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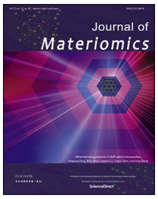

Solvothermal-assisted liquid-phase exfoliation of large size and high quality black phosphorus

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ABSTRACT

Black phosphorus (BP), especially for BP nanosheets, with unique layered structure among two dimensional (2D) materials has attracted much attention due to its outstanding physical properties, such as ultra-high mobility, in-plane anisotropic properties. However, the small horizontal-size of reported BP limits its applications in the integrated circuit or some functional devices. In this work, a solvothermal-assisted liquid-phase exfoliation technique is firstly employed for preparing large size and high-quality BP nanosheets. In the high-polar acetonitrile solvent, solvothermal treatment weakens the Van der Waals forces of block BP. Together with the subsequently ultrasonic processing, effective exfoliation of large size and high-quality BP nanosheets are realized. The TEM, AFM and Raman results indicate that the prepared BP nanosheets are high quality with an average thickness of about 2 nm, and the horizontal-size is up to 10 μm. This facile and effective method for exfoliated BP nanosheets provides a promising strategy for the exfoliation of other 2D materials.

1. Introduction

Since the discovery of graphene in 2004 [1], a large number of two-dimensional (2D) materials are bloomed in the past years. Black phosphorus (BP) is a new-emerging 2D material after Zhang's work in 2014 [2]. Black phosphorus (BP) was first discovered under high pressure at about 100 years ago [3]. It exhibits extraordinary physical properties compared to other 2D materials [4–8]. Due to its puckered structure, BP exhibits strong in-plane anisotropy properties [8]. Also the bandgap tunability of BP enables a wide range of ultrafast electronics (high mobility) and high frequency optoelectronic applications ranging from telecommunications to thermal imaging covering the nearly entire electromagnetic spectrum [4,9]. In addition, in comparison with other phosphorus allotropes, such as red and white phosphorus, BP is more stable [9].

Similar to graphite, BP was consisted by monatomic layer of P atoms, i.e., periodic stacking of phosphorene layers. In each layer, P atom is single-bonded to 3 nearest neighbors [10–12]. BP few layers and phosphorene are promising materials which can be applied in electronics and optoelectronics such as high-performance radio-frequency and logic transistors [6], field-effect transistors [13,14], phototransistors [15], photodetectors [16,17], lithium ion batteries [7], sodium ion batteries [10], solar cells [18] and all-solid-state supercapacitors fields [19,20]. Because of the Van der Waals force between the adjacent layer of BP, it can be exfoliated from bulk BP crystals [21,22] as other 2D materials.

Researchers in this field tried great effects to produce few-layer BP to explore the possible applications of them in different fields. Exfoliation was the earliest method to obtain various 2D materials, including mechanical exfoliation and liquid exfoliation method. Mechanical exfoliation was widely used in getting monolayers or few layers 2D materials from their bulk crystals. This method was also called green exfoliation because it does not pollute the surface of the lamellae, but the inability of mass production and poor reproducibility limit its use in energy storage and catalysis which needs a large amount of samples [10,23,24]. In comparison, liquid-phase exfoliation shows its superiority in obtaining a mass of

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materials. It also has many advantages including solution processability, scalability, stability and an effective path to the preparation of composite materials. At present, ultrasonic bulk BP crystals in organic solvents are the most common way to get few-layer BP, such as in N-Methyl pyrrolidone (NMP) [25], N-Cyclohexyl-2-pyrrolidone (CHP) [26], Dimethyl sulfoxide (DMSO), Dimethylacetamide (DMA) organic solvents [27]. However, in order to obtain fewer-layer BP, ultrasound bulk crystals usually take a long time (>10 h) [10,23,28], and this prolonged and continuous ultrasonication greatly destroys the transverse dimension of the BP sheet. Therefore, most of the obtained black phosphorus sheets are in the nanometer-scale horizontal size of hundreds of nanometer [19,23,29]. However, the small horizontal-size of reported BP limits its applications in the integrated circuit or some functional devices. Large size BP sheets hold many advantages including the high specific surface area and numerous active sites etc., which will provide BP sheets a wider application in energy storage, light emitting diode, gas sensor and other fields. Therefore, the development and preparation of BP sheets with superior size are of great significance.

Herein, for the first time, a facile, novel, and efficient solvothermal-assisted liquid phase exfoliation method was employed to prepare few-layer black phosphorus nanosheets with the size up to 10 μm. The acetonitrile (ACN) solvothermal-assisted liquid-phase exfoliation technique can weaken the van der Waals forces and then shorten the sonication bath time. Thus, this technique can result in large size and high-quality BP sheets. Above processes effectively utilize the volatile advantages of acetonitrile, which is a volatile organic solvent, also, it can be easily removed by the solubilization in water or ethanol. The obtained BP samples are characterized by X-Ray diffraction (XRD), Raman characterizations, Atomic Force Microscope (AFM), scanning electron microscope (SEM) and transmission electron microscope (TEM). Results show that the acetonitrile solvothermal-assisted liquid-phase exfoliation technique can get BP nanosheets with large horizontal size and high quality. This facile and effective technique for exfoliated BP nanosheets provides a promising strategy for the exfoliation of other 2D materials.

2. Experimental section

2.1. Materials preparation

All chemicals (analytical grade) were used as received without further treatment. The bulk BP crystals were purchased from a commercial supplier (Nanjing XFNANO Material Tech. Co., Ltd) and stored in a dark Ar glove box. The BP crystals were grounded into thinner flakes in a mortar, then the processed BP flakes (40 mg) was mixed with ACN (40 mL) in a 50 mL Teflon autoclave, and bubbled Nitrogen for 20 min to remove air from the system before solvothermal treated at 200 °C for 24 h. The reaction products were sonicated for 30 min, 60 min, 120 min and 240 min respectively at 360 W in order to obtain different layers and sizes of BP nanosheets. Afterwards, the mixture was centrifuged at 1500 rpm for 20 min (Beckman Coulter Allegra 64R), and the resulting BP nanosheets supernatant was collected for further structural characterization.

2.2. Materials characterization

The morphologies of the samples were observed on field-emission scanning electron microscopy (FESEM, SU8020) and Tecnai G2 F20 S-Twin Field-emission transmission electron microscopy (FETEM) operated at an acceleration voltage of 200 kV. Raman spectra were measured and collected using a Renishaw in Via Raman microscope with an excitation wavelength of 532 nm. The X-ray diffraction (XRD) patterns were carried out using a D/Max-3c X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å), scanning from 5° to 70° and using an operating voltage and current of 40 kV and 15 mA, respectively.

3. Results and discussion

According to the change of the colour and the characterization, we drew the experimental process and mechanism in Fig. 1. It schematically illustrates the solvothermal-assisted exfoliation and dispersion process of BP nanosheets in ACN. In the bottom of the schematic diagram, the corresponding colours of BP dispersions in each step are shown. Firstly, after the BP crystals were grounded into thinner flakes in a mortar for 5 min, they were mixed with ACN, in the meanwhile, at this stage, the colour of the dispersion is transparent (shown in the bottom of Fig. 1a). Then BP dispersion was transferred into a Teflon-lined autoclave and heated to 200 °C for 24 h. The dispersion did not change significantly and the colour of the dispersion was almost transparent. At this step, ACN molecules are intercalated to the layers of BP. This is the key step for exfoliation of BP. In the third step, the resulting solution was sonicated for an hour, and we found that the colour of the dispersion changed from transparent to dark brown. This was similar to the dispersion which sonicated for 10 h continuously in N-methyl-pyrrolidone (NMP) at the same initial concentration [30]. In the last step, the above solvent was centrifuged at 1500 rpm for 20 min. The resulting BP nanosheets supernatant was collected. Compared to the dark brown samples, the colour of the supernatant is light brown. For the mechanism of the exfoliation, the insertion of ACN between BP layers at the second step effectively weakens the van der Waals forces between BP layers, making them easier to be peeled off. The solvothermal treatment in ACN solution ensured the preparation of the large-size few-layer BP nanosheets.

Obvious Tyndall effect was observed in the solvent with different ultrasonic time in Fig. 2a. This phenomenon indicated that the dispersions have good dispersity and homogeneity. Fig. 2b shows the Raman spectra of as synthesized BP nanosheets with different ultrasonic time and bulk samples. There are three Raman peaks appearing between 300 and 500 cm^{-1}. Raman spectrum of bulk BP crystal and the BP nanosheets with 30 min ultrasonic time exhibits well defined peaks at 362, 437, and 464 cm^{-1} corresponding to the phonon modes A_g^1, B_{2g} and A_g^2, respectively, and this is in good agreement with literatures [31,32]. However, with the increase of ultrasonic time to 60 min, the position of Raman peaks is displaced, because under the influence of covalent bonding, the P atoms collectively oscillate within the monolayers. When another layer of BP is added and bonded by van der Waals forces, the oscillation of the P atoms is hindered. Hence, the corresponding Raman energy becomes smaller resulting in a red-shift [33,34]. And we can see that the dispersions compared with bulk BP, the intensity of Raman peaks became weakened. In addition, the Raman peaks showed a certain degree of blue shift, indicating that with the increase of ultrasonic time, the layer number of BP nanosheets decrease. This is maybe caused by the vibration changes with the decrease of BP nanosheets [33,35].

Fig. 3 shows the TEM images (a-d) and topic microscope photos (d-h) of the dispersions with different ultrasonic time. Compared with the sample after the ultrasonication for 30 min (Fig. 3a, e), the BP layers treated for 60 min display the thinner thickness, and the horizontal sizes of various sheets are up to 10 μm (Fig. 3b, f). When the time extends to 120 min, the sizes of BP layers have decreased to 3–5 μm due to the long-time vibration treatment (Fig. 3c, g). Even, the BP layers have tended to a smaller size with the layer-by-layer stacking after the longer ultrasonication for 240 min (Fig. 3d, h). Therefore, the ultrasonic treatment for 60 min is the optimized

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