

通过简单方法合成先驱体并利用电纺法制备 BCN 微米空心球

李 霞¹ 温广武^{*,1,2} 张 涛¹ 夏 龙² 钟 博²

(¹材料科学与工程学院, 哈尔滨工业大学, 哈尔滨 150001)

(²材料科学与工程学院, 哈尔滨工业大学(威海), 威海 264209)

摘要: 以三氯硼吡啶(B₃N₃H₃Cl₃)和苯胺在 *N*-甲基吡咯烷酮(NMP)溶剂中合成的聚合物为电纺液, 由改进的电纺设备制备具有六方结构的 BCN 微米球。通过控制纺丝电压来控制 BCN 球体的直径。对其进行元素分析, 并通过扫描电子显微镜, 能量色散谱, X 射线衍射和 X 射线光电子能谱进行表征。结果表明 BCN 微米空心球表面微凹, 直径在 10~30 μm 之间。硼碳氮间的比例约为 1:1.12:0.94。

关键词: 聚合; BCN 微米球; 电纺

中图分类号: O613.8⁺1; O613.71; O613.81; TQ128⁺.1

文献标识码: A

文章编号: 1001-4861(2012)11-2458-05

Bulk Quantity BCN Microspheres Fabricated by Electrospray from Easily Prepared Precursor

LI Xia¹ WEN Guan-Wu^{*,1,2} ZHANG Tao¹ XIA Long² ZHONG Bo²

(¹School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China)

(²School of Materials Science and Engineering, Harbin Institute of Technology (Weihai), Weihai, Shandong 264209, China)

Abstract: An easily prepared precursor from polymerization of trichloroborazine (B₃N₃H₃Cl₃) and aniline was selected as the starting material and *N*-methyl pyrrolidone (NMP) was used as the solvent to synthesize hexagonal BCN microspheres in bulk quantity via an improved electrospray method. This approach can control the diameter of the as-prepared spheres by manipulating the voltage of the electrospray apparatus. The product was characterized by scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction and X-ray photoelectron spectrometry. The results show that the fabricated BCN microspheres have smooth and concave surface characters with diameter ranging from 10 to 30 μm. The B:C:N atomic ratio is about 1:1.12:0.94.

Key words: synthesis; BCN microsphere; electrospray

0 Introduction

Recently, a great variety of ternary compounds with different physicochemical properties have attracted considerable attention because of their unique structural characters. Among them, BCN architectures have recently been attracted great deal attention

because BCN compounds have higher thermal and chemical stabilities, and ideal mechanical properties than those of carbon architectures^[1-3]. Analogues to graphite, BCN materials have a two-dimensional network of *sp*²-hybridised structure^[4-5]. These BCN structures have the potential for application as photoluminescent materials, emitters for flat panel

收稿日期: 2011-12-06。收修改稿日期: 2012-03-31。

国家自然科学基金(No.50672018), 863 计划课题(2007AA03Z340)资助项目。

*通讯联系人。E-mail: wgw@hitwh.edu.cn

displays, high temperature transistors, and high temperature lubricants^[6-7]. There are some reports about $B_xC_yN_z$ spheres and nanotubes of different chemical compositions^[8-17]. Commonly, BCN nanotubes are prepared by nitridation of boric oxide in the presence of carbon nanotubes, CuO_4 and Au_2O_3 ^[18]. The products demonstrate different morphologies, and also usually contain oxide or catalysts impurities, thus it is difficult to obtain high-purity BCN structures with good crystallinity. Several groups have achieved BCN architectures through different routes, such as thermolysis of inorganic and polymeric precursors^[19-20]. Ball-milling^[21], Laser ablation^[22] and arc-assisted^[23] methods have been used for synthesis of BCN structures with solid state B, C and N sources.

However, to the best of our knowledge there have been only a few reports on the preparation of high purity BCN microspheres in bulk quantities. Therefore, the selection of a suitable fabrication method and starting materials for the synthesis of high-purity BCN microspheres is important. In this respect, an easily prepared precursor from polymerization of trichloroborazine ($B_3N_3H_3Cl_3$) and aniline was selected as the starting material and N-methyl pyrrolidone was used as the solvent to fabricate BCN green microspheres via an improved electrospray approach. This approach can control the diameter of the as-prepared spheres by manipulating the voltage of the electrospray apparatus.

1 Experimental

A 250 mL single-necked flask equipped with a magnetic stirrer was loaded with 10 g (542 mmol) of trichloroborazine ($B_3N_3H_3Cl_3$)^[17] dissolved in 30wt% of toluene. Then, 6.25 mL (68.5 mmol) of dried aniline was loaded into the mixture at room temperature under vigorous stirring for 2 h. After that, the solution was heated to 65 °C with stirring to remove residual toluene, giving the original product. The polymerization was continued in a nitrogen atmosphere at 120 °C for 20 h. Then, the as-polymerized precursor was dissolved in 40wt% of N-methyl pyrrolidone to form the starting materials for electrospray.

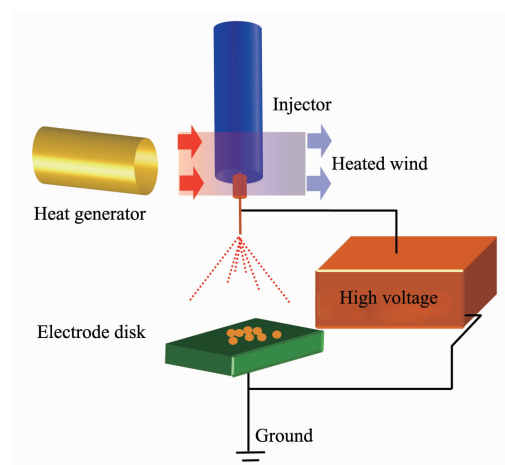


Fig.1 Schematic diagram of improved electrospray approach to spin green BCN microspheres

Fig.1 illustrates the schematic setup for the electrospray of the BCN green microspheres. A high voltage of 9 kV is applied using a high voltage supply (DW-N503-4ACCD of Tianjin Dongwen High Voltage Research Inc). The distance between the source and the collector was 8 cm.

The green microspheres were slowly heated to 1 550 °C at a heating rate of 1 °C · min⁻¹ and maintained at this temperature for 1 h in nitrogen atmosphere. In the end, the as-formed gray product was collected without any further purification. The surface chemical compositions of the product and precursor were examined using X-ray photoelectron spectrometer (XPS, Physical Electronics PHI 5700 with Mg exciting source). The morphology and elemental constituents of the as-prepared products were observed using field emission scanning electron microscopy (SEM, MX2600FE) and energy dispersive spectroscopy (EDS). The structures of the product were characterized by X-ray diffraction (XRD, Rigaku D/Max 2000 VPC with Cu $K\alpha$ radiation, $\lambda=0.15418$ nm). Scan speed (2θ): 4° · min⁻¹, step size: 0.03°(2θ), 30 kV, 60 mA).

2 Results and discussion

The XPS spectrum of full range scanning (Fig.2a) indicates the existence of boron, carbon, nitride, chlorine and oxygen (owing to the absorbed H_2O) in the precursor. Fig.2b shows the XPS spectrum of full range scanning of the products annealed at 1 550 °C. It shows

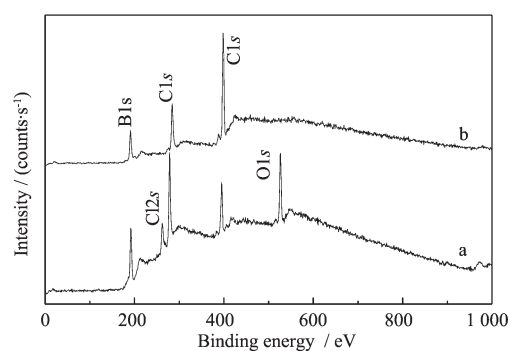


Fig.2 XPS spectra of (a) the precursor and (b) the as-prepared products

that only boron, carbon and nitride are examined after the green sample anneals at 1 550 °C in a heating rate of 1 °C·min⁻¹. No chlorine or oxygen peaks are detected in the XPS spectrum, indicating the absence of oxide compounds such as B₂O₃ in the products. Fig.2b shows a sharp peak at 189.4 eV, indicating the presence of B-C bonding (the binding energy is 188.6 eV) since the typical bonding energy of B-N (the binding energy is 190.2 eV) is higher than 190 eV. The chemical shift toward lower energy suggests a considerable contribution of B-C bonding, since the electronegativity of C atoms is lower than that of N atoms [24]. The binding energy at 285.4 eV and 398.3 eV implies the C1s of graphitic structure (C-C bonding) and N 1s of hybrid structure (B-N and C-N bonding), respectively,

suggesting the hybrid network in chemical compositions of the product. The B:C:N atomic ratio calculated from the XPS spectra is about 1:1.12:0.94.

Scanning electron microscopy (SEM) images of the as-prepared spheres are shown in Fig.3. Fig.3a displays a representative overview of the precursor microspheres, which shows that the as-prepared products are composed of large-scale spherical morphology. The high-magnification SEM image (inset of Fig.3a) shows that the spherical structures have burr-like surface (inset of Fig.3a) and the size of the microspheres are of 10 ~30 μm in diameter. The products annealed at 1 550 °C are shown in Fig.3(b~h). Detailed SEM observations reveal that there exist two types of spherical morphologies: smooth microspheres (Fig.3c, d) and concave-like 3D microspheres (Fig.3e, f). Fig.3d shows the morphology of two smooth spheres with a diameter of about 30 μm. The high magnification SEM image (Fig.3g) of the smooth sphere indicates that the surface of the sphere is composed of uniform nanodots (with a diameter of about 100 nm) and irregular cracked bubbles. Fig.3e shows an individual concave-like sphere with a diameter of about 20 μm. The high-magnification SEM images (Fig.3 f, h) exhibit detailed information about the concave-like sphere, which is composed of massif-like tapers (with a

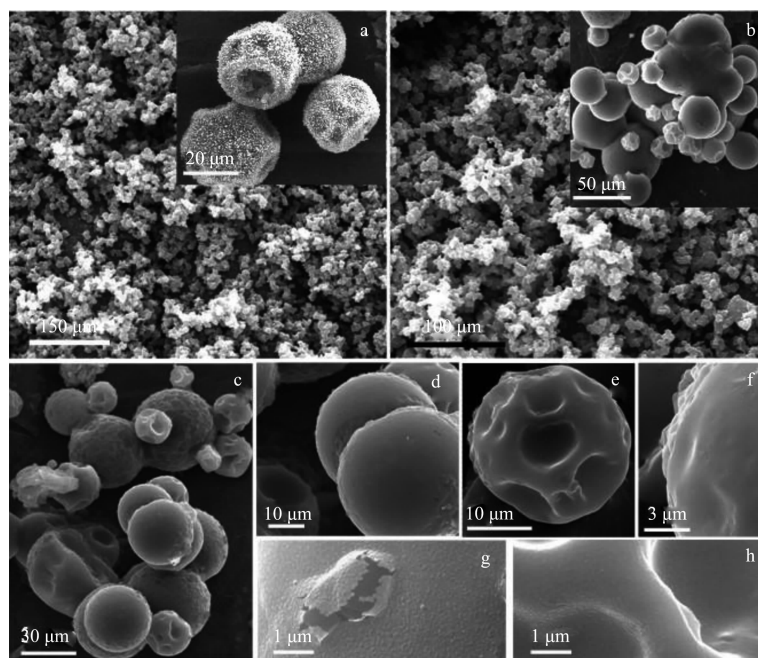


Fig.3 SEM images of (a) the as-produced green microspheres and (b~h) annealed products at different magnifications

diameter of about 800 nm and height about 500 nm) and irregular pits (with a diameter of 3~5 μm and depth about 3 μm) on the surface of the sphere. All the tapers and pits are randomly distributed on the spherical surface leading to the formation of a superstructure. In addition, a few non-spherical particles with a diameter of about 25 μm can be occasionally observed in Fig.3c.

The EDS analysis (Fig.4) shows that the annealed product at 1 550 $^{\circ}\text{C}$ is composed of the elements of B, C and N, indicating the purity of as-synthesized microspheres. The EDS result implies that the entire precursor has been converted to BCN structure.

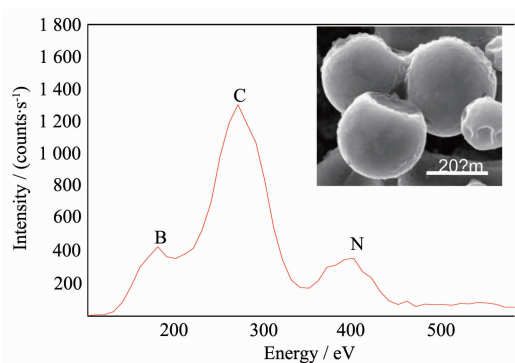


Fig.4 EDS of the annealed microspheres at 1 550 $^{\circ}\text{C}$ and the morphology of the microspheres (inset)

The XRD pattern of the product is shown in Fig.5. The strong and sharp diffraction peaks in Fig.5 indicate that the as-produced BCN structures are principally crystalline. All the peaks of the product can be indexed to a hexagonal structure, similar to the reported BCN structure. The sharp peak at the diffractive plane of (002) indicating, indicating the [100] graphitic sheets is well crystallized. No characteristic peaks of other impurities, such as B_2O_3 or H_3BO_3 , can be detected from

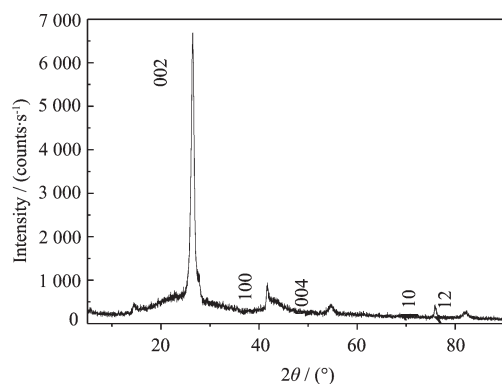


Fig.5 XRD patterns of the as-prepared product

the XRD pattern, indicating that the as-prepared product has high phase purity.

Based on the above experimental observations, a mechanism of the formation of BCN precursor spheres can be proposed. As shown in Fig.6, the procedure of the electrospray of BCN precursor spheres can be divided into four steps. The first step: the precursor filled in the syringe receives surface charges and extrudes from the apex of the syringe at about 90 $^{\circ}\text{C}$ in proper electric field strength. The precursor is stretched to a needle-like structure due to the presence of electric field force. The second step: the needle-like precursor further shrinks to a rod-like structure because of the coexistence of viscoelastic property and surface tension of the precursor at lower temperature. The third step: The precursor forms a spherical structure owing to the presence of surface charge and surface tension at the viscoelastic stage. At this stage burring surface of the precursor spheres is formed because of higher charge density at the external surface than internal (this result has been confirmed by the SEM image of inset in Fig.3a). The fourth step: the spheres shrink to concave-like morphology when the precursor cools to room temperature.

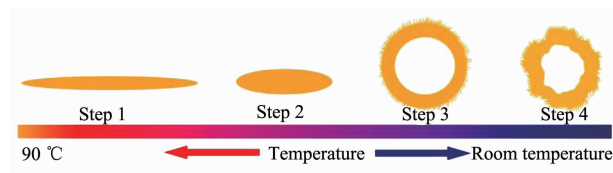


Fig.6 Formation mechanism of the precursor microspheres at the electrospray process

3 Conclusions

In summary, high pur ity hexagonal BCN microspheres with two kinds of morphology were synthesized using an improved electrospray method. The results show that the fabricated BCN microspheres have featureless and concave surface characters with a diameter ranging from 10 to 30 μm . Formation mechanism of the precursor microspheres is proposed according to the observed morphology of the products. A simple, efficient way to synthesize hexagonal

BCN microspheres in large quantity was developed in this work.

Acknowledgements: This work was supported by the National Natural Science Foundation of China (51021002, 51172050, 51102060, 51102063), the Fundamental Research Funds for the Central Universities (HIT. ICRST.2010009), the Natural Scientific Research Innovation Foundation in Harbin Institute of Technology (HIT.NSRIF.2011109, HIT.NSRIF.2010121), and the Scientific Research Foundation of Harbin Institute of Technology at Weihai (HIT(WH)X201108).

References:

- [1] Han W Q, Mickelson W, Zettl A, et al. *Appl. Phys. Lett.*, **2002**,**81**:1110-1112
- [2] Blank V D, Seepujak A, Gutierrez-Sosa A, et al. *Carbon*, **2009**,**47**:3167-3174
- [3] Rao C N R, Biswas K, Subrahmanyam K S, et al. *J. Mater. Chem.*, **2009**,**19**:2457-2469
- [4] Geim A K, Novoselov K S. *Nat. Mater.*, **2007**,**6**:183-197
- [5] Panchakarla L S, Subrahmanyam K S, Saha S K, et al. *Adv. Mater.*, **2009**,**21**:4726-4730
- [6] Terrones M, Grobert N, Terrones H. *Carbon*, **2003**,**41**:1941-1947
- [7] Golberg D, Dorozhkin P S, Bando Y, et al. *Appl. Phys. A*, **2003**,**76**:499-507
- [8] Suenaga K, Colliex C, Demoncey N et al. *Science*, **1997**,**278**:653-655
- [9] Zhang Y, Gu H, Suenaga K, et al. *Chem. Phys. Lett.*, **1997**,**279**:264-269
- [10] Terrones M, Golberg D, Grobert N, et al. *Adv. Mater.*, **2003**,**15**:1899-1903
- [11] Rao C N R, Govindaraj A. *Adv. Mater.*, **2009**,**21**:4208-4233
- [12] Du A J, Chen Y, Smith S C, et al. *J. Am. Chem. Soc.*, **2009**,**131**:1682-1683
- [13] Yin Y D, Lu Y, Gates B, et al. *Chem. Mater.*, **2001**,**13**:1146-1148
- [14] Huang H, Remsen E E. *J. Am. Chem. Soc.*, **1999**,**121**:3805-3806
- [15] Mathlowitz E, Jacob J S, Morrell C, et al. *Nature*, **1997**,**386**:410-414
- [16] Wang X, Xie Y, Guo Q. *Chem. Commun.*, **2003**,**21**:2688-2692
- [17] Zhang T, Wen G, Huang X X, et al. *Cry Eng Comm.*, **2010**,**12**:3506-3510
- [18] Golberg D, Dorozhkin P, Bando Y, et al. *Chem. Phys. Lett.*, **2002**,**359**:220-228
- [19] Han S B, Shi X Y, Zhou F M. *Nano Lett.*, **2002**,**2**:97-100
- [20] Qiu Y, Yu J, Yin J, et al. *Nanotechnology*, **2009**,**20**:345603 (7pages)
- [21] Torres R, Caretti I, Gago R, et al. *Diamond and Related Materials*, **2007**,**16**:1450-1454
- [22] Laidani N, Anderle M, Canteri R, et al. *Appl. Surf. Sci.*, **2000**,**157**:135-144
- [23] Ajayan P M, Stephan O, Colliex C, et al. *Science*, **1994**,**265**:1212-1214
- [24] Watanabe M O, Itoh S, Mizushima K. *Appl. Phys. Lett.*, **1996**,**68**:2962-2964