Exfoliation of hexagonal boron nitride nanosheets assisted with covalent organic frameworks by ball-milling

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Abstract: Boron nitride nanosheets have superior chemical and physical properties. However, there are many problems in the preparation of hexagonal boron nitride nanosheets, and an effective exfoliation method is still lacking. To solve this problem, this paper intends to obtain boron nitride nanosheets by ball milling using TpPa from COFs material as a ball milling aid, and to investigate various factors affecting the ball milling effect. The h-BN obtained by using some other polymer materials such as starch and pvp as ball milling aids were compared with the h-BN peeled by using COFs materials as ball milling aids, and the results showed that the peeling effect of using TpPa as ball milling aids was not satisfactory because the structure of COFs materials was too stable. This paper also further conducted ball milling experiments on a variety of dry auxiliaries and compared them according to the ball milling effect The strength, friction, softening point and hardness were analyzed by machine learning. The analysis revealed that these aspects affect the cross-sectional area, thickness and aspect ratio of h-BN nanosheets. To obtain good h-BN nanosheets, the main conclusions of this paper are as follows: For the cross-sectional area of h-BNNS: the bond strength, friction, hardness and softening point of the ball milling agents have a strong influence on it and are positively correlated with it, while the friction and softening point of the ball milling agents are negatively correlated with it. For the thickness of h-BNNS: the bond strength and decomposition point of ball abrasives have influence on it, but not much, while hardness, softening point and contact angle have more influence on it, and hardness and contact angle are positively correlated with it, and softening point is negatively correlated with it. For the aspect ratio of h-BNNS: the hardness, softening point and contact angle of the ball abrasive have a greater effect on it, while the softening point has the greatest effect on it with a positive trend and the hardness and contact angle with a negative trend.

1. Introduction

The structure of hexagonal boron nitride is similar to that of graphite [1], which is also known as white graphite structure because of the alternating arrangement of N and B atoms in the place of C atoms in graphite. After the discovery of graphene, researchers have focused their attention on a range of similar two-dimensional materials, including two-dimensional boron nitride nanosheets (BNNSs) [3]. Recently, researchers have started studying BNNSs more closely, although they are significantly less explored than graphene. This is because adjacent layers of graphene are stacked together by weak Van der Waals forces, but in BNNSs, the B-N bond is more polar than the carbon-carbon bond, resulting in the presence of lip-lip forces between the two adjacent layers of BNNSs. Therefore, the synthesis approach of BNNSs are difficult to develop and manufacture. Boron nitride exists in four distinct crystalline forms including h-BNNs, r-BNNs, w-BNNs and c-BNNs[2]. Among them, hexagonal boron nitride nanosheets (h-BNNSs) have unusual features. Therefore, commercialization of h-BNNSs has been a goal for researchers. Mechanical exfoliation using transparent tape [4] was the first approach successfully used to generate self-supported graphene and applies to other layered materials such as hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2). Although this approach produces high-quality two-dimensional nanomaterials, the production yields is not satisfied. It is more practical to exfoliate them by introducing a metal or solvent ion between their layers. However, this process is environmentally sensitive, and the re-agglomeration is uncontrollable when the inserted substance is withdrawn [5]. Liquid-phase exfoliation may be used to manufacture vast amounts of two-dimensional h-BNNSs [5-10], but the solvents are costly and difficult to manage. As a result, it is significant to develope a straightforward process for producing vast amounts of h-BNNSs. Developing a mechanical process capable of handling tens of thousands of particles in a single run and exfoliating each one hundreds of times would allow the harvesting of large quantities of high-quality nanosheets for research and practical applications, and ball milling is the answer to these problems.

1.1 Mechanical ball milling method

Mechanical ball milling exfoliation is a frequently used physical process for preparing BNNSs. This method is simple to operate, easy to control, and less sensitive to environmental conditions; it uses ball milling in a sealed tank and can be fed with protective gas to avoid the influence of air during the synthetic process; it consumes relatively little energy; the ball milling process generates low temperatures, resulting in low production costs; it can produce large quantities of BNNSs and disperse them to a solution with high solubility.

BNNSs are primarily exposed to shear and impact pressures during the ball milling process. The sheer force mainly reduces the cross-sectional size, whereas the impact force reduces the flat size. Mechanical ball milling is a process that successfully exfoliatesboron nitride from the sheet by using the impact and shearing action of the ball milling ball on the boron nitride sheet. During the refinement process, impact and shear between the boron nitride sheet and the grinding ball are created continually, stripping the boron nitride sheet to yield BNNSs. The size of BNNSs is continually refined in each boron nitride sheet, from flat to cross-sectional, by the impact and shear of mechanical ball milling. The three-dimensional dimensions of the BNNSs decrease as the ball milling duration rises, but the impact and shear stress flaws on the BNNSs grow. Throughout the ball milling process, as the size of the boron nitride sheet gradually changes, the defect density of some parts of the boron nitride sheet reaches a critical value. The boron nitride sheet begins to refine from the three-dimensional size and continues to refine until the formation of BNNSs. When the ball milling duration reaches a certain value, the impact and shear forces on the boron nitride sheet refining will rise. When the ball milling duration is long enough, the refining effect of impact and shear on the boron nitride flakes reaches a critical value, and the three-dimensional size of BNNSs remains unchanged.

Scalable and economical manufacturing of high-quality BNNS remains difficult due to the strong

interlayer interactions of h-BN. Typically, top-down techniques such as intercalation oxidation [7], ultrasonic liquid stripping [8], and high-pressure spraying [9] are employed to convert layered h-BN blocks to single- or few-layer h-BNNSs. However, most stripping techniques take times, have poor stripping effectiveness (less than 10%), or require significant amounts of organic solvents (N-Methyl-2-Pyrrolidone, N, N-dimethylformamide and alcohols, etc.)

The usage of organic solvents significantly restricts their practical applicability. This shear and impact force is enormous, and as the ball milling process continues, the defect density on the particle surface increases, destroying or disturbing the crystal structure and introducing a large number of defects. A new type of novel mechanical ball milling technique is needed.

In summary, the mechanical ball milling exfoliation technique is the most feasible method for the preparation of BNNSs, since it can produce BNNSs on a large scale and yield high purity BNNSs, so it will be adopted in this work. This work concentrates research efforts to further develop and optimize the mechanical ball milling exfoliation process.

2.Experimental Section

2.1 Ball milling preparation of boron nitride nanosheets

The steps for the preparation of boron nitride nanosheets by mechanical ball milling and exfoliation are as follows.

(1) Weigh the boron nitride flakes, put the boron nitride flakes in the ball mill jar, measure 10 ml of medium-sized balls and 5 ml of small-sized balls into the ball mill jar, then add the ball mill agent in and cover the lid.

(2) Put the ball mill jar on the ball mill and turn it.

(3) After the ball mill stops rotating, take out the sample.

(4) The sample is collected and put into the sample bag for subsequent characterization test.

Then change the ball mill type one by one to get the best ball mill conditions.

3.Results and Discussions
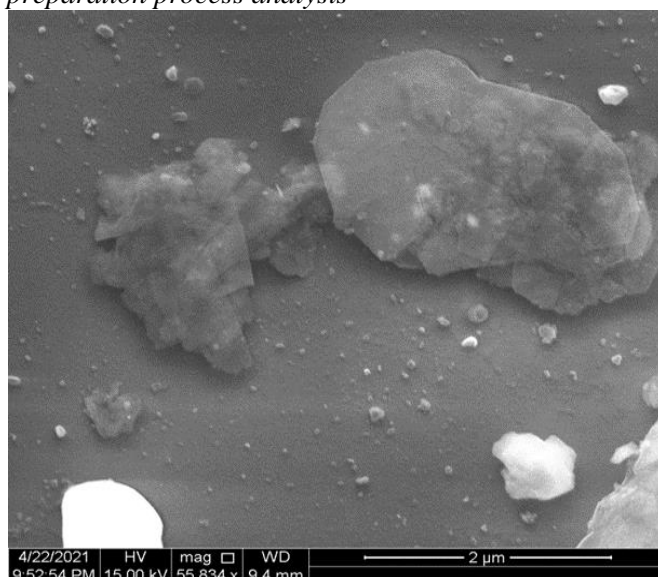
3.1 Ball mill preparation process analysis

Fig.1 SEM image of plain ball milled h-BN
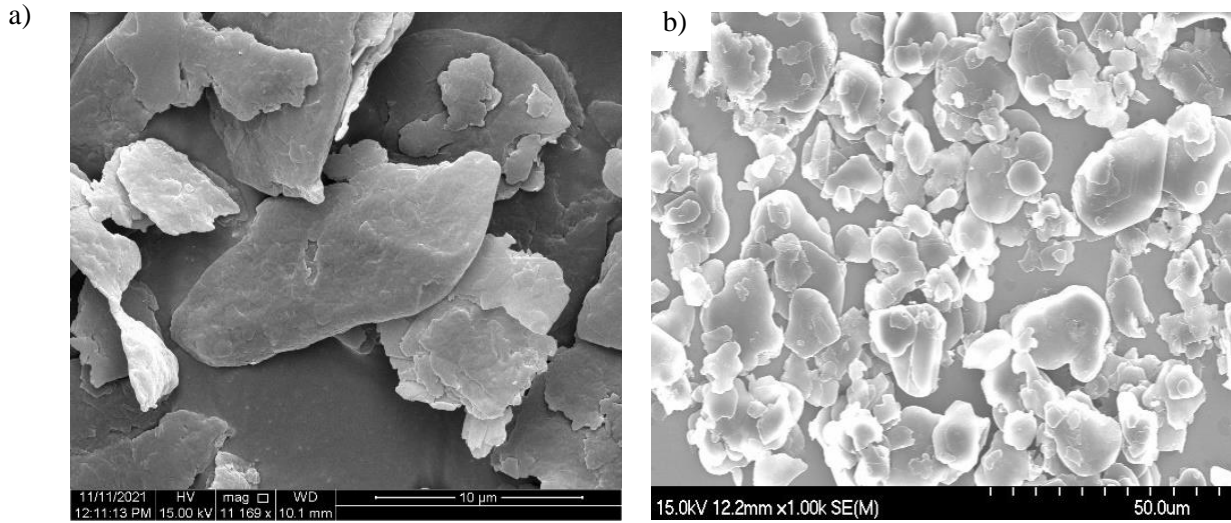
a)
b)

Fig.2 SEM of h-BN obtained with different types of ball milling aids   a) starch; b) TpPa

As shown in Figure 1, SEM images of the flat surfaces of h-BN were obtained at a speed of 500 r/min, a ball milling time of 72 h, a ball-to-material ratio of 150:1, no ball milling aid, and a 2:1 ratio of the number of 2 mm balls to 1 mm balls of zirconia. experiments.

After the addition of the ball milling aid, the larger h-BN was subjected to the shear and impact forces of the ball mill. Under the shear and impact forces of the ball, cracks due to impact and shear appear on the surface of the h-BN in a relatively short period of time, and the cracks extend and fracture on the surface of the h-BN, i.e., a three-dimensional small size is formed, and the h-BN with a smaller size is formed. We used TpPa from COFs material as a ball milling aid

In order to compare the effect of different types of ball milling agents on the ball milling effect, mechanical ball milling was carried out with TpPa, starch as shown in Fig. 2 SEM photographs of zirconia balls obtained with two types of ball milling agents at a speed of 500 r/min, a ball milling time of 2 h, a ball-to-material ratio of 150:1, an aids ratio of 5:1 and a size ratio of 2:1. From Figure 2, it can be seen that a) the h-BN plane size obtained for starch is 13 µm ,b) the average plane size obtained for TpPa is 16 µm, which is due to the over-stable structure of COFs material compared to other ball milling agents and the lack of better viscosity compared to starch.
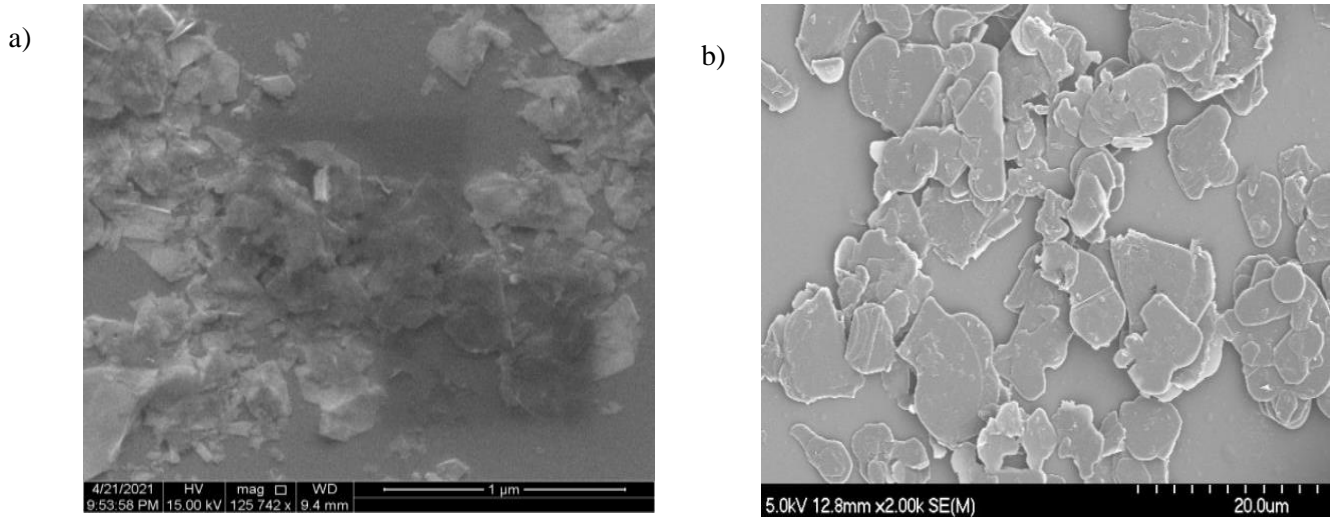
Fig.3 The above two auxiliaries assisted ball milling after 24h h-BN a) starch; b) TpPa

After increasing the ball milling time under the condition of adding ball milling aid, firstly, compared with fig1 ball milling without ball milling aid for 72 h, as fig3 shows that the ball milling time required to reach the same size of plane size after adding the auxiliary ball milling aid is significantly shorter, but as fig3 the average size of h-BN plane obtained by starch as ball milling aid after 24 h of ball milling under the same condition is 5 μm while The average size of the h-BN plane obtained by TpPa as an auxiliary agent is 11μm and the ball milling effect is better with the addition of starch. This is because compared with other solid ball milling aids, starch has moderate viscosity and similar surface tension to h-BNNSs, which can reduce the shear and impact resistance in ball milling and enhance the stripping effect, and can effectively prevent the freshly stripped h-BN from reaggregating.

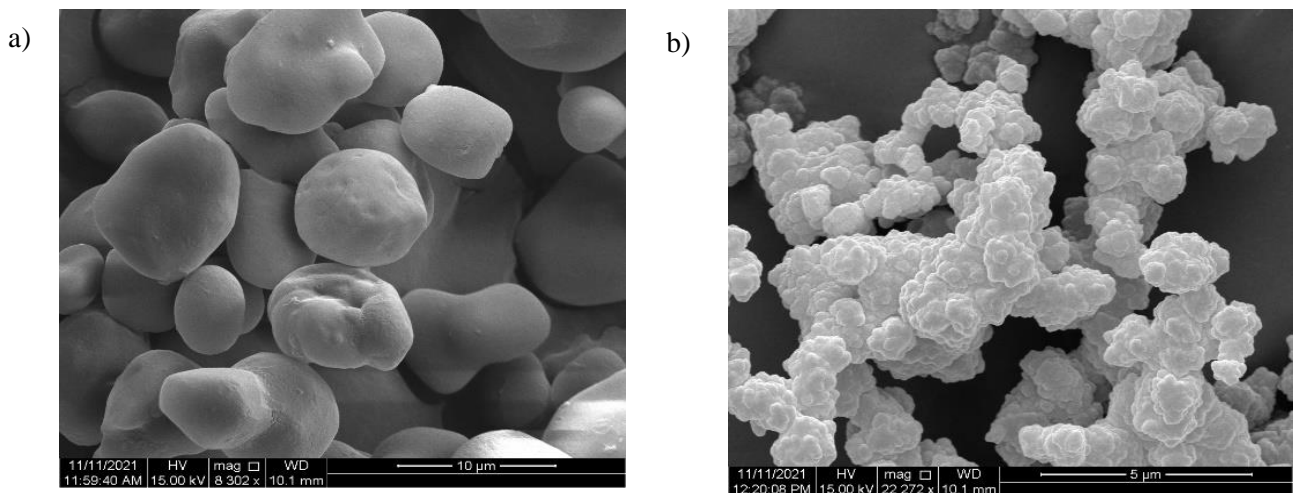*3.2 Effect of COFs material characteristics on ball milling effect*

Fig.4 a) structure of starch; b) structure of TpPa

Figure 4a) shows the SEM image of starch, and b) shows the SEM image of TpPa. It can be seen that the structure of this COFs material is more stable and gathered together and not easy to disperse, so it can not contact well with boron nitride during ball milling, and because the structure is stable so it limits the movementment during ball milling.
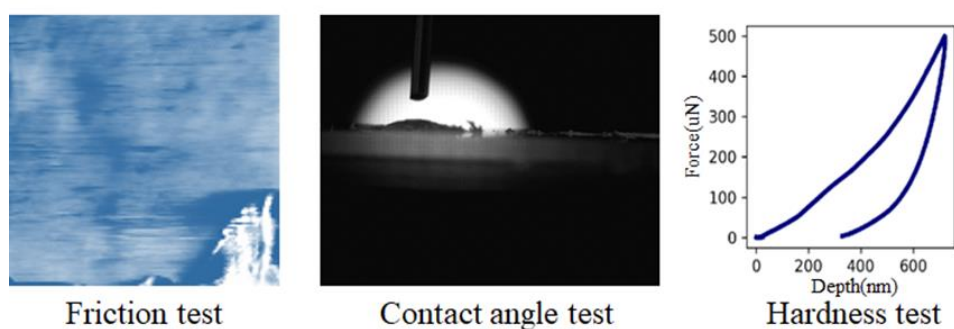
Characterization tests of TpPa-1

Friction test   Contact angle test   Hardness test
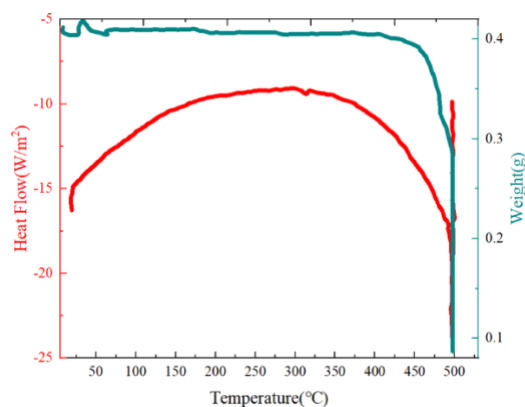
Fig.5 Characterization test of TpPa-1

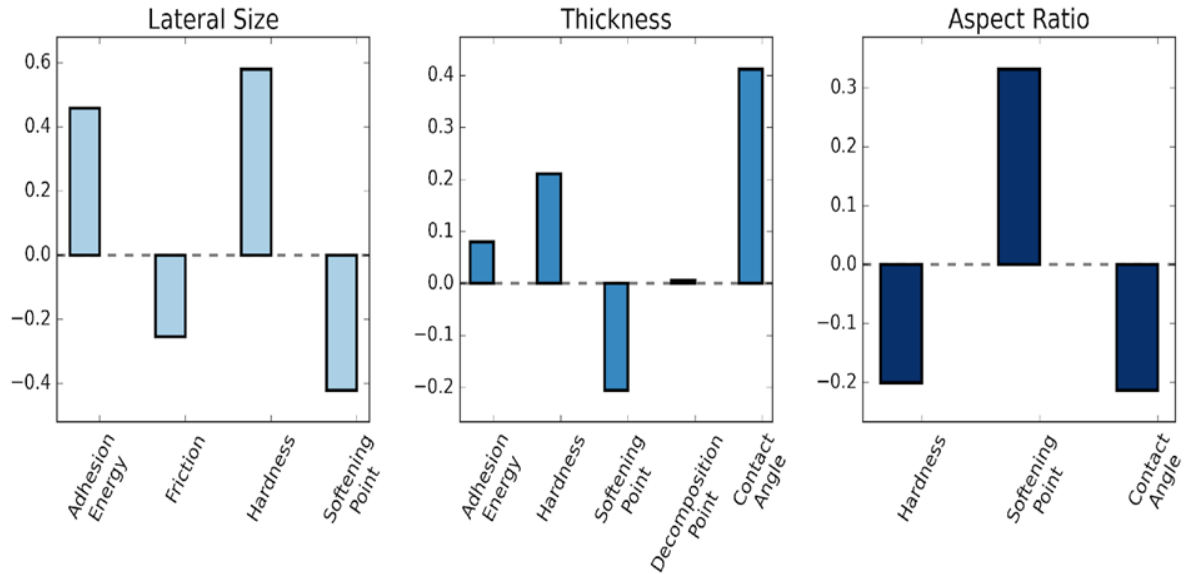
Fig.6 Thermogravimetric analysis

Fig.7 Impact prediction results after machine learning

As shown in Figures 5,6.The properties of different materials such as PVP and starch were tested with the same test method and used as ball milling aids.The results after ball milling were compared with those after TpPa-assisted ball milling and then machine learning methods were used to analyze and predict the effect of these test results on the lateral dimensions, thickness and aspect ratio of the h-BNNSs after ball milling, resulting in the results in Figures 7.

For the lateral size of h-BNNSs: the bond strength, friction, hardness and softening point of the ball abrasives have a strong influence on it and are positively correlated with it, while the friction and softening point of the ball abrasives are negatively correlated with it.

For the thickness of h-BNNSs: the bond strength and decomposition point of ball abrasive have influence on it, but the influence is small, while the hardness, softening point and contact angle have greater influence on it, and the hardness and contact angle are positively correlated with it, and the softening point is negatively correlated with it.

For the aspect ratio of h-BNNSs: the hardness, softening point and contact angle of the ball abrasive have a greater influence on it, among which the softening point has the greatest influence on it and has a positive trend, and the hardness and contact angle have a negative trend.

4. Summary and Prospects

The research in this paper is important and are able to improve the existing ball milling method to obtain h-BNNSs. It improves the accuracy in selecting the suitable ball milling auxiliary and greatly improves the efficiency of exfoliation of h-BNNSs. This work also has a broad research prospect. Further research work to be done in the future including:
1. Synthesize or find a COF material with high hardness, certain bond strength and hydrophilic, and use it as a ball milling aid for synthesis of h-BNNSs.
2. Continue to conduct the same experiments with other polymer materials and keep improving the machine learning procedure to make the prediction results more accurate.

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