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Doctor Thesis Screening Results Reports

論　文　題　目

Thesis Theme

Synthesis, Properties and Applications of B-C-N Nanosheets

Ｂ－Ｃ－Ｎ系ナノシートの創製と特性評価及び応用に関する研究

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Two-dimensional (2D) nanosheets are the rising stars in the new-material family; and sp^2-hybridized mono-/few-layered B-C-N-system nanosheets are the distinctive examples having rich physics and diverse functionalities owing to their low dimensions and special edge structures. The insulating boron nitride (BN) and semimetallic graphene nanosheets are two outstanding electrically neutral representatives equally attractive for understanding the fundamental physics and exploring the applications of nanosheets.

BN nanosheets possess high thermo-conductivity, impressive strength, wide band-gap and excellent thermal and chemical stability resulting from the robust B-N bonding. These properties enable BN nanosheets to be especially useful to make high-performance composite materials. However, the current research progress on BN nanosheets is drowsy, in contrary to the prosperous studies on their isostructural sisters, graphenes. This might be attributed to the lean production of BN nanosheets. The methods of mechanical cleavage, solution exfoliation and chemical vapor deposition (CVD) cannot give a high throughput of BN nanosheets. Moreover, the chemical exfoliation is not available to peel off the BN layers because of their strong inter-layer coupling. Therefore, the lack of mass production of BN nanosheets has notably hindered their scientific studies and immediate applications, and caused a delay in the full realization of their exciting potentials.

Graphenes possess high electrical and thermal conductivity and prominent mechanical strength, which are needed in polymeric composites, electronics and electrode materials. Reduced graphene oxide (RGO) is widely used in these fields; however, the low crystal quality and small lateral dimensions have severely suppressed the intrinsically high performance of graphene. It is still a challenge to synthesize the high-quality graphene products with a high yield.

BN nanosheets are insulators, while graphenes are conductors; both these features are unfavorable for realizing an electrical control. The homogenous combination of BN and C nanosheets is thought to attain a tunable band-gap. Nevertheless, there is still no an effective method to synthesize such materials.

Chapter 1 provided a careful review of the above-mentioned background on the progress and problems of BN, graphene and BN-C nanosheets.

In this dissertation, the author developed a new synthesis technique featuring a bubble-blowing process to solve the regarded problems of B-C-N-system nanosheets. The technology relied on the chemically released gases which blew molten precursor polymers of B-N-H, C-H or C-B-N-H into large polymeric bubbles with ultra-thin walls at 100-400°C; these bubbles were then crystallized at a high temperature of 1200-1400°C. The nanosheets of BN, graphene or C_x-BN were finally obtained from the corresponding crystalline bubbles. The high-yield production of high-quality B-C-N-system nanosheets was thus realized.

In **Chapter 2**, the author achieved the mass production of BN nanosheets through the newly established route of "chemical blowing". The "chemical blowing" method consisted of a facile multistage heating of the ammonia borane precursor, in which the self-released hydrogen blew the polymers derived from ammonia borane into large polymeric bubbles. The best bubbles were optimized at a heating rate of 8^{o}C/min together with a pretreatment under atmospheric pressure. BN nanosheets were subsequently refined from the crystallized BN bubbles.

This technology realized two main characteristics of BN nanosheets, *i.e.* high yield (40wt%) and laterally large dimensions (tens of micrometers). The latter ones are normally larger than those after the liquid exfoliation. The mono-/few- layered BN nanosheets with an average thickness of 3-5 nm were presented, and they possessed a hexagonal crystalline structure, a large surface area of 140 m^2/g and strong luminescence. Also, this catalyst- and substrate-free approach is simpler than the normal CVD method; it not only provides large-enough nanosheets readily available for their electrical and mechanical performance explorations, but also gives enough nanosheets' mass for fabricating ultimately strong polymeric composites.

In **Chapter 3**, C_x-BN nanosheets were produced through introducing ethanol atmosphere into the above-mentioned "chemical blowing" process. The different carbon contents and phase-separated structures of C_x-BN nanosheets were identified. The carbon domains with sizes of around 10 nm were attached to the surface of BN matrices. This is similar to the superlattice of graphene quantum dots. The first-principle calculation indicated that these C_x-BN nanosheets had the increased band-gap with decreasing the carbon content. This further determined the tunable conductivity varying from 10 to 0.01 S/m for $C_{0.7}$-BN and $C_{0.3}$-BN nanosheets, respectively, which is valuable for graphene-based electronics.

Graphene nanosheets were subsequently synthesized using a glucose precursor by an improved "chemical blowing" method, in which ammonium chloride served as an assistant exotic blowing agent. This route is different from the previous exfoliation and bottom-up methods; it thus can be added as a new member into the family of graphene syntheses. The obtained graphene nanosheets possessed high quality and conductivity (20,000 S/m), which is larger than those of typical RGO. Therefore, they acted as excellent electrodes for their electrochemical capacitors with a high capacitance.

In **Chapter 4**, the BN and graphene nanosheets were filled into polymer matrices to make composites, based on their high throughput by the established “chemical blowing” route. The mechanical strength was increased by tens of percents while filling polymethyl methacrylate (PMMA) or polycarbonate (PC) with a few weight percents of BN or graphene nanosheets. The significant 17-fold-enhanced thermo-conductivity together with the 18^oC increased glass transition temperature for 23wt% BN-filled PMMA was achieved, while the insulating properties were kept unchanged. This indicates that such highly insulating, thermo-conductive and thermo-stable polymeric composites are valuable for diverse functional applications in many fields, especially for the new-generation long-lifetime heat-release packaging in electrical circuits and power modules.

In conclusion, this work established a new technology featuring the bubble-blowing to produce high-yield and high-quality BN, C_x-BN and graphene nanosheets for the first time. BN nanosheets were applied as novel fillers to achieve the highly insulating and thermo-conductive polymeric composites, to satisfy the strong demand for heat-releasing packaging in electronics. The largely tunable conductivity of C_x-BN nanosheets was also realized, which is potentially useful for semiconductor electronics. Graphene nanosheets provided the mechanical reinforcement in their polymeric composites, and they also served as good electrodes for supercapacitors. In our opinion, the abundant nanosheet products must enable their wide applications and accelerate the full realization of their rich potentials in nanotechnology; and the developed herein synthesis technology opens up a wide horizon for the analogous growth of other 2D nanosheets. This work definitely deserves to be awarded with a Doctor of Engineering degree.

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