ELSEVIER



Materials Research Bulletin



journal homepage: www.elsevier.com/locate/matresbu

Synthesis of rose-like boron nitride particles with a high specific surface area

Hongming Yu^a, Xiaoxiao Huang^a, Guangwu Wen^{a,b,*}, Bo Zhong^a, Tao Zhang^a, Hongwei Bai^a

^a School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
^b School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, Weihai 264209, China

ARTICLE INFO

Article history: Received 22 August 2009 Received in revised form 31 March 2010 Accepted 1 April 2010 Available online 7 April 2010

Keywords: A. Nitrides B. Crystal growth B. Chemical synthesis D. Crystal structure

1. Introduction

Hexagonal boron nitride (h-BN) has received considerable attention due to its wide-band gap semiconducting properties, high melting point, low density, high mechanical strength, corrosion resistance, oxidation resistance, outstanding thermal and electrical properties and the capability of hydrogen uptake [1–3]. Boron nitride nanostructures commonly inherit the superior properties of h-BN. Boron nitride nanotube (BNNT) is a structural analogue of carbon nanotube in nature [4]: alternating B and N atoms entirely substitute for C atoms in a graphitic-like sheet with almost no change in atomic spacing. BNNT was first theoretically predicted in 1994 [5,6] and experimentally realized in the following year [7]. Thereafter, other nanostructures including fullerenes [8], nanocones [9], acetabuliform boron nitride nanoparticles [10] and so on have been successfully synthesized using various techniques.

Hexagonal BN proves to be an excellent support for catalysts [11,12] owing to its super-resistance to oxidation at high temperatures and its excellent chemical inertness. However, h-BN has been less extensively used as catalytic supports compared with traditional oxide materials such as Al_2O_3 and SiO_2 , mainly due to the difficulties in the synthesis of BN with high surface area [13]. Although BN fullerene-like nanocages have been fabricated [14], they were obtained as by-products during the production of BN nanotubes and thus the yield was disappointingly low. Recently, it has been shown that mesoporous BN materials can be fabricated

ABSTRACT

Novel rose-like BN nanostructures were synthesized on a large scale via a two-step procedure. The products were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectrometer and nitrogen porosimetry. The results show that the obtained rose-like nanostructures are composed of a large amount of h-BN crystalline flakes and have a surface area of 90.31 m²/g. A mechanism was proposed to explain the formation process of the rose-like BN nanostructures.

© 2010 Elsevier Ltd. All rights reserved.

via substitution reactions method using mesoporous C as templates [15,16]. However, the purification processes of the product are complicated and the impurity cannot be removed effectively. Herein, we present a facile, two-step repeatable approach to fabricate rose-like BN particles on a large scale. Such particles possess a BET specific surface area of 90.31 m²/g, and can be potentially used as hydrogen storage containers or catalyst supports.

2. Experimental

To synthesize the rose-like BN nanostructures, a precursor was first prepared. Firstly, $40.4 \text{ g} \text{ Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $120.12 \text{ g} \text{CO}(\text{NH}_2)_2$ powders were dissolved in 800 ml deionized water at room temperature with 1.1 g amorphous boron powder adding into the solution. Then the mixture was heated at 80 °C and kept stirring for 5 h. During this heating process, urea was hydrolyzed according to the following Eq. (1):

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + CO_2 + 2OH^-$$
(1)

Fe $(OH)_3$ precipitate appeared owing to the reaction between OH^- and Fe^{3+} in the solution. The slurry was aged for 24 h to guarantee the sufficient reaction, and then the filter process for the suspensions was conducted followed by an absolute washing with deionized water and ethanol to remove residual nitric ions. After washing, the product was dried at 50 °C for 10 h resulting in loose precursors. The as-obtained precursors were loaded into a graphite crucible and calcined in a gas pressure furnace at 800 °C for 30 min and then at 1350 °C for 2 h under nitrogen atmosphere. The initial and final pressures were 0.5 and 1.2 MPa, respectively. A sketch of the gas pressure furnace is shown in Fig. 1. The furnace chamber was evacuated to 10^{-3} mbar before the vacuum pump was

^{*} Corresponding author at: Harbin Institute of Technology, West-Da Street No. 92, Harbin 150001, China. Tel.: +86 451 86418860; fax: +86 451 86413922.

E-mail address: wgw@hitwh.edu.cn (G. Wen).

^{0025-5408/\$ -} see front matter \circledcirc 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.materresbull.2010.04.003



Fig. 1. Scheme of the gas pressure furnace.



Fig. 2. XRD pattern of the rose-like boron nitride particles.



Fig. 3. SEM and TEM images of the rose-like boron nitride nanostructures: (a) low-magnification SEM image indicating that the yield of the product is in large scale; (b and c) high-magnification SEM images showing the rose-like morphology; (d) low-magnification TEM image of the sample; (e and f) high-magnification TEM image and corresponding electron diffraction pattern of the rose-like BN.

shut down, and then it was filled with ultra-pure nitrogen gas to 0.5 MPa. A layer of white powder was collected from the bottom of the graphite crucible after cooling the furnace to room temperature.

The crystal structure and phase purity of the products were examined by means of X-ray diffraction analysis (XRD) with Cu K α radiation (λ = 0.15418 nm), and by Fourier transform infrared spectroscopy (FT-IR, Bruker VECTOR 22 spectrometer). The overview of the sample morphology was checked by scanning electron microscopy (SEM, MX2600FE). The products were also ultrasonically dispersed in acetone for 20 min and dropped onto a carbon-coated copper grid for transmission electron microscopy and the selected area electron diffraction (SAED) analysis (TEM, TECNAI20). The surface elemental analysis of the sample was performed on a PHI 5700 ESCA System X-ray photoelectron spectrometer (XPS). Barrett–Emmett–Teller (BET) surface area was examined via nitrogen adsorption experiments at 77 K using a Quantachrome Nova 4200 analyzer.

3. Results and discussion

Typical XRD pattern of the as-obtained products is shown in Fig. 2. The dominant diffraction peaks at d-spacings of 3.3334, 2.1661, 2.0687, 1.8111, 1.6648 and 1.2514 Å can be indexed to h-BN (002), (100), (101), (102), (004) and (110) planes, respectively, which are consistent with the literature values (PCPDF#34-0421) very well. The intense and sharp diffraction peaks indicate that the obtained h-BN is well crystallized.

The morphology of the products was investigated by SEM and TEM, and their typical images are displayed in Fig. 3. As shown in Fig. 3a, a high yield of the BN particles was obtained. Two high-magnification SEM images (Fig. 3b and c) clearly show that the products possess a novel uniform rose-like morphology with diameters ranging from 1 to 5 μ m. To investigate the real structure feature of the rose-like BN nanostructures more TEM examinations were performed. Fig. 3d and e shows the typical TEM images, which reveal that the rose-like nanostructures are formed by a large quantity of the crystalline flakes agglutinating together, and



Fig. 4. FT-IR spectrum of the rose-like boron nitride products.

the SAED pattern (Fig. 3f) taken on a selected flake indicates the hexagonal structure of the products. This result suggests that the rose-like morphology is constructed by h-BN crystals, which is in agreement with the XRD analysis.

Fig. 4 displays the FT-IR spectrum of the h-BN sample. Two strong characteristic absorption bands near 1363 and 796 cm⁻¹ can be assigned to the in-plane B–N TO mode of the sp²-bonded h-BN and the B–N–B bending vibrations out of the plane, respectively [17,18]. The high frequency peaked at 3425 cm⁻¹ represents a typical –OH stretching vibration from surface atmosphere species, which has been widely observed in BN system [19].

Further evidence for the formation of BN can be obtained from the XPS analysis of the as-prepared sample, as shown in Fig. 5a. The full range survey XPS spectrum demonstrates the existence of nitrogen, boron, oxygen and carbon elements in the sample, with binding energies at 532.5 eV for O 1s, 398.0 eV for N 1s, 284.6 eV for C 1s and 190.2 eV for B 1s, respectively. The C 1s and O 1s peaks indicate that there exist a small amount of impurity elements such as C and O due to the adsorption of CO₂, H₂O and O₂ on the surface



Fig. 5. XPS spectra of the rose-like boron nitride particles: (a) survey spectrum; (b) B 1s spectrum; (c) N 1s spectrum.

of the sample. The binding energies centered at 190.2 eV for B 1s (Fig. 5b) and 398.0 eV for N 1s (Fig. 5c) are well consistent with the values of bulk BN reported in the literature [20]. The quantitative analysis of the peaks confirms that the atomic ratio of N:B is 1.09:1, which is in good agreement with stoichiometric composition of BN.

Fig. 6 shows nitrogen adsorption/desorption isotherms of the sample. From the N₂-adsorption data, the total specific surface area of 90.31 m^2/g is calculated, which is much larger than that of the commercial h-BN (25.31 m²/g) [21]. Therefore, it is regarded as a promising catalyst support for various catalytic reactions and hydrogen storage medium.

The formation of the rose-like BN nanostructure probably occurs based on the following reactions:

$$2Fe(OH)_3 \to Fe_2O_3 + 3H_2O(<500\,^{\circ}C) \tag{2}$$

 $Fe_2O_3 + 3B \to Fe \ + \ FeB \ + \ B_2O_3(800\ ^\circ C)$ (3)

$$FeB + \frac{1}{2}N_2 \rightarrow Fe + BN \quad (1100^{\circ}C) \tag{4}$$

$$B_2O_3 + 4C \,+\, N_2 + 5H_2O \rightarrow 2BN \,+\, 4CO_2 + 5H_2(1350\,^\circ C) \eqno(5)$$

We propose a two-stage growth process for the unique structure. Firstly, boron particles reduce neighboring Fe₂O₃ particles to give metallic Fe particles, and subsequently the metallic Fe particles react with surplus boron to generate a Fe-B compound with the chemical reaction shown in Eq. (3) [22]. And then the Fe-B reacts with N2 to generate BN shell around the particle free surface (Eq. (4)). Pan et al. [23] have discussed the synthesis of boron nitride by nitriding Fe-B compounds in detail. With the consumption of the surface B atoms, the inner B atoms of the compounds diffuse outwards to the particle surface due to the concentration gradient, and the h-BN shell gradually grows inward around the Fe-B particle. The shell thickness gradually increases and the inner diameter of the shell decreases as the growth continues, which build up strain energy between BN shell walls and the Fe-B particle. When the BN shell reaches a critical thickness, the Fe-B core is expelled from the BN shell by a straininduced ejection, so the core of the rose-like structure is a BN cage or a solid particle. While, a very weak diffraction peak of α -Fe is observed (in Fig. 2), it may not be expelled absolutely. The second stage is a deposition and growth process. The surfaces of the BN particles are generally rather rough and have many defects (it is convincingly supported by in situ HRTEM observations [24]), so the curved surfaces of BN particles behave as the substrates for nucleation and deposition sites, and they are closely covered around by B₂O₃ vapor under the gas pressure assistance; meanwhile, crucible C reacts with H₂O at high temperature to generate CO and H₂, which guarantee B₂O₃ vapor react with N₂ to form BN flakes (Eq. (5) [25]) attaching on curved surfaces of BN particles and then agglutinate together to form rose-like morphology.

4. Conclusion

In summary, we presented a two-step synthesis route to fabricate a novel rose-like BN nanostructure. The obtained unique rose-like nanostructures consisting of numerous curved BN flakes and have a large surface area of 90.31 m^2/g , which is a promising material for catalyst support and hydrogen absorption. In this



Fig. 6. Nitrogen adsorption/desorption isotherms of rose-like boron nitride particles.

synthetic method, the as-produced sample can avoid complicated purification process.

Acknowledgments

The authors are grateful to the financial support from the National Natural Science Foundation of China (No. 50672018), the 863 Program of China (No. 2007AA03Z340) and the excellent team in Harbin Institute of Technology.

References

- [1] R.T. Paine, C.K. Narula, Chem. Rev. 90 (1990) 73.
- [2] C. Tang, Y. Bando, C. Liu, S. Fan, J. Zhang, X. Ding, D. Golberg, J. Phys. Chem. B 110 (2006) 10354.
- [3] R. Ma, Y. Bando, H. Zhu, T. Sato, C. Xu, D. Wu, J. Am. Chem. Soc. 124 (2002) 7672.
- A. Oberlin, M. Endo, T. Koyama, J. Cryst. Growth 32 (1976) 335.
- [5] X. Blase, A. Rubio, S.G. Louie, M.L. Cohen, Europhys. Lett. 28 (1994) 335.
- A. Rubio, J.L. Corkill, M.L. Cohen, Phys. Rev. B 49 (1994) 5081.
- [7] N.G. Chopra, R.J. Luyken, K. Cherrey, V.H. Crespi, M.L. Cohen, S.G. Louie, A. Zettl, Science 269 (1995) 966.
- [8] O. Stephan, Y. Bando, A. Loiseau, F. Willaime, N. Shramchenko, T. Tamiya, T. Sato, Appl. Phys. A 67 (1998) 107.
- [9] C. Zhi, Y. Bando, C. Tang, D. Golberg, Appl. Phys. Lett. 87 (2005) 063107.
- [10] L. Lin, Y. Zheng, Z. Li, K. Wei, Scripta Mater. 59 (2008) 1151.
- [11] G. Postole, A. Gervasini, C. Guimon, A. Auroux, B. Bonnetot, J. Phys. Chem. B 110 (2006) 12572.
- [12] S.H. Taylor, A.J.J. Pollard, Catal. Today 81 (2003) 179.
- [13] G. Postole, A. Gervasini, M. Caldararu, B. Bonnetot, A. Auroux, Appl. Catal. A: Gen. 325 (2007) 227.
- [14] D. Golberg, Y. Bando, T. Sato, N. Grobert, M. Reyes-Reyes, H. Terrones, M. Terrones, J. Chem. Phys. 116 (2002) 8523.
- [15] A. Vinu, M. Terrones, D. Golberg, S. Hishita, K. Ariga, T. Mori, Chem. Mater. 17 (2005) 5887.
- [16] W. Han, R. Brutchey, T.D. Tilley, A. Zettl, Nano Lett. 4 (2004) 173.
- [17] M. Zheng, Y. Gu, Z. Xu, Y. Liu, Mater. Lett. 61 (2007) 1943.
- [18] J. Pai, L.Q. Xu, Z.L. Fang, D.P. Sheng, Q.F. Guo, Z.Y. Ren, K. Wang, Y.T. Qian, Chem. Phys. Lett. 440 (2007) 253.
- [19] S.D. Yuan, L.H. Zhu, M.X. Fan, X.B. Wang, D.J. Wan, S.X. Peng, H.Q. Tang, Mater. Chem. Phys. 112 (2008) 912.
- [20] R.M. Desrosiers, D.W. Greve, A.J. Gellman, Surf. Sci. 382 (1997) 35.
- [21] L. Hou, F.M. Gao, G.F. Sun, H.Y. Gou, M. Tian, Cryst. Growth Des. 7 (2007) 535. [22] H. Tokoro, S. Fujii, T. Oku, Mater. Chem. Phys. 114 (2009) 204.
- [23] Y. Pan, K. Huo, Y. Hu, J. Fu, Y. Lu, Z. Dai, Z. Hu, Y. Chen, Small 1 (2005) 1199.
- [24] M. Yeadon, M. Lin, K.P. Loh, C.B. Boothroyd, J. Fu, Z. Hu, J. Mater. Chem. 13 (2003) 2573
- [25] T. Ishii, T. Sato, Y. Sekikaw, M. Iwata, J. Cryst. Growth 52 (1981) 285.