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Advances of Synthesis of Hexagonal Boron Nitride for Industrial Applications: A Review

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Abstract: During the last decade, two-dimensional (2D) hexagonal boron nitride (h-BN), an isomorph of graphene, has shown tremendous importance as the building block for a number of remarkable products of the future. The active edges of N- and B-, high specific surface area, structural defects, excellent electrocatalytic activity, chemical functionalization, and adjustable band gap through interaction with other nanomaterials make 2D-hBN material ideal for many industrial applications. Its strong ability to undergo phase transformations to super lightweight, thermally and chemically stable, oxidation-resistant films makes it a promising material for deep-UV light emitters, protective coatings, nanotechnology thermal applications, and much more. Although h-BN is electrically insulating, strategies can be made to tune it for differing properties such as functionalization, doping, substitution, hybridization, etc. Interestingly, the conventional methods of preparing h-BN, including vapor deposition, solid-state reaction, solvothermal synthesis, microwave heating, etc., are well documented. Yet, the controlled synthesis of 2D h-BN is extremely hard and still a great challenge for researchers. This review aims to summarize the various synthesis methods of this unique class of 2D material to guide researchers on h-BN. This review paper describes the advances in synthetic approaches of h-BN and their emerging potential applications.

Keywords: boron nitride; 2D h-BN; synthesis; industrial applications.

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1. Introduction

Boron nitride, a structural analog of carbon and graphite, consists of boron and nitrogen atoms. Due to the similarity in structure with graphite, it is called "Inorganic graphite" or "white graphite due to its white color. It has superior chemical stability, high thermal conductivity, and mechanical and electrical insulation properties. It is an excellent substitute for commonly used lubricants in metal processing, and it is non-toxic, chemically inert, and a non-conductor of electricity. Boron nitride can exist in several different structures that are isoelectronic to carbon lattice. Although the cubic form resembles a diamond, it is comparatively softer and more stable than a diamond. Among all the structures, the hexagonal form is the softest, most common, and stable form, corresponding to the structure of graphite. It is found to be very useful in manufacturing lubricants and cosmetic products. While graphite has homonuclear, nonpolar C-C intralayer bonds, hexagonal boron nitride (h-BN) possesses highly polar B-N bonds, resulting in different optimal stacking modes in the bulk form. H-BN has emerged as a strong candidate for two-dimensional (2D) material due to its exciting optoelectrical properties, mechanical robustness, thermal stability, and chemical inertness. Due to the extremely large band gap and luminescence, this 2D material may be utilized in UV detectors, ultraviolet lasing, and photoemission. It also safeguards metals from corrosion and oxidation due to their non-reactivity towards chemicals and great impermeability. Besides, it does not produce galvanic corrosion due to its electrically insulated nature. It can be a potential material for spaceship applications due to its good shielding effect against radiation from space. As h-BN is biocompatible, it is also used in drug delivery and tissue scaffolds to improve the thermal and mechanical properties of bio-composites. However, the controlled synthesis of high-quality h-BN is still a great challenge. This review represented the recent trends of synthesis of often overlooked h-BN material, current challenges, and future perspectives for the utilization of 2D-hBN for the next generation. It also highlighted a comprehensive overview of the synthesis approaches for h-BN, which is crucial for future opportunities in this field.

2. Crystallinity and Special Features of Boron Nitride

As a structural counterpart of graphite, it has an equal number of boron and nitrogen atoms, where the length of the B-N bond is 1.44 Å, extremely close to the C-C bond length of graphene. Boron nitride can exist in wurtzite, cubic zinc blende, or hexagonal structures, and a perfect crystallographic analogy can be observed between the carbon allotropes and boron nitride polymorphs. H-BN is similar to graphite in the crystal lattice; rhombohedral boron nitride is similar to rhombohedral graphite; cubic boron nitride has a crystal lattice similar to diamond and wurtzite boron nitride, possessing similar crystal lattice as lonsdaleite variety of diamond. Besides, boron nitride can be prepared as low density-low hardness as well as high density–high hardness polymorphs, similar to carbon. The crystal structures determine various advantages of boron nitride, such as high electrical resistance, unique heat resistance under any thermal shock, stable dielectric properties, chemical inertness to molten metals, glasses, concentrated acids, organic solvents, etc. Currently, more than thirty compounds have been established with decomposition temperatures of about 3000°C and hence have a variety of applications in precision metallurgy, space, nuclear, ceramics, chemical industries, etc. Interestingly, graphene is considered brittle, but its h-BN fracture resistance is about 10 times higher than graphene. Moreover, h-BN's surprising toughness could also make it the ideal option for adding tear resistance to flexible electronics made from 2D materials, which tend to be brittle.

3. Recent Methods of Synthesis of Hexagonal Boron Nitride for Industrial Applications

In the recent few years, 2D hexagonal boron nitride (h-BN) has become a highly demanded material for diversified applications, and this recent wave of research originated from the synergistic impacts of superior thermal conductivity, electrically insulative nature as well as high thermal and chemical stabilities. It is well known that from the successful isolation of graphene from graphite in 2004, the research on graphene and other 2D materials has exploded due to their peculiar, fascinating, and unique properties, in contrast to their bulk counterparts. In the past few years, tremendous attention has been paid to 2D hexagonal boron nitride (hBN), which is by itself an electrical insulator with an ultra-flat surface and a highly stable structure. Mehmet Enes Arslan *et al*. reported the synthesis of hexagonal boron nitride (h-BN) at 300°C in a muffle furnace using boric acid, hydrazine monohydrate, and sodium azide as the starting materials under nitrogen atmosphere for potential application in the nano pharmacological and nano medicinal field [1]. H. Wang *et al*. prepared h-BN flakes on quartz substrate by mechanical exfoliation method [2]. Tomoki Machida *et al*. synthesized h-BN using metal alloy solvent under ambient pressure and elevated temperature, which can be used as a high-grade substrate for 2D materials [3]. Kaihui Liu *et al*. prepared the h-BN films directly capped on Cu substrate using ammonia borane and chemical vapor deposition method at a temperature of 1000℃ [4]. Zonghoon Lee *et al*. reported the growth of h-BN on Cu nanoparticles using ammonia borane by CVD process, where tungsten foil was used as a Cu support substrate [5]. Siyuan Dai *et al*. synthesized the single-layer and bilayer of h-BN on iron foil using borazine as the precursor under low-pressure chemical vapor deposition (LP-CVD) [6]. Wanlin Guo *et al*. reported the growth of large domains of h-BN from ammonia borane on Si and Cu substrate by the CVD method, which can be used for various applications [7]. Dacheng Wei *et al*. successfully produced thin films of two-dimensional h-BN using ammonia borane as a SiO_2/Si substrate precursor in a plasma-enhanced chemical vapor deposition (PECVD) [8]. Marin Petrović *et al*. synthesized a monolayer of h-BN on Ir (111) as the substrate from borazine using the CVD method [9]. Hannah L. Stern and co-workers grew single layer h-BN from borazine on platinum catalyst at 1000°C using the same CVD method. The large crystalline domains of h-BN possess emitters that can be used for optical quantum applications [10]. Kaihui Liu *et al*. reported the epitaxial growth of a single crystal h-BN monolayer with a size of 100 cm^2. They have used Cu (110) vicinal surface, obtained from Cu foils as substrate and ammonia borane as precursors [11].

Tianru Wu *et al*. discussed the controlled synthesis of multilayered h-BN films using nitrogen as a precursor and iron boride alloy, and it has wide applications in optoelectronics and 2D electronics [12]. Milos Toth *et al*. prepared growth of poly-layer h-BN films on metal substrates, i.e., Cu foils, by heating ammonia borane in the 50 cm length heating zone of CVD using low pressure. These thin films host high photostable SPEs, which can help in the progress of scalable quantum emitters [13]. Xingwang Zhang *et al*. demonstrated the synthesis of polycrystalline h-BN layers on Cu foils using ion beam sputter deposition method for using it as a buffer layer for the growth of hafnium disulfide (HfS_2) thin film on a sapphire substrate involving remote heteroepitaxy technique [14]. Si-Young Choi *et al*. successfully synthesized h-BN on sapphire substrates using the metal-organic chemical vapor deposition (MOCVD) method. They observed that the synthesized h-BN showed improved optical properties and better crystallinity and can be used in the field of 2D electronic devices [15]. Mustafa Çulha *et al*. synthesized h-BNs using boric acid and ammonia as a source of boron and nitrogen using a silicon carbide boat using the CVD method. The synthesis was performed to investigate h-BN as a potential therapeutic agent for wound healing therapy [16]. Ping An Hu *et al*. reported the growth of single-layer h-BN utilizing borane ammonia as the precursor on pure Cu and Ni/Cu alloy as the substrates at 1065°C using an atmospheric chemical vapor deposition. This h-BN can be used to detect high ultraviolet [17].

BN acts as an insulator due to a wide band gap and does not possess significant electrochemical activity; however, h-BN has sparked remarkable scientific interest because of its superior thermal conductivity, high thermal and chemical stability, and high optoelectronic characteristics. Hiroki Ago *et al*. used borazine as a precursor and demonstrated epitaxial growth of single-layered h-BN on top of Ni thin film as the substrate, using high-temperature chemical vapor deposition. They achieved the alignment of the h-BN grains by two two-step growth processes; first, the h-BN was grown in random orientation, and second, the substrate was rotated. This resulted in the formation of highly aligned h-BN grains up to the size of 0.5 mm [18]. Jong Kyu Kim *et al*. discussed the growth of h-BN films using tri-ethyl-borane and ammonia as precursors and metal-organic chemical vapor deposition on Ni template [19]. Jigang Wang *et al*. synthesized h-BN within a period of 40 min only using boric acid and melamine as starting materials under microwave heating without using any protective gas or catalyst during the synthesis. They have obtained h-BN with a length of 15–25 mm and 200–500 nm in diameter, which can be used in wastewater cleaning [20]. Rupesh Singh *et al*. reported the synthesis of h-BN using ammonia borane on a silicon wafer as a non-catalytic substrate and copper foil as a catalyst at a relatively lower temperature using CVD. This synthesized h-BN can be used to fabricate in solar-blind photodetector [21]. Tuba Tarhan *et al*. successfully synthesized h-BN at a very high temperature in the furnace using boric acid, which was used as an application to differentiate between the adsorption behavior of anionic and cationic dyes in an aqueous solution [22]. Ping Hu *et al*. grew multilayered h-BN thin films CVD on Au foils as substrate, where ammonia borane was subjected to heat treatment at 90°C for 5-60 to grow h-BN. They have synthesized h-BN to detect ultraviolet light only, not visible or infrared light [23]. Wen-Hao Chang *et al*. reported the growth of single-crystal h-BN monolayers using low-pressure chemical vapor deposition (LPCVD) on a Cu (111) substrate in the presence of ammonia borane [24]. Ruth H.G.A. Kiminami *et al*. synthesized nanocrystalline h-BN, where melamine and boric acid were used as precursors in different ratios using microwave-assisted melamine [25].

Ceramic objects such as monoliths, fibers, and coatings with tailored textural and structural properties can be developed via the derived ceramics (PDC) route, where structural homogeneities at an early fabrication stage are possible at the molecular scale. Catherine Journet *et al*. synthesized h-BN nanosheets using borazine under normal atmospheric pressure conditions and at low temperatures through the PDC route [26]. Li Shi *et al*. reported the synthesis of h-BN foams on nickel powder templates using the atmospheric pressure chemical vapor deposition technique, which can be used in solid thermal conductivity, as gaseous precursors, etc. [27]. Hiroki Ago *et al*. investigated the CVD process to monitor the growth of poly-layered h-BN sheets using borazine on thin iron and nickel films deposited on different sapphire substrates [28]. Bérangère Toury *et al*. prepared h-BN nanosheets using borazine and polymer-derivative ceramic pathways, which require high temperatures to grow mm-scale crystal structures of h-BN [29]. Haomin Wang *et al*. demonstrated the synthesis of multilayered h-BN on sapphire substrate using N_2 gas as reactants and iron alloy using vapor–liquid–solid growth method [30]. Jiangtao Lia *et al*. prepared h-BN nanoplates by combustion using magnesium powder of large particle size. The thickness of nanoplates was 50nm, along with a diameter of 20 μm having high crystallinity, huge aspect ratio, and high purity. This method can produce high-quality h-BN nanoplates in large amounts [31]. Song Zhang *et al*. reported monolayer synthesis of h-BN on copper-nickel alloy substrate using ammonia borane and a low-pressure chemical vapor deposition method [32]. Yiming He and his co-workers synthesized h-BN within 50 min using urea and boric acid as raw materials by microwave-assisted heating method. The synthesized h-BN can perform well in photocatalytic hydrogen diatomic evolution applications [33]. Hui Chen *et al*. prepared porous-natured few layers of h-BN nanosheets using graphitic carbon nitride as a template, resulting in high crystallinity and a thickness of ~5.5 nm. It also displayed excellent CO_2 adsorption properties due to its porous nature, with optimal CO_2 adsorption capacity of 19.26 $cm^3\ g^{-1}$ at 25°C under atmospheric pressure [34]. Janghwan Cha *et al*. reported the synthesis of poly-layered h-BN films on copper foil substrate using ammonia borane and the CVD method. They observed twin boundaries at different stacking in h-BN with promising conducting channels and can be utilized in single h-

BN electronic devices [35]. Wen Hua *et al*. fabricated monolayer h-BN on copper foil using ammonia borane by CVD method [36]. Wenshuai Zhu *et al*. synthesized high-efficiency poly-layered h-BN using boric acid and urea at 1000°C in a tube furnace. The prepared h-BN can be used as a metal-free catalyst to remove sulfur compounds from fuel oils in the presence of hydrogen peroxide as an oxidizing agent, i.e., oxidative desulfurization [37].

Zhanguo Chen *et al*. reported the synthesis of h-BN on silicon substrate using ammonia and boron trichloride as precursors under low pressure of 100 Pa and temperature of 900-1300°C and used them in solar-blind photodetectors [38]. Dominique Vignaud *et al*. successfully synthesized h-BN layers directly grown on nickel foils from borazine using a molecular beam epitaxy chamber [39]. Xingwang Zhang *et al*. discussed synthesizing h-BN thin films grown on sapphire substrates. They utilized the pulsed laser deposition method without the involvement of any catalyst for applications in optoelectronics [40]. James H. Edgar *et al*. demonstrated the growth of h-BN crystals using iron flux under atmospheric pressure, and the obtained single crystal of h-BN can be used in 2D materials devices [41]. Daiyu Kondo *et al*. synthesized h-BN on an epitaxial copper film catalyst formed on a sapphire substrate using the CVD method under low pressure, where ammonia and diborane were used as precursors. The chamber was diluted with hydrogen and argon sources, and the resultant product showed good insulating properties [42]. Aymeric Delteil *et al*. showed directly grown h-BN on silicon substrate under high pressure and high temperature using barium boron nitride, which paved the way for devices based on quantum emitters [43]. Toan Trong Tran *et al*. demonstrated the synthesis of h-BN nanoparticles with "stable quantum light sources using melamine and boric acid as resources and hydrothermal approach [44]. Donghyun Hwang and his co-workers reported the same boric acid, melamine, as precursors but doped with Ce^{3+} to synthesize h-BN pyrolysis at a very high temperature of 900°C under a nitrogen atmosphere. They also re-heated the h-BN samples from 1100°C to 1400°C to check the photoluminescence properties and crystalline structure according to annealing temperatures [45]. Gürcan Yıldırım *et al*. used the modified O'Connor method and synthesized the h-BN materials, using boron oxide, a mixture of urea powder, and different types of borates as starting materials. In the presence of an ammonia stream, they heated the tube furnace using high temperatures to understand the effects of different borates in the nanoscale h-BN formation [46]. Among the different parameters of growth, the temperature of the substrate has the greatest influence on the crystallinity of the h-BN films, where the variation of optimal pressure largely depends on the target substrate distance. Besides, synthesizing h-BN films on non-catalytic dielectric substrates is also desirable for electronic applications. Looking at this aspect, Igor Aharonovich *et al*. grew the h-BN on dielectric substrates using a CVD chamber. They used the ammonia borane powder as a precursor and discussed the fabrication of single-photon emitters (SPEs) arrays in h-BN for quantum photonic applications [47]. Yifei Li *et al*. reported the growth of nanoscale high-grade multi-crystalline thin films of h-BN [48]. Jayeeta Lahira *et al*. successfully synthesized a few layers of h-BN on Cu foil using atmospheric pressure chemical vapor deposition using ammonia borane powder. They aimed to investigate the surface-enhanced raman spectroscopy activity [49]. Liming Zhang *et al*. synthesized the single layer h-BN on Cu foil at a high temperature in a tube furnace using ammonia borane as a precursor. They reported the work for sustainable energy conversion by CO_2 reduction electrocatalysts [50]. Gyu-Chul Yi *et al*. reported multi-crystalline thin h-BN layers using chemical vapor deposition. This deposition was done on copper foil using NH_3 and BCl_3 as sources, leading to large-scale productions of 2D insulating layers [51]. Raj N. Singh *et al*. successfully synthesized h-BN thin films on silicon and sapphire substrates using low-pressure chemical vapor deposition at a temperature of 1100°C. They used ammonia borane as a precursor, and the crystal size of the h-BN films on sapphire and silicon was found to be 6.13 nm and 6.37, respectively [52]. Lei Qian *et al*. prepared h-BN nanofibers using melamine, polyethylene glycol, and boric acid by mixing them in different molar ratios followed by pyrolysis [53]. Hong Yin *et al*. reported the synthesis of h-BN nano-size films grown on stainless steel surfaces using a magnetron sputtering method. The synthesized h-BN acted as a barrier coating for prevention from corrosion [54]. Eric Pop *et al*. prepared monolayer h-BN films on platinum substrates using ammonia borane as a precursor using the chemical vapor deposition method [55].

Hong Yin *et al*. successfully synthesized thick layers of h-BN on dielectric substrates at low temperatures using ion beam-assisted deposition without the use of a catalyst. This work paved the way for using them to develop photodetectors [56]. Hyeon Suk Shin *et al*. reported the growth of high-quality, large-area crystalline multilayered h-BN using BN multilayers; they have used chemical vapor deposition, involving heating a mixture of boron and nitrogen precursors in the presence of a Ni substrate. They also demonstrated that the h-BN layers were epitaxially aligned with the Ni substrate. This work has important implications for the development of h-BN-based devices [57]. Mindaugas Lukosius *et al*. reported the growth of h-BN thin films using a thin layer of germanium (Ge), which grows epitaxially on top of a silicon substrate, creating a Ge/Si heterostructure. Borazine was used as a precursor along with chemical vapor deposition at the temperature of 900°C and 980°C and pressure range of 10^{-7} mbar to 10^{-3} mbar [58]. Thanikaivelan Palanisamy *et al*. successfully synthesized h-BN nanoparticles from boric acid and urea using the hydrothermal method. After synthesis, h-BN was dispersed along with polyethylene glycol to yield h-BN/PEG-treated leathers. The treated leathers were examined for thermal insulations, which could be utilized in different applications [59]. R. Thamankar *et al*. reported nanoscale h-BN using a facile synthesis from boric acid and melamine, where they heated the sources under standard conditions and studied their light emissions properties due to defects for utilizing in quantum computation and photonic applications [60]. Zhigiang Yao *et al*. reported the self-assembled growth of macroscopic-scale quasi-single-crystalline h-BN films using ammonia borane as a precursor and liquid Cu substrate for future applications in advanced electronics [61]. Junhua Meng *et al*. reported direct growth of premium quality multilayered h-BN on sapphire substrates by ion beam sputtering deposition method under a temperature of 700°C by unveiling NH_3 into the vacuum chamber [62]. A. Ougazzaden *et al*. showed the growth of h-BN thin films on epi-graphene, which is grown on a silicon carbide substrate by a metal-organic vapor phase epitaxy. The resultant h-BN showed high thermal stability for use in high-temperature applications [63].

Mingzai Wu *et al*. designed a CVD method that can produce large quantities of high-quality h-BN films on copper foil in a sealed chamber containing boron and nitrogen gas. The properties of h-BN can make it an attractive material for anticorrosion applications, including its high chemical stability, low friction, and good thermal conductivity [64]. Pulickel M. Ajayan *et al*. discussed the direct growth of h-BN thin films on sapphire by pulsed laser deposition, which was found to be highly insulating. It was also beneficial for high-performance 2D materials electronics [65]. Haolin Wang *et al*. reported selective growth of h-BN bilayer on Cu foil/sapphire substrate using ammonia borane by two-step low-pressure CVD [66]. Tianru Wu *et al*. produced high-quality h-BN thin films using the CVD method, utilizing nickel-boron as a substrate and boron as a precursor [67]. Bharat K. Jasthi *et al*. synthesized h-

BN thin films on an iron substrate using a pulsed laser deposition technique at around 600°C with improved crystallinity. This h-BN acted as a protective barrier to prevent corrosion even in saline environments [68]. Hiroki Ago *et al*. synthesized high-quality h-BN multilayers using borazine on iron-nickel alloy foil as substrate by low-pressure chemical vapor deposition for suitable applications in electronic devices [69]. Jong Kyu Kim *et al*. accomplished the growth of h-BN films using triethyl-borane and ammonia as precursors on silicon substrate by metal-organic chemical vapor deposition within a pressure of 600 mbar and high temperature of 1050°C. These can have a huge impact on silicon-based microelectronic applications [70]. Jing Kong *et al*. grew single-layered h-BN using epitaxial chemical vapor deposition under a stabilized temperature and low pressure inside the furnace. They synthesized monolayers of h-BN with borazine as precursors on the single crystalline structure Cu-(III) as substrate [71]. Xingwang Zhang *et al*. reported a submicron-spacing vapor deposition method for the direct growth of wafer-scale highly single crystalline 2D structured h-BN using boron films as a precursor and was found to be dielectric [72]. Luxiang Wang *et al*. reported the synthesis of γ-aminopropyl tri-ethoxy silane-modified h-BN, which exhibited a good high yield and good dispersion stability of the resultant nanosheets. It also helped develop high thermal conductivity and thermomechanical properties of epoxy nanocomposites [73].

Yanming Xue *et al*. successfully developed micro-spherical h-BN using pyrolysis at a high temperature, followed by polymerization of spherical precursors. This preparation upgraded extensive applications of porous bulk materials of h-BN ceramics [74]. Wenhong Sun *et al*. reported a one-step synthesis of vertically oriented hexagonal shape boron nitride (h-BN) thin films on Gallium Nitride by the method of chemical vapor deposition (CVD). They grew the h-BN in GaN using the Boron powder and ammonia gas as the precursors. The temperature went up to 1100°C in the furnace while preparing the h-BN on the Gallium Nitride epilayer [75]. Agustin Schiffrin *et al*. demonstrated monolayer h-BN on a substrate of Cu-(III) using a chamber of ultrahigh vacuum at a high temperature ∼1190k and partial pressure (∼10−6 mbar) [76]. Myung Jong Kim *et al*. used the thermal plasma method to prepare a highly crystalline structure of double-walled h-BN nanotubes at high temperatures using ammonia borane. The resultant product had fewer walls with decreased diameter and a significantly increased production rate (∼50 g/h) [77]. Pulickel M. Ajayan *et al*. proposed the growth of 2D h-BN by pulsed laser deposition method at normal room temperature [78]. Katsuhisa Murakami *et al*. reported multilayered h-BN at low temperatures, i.e., between 400 and 500°C, using the inductively coupled plasma-enhanced chemical vapor deposition. They also studied the effect of crystal quality on different parameters such as input radio frequency power, nitrogen and hydrogen flow rate, temperature, etc. [79]. Sheng Dai *et al*. reported the synthesis of h-BN nanomaterials using both top-down and bottom-up approaches. Urea and boron trioxide were used as starting materials to prepare h-BN. This h-BN showed great potential for catalytic applications due to its unique properties, and it also enhanced the catalytic activity of h-BN-based materials through nanostructured interfaces [80].

4. Conclusions

As an isostructural and isoelectronic material similar to graphite, h-BN has similar properties. Due to high-temperature resistance, excellent chemical corrosion resistance, pressure resistance, anti-oxidation properties, and good neutron radiation shielding performance, h-BN has become a new 2D material with excellent performance and great potential for future research. There are several approaches regarding the synthesis of h-BN where the precursor of boron, catalyst, temperature, substrates, and the duration of heating are the key factors. It is now well established that its properties depend highly on the synthesis methods, so the controlled synthesis of h-BN is still a great challenge for scientists and researchers. This review aims to highlight the current progress and the synthetic approaches of h-BN, where the details of the reaction conditions were mainly discussed, which will give new insights for further development and practical applications. It will give a thorough overview of the growth process of h-BN, formation mechanisms, and application areas for a better understanding of future research in this area.

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Conflicts of Interest

The authors declare that they have no conflict of interest.

References

1. Türkez, H.; Arslan, M.E.; Sönmez, E.; Açikyildiz, M.; Tatar, A.; Geyikoğlu, F. Synthesis, characterization and cytotoxicity of boron nitride nanoparticles: emphasis on toxicogenomics. *Cytotechnology* **2019**, *71*, 351-361, https://doi.org/10.1007/s10616-019-00292-8.
2. Ni, G.X.; Wang, H.; Jiang, B.-Y.; Chen, L.X.; Du, Y.; Sun, Z.Y.; Goldflam, M.D.; Frenzel, A.J.; Xie, X.M.; Fogler, M.M.; Basov, D.N. Soliton superlattices in twisted hexagonal boron nitride. *Nat. Commun.* **2019**, *10*, 4360, https://doi.org/10.1038/s41467-019-12327-x.
3. Onodera, M.; Taniguchi, T.; Watanabe, K.; Isayama, M.; Masubuchi, S.; Moriya, R.; Machida, T. Hexagonal Boron Nitride Synthesized at Atmospheric Pressure Using Metal Alloy Solvents: Evaluation as a Substrate for 2D Materials. *Nano Lett.* **2019**, *20*, 735–740, https://doi.org/10.1021/acs.nanolett.9b04641.
4. Chen, D.; Qiao, R.; Xu, X.; Dong, W.; Wang, L.; Ma, R.; Liu, C.; Zhang, Z.; Wu, M.; Liu, L.; Bao, L.; Wang, H.-T.; Gao, P.; Liu, K.; Yu, D. Sub-10 nm stable graphene quantum dots embedded in hexagonal boron nitride. *Nanoscale* **2019**, *11*, 4226-4230, https://doi.org/10.1039/C9NR00412B.
5. Park, H.J.; Tay, R.Y.; Wang, X.; Zhao, W.; Kim, J.H.; Ruoff, R.S.; Ding, F.; Toe, E.H.T.; Lee, Z. Double-Spiral Hexagonal Boron Nitride and Shear Strained Coalescence Boundary. *Nano Lett.* **2019**, *19*, 4229–4236, https://doi.org/10.1021/acs.nanolett.8b05034.
6. Dai, S.; Fang, W.; Rivera, N.; Stehle, Y.; Jiang, B.-Y.; Shen, J.; Tay, R.Y.; Ciccarino, C.J.; Ma, Q.; Rodan-Legrain, D.; Jarillo-Herrero, P.; Teo, E.H.T.; Fogler, M.M.; Narang, P.; Kong, J.; Basov, D.N. Phonon Polaritons in Monolayers of Hexagonal Boron Nitride. *Adv. Mater.* **2019**, *31*, 1806603, https://doi.org/10.1002/adma.201806603.
7. Li, J.; Hu, Z.; Yi, Y.; Yu, M.; Li, X.; Zhou, J.; Yin, J.; Wu, S.; Guo, W. Hexagonal Boron Nitride Growth on Cu-Si Alloy: Morphologies and Large Domains. *Small* **2019**, *15*, 1805188, https://doi.org/10.1002/smll.201805188.
8. Liu, D.; Chen, X.; Yan, Y.; Zhang, Z.; Jin, Z.; Yi, K.; Zhang, C.; Zheng, Y.; Wang, Y.; Yang, J.; Xu, X.; Chen, J.; Lu, Y.; Wei, D.; Wee, A.T.S.; Wei, D. Conformal hexagonal-boron nitride dielectric interface for tungsten diselenide devices with improved mobility and thermal dissipation. *Nat. Commun.* **2019**, *10*, 1188, https://doi.org/10.1038/s41467-019-09016-0.
9. Petrović, M.; Hoegen, M.H.-v.; Meyer zu Heringdorf, F.-J. Equilibrium shape of single-layer hexagonal boron nitride islands on iridium. *Sci. Rep.* **2019**, *9*, 19553, https://doi.org/10.1038/s41598-019-56000-1.
10. Stern, H.L.; Wang, R.; Fan, Y.; Mizuta, R.; Stewart, J.C.; Needham, L.-M.; Roberts, T.D.; Wai, R.; Ginsberg, N.S.; Klenerman, D.; Hofmann, S.; Lee, S.F. Spectrally Resolved Photodynamics of Individual Emitters in

Large-Area Monolayers of Hexagonal Boron Nitride. *Acs Nano* **2019**, *13*, 4538-4547, https://doi.org/10.1021/acsnano.9b00274.

11. Wang, L.; Xu, X.; Zhang, L.; Qiao, R.; Wu, M.; Wang, Z.; Zhang, S.; Liang, J.; Zhang, Z.; Zhang, Z.; Chen, W.; Xie, X.; Zong, J.; Shan, Y.; Guo, Y.; Willinger, M.; Wu, H.; Li, Q.; Wang, W.; Gao, P.; Wu, S.; Zhang, Y.; Jiang, Y.; Yu, D.; Wang, E.; Bai, X.; Wang, Z.-J.; Ding, F.; Liu, K. Epitaxial growth of a 100-square-centimetre single-crystal hexagonal boron nitride monolayer on copper. *Nature* **2019**, *570*, 91-95, https://doi.org/10.1038/s41586-019-1226-z.
12. Shi, Z.; Lu, G.; Yang, P.; Wu, T.; Yin, W.; Zhang, C.; Jiang, R.; Xie, X. Controlled synthesis of uniform multilayer hexagonal boron nitride films on Fe_2B alloy. *RSC Adv.* **2019**, *9*, 10155-10158, https://doi.org/10.1039/c9ra00595a.
13. Mendelson, N.; Xu, Z.-Q.; Tran, T.T.; Kianinia, M.; Scott, J.; Bradac, C.; Aharonovich, I.; Toth, M. Engineering and Tuning of Quantum Emitters in Few-Layer Hexagonal Boron Nitride. *ACS Nano* **2019**, *13*, 3132-3140, https://doi.org/10.1021/acsnano.8b08511.
14. Wang, D.; Lu, Y.; Meng, J.; Zhang, X.; Yin, Z.; Gao, M.; Wang, Y.; Cheng, L.; You, J.; Zhang, J. Remote heteroepitaxy of atomic layered hafnium disulfide on sapphire through hexagonal boron nitride. *Nanoscale* **2019**, *11*, 9310-9318, https://doi.org/10.1039/c9nr01700c.
15. Lee, H.S.; Jeong, H.; Okello, O.F.N.; Xiao, S.; Moon, S.; Kim, D.Y.; Kim. G.-Y.; Lo, J.-I.; Peng, Y.-C.; Cheng, B.-M.; Miyake, H.; Choi, S.-Y.; Kim, J.K. Improvements in structural and optical properties of wafer-scale hexagonal boron nitride film by post-growth annealing. *Sci. Rep.* **2019**, *9*, 10590, https://doi.org/10.1038/s41598-019-47093-9.
16. Sen, Ö.; Emanet, M.; Çulha, M. Stimulatory Effect of Hexagonal Boron Nitrides in Wound Healing. *ACS Appl. Bio Mater.* **2019**, *2*, 5582-5596, https://doi.org/10.1021/acsabm.9b00669.
17. Yang, H.; Wang, L.; Gao, F.; Dai, M.; Hu, Y.; Chen, H.; Zhang, J.; Qiu, Y.; Jia, D.C.; Zhou, Y.; Hu, P.A. Shape evolution of two-dimensional hexagonal boron nitride single domains on Cu/Ni alloy and its applications in ultraviolet detection. *Nanotechnology* **2019**, *30*, 245706, https://doi.org/10.1088/1361-6528/ab0d3d.
18. Taslim, A.B.; Nakajima, H.; Lin, Y.-C.; Uchida, Y.; Kawahara, K.; Okazaki, T.; Suenaga, K.; Hibino, H.; Ago, H. Synthesis of sub-millimeter single-crystal grains of aligned hexagonal boron nitride on an epitaxial Ni film. *Nanoscale* **2019**, *11*, 14668-14675, https://doi.org/10.1039/c9nr03525g.
19. Jeong, H.; Kim, D.Y.; Kim, J.; Moon, S.; Han, N.; Lee, S.H.; Okello, O.F.N.; Song, K.; Choi, S.-Y.; Kim, J.K. Wafer-scale and selective-area growth of high-quality hexagonal boron nitride on Ni(111) by metal-organic chemical vapor deposition. *Sci. Rep.* **2019**, *9*, 5736, https://doi.org/10.1038/s41598-019-42236-4.
20. Shen, T.; Liu, S.; Yan, W.; Wang, J. Highly efficient preparation of hexagonal boron nitride by direct microwave heating for dye removal. *J. Mater. Sci.* **2019**, *54*, 8852-8859, https://doi.org/10.1007/s10853-019-03514-8.
21. Singh, R.; Kalita, G.; Mahyavanshi, R.D.; Adhikari, S.; Uchida, H.; Tanemura, M.; Umeno, M.; Kawahara, T. Low temperature wafer-scale synthesis of hexagonal boron nitride by microwave assisted surface wave plasma chemical vapour deposition. *AIP Adv.* **2019**, *9*, 035043, https://doi.org/10.1063/1.5091529/s10.1063/1.5091529.
22. Tarhan, T. Synthesis and characterization of hexagonal boron nitride used for comparison of removal of anionic and cationic hazardous azo-dye: kinetics and equilibrium studies. *Turk. J. Chem.* **2020**, *44*, 1471-1482, https://doi.org/10.3906/kim-2004-23.
23. Tan, B.; Yang, H.; Hu, Y.; Gao, F.; Wang, L.; Dai, M.; Zhang, S.; Shang, H.; Chen, H.; Hu, P.A. Synthesis of High-Quality Multilayer Hexagonal Boron Nitride Films on Au Foils for Ultrahigh Rejection Ratio Solar-Blind Photodetection. *ACS Appl. Mater. Interfaces* **2020**, *12*, 28351-28359, https://doi.org/10.1021/acsami.0c00449.
24. Chen, T.-A.; Chuu, C.-P.; Tseng, C.-C.; Wen, C.-K.; Wong, H.-S.P.; Pan. S.; Li, R.; Chao, T.-A.; Chueh, W.-C.; Zhang, Y.; Fu, Q.; Yakobson, B.I.; Chang, W.-H.; Li, L.-J. Wafer-scale single-crystal hexagonal boron nitride monolayers on Cu(111). *Nature* **2020**, *579*, 219-223, https://doi.org/10.1038/s41586-020-2009-2.
25. Yasnó, J.P.; Kiminami, R.H.G.A. Short time reaction synthesis of nano-hexagonal boron nitride. *Adv. Powder Technol.* **2020**, *31*, 4436-4443, https://doi.org/10.1016/j.apt.2020.09.018.
26. Matsoso, B.; Hao, W.; Li, Y.; Vuillet-a-Ciles, V.; Garnier, V.; Steyer, P.; Toury, B.; Marichy, C.; Journet, C. Synthesis of hexagonal boron nitride 2D layers using polymer derived ceramics route and derivatives. *J. Phys. Mater.* **2020**, *3*, 034002, https://doi.org/10.1088/2515-7639/ab854a.

27. Jia, Q.; Shi, L. Synthesis and thermal transport properties of high-surface area hexagonal boron nitride foam structures. *Int. J. Heat Mass Transf.* **2020**, *161*, 120268, https://doi.org/10.1016/j.ijheatmasstransfer.2020.120268.
28. Uchida, Y.; Kawahara, K.; Fukamachi, S.; Ago, H. Chemical Vapor Deposition Growth of Uniform Multilayer Hexagonal Boron Nitride Driven by Structural Transformation of Metal Thin Film. *ACS Appl. Electron. Mater.* **2020**, *2*, 3270–3278, https://doi.org/10.1021/acsaelm.0c00601.
29. Li, Y.; Garnier, V.; Steyer, P.; Journet, C.; Toury, B. Millimeter-Scale Hexagonal Boron Nitride Single Crystals for Nanosheet Generation. *ACS Appl. Nano Mater.* **2020**, *3*, 1508–1515, https://doi.org/10.1021/acsanm.9b02315.
30. Shi, Z.; Wang, X.; Li, Q.; Yang, P.; Lu, G.; Jiang, R.; Wang, H.; Zhang, C.; Cong, C.; Liu, Z.; Wu, T.; Wang, H.; Yu, Q.; Xie, X. Vapor–liquid–solid growth of large-area multilayer hexagonal boron nitride on dielectric substrates. *Nat. Commun.* **2020**, *11*, 849, https://doi.org/10.1038/s41467-020-14596-3.
31. Wu, X.; He, G.; Wang, L.; Yang, Z.; Li, J. Combustion synthesis of hexagonal boron nitride nanoplates with high aspect ratio. *Ceram. Int.* **2020**, *46*, 20717-20723, https://doi.org/10.1016/j.ceramint.2020.05.004.
32. Zhu, T.; Liang, Y.; Zhang, C.; Wang, Z.; Dong, M.; Wang, C.; Yang, M.; Goto, T.; Tu, R.; Zhang, S. A high-throughput synthesis of large-sized single-crystal hexagonal boron nitride on a Cu–Ni gradient enclosure. *RSC Adv.* **2020**, *10*, 16088-16093, https://doi.org/10.1039/D0RA00734J.
33. Chen, L.; Chen, P.; Dai, X.; Zhang, W.; Xing, P.; He, Y. Facile and rapid preparation of hexagonal boron nitride via microwave heating method and its application in photocatalytic H_2 evolution. *Mater. Lett.* **2020**, *266*, 127477, https://doi.org/10.1016/j.matlet.2020.127477.
34. Li, S.; Zeng, X.; Chen, H.; Fang, W.; He, X.; Li, W.; Huang, Z.H.; Zhao, L. Porous hexagonal boron nitride nanosheets from g-C_3N_4 templates with a high specific surface area for CO_2 adsorption. *Ceram. Int.* **2020**, *46*, 27627-27633, https://doi.org/10.1016/j.ceramint.2020.07.257.
35. Park, H.J.; Cha, J.; Choi, M.; Kim, J.H.; Tay, R.Y.; Teo, E.H.T.; Park, N.; Hong, S.; Lee, Z. One-dimensional hexagonal boron nitride conducting channel. *Sci. Adv.* **2020**, *6*, eaay4958, https://doi.org/10.1126/sciadv.aay4958.
36. Bilal, M.; Xu, W.; Wang, C.; Wen, H.; Zhao, X.; Song, D.; Ding, L. Optoelectronic Properties of Monolayer Hexagonal Boron Nitride on Different Substrates Measured by Terahertz Time-Domain Spectroscopy. *Nanomaterials* **2020**, *10*, 762, https://doi.org/10.3390/nano10040762.
37. Wu, P.; Lu, L.; He, J.; Chen, L.; Chao, Y.; He, M.; Zhu, F.; Chu, X.; Li, H.; Zhu, W. Hexagonal boron nitride: A metal-free catalyst for deep oxidative desulfurization of fuel oils. *Green Energy Environ.* **2020**, *5*, 166-172, https://doi.org/10.1016/j.gee.2020.03.004.
38. Chen, X.; Tan, C.; Liu, X.; Luan, K.; Guan, Y.; Liu, X.; Zhao, J.; Hou, L.; Gao, Y.; Chen, Z. Growth of hexagonal boron nitride films on silicon substrates by low-pressure chemical vapor deposition. *J. Mater. Sci.: Mater. Electron.* **2021**, *32*, 3713–3719, https://doi.org/10.1007/s10854-020-05116-6.
39. Hadid, J.; Colambo, I.; Boyaval, C.; Nuns, N.; Dudin, P.; Avila, J.; Wallart, X.; Vignaud, D. Molecular beam epitaxial growth of hexagonal boron nitride on Ni foils. *2D Mater.* **2021**, *8*, 045007, https://doi.org/10.1088/2053-1583/ac1502.
40. Wang, G.; Chen, J.; Meng, J.; Yin, Z.; Jiang, J.; Tian, Y.; Li, J.; Wu, J.; Jin, P.; Zhang, X. Direct growth of hexagonal boron nitride films on dielectric sapphire substrates by pulsed laser deposition for optoelectronic application. *Fundam. Res.* **2021**, *1*, 677-683, https://doi.org/10.1016/j.fmre.2021.09.014.
41. Li, J.; Wang, J.; Zhang, X.; Elias, C.; Ye, G.; Evans, D.; Eda, G; Redwing, J.M.; Cassabois, G.; Gil, B.; Valvin, P.; He, R.; Liu, B.; Edgar, J.H. Hexagonal Boron Nitride Crystal Growth from Iron, a Single Component Flux. *ACS Nano* **2021**, *15*, 7032–7039, https://doi.org/10.1021/acsnano.1c00115.
42. Kondo, D.; Kataoka, M.; Hayashi, K.; Sato, S. Few-layer hexagonal boron nitride synthesized by chemical vapor deposition and its insulating properties. *Nano Ex.* **2021**, *2*, 030001, https://doi.org/10.1088/2632-959X/ac0d9d.
43. Fournier, C.; Plaud, A.; Roux, S.; Pierret, A.; Rosticher, M.; Watanabe, K.; Taniguchi, T.; Buil, S.; Quelin, X.; Barjon, J.; Hermier, J.-P.; Delteil, A. Position-controlled quantum emitters with reproducible emission wavelength in hexagonal boron nitride. *Nat. Commun.* **2021**, *12*, 3779, https://doi.org/10.1038/s41467-021-24019-6.
44. Chen, Y.; Xu, X.; Li, C.; Bendavid, A.; Westerhausen, M.T.; Bradac, C.; Toth, M.; Aharonovich, I.; Tran, T.T. Bottom-Up Synthesis of Hexagonal Boron Nitride Nanoparticles with Intensity-Stabilized Quantum Emitters. *Small* **2021**, *17*, e2008062, https://doi.org/10.1002/smll.202008062.

45. Jung, J.Y.; Kim, J.; Kim, Y.D.; Kim, Y.-K.; Cha, H.-R.; Lee, J.-G.; Son, C.S.; Hwang, D. Enhanced Crystallinity and Luminescence Characteristics of Hexagonal Boron Nitride Doped with Cerium Ions According to Tempering Temperatures. *Materials* **2021**, *14*, 193, https://doi.org/10.3390/ma14010193.
46. Öz, M.; Bozkurt, C.; Yılmaz, B.K.; Yıldırım, G. Effect of borates on the synthesis of nanoscale hexagonal boron nitride by a solid-state method. *Microsc. Res. Tech.* **2021**, *84*, 2677-2684, https://doi.org/10.1002/jemt.23817.
47. Li, C.; Mendelson, N.; Ritika, R.; Chen, Y.L.; Xu, Z.-Q.; Toth, M.; Aharonovich, I. Scalable and Deterministic Fabrication of Quantum Emitter Arrays from Hexagonal Boron Nitride. *Nano Lett.* **2021**, *21*, 3626-3632, https://doi.org/10.1021/acs.nanolett.1c00685.
48. Li, Y.; Wen, X.; Tan, C.; Li, N.; Li, R.; Huang, X.; Tian, H.; Yao, Z.; Liao, P.C.; Yu, S.; Liu, S.; Li, Z.; Guo, J.; Huang, Y.; Gao, P.; Wang, L.; Bai, S.; Liu, L. Synthesis of centimeter-scale high-quality polycrystalline hexagonal boron nitride films from Fe fluxes. *Nanoscale* **2021**, *13*, 11223-11231, https://doi.org/10.1039/d1nr02408f.
49. Basu, N.; Satya Bharathi, M.S.; Sharma, M.; Yadav, K.; Parmar, A.S.; Soma, V.R.; Lahiri, J. Large Area Few-Layer Hexagonal Boron Nitride as a Raman Enhancement Material. *Nanomaterials* **2021**, *11*, 622, https://doi.org/10.3390/nano11030622.
50. Chen, S.; Zhu, C.; Gu, H.; Wang, L.; Qi, J.; Zhong, L.; Zhang, Z.; Yang, C.; Shi, G.; Zhao, S.; Li, S.; Liu, K.; Zhang, L. Enhanced Electrochemical Methanation of Carbon Dioxide at the Single-Layer Hexagonal Boron Nitride/Cu Interfacial Perimeter. *Nano Lett.* **2021**, *21*, 4469-4476, https://doi.org/10.1021/acs.nanolett.1c01258.
51. Oh, H.; Yi, G.-C. Synthesis of Atomically Thin h-BN Layers Using BCl_3 and NH_3 by Sequential-Pulsed Chemical Vapor Deposition on Cu Foil. *Nanomaterials* **2022**, *12*, 80, https://doi.org/10.3390/nano12010080.
52. Singhal, R.; Echeverria, E.; McIlroy, D.N.; Singh, R.N. Synthesis of hexagonal boron nitride films on silicon and sapphire substrates by low-pressure chemical vapor deposition. *Thin Solid Films* **2021**, *733*, 138812, https://doi.org/10.1016/j.tsf.2021.138812.
53. Liu, H.; Yan, Z.; Sun, Z.; Li, A.; Guo, Z.; Lei, Q. Highly Efficient Synthesis of Hexagonal Boron Nitride Nanofibers with High Specific Surface Area. *ES Mater. Manuf.* **2021**, *16*, 56-65, https://doi.org/10.30919/esmm5f561.
54. Tang, X.; Wang, H.; Liu, C.; Zhu, X.; Gao, H.; Yin, H. Direct Growth of Hexagonal Boron Nitride Nanofilms on Stainless Steel for Corrosion Protection. *ACS Appl. Nano Mater.* **2021**, *4*, 12024-12033, https://doi.org/10.1021/acsanm.1c02590.
55. Chen, V.; Shin, Y.C.; Mikheev, E.; Lin, Q.; Martis, J.; Zhang, Z.; Chatterjee, S.; Majumder, A.; Wong H.-S.P.; Goldhaber-Gordon, D.; Pop, E. Application-driven synthesis and characterization of hexagonal boron nitride deposited on metals and carbon nanotubes. *2D Mater.* **2021**, *8*, 045024, https://doi.org/10.1088/2053-1583/ac10f1.
56. Li. D.; Gao, W.; Sun, X.; Yu, H.; Liu, C.; Yin, H. Direct Growth of Hexagonal Boron Nitride Thick Films on Dielectric Substrates by Ion Beam Assisted Deposition for Deep-UV Photodetectors. *Adv. Opt. Mater.* **2021**, *9*, 2100342, https://doi.org/10.1002/adom.202100342.
57. Ma, K.Y.; Zhang, L.; Jin, S.; Wang, Y.; Yoon, S.I.; Hwang, H.; Oh, J.; Jeong, D.S.; Wang, M.; Chatterjee, S.; Kim, G.; Jang, A.-R.; Yang, J.; Ryu, S.; Jeong, H.Y.; Ruoff, R.S.; Chhowalla, M.; Ding, F.; Shin, H.S. Epitaxial single-crystal hexagonal boron nitride multilayers on Ni (111). *Nature* **2022**, *606*, 88-93, https://doi.org/10.1038/s41586-022-04745-7.
58. Franck, M.; Dabrowski, J.; Schubert, M.A.; Wenger, C.; Lukosius, M. Towards the Growth of Hexagonal Boron Nitride on Ge(001)/Si Substrates by Chemical Vapor Deposition. *Nanomaterials* **2022**, *12*, 3260, https://doi.org/10.3390/nano12193260.
59. Bhasi, A.P.; Wilson, N.H.; Palanisamy, T. Nanosized Hexagonal Boron Nitride and Polyethylene Glycol-Filled Leathers for Applications Demanding High Thermal Insulation and Impact Resistance. *ACS Omega* **2022**, *7*, 45120-45128, https://doi.org/10.1021/acsomega.2c05567.
60. Sunny, A.; Balapure, A.; Ganesan, R.; Thamankar, R. Room-Temperature Deep-UV Photoluminescence from Low-Dimensional Hexagonal Boron Nitride Prepared Using a Facile Synthesis. *ACS Omega* **2022**, *7*, 33926-33933, https://doi.org/10.1021/acsomega.2c02884.
61. Zhang, Q.; Chen, H.; Liu, S.; Yu, Y.; Wang, C.; Han, J.; Shao, G.; Yao, Z. Self-aligned stitching growth of centimeter-scale quasi-single-crystalline hexagonal boron nitride monolayers on liquid copper. *Nanoscale* **2022**, *14*, 3112-3122, https://doi.org/10.1039/d1nr06045g.

62. Chen, J.; Wang, G.; Meng, J.; Cheng, Y.; Yin, Z.; Tian, Y.; Huang, J.; Zhang, S.; Wu, J.; Zhang, X. Low-Temperature Direct Growth of Few-Layer Hexagonal Boron Nitride on Catalyst-Free Sapphire Substrates. *ACS Appl. Mater. Interfaces* **2022**, *14*, 7004-7011, https://doi.org/10.1021/acsami.1c22626.
63. Ottapilakkal, V.; Juyal, A.; Sundaram, S.; Vuong, P.; Mballo, A.; Beck, L.; Nunn, G.; Su, Y.; Loiseau, A.; Fossard, F.; Mérot, J.S.; Chapron, D.; Kauffmann, T.H.; Salvestrini, J.P.; Voss, P.L.; de Heer, W.A.; Berger, C.; Ougazzaden, A. Thermal stability of thin hexagonal boron nitride grown by MOVPE on epigraphene. *J. Cryst. Growth* **2023**, *603*,127030, https://doi.org/10.1016/j.jcrysgro.2022.127030.
64. Wang, R.; Huang, M.; Hou, J.; Zhou, S.; Mei, K.; Yu, X.; Wu, M. Large-Scale Growth of Hexagonal Boron Nitride for Anticorrosion. *ACS Appl. Eng. Mater.* **2023**, *1*, 1408–1415, https://doi.org/10.1021/acsaenm.3c00083.
65. Biswas, A.; Ruan, Q.; Lee, F.; Li, C.; Iyengar, S.A.; Puthirath, A.B.; Zhang, X.; Kannan, H.; Gray, T.; Birdwell, A.G.; Neupane, M.R.; Shah, P.B.; Ruzmetov, D.A.; Ivanov, T.G.; Vajtai, R.; Tripathi, M.; Dalton, A.; Yakobson, B.I.; Ajayan, P.M. Unidirectional domain growth of hexagonal boron nitride thin films. *Appl. Mater. Today* **2023**, *30*, 101734, https://doi.org/10.1016/j.apmt.2023.101734.
66. Zhao, Y.; Li, X.; Feng, L.; Liu, T.; Wang, H. Layer-selective growth of 2D hexagonal boron nitride using two-step chemical vapor deposition. *Vacuum* **2023**, *213*, 112126, https://doi.org/10.1016/j.vacuum.2023.112126.
67. Chen, D.; Shen, H.; Liu, B.; Wang, Z.; Liao, B.; Mao, W.; Li, Y.; Wu, T. Controllable Synthesis of High-Quality Hexagonal Boron Nitride Films on Ni-B Alloy. *J. Electron. Mater.* **2023**, *52*, 4913–4920, https://doi.org/10.1007/s11664-023-10433-7.
68. Kandadai, V.A.S.; Petersen, J.B.; Gadhamshetty, V.; Jasthi, B.K. Synthesis of hexagonal boron nitride nanocoatings for corrosion prevention of iron substrates. *Surf. Coat. Technol.* **2023**, *468*, 129736, https://doi.org/10.1016/j.surfcoat.2023.129736.
69. Fukamachi, S.; Solís-Fernández, P.; Kawahara, K.; Tanaka, D.; Otake, T.; Lin, Y.-C.; Suenaga, K.; Ago, H. Large-area synthesis and transfer of multilayer hexagonal boron nitride for enhanced graphene device arrays. *Nat. Electron.* **2023**, *6*, 126-136, https://doi.org/10.1038/s41928-022-00911-x.
70. Kim, J.; Doh, K.-Y.; Moon, S.; Choi, C.-W.; Jeong, H.; Kim, J.; Yoo, W.; Park, K.; Chong, K.; Chung, C.; Choi, H.; Choi, S.-Y.; Lee, D.; Kim, J.K. Conformal Growth of Hexagonal Boron Nitride on High-Aspect-Ratio Silicon-Based Nanotrenches. *Chem. Mater.* **2023**, *35*, 2429–2438, https://doi.org/10.1021/acs.chemmater.2c03568.
71. Park, J.-H.; Lu, A.-Y.; Tavakoli, M.M.; Kim, N.Y.; Chiu, M.-H.; Liu, H.; Zhang, T.; Wang, Z.; Wang, J.; Martins, L.G.P.; Luo, Z.; Chi, M.; Miao, J.; Kong, J. Revealing Variable Dependences in Hexagonal Boron Nitride Synthesis via Machine Learning. *Nano Lett.* **2023**, *23*, 4741-4748, https://doi.org/10.1021/acs.nanolett.2c04624.
72. Wang, G.; Huang, J.; Zhang, S.; Meng, J.; Chen, J.; Shi, Y.; Jiang, J.; Li, J.; Cheng, Y.; Zeng, L.; Yin, Z.; Zhang, X. Wafer-Scale Single Crystal Hexagonal Boron Nitride Layers Grown by Submicron-Spacing Vapor Deposition. *Small* **2023**, *19*, 2301086, https://doi.org/10.1002/smll.202301086.
73. Tang, B.; Cao, M.; Yang, Y.; Guan, J.; Yao, Y.; Yi, J.; Dong, J.; Wang, T.; Wang, L. Synthesis of KH550-Modified Hexagonal Boron Nitride Nanofillers for Improving Thermal Conductivity of Epoxy Nanocomposites. *Polymers* **2023**, *15*, 1415, https://doi.org/10.3390/polym15061415.
74. Li, Z.; Yang, J.; Gao, H.; Qiao, J.; Qiao, W.; Wang, P.; Zhang, J.; Tang, C.; Xue, Y. Boron Nitride Microspheres via Pyrolysis of Polymerized Precursors. *ACS Omega* **2023**, *8*, 15239-15248, https://doi.org/10.1021/acsomega.3c00313.
75. Peng, Y.; Yang, Y.; Xiao, K.; Yang, Y.; Ding, H.; Deng, J.; Sun, W. Direct Synthesis of Vertical Self-Assembly Oriented Hexagonal Boron Nitride on Gallium Nitride and Ultrahigh Photoresponse Ultraviolet Photodetectors. *Nanomaterials* **2023**, *13*, 1546, https://doi.org/10.3390/nano13091546.
76. Kumar, D.; Hellerstedt, J.; Lowe, B.; Schiffrin, A. Mesoscopic 2D molecular self-assembly on an insulator. *Nanotechnology* **2023**, *34*, 205601, https://doi.org/10.1088/1361-6528/acba20.
77. Bae, D.; Jung, U.; Lee, H.; Yoo, H.; Moon, S.Y.; Lee, K.-H.; Kim, M.J. Synthesis of Double-Walled Boron Nitride Nanotubes from Ammonia Borane by Thermal Plasma Methods. *ACS Omega* **2023**, *8*, 21514-21521, https://doi.org/10.1021/acsomega.3c00498.
78. Biswas, A.; Maiti, R.; Lee, F.; Chen, C.Y.; Li, T.; Puthirath, A.B.; Iyengar, S.A.; Li, C.; Zhang, X.; Kannan, H.; Gray, T.; Saadi, M.A.S.R.; Elkins, J.; Birdwell, A.G.; Neupane, M.R.; Shah, P.B.; Ruzmetov, D.A.; Ivanov, T.G.; Vajtai, R.; Zhao, Y.; Gaeta, A.L.; Tripathi, M.; Dalton, A.; Ajayan, P.M. Unravelling the room

temperature growth of two-dimensional h-BN nanosheets for multifunctional applications. *Nanoscale Horiz.* **2023**, *8*, 641-651, https://doi.org/10.1039/d2nh00557c.

79. Yamamoto, M.; Murata, H.; Miyata, N.; Takashima, H.; Nagao, M.; Mimura, H.; Neo, Y.; Murakami, K. Low-Temperature Direct Synthesis of Multilayered h-BN without Catalysts by Inductively Coupled Plasma-Enhanced Chemical Vapor Deposition. *ACS Omega* **2023**, *8*, 5497-5505, https://doi.org/10.1021/acsomega.2c06757.
80. Chen, H.; Jiang, D.-E.; Yang, Z.; Dai, S. Engineering Nanostructured Interfaces of Hexagonal Boron Nitride-Based Materials for Enhanced Catalysis. *Acc. Chem. Res.* **2023**, *56*, 52-65, https://doi.org/10.1021/acs.accounts.2c00564.