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Boron nitride hollow nanospheres: Synthesis, formation mechanism and dielectric property

B. Zhong [a], X.H. Tang [a], X.X. Huang [b,**], L. Xia [a], X.D. Zhang [b], C.J. Wang [a], G.W. Wen [a,b,*]

[a] School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, Weihai 264209, People's Republic of China
[b] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

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ABSTRACT

Boron nitride (BN) hollow nanospheres have been successfully fabricated by pyrolyzing vapors decomposed from ammonia borane (NH_3BH_3) at 1300 °C. The final products have been extensively characterized by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. The BN hollow nanospheres were ranging from 100 to 300 nm in diameter and around 30–100 nm in thickness. The internal structure of the products was found dependent on the reaction temperatures. A possible formation mechanism of the BN hollow nanospheres was proposed on the basis of the experimental observations. Dielectric measurements in the X-band microwave frequencies (8–12 GHz) showed that the dielectric loss of the paraffin filled by the BN hollow nanospheres was lower than that filled by regular BN powders, which indicated that the BN hollow nanospheres could be potentially used as low-density fillers for microwave radomes.

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1. Introduction

Hexagonal boron nitride (h-BN, hereinafter referred to as BN) has long been known for its advantageous physical and chemical properties, such as self-lubrication, high temperature stability, high thermal conductivity, low dielectric constant and chemical inertness [1]. Therefore, BN has been traditionally used as high-temperature crucible material, microwave-transparent window material, mould release agent, and so forth [2,3]. In the past two decades, BN has attracted renewed interests because of its structural similarity to carbon which can exit in a variety of interesting morphologies. Many BN micro/nanomaterials with different morphologies, including nanotubes [4–7], whiskers [8,9], nanoribbons [10], cones [11], and nanosheets [12–15], have been successfully fabricated. Among them, BN hollow nanospheres with hollow cavity, low density and high specific surface area, have received increasing attention because of their potential application as hydrogen storage media, sensors or in drug delivery systems [16–20].

Although BN nanostructures like nanotubes and nanosheets have been intensively investigated, very few studies on the fabrication of BN hollow nanospheres have been made. Sun et al. synthesized BN hollow spheres via the reaction of $NaBF_4$ and NaN_3 and demonstrated that they are promising candidates for hydrogen storage container or catalyst [16]. Chen et al. successfully prepared BN hollow spheres at room temperature, using BBr_3 as the boron source and $NaNH_2$ as nitrogen [17]. Lian et al. used NH_4BF_4, NaN_3 and sulphur to produce BN hollow spheres and investigated its potential ability in hydrogen storage and waste-water treatment [18]. Xu et al. fabricated BN hollow spheres with diameters ranging from 100 nm to a few micrometers by co-pyrolysis of NH_4BF_4, KBH_4 and zinc powder [19]. Wang et al. reported a simple chemical route to prepare high quality BN hollow spheres with the yield reaching 30–40% by using BBr_3 and NaN_3 [20]. These pioneering efforts undoubtedly enrich our knowledge about the BN-nanomaterial family, but the synthetic routes are generally complex and product purity and yield are limited. Moreover, highly toxic starting materials like sodium azide (NaN_3) are employed in most experiments, which inevitably burdens operating staffs and the environment. In order to further investigate the properties and applications, it is absolutely necessary to develop safe and reliable methods to fabricate the BN hollow nanospheres with high yield and purity.

In the present work, we report the synthesis of unique BN hollow nanospheres by a chemical vapor reaction approach employing easily available tube furnaces using ammonia borane (AB, NH_3BH_3) as a precursor. AB is a stable solid at normal conditions. Compared with other BN precursors (such as NaN_3

* Corresponding author at: School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China.
Tel.: +86 451 86418860; fax: +86 451 86413922.
** Corresponding author.
E-mail addresses: swliza@hit.edu.cn (X.X. Huang), g.wen@hit.edu.cn (G.W. Wen).

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and BBr_3), AB is not only insensitive to moisture and thus easy to manipulate, but also less hazardous to human bodies and environment. The morphology and structure of the BN hollow microspheres are elucidated by means of complementary analytical techniques. A possible formation mechanism of the hollow microspheres was proposed based on our experimental observations. The dielectric properties of the BN hollow microspheres were investigated in the X-band microwave frequencies (8–12 GHz).

2. Experimental

All the chemical reagents used in this study were analytical grade unless otherwise specified. Ammonia borane was synthesized according to a previous literature procedure developed by Ramachandran and Gagare with minor modifications [21]. The boron nitride hollow nanospheres were fabricated using an experimental apparatus with two furnaces connected together, as schematically shown in Fig. 1a. AB powders were molded into blocks and filled into the low-temperature furnace which was subsequently heated up to ~300 °C at a heating rate of about 3 °C/min. During this process, large quantities of B and N containing gases decomposed from AB were introduced by high purity argon (~100 ml/min) into the high-temperature furnace which had already been heated up to 1300 °C. The reaction lasted for about 60 min before both furnaces were cooled down to the room temperature. It was found that products from different regions exhibited different colors. Products from the central regions with higher reaction temperatures were white powders, while those from the edge regions with lower reaction temperatures were brown powders. Both samples were collected and directly used for characterizations without further treatments. In addition, to investigate the influence of the temperature nonuniformity on the products, the temperature distribution along the high-temperature furnace tube (from the left end to the center) was measured and the results are shown in Fig. 1b.

The morphology, crystal structure, and chemical composition of the products were characterized by a variety of techniques including X-ray powder diffraction (XRD, Rigaku D/max-γB X-ray diffractometer with Cu K radiation (λ = 0.154178 nm)), field emission scanning electron microscopy (FESEM, FEI Helios Nano-Lab 600i), high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100 equipped with energy dispersive spectroscopy (EDS)), and X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5700 ESCA System with a PC-ACCESS data analysis system). Dielectric properties (dielectric constant and dielectric loss tangent) of the samples were estimated in the frequency range from 8 to 12 GHz (X band) using a microwave network analyzer (Agilent N5245A).

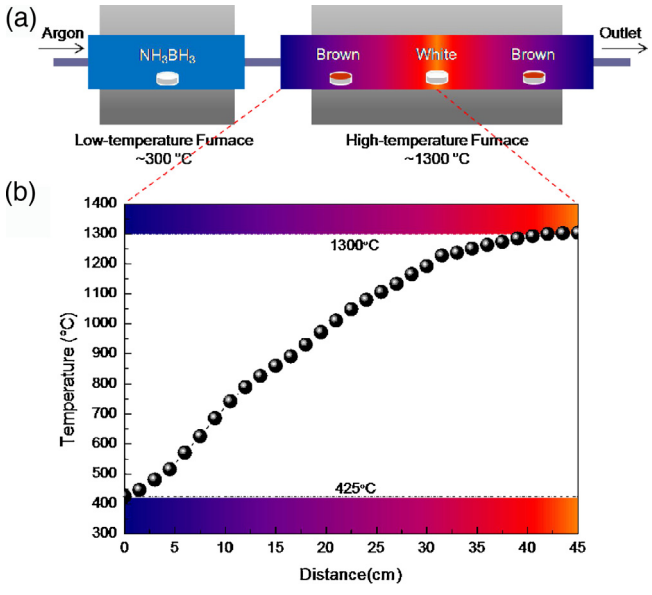

Fig. 1. (a) Schematic illustration of the experimental setup; (b) temperature distribution along the high-temperature furnace tube (from the left end to the center).

3. Results and discussion

3.1. Characterization of BN hollow nanospheres

A typical XRD pattern of the as-prepared products collected from the central region of the high-temperature furnace is shown in Fig. 2. Two diffraction peaks at about 26° and 42° are distinctly identified, which can be assigned to the (0 0 2) and (1 0 0) planes of hexagonal BN (space group: P63/mmc (194), lattice constants: $a = 2.504$ Å, $c = 6.656$ Å; Joint Committee on Powder Diffraction Standards [JCPDS] card no. 34-0421), demonstrating the products are composed of BN. It is noted that the diffraction peaks are broadened, suggesting that the BN is not well crystallized. The inset of Fig. 2 shows a digital photograph of the products. It can be seen that the alumina substrate is uniformly covered by a thick layer of powders exhibiting the white color of BN. Typically, ~0.5 g of BN hollow nanospheres could be obtained in one batch and the fractional yield could reach ~50 wt.% with respect to the starting reactive gases, but the process could be easily scalable to larger amounts.

Fig. 3 shows typical SEM images (with different magnifications) of the as-prepared products. Low magnification SEM images shown in Fig. 3a and b suggest that a large number of spherical nanoparticles are obtained. High magnification SEM images further reveal that the products actually consist of nanoparticles with typical diameters ranging from 100 to 300 nm (Fig. 3c and d).

The structure and chemical composition of the BN nanospheres were further investigated by TEM, selected area electron diffraction (SAED), and EDS. Fig. 4a and b shows typical low-magnification bright-field TEM images of the nanospheres. A number of randomly distributed nanospheres with distinct contrast between the outer and the inner regions could be observed, revealing the hollow nature of the nanospheres. A high-magnification bright-field TEM image displayed in Fig. 4c shows an individual

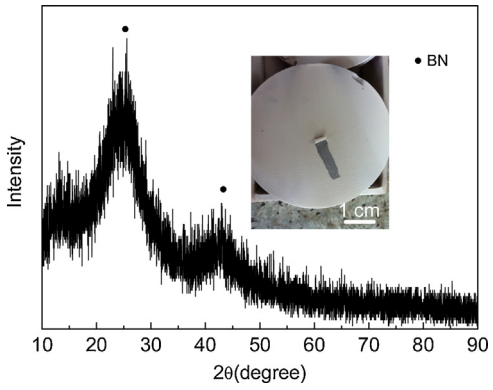

Fig. 2. XRD pattern and digital photograph (inset) of as-prepared BN hollow nanospheres.

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