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Highly-dispersible boron nitride nanoparticles by spray drying and pyrolysis

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ABSTRACT

A spray drying and pyrolysis synthesis route was developed and it successfully prepared boron nitride (BN) nanoparticles with high dispersivity. During the experiment, the extremely rapid drying of the boric acid/urea solution during the spray-drying process resulted in the formation of homogeneous precursors, which was the key for the final pyrolysis synthesis of BN nanoparticles with high dispersibility and uniform diameters (~20 nm). Compared with boron nitride synthesized without using spray drying, the as-prepared BN nanoparticles possess higher specific surface area (145.01 $m^2 g^{-1}$) and larger pore volume (0.41 $cm^3 g^{-1}$). Especially, we used the BN nanoparticles as lubricant and incorporated it into the liquid paraffin (LP). The experiment results show that the LP presents outstanding antifriction properties for a BN content of 1.5 wt%. These results suggest that the h-BN nanoparticles have significant potential applications in the field of tribology.

1. Introduction

Inorganic nanoparticles have been widely used in various fields, including thermotics [1], biomedicine [2], electronics [3] and photonics [4] because of their unique physical and chemical properties. Previous researches on inorganic nanoparticles predominantly focused on synthetic method, morphology and composition rather than their application. With the rapid development of society and science technology, the applications of inorganic nanoparticles have become more and more important. Hence, it is meaningful to conduct a research on the applications of inorganic nanoparticles.

Among inorganic nanoparticles, hexagonal boron nitride (h-BN) nanoparticles have attracted great interest due to their unique physical and chemical properties, including high specific surface area, numerous structural defects, lubricating characteristics, low density, high thermal conductivity, chemical durability and oxidation resistance [5–8]. Various methods have been used for producing BN nanoparticles, such as template method [9], hydrothermal method [10], ball-milling peeling method [11], chemical vapor deposition (CVD) techniques [12] and other methods [13]. For example, graphene analogues of BN nanoparticles were fabricated by solid state thermal annealing method using boric acid and urea as starting materials [14]. Water-dispersible boron nitride nanoparticles had been successfully synthesized by adjusting the reaction temperature and time in the pyrolysis process [15]. Xu et al. found that BN nanoparticles were prepared by using BBr_3, NH_4Br and metallic Na as reactants in stainless steel autoclaves at 450 °C for 24 h. [16]. BN nanospheres can be prepared through aerosol-assisted method [17]. The CVD method was selected to fabricate spherical h-BN by using trimethoxyborane as the reactant under an NH_3 atmosphere [24]. In addition, a modified solid state metathesis reaction route was also used to prepare h-BN nanoparticles with low agglomeration degree [18]. But these methods have disadvantages more or less, such as high cost, low purity, high temperature and low yield etc. Spray drying has the characteristics of fast heat transfer, rapid water evaporation and short drying time [19]. Besides, the as-prepared products possess high purity and good uniformity [20]. The hollow capsules of organic materials have been reported by spray-drying technology in a single-step route [21]. Recently, the technology has been extended to metal-organic-frameworks (MOFs) which can be crystallized at mild temperatures [22]. Moreover, spray pyrolysis is appropriate for the mass-production of highly crystalline fine particles with reduced processing time and solvent. However, to the best of our knowledge, investigations on the fabricating BN nanoparticles via spray-drying method have been rarely reported.

In addition, it is well known that morphologies and sizes of BN nanomaterials are significant to understand the shape–property relationship and to develop functional materials for specific applications. Various morphologies of BN micro/nanomaterials have been reported since the first discovery of BN nanotubes in 1995, including nanotubes [23], nanoparticles [24], nanoribbons [25], nanosheets [26], micro/nanospheres [27], nanowires [28] and nanofibers [29]. The different morphologies of boron nitride materials have been applied in many

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fields. For instance, BN nanotubes (BNNT) as filler were added into composites to improve mechanical strength owing to their unique properties [30]. They were also used in enhancing thermal conductivity, and decreasing dielectric constant and loss of polymer-matrix composite [31]. The highly porous BN microbelts with large specific surface area (up to 1488 $m^2 g^{-1}$) were used for hydrogen storage. The results show that the sample possesses the largest reversible H_2 uptake capacity of 2.3 wt% at 77 K and 1 MPa [32]. Boron nitride nanosheets exhibited superhydrophobicity, high selective absorption and adsorption capacities for oils, organic solvents and dyes, and they afforded a new strategy in water purification and treatment [33]. Novel BN hollow microspheres with open mouths had potential applications in the field of ultraviolet lasing due to intense cathodoluminescence emissions at 338.7, 403.1 and 458.2 nm [34]. Furthermore, nanoporous BN materials had important applications in biological fields when their surfaces were engineered to be hydrophilic. Highly hydroxylated nanoporous BN were water-soluble and nontoxic, and they served as efficient transports vehicles for drug delivery up to 309 wt% [35]. Tribological performance as an important technical index has been widely used in many fields. Steel, plastic, nylon, rubber and Al-Si alloy as friction materials have been used in manufacture, mechanical processing industry, architecture industry and chemical industry. However, the improvements of tribological properties still keep an enormous technical challenge. Recently, many investigations focused on carbonaceous material reinforced polymer or alloys to improve the tribological properties [36]. However, the application of highly-dispersible and small-sized hexagonal boron nitride nanoparticles for antifriction of liquid paraffin has not been reported yet.

In this work, highly-dispersible h-BN nanoparticles were successfully synthesized by two-steps (spray drying and pyrolysis). Spray drying is the unique aspect of our study compared with previous reports and is also an essential step for the uniformity of highly-dispersible BN nanoparticles. The as-synthesized samples were researched and analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (SEM) and transmission electron microscope (TEM). Moreover, the tribological behaviors of the as-synthesized BN nanoparticles as additive to liquid paraffin were researched. The friction behavior of the as-obtained products is superior to that of BN nanoparticles without using spray drying method.

2. Experiment

2.1. Materials

Boric acid (H_3BO_3, analytically pure) and urea ($CO(NH_2)_2$, analytically pure) were supplied by Sinopharm Chemical Regent Co. Ltd. China to prepare the boron nitride. Ltd. Ethanol (C_2H_5OH, 75.0% purity) and hydrochloric acid (HCl, 36.0–38.0% purity) were purchased from Sinopharm Chemical Reagent Co. Ltd. China to remove the byproducts of products. All chemicals were used as received without any further purification.

2.2. Synthesis of BN powders

In a typical procedure, boric acid and urea were selected as the raw materials. Firstly, boric acid and urea were dissolved in distilled water (H_2O) and stirred for 24 h at 40 °C using a hot magnetic stirrer. The molar ratio ($R_{B/U}$) of boric acid and urea are 1:1, 1:2, 1:4, and 1:6. The resultant solution was spray-dried using a mini lab spray drier L-117 (Beijing laiheng scientific Co. Ltd. China). A peristaltic pump was used to deliver the liquid through the bi-fluid nozzle (0.7 mm) into the spray-drying chamber with a feed flow-rate of 10 mL/min and a nozzle pressure of 2 bars. The inlet temperature was set 110 °C. The spray-dried homogeneous precursor was obtained and stored in plastic vessel at 20 °C before being used. The precursors were put into the bottom of an alumina boat, which was then placed at the center of a tube furnace. After that, the precursors were calcined at 500 °C for 1 h and then calcined at 900–1200 °C for 2 h in N_2 condition with heating rate of 5 °C/min. The tube furnace was naturally cooled to ambient temperature under N_2 atmosphere. The as-obtained samples were put into dilute hydrochloric acid and stirred for 12 h at room temperature. Afterwards, the products were washed with distilled water and ethanol for three times in order to remove all residual impurities. Finally, the final product powders had been obtained after being dried at 110 °C for 12 h in vacuum drying oven.

2.3. Characterization of the prepared BN powders

The structure and morphology of the h-BN samples were measured by XRD, FT-IR, SEM and TEM. XRD patterns were performed using a Germany Bruker D8 Advance powder X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ=0.15406 Å) at a scanning step of $0.5°s^{-1}$ over the 2θ range of 10–70°. FT-IR was recorded on an America Elmer Spectrum One Spectrometer (KBr disks) within a wavelength range of 500–4000 cm^{-1}. SEM and TEM were performed by Japan Hitachi Corporation JSM-6701F and JEM-2100 to determine the surface morphology and size. The surface elemental compositions of product was analyzed by a Thermo Scientific ESCA Lab 250Xi using a 200 W monochromated Al Kα as radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Specific surface area, pore volume and pore diameter were measured by an America Micromeritics ASAP 2010 at 77 K.

2.4. Friction and wear test

The friction and wear behavior of the as-prepared samples were measured by a microcomputer controlled omnipotence friction wear testing machine (MMW-1A, Jinan Yihua Tribology Testing Technology Co. Ltd. China). The test machine consisted of four standard test steel ball (GB308-84, a ball on top and three balls at the bottom) rotate against each other. The screw locking ring was fixed standard test steel ball. The distance between the upper and the lower balls: a vertical one, which allowed normal load application, and a horizontal one, for friction measurement. Prior to each test, the standard test steel balls were washed by water and acetone to remove surface contamination. The friction and wear behaviors were performed at 75 °C, with a rotating speed of 1450 rpm and with the applied load of 300 N.

3. Results and discussion

Boron nitride was fabricated by two-steps and boric acid and urea were chosen as the reactants. Through theoretical calculation, it is predicted that boric acid binds to urea mainly by hydrogen bond to form BN precursor in the spray drying process (as shown in Fig. 1). The $R_{B/U}$ and reaction temperature as two important conditions on the formation of highly-dispersed BN nanoparticles were investigated in the pyrolysis process. The spray drying technology is the unique aspect of our study compared with previous reports [15–18].

Fig. 2 displays the typical SEM image of h-BN products synthesized by spray drying and pyrolysis process at 1100 °C under different molar ratios of boric acid to urea ($R_{B/U}$). It is clearly indicated that the morphology of the products is strongly affected by the $R_{B/U}$. When equimolar amounts of $CO(NH_2)_2$ and H_3BO_3 present ($R_{B/U}$=1:1), the obtained BN particles were consisted of somewhat irregular and spherical in shape (Fig. 2a). At $R_{B/U}$=1:2, the spherical BN was observed (Fig. 2b). The size of the as-obtained spheres was about 25–30 nm. With $R_{B/U}$ increased to 4, the products were composed of nearly uniform spheres with about 20 nm in diameter in Fig. 2c. The dispersibility of the BN nanospheres is better than that of the BN

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