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Fabrication and characterization of hexagonal boron nitride powder by spray drying and calcining–nitriding technology

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ABSTRACT

Hexagonal boron nitride (hBN) powder was fabricated prepared by the spray drying and calcining–nitriding technology. The effects of nitrided temperature on the phases, morphology and particle size distribution of hBN powder, were investigated. The synthesized powders were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), Fourier transformed infrared spectrum, ultraviolet–visible (UV–vis) spectrum and photoluminescence (PL) spectrum. UV–vis spectrum revealed that the product had one obvious band gap (4.7 eV) and PL spectrum showed that it had a visible emission at 457 nm ($\lambda_{ex} = 230$ nm). FESEM image indicated that the particle size of the synthesized hBN was mainly in the range of 0.5–1.5 μm in diameter, and 50–150 nm in thickness. The high-energy ball-milling process following 900 °C calcining process was very helpful to obtain fully crystallized hBN at lower temperature.

1. Introduction

Boron nitride (BN) is a synthetically refractory material, which is widely applied due to its fascinating physical and chemical properties [1–4]. BN exists in the form of hexagonal BN (hBN), cubic BN (cBN), turbostratic BN (tBN), wurtzitic BN (wBN), rhombohedral BN (rBN), and explosive BN (eBN) [5–8].

hBN is also known as 'white graphite,' has similar crystal structure as of graphite [9,10]. This crystal structure provides excellent lubricating properties. Moreover, it has key properties such as high thermal conductivity, low thermal expansion, good thermal shock resistance, high electrical resistance, low dielectric constant and loss tangent, microwave transparency, nontoxic, easily machined-nonabrasive and lubricious, chemically inert and not wet by most molten metals [11–13]. Materials for electronics and nuclear energy, lubricants, and refractories are an incomplete list of applications of hBN [14,15]. The layered structure of hBN makes the material mechanically weak, but it has greater chemical and thermal stability than GaN and AlN. The interesting optical properties of hBN, such as its huge exciton-binding energy, are due to its anisotropic structure [1]. It is a promising material for its optical characteristics.

There are different methods to synthesis hBN. Traditionally, hBN has been prepared by the classical high-temperature synthesis routes [16] and the direct combination of boron with nitrogen [17]. Hirano et al. [18] reported that pyrolysis of the adduct $Al(BH_4)_3 \cdot 4NH_3$ below 5.0 GPa at 600 °C led to a mixture of hBN and AlN. Rao et al. [19] and Solozhenko et al. [20] reported a self-propagation route to synthesize crystalline BN powders by reacting MBF_4 (M = K or Na) with Li_3N and NaN_3. Hao et al. [21] reported that BN nanoparticles were obtained when reacting Li_3N with BBr_3 at 250–550 °C by benzene-thermal methods. Lin et al. [12] prepared hBN fibers and flowers by the reaction of KBH_4 and NH_4Cl at 1250 °C for 10 h. At the same time, there are many researches on the synthesis of BN with organic precursors. But it is not really convenient to obtain appropriate organic precursors.

However, most of the methods could not synthesize hBN powder with uniform, fine grain size and high crystallinity, high-yield, at the same time with low cost and energy-consuming. For the sake of practicality, developing low-cost, and high-yield synthetic routes to synthesize BN with uniform and fine grain size is urgently expected. In this paper, the precursor was facile synthesized by the reaction of HBO_3, $Na_2B_4O_7$ and $(NH_2)_2CO$ at 900 °C for 20 m. Then hBN was obtained by heating the intermediate material at 1200, 1300, 1400, 1550 °C for 3 h, respectively. The effects of nitrided temperature and high-energy

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ball-milling of the calcined precursor on the phases, grain size and morphology were investigated.

2. Experimental

BN powder was prepared from commercial HBO_3, $Na_2B_4O_7$ and $(NH_2)_2CO$ (all 99.9% purity). The weight ratio of HBO_3 and $Na_2B_4O_7$ was 93:7. An appropriate amount of HBO_3 and $Na_2B_4O_7$ were dissolved into deionized water to form aqueous solution with a weight percentage of 50%. The solution was churned up and fed into the nozzle with a solution feed rate of 500 mL/h, and spray dried in a hot air of 250 °C. In this way, the mixture of HBO_3 and $Na_2B_4O_7$ was prepared. The appropriate amount of spray dried powder and $(NH_2)_2CO$ with the molar ratio of N:B = 2:1 was put into five alumina crucible with alumina lid, then calcined at 900 °C for 20 m in a muffle. In order to investigate the effects of nitrided temperature on the phases, grain size and morphology of the following heat-treated process, the appropriate amount of 900 °C calcined precursor powder was put into five graphite crucible, then nitrided at 1200, 1300, 1400, and 1550 °C for 3 h in tube furnace with a N_2 ambience, respectively. In a parallel run, an appropriate amount of 900 °C calcined precursor powder were high-energy ball-milled in ethanol using a Teflon-lined vial and balls with a speed of 350 rpm for 24 h. After milling it was dried at 110 °C in a desiccator, then nitrided at 1400 °C for 3 h in tube furnace with a N_2 ambience. The resulted products were filtered, washed with distilled water for 3 times, then with ethanol for 2 times. The samples were dried at 110 °C in a desiccator. The as-prepared powders were identified by X-ray diffraction (XRD) analysis using a D/MAX-RB X-ray diffractometer. The mixture of HBO_3 and $Na_2B_4O_7$ prepared by spray drying was annealed at the temperature according to the XRD analysis of BN powder from the ball-milled powder, in order to obtain hBN powder. A Hitachi S-4800 field emission scanning electron microscope (FESEM) was employed in the morphology and grain size analysis of the hBN powders and the spray dried precursor powder from the mixture of HBO_3 and $Na_2B_4O_7$. Fourier transformed infrared spectrum (FT-IR) was recorded with a Nicolet Nexus Fourier transform infrared spectroscopy in transmission mode in a KBr pellet. Ultraviolet–visible (UV–vis) spectrum was obtained from powders suspended in water using a HITACHI UV–visible recording spectrophotometer (U-3010) between 200 and 800 nm. Photoluminescence (PL) spectrum of powders suspended in water was recorded with a Fluoro Max-P fluorescence spectrophotometer.

3. Results and discussion

Fig. 1 showed FESEM micrographs of the spray dried precursor powder from the mixture of HBO_3 and $Na_2B_4O_7$. As Fig. 1(a, b) shown, the powder was not comprised of spherical agglomerates that usually existed in other spray dried powder. At the same time, there was not the hollow structure in the spray dried precursor powder.

Fig. 2 showed XRD patterns of the BN powders prepared from spray dried powder and $(NH_2)_2CO$ with the molar ratio of N:B = 2:1, which were calcined at 900 °C for 20 min in a muffle, respectively, then nitrided in tube furnace at 1200, 1300, 1400, and 1550 °C for 3 h in tube furnace with a N_2 ambience, respectively. As shown in Fig. 2(a–c), the XRD pattern of BN powder prepared from the calcined precursor powder nitrided in tube furnace at 1200, 1300, and 1400 °C, respectively, displayed seven crystal planes, (002), (100), (101), (004), (103), (104), (110), (112), and (006), which were basically in agreement with the reported values Joint Committee on Powder Diffraction Standards (JCPDS) card no.

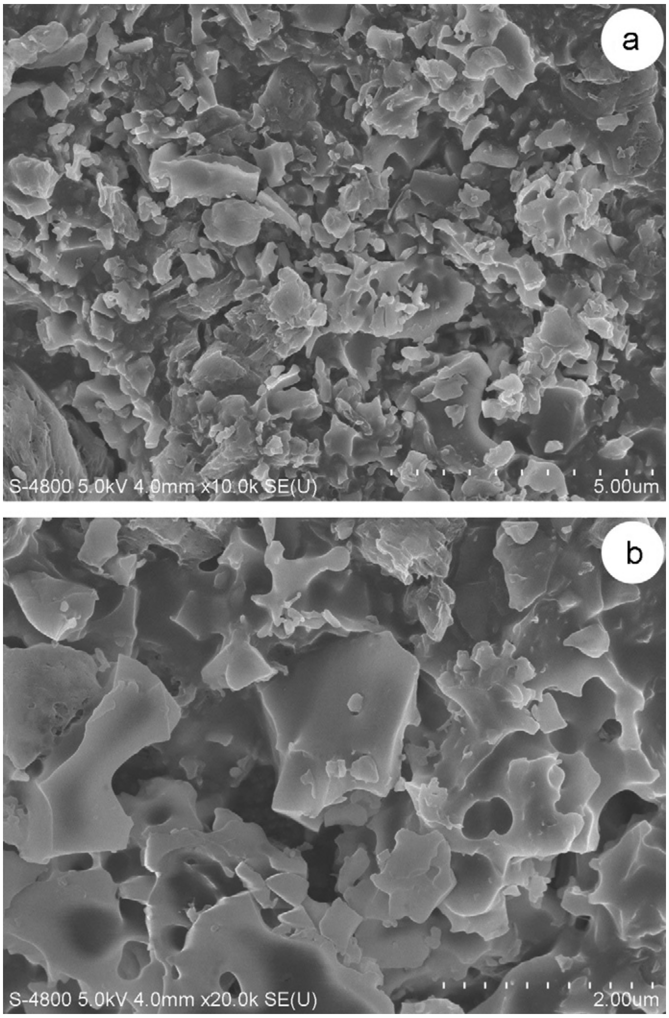

Fig. 1. FESEM micrographs of the spray dried precursor powder from the mixture of HBO_3 and $Na_2B_4O_7$.

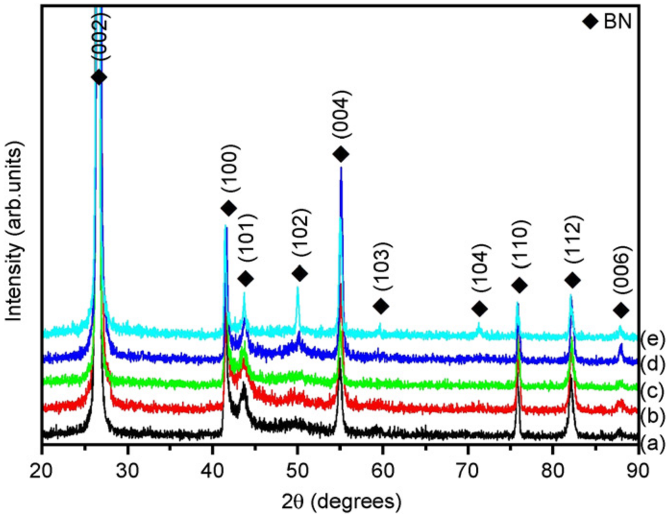

Fig. 2. XRD patterns of the BN powders prepared from spray dried powder and $(NH_2)_2CO$ with the molar ratio of N:B = 2:1, calcined at 900 °C for 20 min, then nitrided in tube furnace at 1200 °C (a), 1300 °C (b), 1400 °C (c), 1550 °C(d), and 1400 °C. (e) High-energy ball-milled for 24 h before calcining) for 3 h with a N_2 ambience.

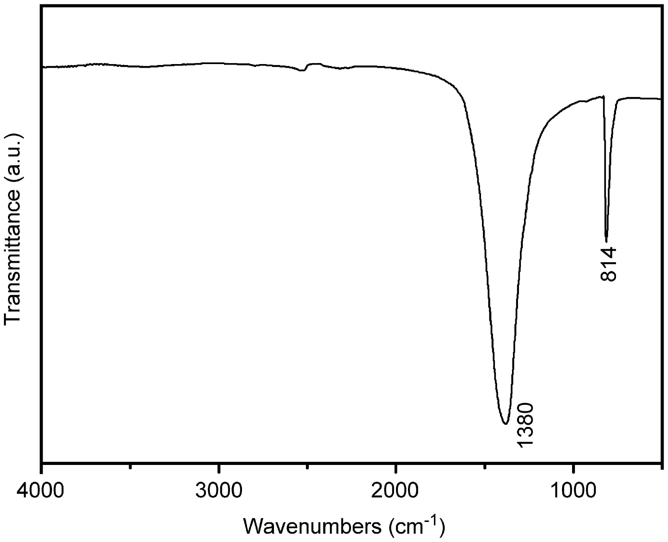

Fig. 3. Fourier transformed infrared spectrum (FT-IR) of as-prepared BN powder nitrided at 1400 °C from high-energy ball-milled 900 °C calcined precursor powder.

34-0421. But the (102), (103), and (104) reflections did not become visible. The (100) and (101) peaks were not separated completely, which was usually defined as (10) reflection. It showed that the as-prepared BN powder had a semi-crystalline structure called tBN [5]. With the increasing of nitrided temperature, at 1550 °C, the (102) reflection became visible, as shown in Fig. 1(d), while the (103) and (104) reflections did not become visible. The as-prepared BN powder nitrided at 1400 °C from high-energy ball-milled 900 °C calcined precursor powder displayed 10 crystal planes, (002), (100), (101), (102), (004), (103), (104), (110), (112), and (006), and the (102), (103), and (104) reflections became visible. The (100) and (101) peaks were separated completely. It showed that fully crystallized hBN powder had been fabricated. Although the 1400 °C nitrided temperature was lower than the 1550 °C nitrided temperature with the same time, the high-crystallinity hBN was obtained at lower nitrided temperature. It showed that the high-energy ball-milled process following the 900 °C calcined process is very helpful for the phase changing from tBN to hBN. The bragg angles of these peaks were coincident with the bragg angles of (001) and (10) reflections of hBN and indicate the presence of a turbostratic structure, as was also illustrated by Alkoy et al. [5]. With the increasing of calcined temperature of precursor powder, the (10) reflection was divided into (100) and (101) peaks. The interlayer spacing of the (002)

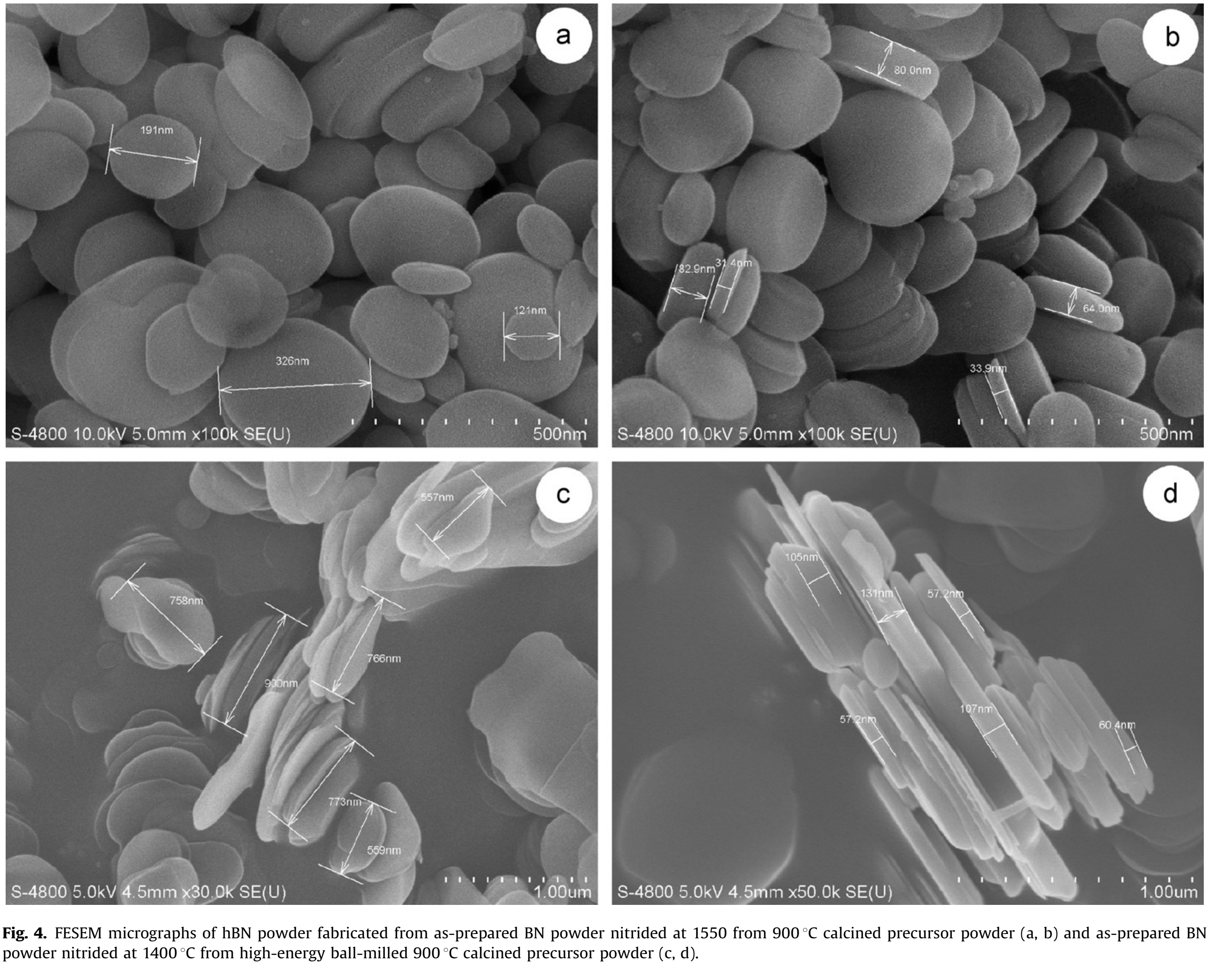

Fig. 4. FESEM micrographs of hBN powder fabricated from as-prepared BN powder nitrided at 1550 from 900 °C calcined precursor powder (a, b) and as-prepared BN powder nitrided at 1400 °C from high-energy ball-milled 900 °C calcined precursor powder (c, d).

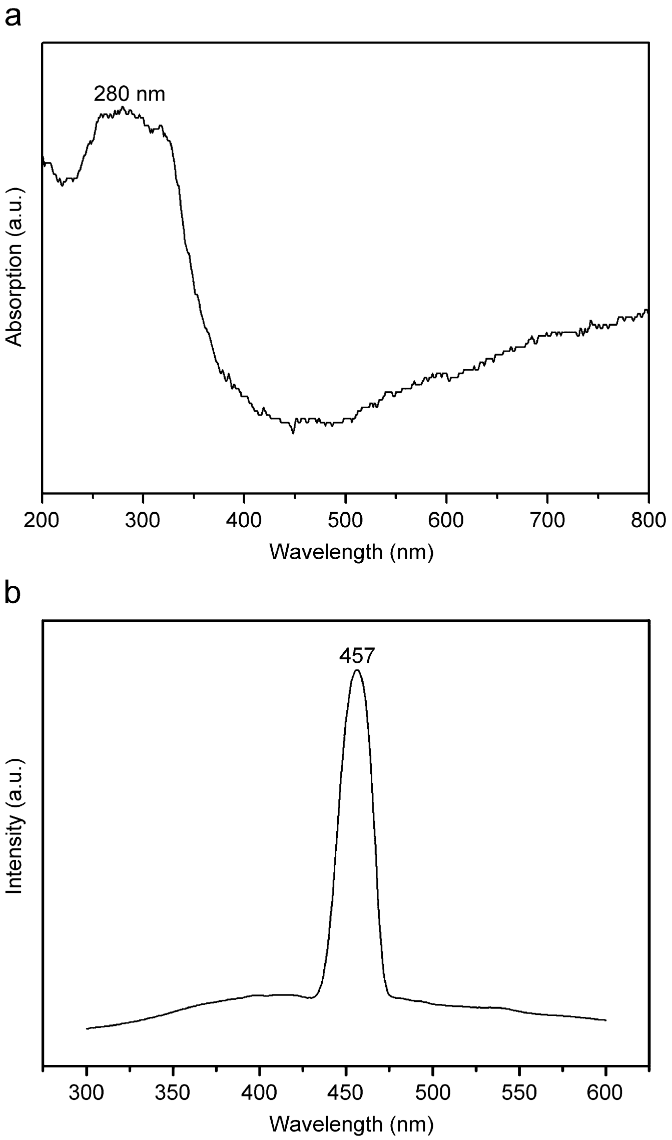

Fig. 5. UV absorption spectrum (a) and PL spectrum (b) of the as-prepared BN powder nitrided at 1400 °C from high-energy ball-milled 900 °C calcined precursor powder.

atomic plane of the sample approached to a value of 3.3484 Å, which was closer to the ideal value of 3.3306 Å for hexagonal BN.

Fig. 3 showed the FT-IR of hBN powder fabricated from as-prepared BN powder nitrided at 1400 °C from high-energy ball-milled 900 °C calcined precursor powder. As shown in Fig. 3, two strong characteristic absorption bands near 1380 and 814 cm^{-1} were observed, which were close to the reported result of hBN. The peak around 1380 cm^{-1} results from the in-plane TO models of the sp^2-bonded BN, while the peak centered at 814 cm^{-1} can be attributed to the B–N–B bonding vibrations [22,23].

As shown in Fig. 4, hBN particles, obtained with the method utilized in this study, had a plate-like shape, where the (002) atomic planes of the hexagonal structure of BN align paralleled to the particle's major flat surface [5]. From FESEM micrographs of as-prepared BN powder nitrided at 1550 °C from 900 °C calcined precursor powder, shown in Fig. 4(a, b), mean particle sizes of the fully crystallized powders could be estimated in the following ranges, 100–400 nm in diameter, and 30–90 nm in thickness. As shown in Fig. 4(c, d), hBN powder fabricated from as-prepared BN powder nitrided at 1400 °C from high-energy ball-milled 900 °C calcined precursor powder, had an irregular and plate-like shape, mean particle sizes of the fully crystallized powders could be estimated in the following ranges, about 0.5–1.5 μm in diameter, and 50–150 nm in thickness. The average particle size of as-prepared BN powder nitrided at 1550 °C from 900 °C calcined precursor powder was much smaller than that of as-prepared BN powder nitrided at 1400 °C from high-energy ball-milled 900 °C. It showed that high-energy ball-milling improved the crystallinity from tBN to hBN, at the same time the grain grew larger. The special shape of hBN powder obtained with the method could be well utilized used as a lubricant additive and dispersed in lubricating oil, grease, water, and solvents.

Fig. 5 showed the UV absorption spectrum (Fig. 5(a)) and PL spectrum (Fig. 5(b)) of the as-prepared BN powder nitrided at 1400 °C from high-energy ball-milled 900 °C calcined precursor powder. UV absorption spectrum and PL spectrum were used to investigate the band-gap energy (E_g) of the synthesized hBN. Despite the fact that h-BN is the best-studied polymorph of BN, no agreement concerning its E_g has been obtained so far. The measured E_g values of hBN are widely dispersed in the range between 3.6 and 7.1 eV, according to the data available in the literature [21]. The dispersed values of E_g should be related to the variation of their microstructures. BN has numerous structures, which are composed of various contents of sp^3- and/or sp^2-bonded structures depending on the preparation conditions. The difference between these BN structures is reflected by changes of their vibration modes. The structural changes certainly lead to changes in the electronic state, and resultantly lead to changes of the band-gap energy. This is the reason the band-gap energy of BN is reported to be widely dispersed [24]. Herein, we report our measured E_g values of hBN. UV–vis absorption spectrum (Fig. 4a) showed one broad absorption band near 280 nm, which corresponded to the estimated E_g values of 4.4 eV. PL spectrum (Fig. 5b) showed one intense narrow emission band at $\lambda_{em} = 457$ nm when hBN was excited by ultraviolet light with $\lambda_{ex} = 230$ nm. The corresponding E_g value was 2.7 eV. While reference reports that hBN shows a broad emission [25]. Moreover, the as-prepared hBN powder had no emission at 340 nm although it was excited below 310 nm [24].

4. Conclusions

High-crystallinity hBN powder had been fabricated from high-energy 900 °C calcined precursor powder crystallized in tube furnace at 1400 °C for 3 h with a N_2 ambience, which had an irregular and plate-like shape, mean particle sizes of the fully crystallized powders could be estimated in the following ranges, 0.5–1.5 μm in diameter, and 50–150 nm in thickness. The spray drying and calcining–nitriding technology assisted with the high-energy ball-milling process following the calcined process of mixture of spray dried powder and $(NH_2)_2CO$ was a hopeful way to manufacture hBN powder with high crystallinity in industrial scale. The investigation of PL spectrum and UV absorption showed that the as-prepared hBN, synthesized in this study, provided researchers with an opportunity to expediently investigate its optical characteristics and structure transformations in detail.

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