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Synthesis, microstructure and thermal stability of graphene nanoplatelets coated by hexagonal boron nitride (h-BN)

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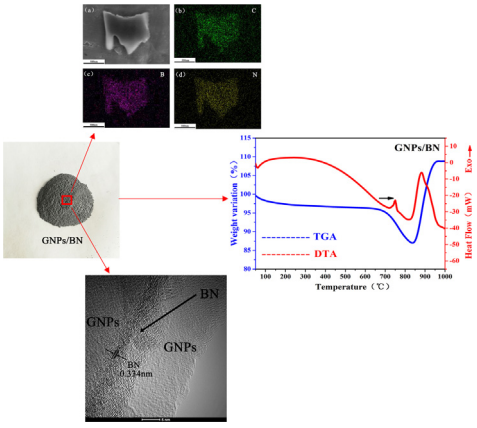
HIGHLIGHTS

- A boron nitride coating layer was successfully synthesized at the temperature as low as 950 °C.
- The precursor sedimentary layer more prone to deposit with surfactants and adhesives.
- The coating more uniform and extensive through van der Waals interplanar interaction by the precursor-assisted.
- The antioxidant capacity is achieved a 31% increase compared to pristine GNPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene nanoplatelets/Boron nitride (GNPs/BN) nanocomposites were prepared by precursor-assisted high-temperature sintering technique using carbamide (CH_4N_2O) and boric acid (H_3BO_3) at the temperature as low as 950 °C. The multilayer and single BN coverage combine with GNPs through van der Waals interplanar interaction without damaging the structures of GNPs. Specifically, GNPs/BN with oxidation temperature of 730 °C shows remarkable thermal stability compared to the original GNPs, indicating an increase of 31% in antioxidant performance, which provides great potential for GNPs in high-temperature heat-insulating coatings, inorganic refractories and heat-resisting binder, etc.

1. Introduction

Graphene, two-dimensional allotrope of carbon, has a specific surface area of 2630 m^2g^{-1}, a high Young's modulus of 1000 GPa, a thermal conductivity of 5000 $W\,m^{-1}K^{-1}$ and extraordinary carrier mobility [1–7]. Graphene nanoplatelets, known as inexpensive alternatives to pure graphene, have been explored widely attention and application due to its high thermal conductivity, excellent electrical conductivity, high mechanical and wear resistance properties [8–10]. However, the inherent nature of GNPs displays inferior thermal

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stability in air atmosphere under elevated temperatures, which limits the practical applications of GNPs at high temperatures. Therefore, it is imperative to find a way to improve the thermal stability of GNPs, and the common method is to compound it with another material.

Boron nitride is considered as a widely applicable material possessing the properties of high thermal stability and conductivity, low density and excellent corrosion resistance [11–16]. The structural and features similarities between GNPs and BN enable them integrated with each other so well that BN seem to be the impeccable candidate to be the antioxidant performance coating for GNPs [17]. Coating a uniform boron nitride films layers onto the surface of graphene nanoplatelets is not only a promising method for avoiding oxidation of the GNPs at high temperatures, but also an effective way for retaining the advantageous properties of GNPs. Different methods have been implemented to prepare the GNPs/BN nanocomposites. Shi [18] has synthesized a monolayer materials of boron nitride-graphene electrodes in nanocapacitor by chemical vapour deposition (CVD). Gao [19] has prepared artificially stacked boron nitride-graphene solids using liquid phase exfoliation methods by van der Waals interaction. Sun [20] has used an aqueous sodium borohydride-ammonium sulfate solution followed by a heat-treatment in stainless steel autoclave systems for BN coating synthesized on the functionalized RGO. However, the above methods cannot be well applied in industrial applications due to the complex apparatus, high-budget, high temperature, complicated operation and difficulties in producing continuous BN layers, etc.

In this study, graphene nanoplatelets/boron nitride (GNPs/BN) nanocomposites were prepared by the reaction of carbamide and boric acid, which had the advantages of convenient operation, simple technology and encapsulation effective method. GNPs/BN samples were characterized by a series of detection equipments, the results indicate that uniform and extensive boron nitride coating were attached to the surface of graphene nanoplatelets successfully. The thermal stability of the GNPs/BN composites was determined by thermal gravimetric analysis and differential thermal analysis (TG-DTA), indicating that the antioxidant performance properties of GNPs greatly improved, which expands the application potential of GNPs at elevated temperatures.

2. Experimental

2.1. Materials

The original materials of boric acid (H_3BO_3, 99.95%) and carbamide (CH_4N_2O, 99.95%) were supplied by Tianjin Wind Boat Chemical Reagent Technology Co. Ltd and Tianjin Guangfu Fine Chemical Research Institute, respectively. Sodium dodecyl sulfate (SDS, $NaC_{12}H_{25}SO_4$, 99.95%) was used as surfactant and binder, which was purchased from Tianjin Bodi Chemical Co. Ltd. The materials were analytical-grade and used as received without further purification. The industrial grade graphene nanoplatelets (GNPs, 99.8%) with average particle size of $4 < M < 20$ μm were purchased from Suzhou Carbon Technology Co., Ltd.

2.2. The synthesis of samples

Fig. 1 illustrates the preparation procedure schematic of GNPs/BN nanocomposites. First, 1.201 g of CH_4N_2O and 2.472 g H_3BO_3 were dissolved in ethanol of 60 ml. Next, GNPs of 0.12 g and 1.442 g SDS were added in the solution. The mixed solution was then sonicated for 2 h and stirred for 12 h under a magnetic stirrer. After that, the intermixture was heated in a water-bath of 40°Cmild condition until it forms clumpy. Then, the precipitate was washed and vacuum dried. Finally, GNPs/BN nanoparticles were obtained after that the precipitate was sintered in an ammonia atmosphere at 950 °C.

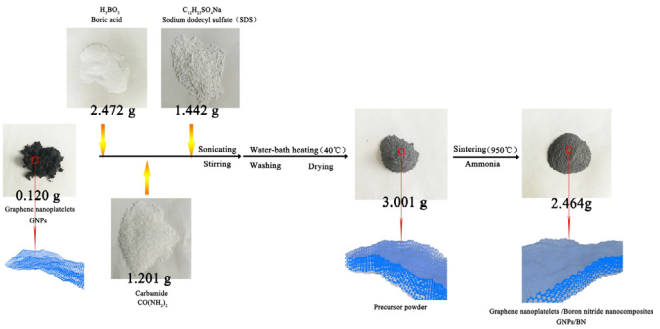

Fig. 1. Schematic of the preparation of GNPs/BN nanocomposites.

2.3. Characterization

X-ray powder diffraction (XRD, Germany, Vinci) patterns were characterized at a scanning speed of 8°/min in the 2 θ range from 10° to 80° on a Rigaku smartlab diffractometer with Ni-filtered Cu Kα radiation. The types of chemical bonds were performed by Fourier transform infrared Spectroscopy (FTIR, Germany, Vector 22) in the range of 500^{-1} to 4000 cm^{-1}. Surface morphology and structure of the films were carried out by scanning electron microscope (SEM, American FEI Company, NovaNanoSEM450) and transmission electron microscope (TEM, Japan JEOL, JEM-2010FEF), respectively. X-ray photoelectron spectroscopy (XPS, America, ESCALAB-250Xi) was used to investigate its surface compositions from the Thermo Fisher Scientific Co. Ltd with a source of monochromatized AIKa. The BN layers on the surface of GNPs with their uniformity and universality of the samples were also studied by FESEM (American FEI Company, NovaNanoSEM450) and STEM-HAADF (Talos F200X, American FEI Company) with the correlative elemental maps of B, C and N. Oxidation mechanism of original GNPs and GNPs/BN was obtained using thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) instrument (TG-DTA, America TA Instruments-water, LLCSDTQ-600) at a heating rate of 5 °C/min from room temperature to 1000 °C in flowing air.

3. Results and discussions

Crystal phase and structure analysis were characterized by XRD. Fig. 2 shows the XRD patterns of the (a) GNPs/BN and (b) GNPs. It can be clearly observed from Fig. 2(a) that GNPs/BN with a well-crystallized structure has two typical diffraction peaks at $2\theta = 26.45°$ and 54.60° corresponding to the lattice planes (002) and (004), respectively [21–24]. As can be observed in Fig. 2 (b), there are two distinct characteristic diffraction peaks at 26.55°and 54.65°, corresponding to the (002) and (004) reflections of GNPs, respectively [8]. The structural similarities between BN and GNPs cause them combined with each other perfectly so that it is hard to distinguish the diffraction peaks between them [25]. In addition, GNPs/BN also shows three different peaks at 41.65°, 43.99° and 77.37°besides the typical characteristic peaks of GNPs, which are analogous to that lattice planes (100), (101) and (110) of BN, indicating that GNPs/BN nanocomposites were successfully synthesized [26].

The crystal defects of GNPs and GNPs/BN were investigated by Raman spectroscopy, as depicted in Fig. 3. GNPs reveal two prominent peaks at 1352 cm^{-1} and 1583 cm^{-1}, corresponding to the well-documented D and G bands, respectively [8]. The D band is ascribed to the degree of lattice disorder in graphene, whereas the G peak is commonly related to the in-plane stretching mode of sp2 carbon atoms [25]. The intensity ratios of I_D/I_G are usually used as an characterization methods of the defect density. As can be seen in curve (a), GNPs/BN has two distinct peaks at 1356 cm^{-1} and 1585 cm^{-1}, which exhibits a trace deviation of the peak in comparison with GNPs, indicating that the structures of GNPs are unalterable in reaction process [27–29].