n \) clusters than CNT, which can effectively inhibit the shuttle effect of polysulphides and accelerate their decomposition at the same time. These should be responsible for the extraordinary catalytic activity of \( \beta_{12}\)-borophene towards polysulphides in the CNT/B-based Li-S cell. Therefore, our strategy will pave a new way for the design of high-energy rechargeable batteries through the exploration of 2D boron-based nanomaterials.

**Methods**

**Synthesis of few-layer \( \beta_{12}\)-borophene sheets.** The low-temperature liquid exfoliation (LTLE) method was firstly developed to synthesize \( \beta_{12}\)-borophene sheets at milligram scale by using boron powder (99.8 %, Zhongnuo Incorp., China) as source materials. Firstly, 20 ~ 50 mg boron powers were added into 50 ml N,N-Dimethylformamide (NMP, 99.9 %, Innochem. Incorp., China) to form uniform and well-dispersed solution by several minutes’ stirring, as seen in Figure S1. Secondly, the boron-power solution was transferred into the ethanol path and treated at -20~-25 °C in the tip-type ultrasonicator equipped with cooling system (SXSONIC Incorp., China), where the ultrasonic power was kept at 800 W and the treatment lasted for 4 ~ 8 h. Thirdly, the product solution was statically settled at room temperature for 48 ~ 72 h to enough precipitate the undissolved boron powder. Finally, the suspension was centrifuged at...
about 10000 ~ 11000 revolutions per minute (rpm) for 30 minutes to obtain solid products. After the above synthesis process, the mass of the collected 2D sheets was ranging from 4 to 10 mg. Accordingly, the yield of 2D few-layer borophene by LTLE way can reach as high as over 20 %, which is much higher than those by many other methods in previous reports (Supplementary Table 1) 48,49.

**Material characterizations.** The morphology of β12-borophene sheets was investigated by SEM (Zeiss Supra 60) and AFM (Bruker Dimension Fastscan). XPS (Thermofisher Nexsa), XRD (D-MAX 2200 VPC) and Raman spectroscopic (inVia Reflex, 532-nm laser) were respectively used to analyze the chemical compositions of the sample. UV-vis spectroscopy (UV-3600) was applied to determine the energy-band structure and absorption coefficient of β12-borophene sheets. TEM and HRTEM (FEI Titan 80−300) were employed to ascertain the lattice structure of the product. The STEM and elemental mapping were performed on a JEM ARM200F thermal-field emission microscope with a probe Cs-corrector working at 200 kV. For the HAADF imaging, the convergence angle of ~ 23 mrad and collection angle range of 68 ~ 174 mrad were adopted for the incoherent atomic number imaging. Both the elemental composition and distribution were analyzed on the energy dispersive X-ray analyzer (EDS, EX-230 100m² detector) equipped with the microscope.

**Preparation of Li₂S₈ catholyte.** The sources of sulfur and Li₂S with a molar ratio of 7:1 were put into an appropriate amount of 1 mol l⁻¹ lithium bis (trifluoromethanesulfonyl) imide (LiTFSI). Secondly, the LiTFSI solution was added into the mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (volume ratio (v:v): 1:1). Thirdly, 1 wt.% LiNO₃ was used as additive by vigorous magnetic stirring at 50 °C until the sulfur powder were fully dissolved. The concentration of Li₂S₈ was ranging from 0.15 to 2 mol l⁻¹.

**Fabrication of CNT electrodes.** 5 g commercial multiwalled CNT (length ~ 50 nm, Aladdin, China) powders were dispersed into 50 ml Triton X-100 aqueous solution (0.01 wt.%, Secco Romeo, China) to form uniform and homodisperse solution by ultrasonication for 2 h. Subsequently, the obtained CNT solution was filtered through nylon film under vacuum. After three-time washing by deionized water and drying for 2 h at 60 °C in vacuum oven, the free-standing CNT paper was peeled from the nylon film. Finally, the obtained CNT paper was cut into desired disks as the free-standing electrode.

**Assembly of symmetric cells for kinetic evaluation of polysulfide conversion.** CNT/B (with a mass loading of about 1 mg β12-borophene sheets) or bare CNT electrodes were used as both working and counter electrodes. And 40 µl catholyte (0.5 mol l⁻¹ Li₂S₆ and 1.0 mol l⁻¹ solution of LiTFSI with 1 wt.% LiNO₃ in DOL and DME, v/v = 1:1) was added into each coin cell. The CV behaviors of the symmetric cell were tested at a scan rate of 10 mV s⁻¹, in which the voltage window ranged from −0.8 to 0.8 V.

**Measurement on the nucleation and dissolution of Li₂S.** The CNT/B or CNT film electrodes were used as cathodes and Li foils were employed as the anodes. Also, 20 µl Li₂S₈ solution (0.15 mol l⁻¹) was applied as catholyte, and 20 µl electrolyte without Li₂S₈ was used as anolyte. For the nucleation and growth of
Li$_2$S, the assembled cells were first discharged galvanostatically to 2.06 V at 0.112 mA, and then discharged potentiostatically to 2.05 V until the current dropped to below $10^{-5}$ A. The deposition capacities of Li$_2$S were calculated according to the Faraday's law. For the Li$_2$S dissolution, the assembled cells were firstly galvanostatically discharged to 1.80 V at 0.10 mA, and subsequently galvanostatically discharged to 1.80 V at 0.01 mA for fully transforming sulfur species into solid Li$_2$S. Then the cells were potentiostatically charged at 2.40 V to oxidize Li$_2$S into soluble polysulfides. The potentiostatic charge was accomplished when the charge current was below $10^{-5}$ A.

**Assembly and performance evaluation of Li–S cells.** CR-2016 coin cells were assembled in an argon-protected glove box, where the CNT/B or CNT films were employed as the cathodes and 20 µl Li$_2$S$_8$ catholyte was dropped onto the CNT film as the sulfur cathode. Also, Li foil was applied as the counter electrode, and 1.0 M solution of LiTFSI with 1 wt.% LiNO$_3$ in DOL and DME ($\nu/\nu = 1:1$) was used as the electrolyte. In experiments, the common areal loading of sulfur was about 1 mg cm$^{-2}$, and the electrolyte/sulfur ratio was fixed at 15 µl mg$^{-1}$. The electrochemical performances of Li–S batteries were measured by a LANDCT2001A analyzer, where the voltage interval ranged from 1.7 to 2.8 V. And the cyclic voltammograms (CV) curves were collected at 0.1 mV s$^{-1}$ on a CHI-760E electrochemical workstation (Chenhua Instrument, Shanghai), in which EIS analysis was in the range of 10 kHz-0.01 Hz.

**Theoretical model of few-layer $\beta_{12}$-borophene sheets.** All the calculations except superconducting properties were carried out using Vienna *ab initio* simulation package (VASP 5.4) with projector augmented wave (PAW) pseudopotential method and Perdew-Burke-Ernzerhof (PBE) functional. Both lattice parameters and atomic positions were optimized by conjugate gradient method, and the convergence criteria for energy and force were eV and eVÅ$^{-1}$, respectively. The kinetic energy cutoff for plane waves was set at 450 eV. The Brillouin zones were sampled with Å$^{-1}$ spacing in reciprocal space by the Monkhorst-Pack scheme. The high symmetry K-points for band structure and phonon dispersion curves were generated by AFLLOW package. And Grimme's DFT-D3 van der Waals corrections with the Becke-Jonson damping was employed. The phonon spectrum was calculated by DFPT method implemented in Phonopy program. Also, the crystal structures were visualized by VESTA package.

**Computational methods of the adsorption energy of few-layer $\beta_{12}$-borophene.** First-principle calculations were implemented using VASP software package. The PBE functional of generalized gradient approximation (GGA) was used for the exchange-correlation. The basis set utilized PAW pseudopotential method, and the energy cutoff was set at 400 eV. The self-consistent field (SCF) tolerance was eV and the force convergence criterion for atomic relaxation was 0.02 eV Å$^{-1}$. A Monkhorst-Pack k-point mesh with different sizes was chosen to meet various requirements, where is for the geometrical relaxation, is for the calculation of electronic structure and is for the calculation of adsorption. The vdW forces between Li$_2$S$_n$ and $\beta_{12}$-borophene sheet or CNT were accurately obtained by the DFT-D3 method. The supercell of $\beta_{12}$-borophene and
CNT was used for the adsorption energy and CI-NEB calculations, respectively. The adsorption energy ( ) was derived using the following equation:

\[ E_{\text{sub}} - E_{\text{Li}_2S_8/S_8}, \]

In this equation, \( E_{\text{sub}} \), \( E_{\text{Li}_2S_8/S_8} \), and \( E_{\text{sub@Li}_2S_8/S_8} \) represent the energy of free \( \beta_{12} \)-borophene or CNT supercell substrate, the energy of free \( \text{Li}_2S_8 \) or \( S_8 \) species, and the energy of \( \beta_{12} \)-borophene or CNT substrate after the adsorption of polysulphide species, respectively. Positive energy values suggest the kinetically stable adsorption of \( \text{Li}_2S_n \) or \( S_8 \) on the substrate, and higher adsorption energy implies the adsorption sites are energy favorable.

**Data availability**

The authors declare that all the data supporting the findings of this study are available within the article and its Supplementary Information or from the corresponding authors upon reasonable request.

**Declarations**

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**Author contributions**
B. Y., Z. -S. W. and F. L. proposed and supervised the projects. H.J.L. synthesized the borophene sheets, and characterized their surface morphology and chemical compositions. H. D. S. fabricated the CNT- and CNT/B-based Li-S batteries, and carried out the electrochemical measurements. Z. W. carried out the TEM analysis of the borophene sheets and calculated the adsorption energies of Li$_2$S$_n$ clusters on monolayer borophene or CNT by DFT model. Y. W. M. proposed the DFPT model of the surface configuration of the $\beta_{12}$-borophene. H. J. L., H. D. S, Z. W., Y. W. M., S. D. L., B. Y., Z. -S. W. and F. L. wrote the paper. All the authors involved in the analysis and discussion of the experimental results. And all authors approve to submit the final version of the manuscript.

Additional information

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References


**Figures**
Figure 1

Synthesis process and characterization of 2D few-layer borophene sheets. (a) Schematic diagram of the LTLE process of 2D few-layer borophene sheets. (b) Photograph of 2D borophene sheets in NMP solution. (c, d) SEM and AFM images of 2D borophene sheets, respectively. (e) Typical XPS spectrum and peak deconvolution of borophene sheets. (f) Raman spectra of pristine boron powder and 2D borophene sheets. Scale bar: (c) 2 μm, and (d) 100 nm.
Figure 2

Surface configuration of few-layer borophene. (a) TEM image of a 2D borophene sheet (scale bar: 200 nm). The inset presents the cross-sectional image of a few-layer sheet (scale bar: 2 nm). (b) Typical HRTEM image of the borophene sheet (scale bar: 1 nm). The corresponding selected area electron diffraction (SAED) pattern is shown as the inset. (c) Side and top views of the \( \beta_{12} \)-B5 allotrope labelled with lattice parameters by DFT model. (d) Phonon dispersion curves and density of states (PhDOS) for the \( \beta_{12} \)-B5 allotrope based on DFPT method. (e) HAADF-STEM image of a borophene sheet. (f-h) The corresponding EDX element-mapping images of B, O and C, respectively (scale bar: 500 nm).
Figure 3

Electrocatalytic activity of borophene sheets for polysulfides. (a) Potentialstatic discharge curves of the Li2S8/tetraglyme solution using CNT/B and CNT electrodes at 2.05 V, respectively. (b) Potentiostatic charge profiles of the CNT/B and CNT electrodes at 2.40 V to evaluate dissolution behaviors of Li2S. (c) CV curves of Li2S6 symmetric batteries employing CNT/B and CNT electrode at 5 mV s⁻¹. (d) CV curve comparisons of the cells using CNT/B and CNT electrodes as sulfur hosts at a scan rate of 1 mV s⁻¹. (e) Corresponding Tafel plots for the oxidation peaks, and (f) Nyquist plots of Li-S batteries using CNT/B and CNT cathodes, respectively.
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Electrochemical performances of the CNT- and CNT/B-based Li-S batteries. (a) CV curves of the Li-S battery using CNT/B electrode at a scan rate of 0.1 mV s⁻¹. (b) The galvanostatic charge/discharge curves of the CNT/B-based Li-S battery at different rates. (c) The rate performances of the Li-S batteries using bare CNT and CNT/B cathodes. (d) Galvanostatic charge/discharge profiles at 0.5 C. (e) Cycling stability and coulombic efficiency of the CNT-and CNT/B-based batteries at 0.5 C, respectively. (f) Cycling performances of the CNT/B-based batteries with high sulfur loading of 5.3 and 7.8 mg cm⁻² at 0.3 C. (g) Long-term cycling stability and coulombic efficiency of the CNT/B-based Li-S battery at 5 C.
Figure 5

Theoretical study of the working mechanism of the CNT/B-based Li-S batteries. (a) Optimized adsorption configurations of S8 and Li2Sn (n = 1, 2, 4, 6, 8) on a monolayer β12-borophene. (b) Comparison of the adsorption energies of Li2Sn on monolayer borophene and CNT. (c, d) Partial density of states (PDOS) and charge density difference of Li2S4 on borophene. The yellow and blue colors represent the spatial distribution with increased and decreased charge density, respectively. (e) Diffusion energy barrier of Li+ on borophene.

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