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Synthesis of boron nitride nanotubes and its hydrogen uptake

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Abstract

Boron nitride nanotubes (BNNT) were synthesized by annealing ball-milled boron-nickel catalyst in nitrogen/hydrogen gas mixture at a temperature of 1025 °C. The BNNTs were characterized by TEM, XRD, FTIR and Raman spectroscopy. The pressure-composition isotherms (PCI) and temperature-programmed desorption (TPD) techniques were used to investigate the H_2 uptake properties of BN nanotubes. The BNNTs show a reproducible room temperature hydrogen sorption of 1.8–2.2 wt% under 6 MPa.

Keywords: Boron nitride nanotubes; Pressure-composition isotherms; Temperature-programmed desorption; Hydrogen uptake

1. Introduction

Intensive research efforts on carbon nanotubes (CNTs) [1–3] have led to the postulation and synthesis of other non-carbonaceous nanostructured materials such as layered metal chalocogenides (MS_2, M = Mo, Ti) [4,5], hexagonal boron nitride [6–10], metal carbides, nitrides and oxides in the forms of nanotubes, nanowires, nanorods and nanobelts [11]. CNTs have been suggested as potential candidates for hydrogen storage materials [3]. However as the synthesis of nanostructured materials matures, there is a growing interest to study the hydrogen storage of new nanostructured materials. Nanostructured compounds are one of the most promising classes of advanced materials for hydrogen storage, owing to their unique chemical, physical, thermodynamic and transport properties as compared to their bulk forms. Recently, we have reported the hydrogen sorption behaviour of TiO_2 nanotubes with a storage of ~2 wt% [12], but the hydrogen sorption kinetics of TiO_2 nanotubes are rather slow [13]. Other non-carbonaceous nanomaterials (e.g. TiS_2, MoS_2 and BN) show a hydrogen sorption capacity of ~1–4 wt% at room temperatures (see Table 1), and particular attentions are given to collapsed BN nanotubes which show a promising level of 4.2 wt% [8].

Boron nitride nanotube (BNNT) is isoelectronic and isostructural to carbon nanotube. Unlike carbon nanotube which can be metallic or semiconducting, BNNT is semiconducting with a bandgap of ~5.5 eV and it is nearly independent of the tube diameter, chirality and the number of BN layers; a phenomeon that has been attributed to the ionic origin of the BN bonding. Both BN nanotube and BN nanowire (BNNW) have been succuessfully synthesized using similar techniques applied for the growth of CNT such as arc-discharge, laser ablation and chemical vapor deposition (CVD) [6–10]. However, most of the methods reported may require sophiscated equipment, usage of harmful precursors such as borazine and ammonia, and high synthesis temperatures >1200 °C. In light of the promising hydrogen uptake of BN nanostructured materials, a simple and scalable synthesis method will be desirable.

In this work, we had prepared boron nitride nanotubes via a simple chemical reaction between nitrogen/hydrogen gas mixture and boron-nickel powders at 1025 °C. The BNNTs were characterized with transmission electron microscopy (TEM, JEOL 2010F 200 kV), X-ray diffraction (XRD, Bruker D8 with Cu Kα radiation), Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer 2000) and Raman spectroscopy (Reinshaw micro-Raman 2000 system with 514 nm). The hydrogen sorption properties of BN nanotubes were investigated by pressure-composition isotherms (PCI) and temperature-programmed desorption (TPD). The BNNTs exhibit reproducible room temperature hydrogen uptakes of 1.8–2.2 wt% at 6 MPa.

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Table 1
A comparison of H_2 uptake by various nanostructured materials

Reference	Sample	H_2 sorption/wt%	Conditions
[a]	BN nanotubes	2.2	6 MPa, room temperature
[6]	BN nanofibers	2.9	9 MPa, room temperature
[7]	BN nanotubes	1.8–2.6	10 MPa, room temperature
[8]	Collapsed BN nanotubes	4.2	10 MPa, room temperature
[9][b]	BN nanotubes, cages, capsules	1–3	20–300 °C
[22]	Milled *h*-BN powder	2.6	Ball-milled in H_2 atmosphere
[4]	MoS_2 nanotubes	1.2	3 MPa, room temperature
[5]	TiS_2 nanotubes	2.5	4 MPa, room temperature
[1]	SWNT	4.2	10 MPa, room temperature
[2]	MWNT (template-synthesized)	1.1 (6.4)	10 MPa, room temperature (77 K)
[12]	TiO_2 nanotubes	2.0	6 MPa, room temperature

[a] This work.

[b] H_2 pressure is not stated.

2. Experimental

2.1. Preparation of boron-nickel catalyst

The boron-nickel catalyst was prepared by ball-milling nickel boride (NiB_x) and boron powders. The nickel boride was prepared by reduction of nickel chloride with potassium tetrahydridoborate (KBH_4). Three hundred millimolar of KBH_4 aqueous solution and 50 mM of $NiCl_2$ solution ($NiCl_2 \cdot 6H_2O$ was dissolved in methanol/water, 1:1 volume ratio, solution) were prepared separately. Two hundred millilitre of KBH_4 solution was added dropwise to 400 ml of $NiCl_2$ solution under vigorous stirring. The resulting NiB_x powder were filtered and rinsed with distilled water. Ball-milling of boron and NiB_x powders were performed in N_2 atmosphere for 48 h at 180 rpm (Planetary ballmill, Fristsch Pulverisette 5). The ball-milled B-Ni powder was loaded into a horizontal quartz tube reactor flowing with a mixture of N_2:H_2 gases with their flow rates at 15 ml/min versus 35 ml/min, respectively. The continuous supply of H_2 is noted to be crucial for the efficient growth of the BN nanotubes. The reactor was heated up at 7.5 °C/min to a maximum temperature of 1025 °C and held for 2 h. The as-prepared BNNTs were sonicated in 8 M HCl acid to remove the residual Ni particles.

2.2. Hydrogen uptake measurements

The hydrogen uptake of BN systems was measured with a commercial pressure-composition isotherm unit (PCI, Advanced Materials) as previously described [12]. The PCI system was calibrated with $LaNi_5$ alloy. An expected 1.5 wt% of $LaNi_5H_{6.5}$ was observed. No gas leakage was found when the pressures of the PCI manifold and blank sample chamber were manually increased to a pressure up to 900 psi. For an arbitrary pressure (800–900 psi), the pressure fluctuation was monitored over a period of $\geq$12 h. The drop in the pressure was always less than 2 psi. Generally, ~500 mg of the BN samples were loaded into the PCI sample holder. The samples were degassed at 350 °C and 1×10^{-3} Pa for at least 2 h. When the sample was cooled to room temperature, the hydrogen sorption process began. The PCI measurements were repeatable. For comparison, the hydrogen uptakes of bulk BN and multi-walled carbon nanotubes (MWNT with diameter 10–20 nm, which was home-made according to our method [14]) were carried out under identical conditions in the same equipment. The measured 0.1 and 0.2 wt% for bulk BN and MWNT, respectively are low, but consistent with the reported data.

2.3. Temperature-programmed desorption (TPD)

TPD was performed on a home-built stainless steel microreactor equipped with an online mass spectrometer (HPR20 mass spectrometer, Hiden Analytical Ltd.). Approximately 100 mg of purified BN nanotube was loaded into the middle of the microreactor and vacuum degassed at 350 °C for 2 h. The BN nanotube was then soaked under ~9 MPa of H_2 pressure (purity 99.9995%) for 4 h at room temperature. After the hydrogen pressure was released back to ambient conditions, the BNNT sample was purged with argon for ~45 min. The desorption process of the H_2-pressurized BN nanotube was monitored from room temperature to 400 °C at a heating rate of 10 °C/min with argon as the carrier gas. During TPD

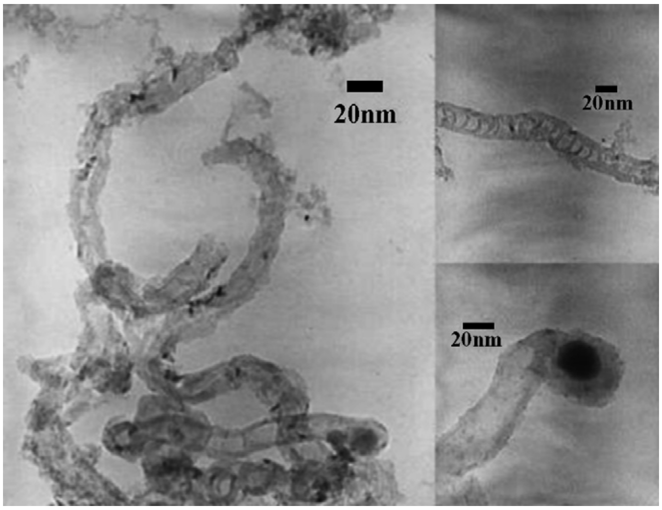

Fig. 1. TEM images of boron nitride nanotubes synthesized from ball-milled boron-nickel catalyst in nitrogen/hydrogen gas mixture at 1025 °C.

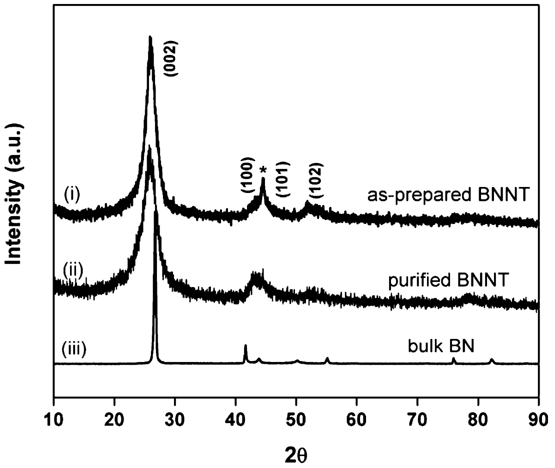

Fig. 2. XRD patterns of (i) as-prepared BNNT, (ii) purified BNNT, and (iii) bulk BN powders (asterisk (*) indicates the presence of Ni nanoparticles in as-prepared BNNTs).

measurements, H_2, N_2, O_2 and H_2O desorption were monitored simultaneously. No N_2, O_2 and H_2O desorption signals were observed.

3. Results and discussion

Fig. 1 shows the TEM images of the BN nanotubes. The diameters and lengths of the BNNTs ranged from 20–40 nm and >250 nm, respectively. Ammonia gas is not essential since it is known that NH_3 decomposes into N_2 and H_2 gases at >550 °C [15]. It is inferred that extensive ball-milling of boron and NiB_x powders resulted in a nanometeric boron–nickel mixture, which is essential for the synthesis of BNNTs. It is noted that H_2 gas is crucial to the efficient growth of BNNTs in terms of the activation of the metallic Ni, which could absorb nitrogen into the B–Ni alloy. At 1025 °C the formation of Ni-BN eutectics yields anisotropic growth of BN nanotubes. Ni nanoparticles encased at the tip of the BNNT can be observed from the TEM micrograph.

The XRD patterns of the BN nanotubes are shown in Fig. 2. The XRD pattern of the as-prepared BNNTs has a Ni peak at ~44.4° (indicated by an asterisk), which is removed after the HCl acid treatment. All reflection peaks can be indexed as hexagonal-phase boron nitride with lattice constants of $a = 2.48$ Å and $c = 6.79$ Å, which are consistent with literature (JPDCS, No. 45–895, $a = 2.5044$ Å and $c = 6.6562$ Å). All (0 0 2) peaks of BNNTs are slightly shifted to lower angle as compared to bulk *h*-BN crystal, indicating a slight expansion of the interplanar spacing (from 3.33 to 3.40 Å) in nanometric tube-like morphology.

The FTIR spectrum of purified BNNTs exhibit two strong characteristic peaks located at ~1380 and ~805 cm^{-1} (Fig. 3a). The former is the B–N vibration along the axis of the nanotubes, while the latter is the B–N vibration perpendicular to the axis [16]. Computational simulations [17] and LEED study [18] have shown the substantial buckling of B–N bonds in the bulk sp^2-based layered structure. Outward displacement of nitrogen atoms has been predicted and experimentally observed. Due to the curvature of the BN nanotube this buckling becomes more evident. This structural buckling results in some sp^3 admixture in sp^2 BN bonding so that the softening of the FTIR vibration modes can be observed. Indeed in comparison with bulk *h*-BN, the B–N vibration perpendicular to the axis of the BN nanotube is shifted to lower frequency (from 811 to 805 cm^{-1}) by 6 cm^{-1}, indicating the buckled structure in BNNTs.

The Raman scattering spectrum of purified BNNTs exhibits only one Raman active mode, E_{2g}, in the range of 1100–1600 cm^{-1} (Fig. 3b). The E_{2g} mode of boron nitride is due to the in-plane atomic displacement of B and N atoms against each other. This peak is located at 1356 cm^{-1} for the purified BNNTs and the full-width at half maximum (FWHM) is 32 cm^{-1}. The E_{2g} Raman peak of BNNTs, compared to bulk BN, was broader and downshifted by 12 cm^{-1}. This is attributed to the buckled structure of BN nanotubes.

Fig. 4a shows the pressure-composition isotherms of purified BNNT at 24, 180 and 250 °C. The H_2 uptake of the

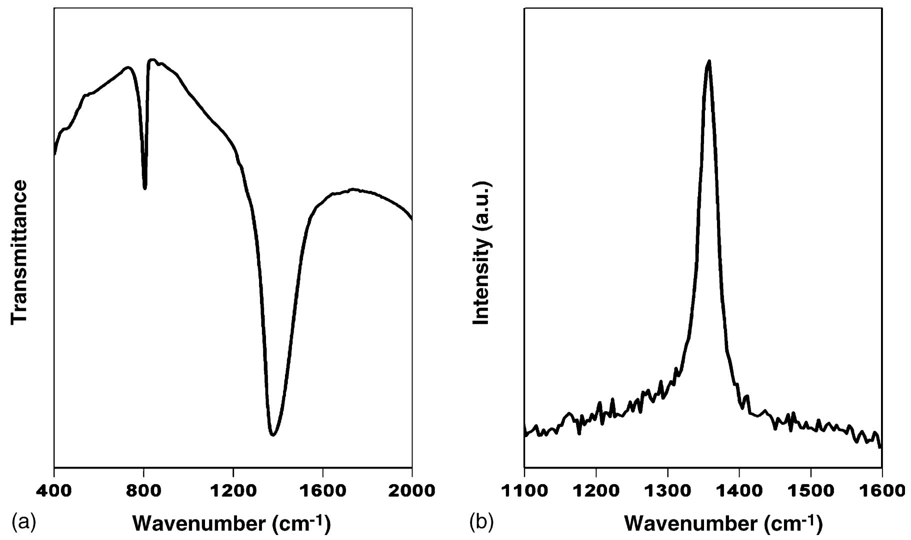

Fig. 3. (a) FTIR and (b) Raman spectra of the purified BNNTs.

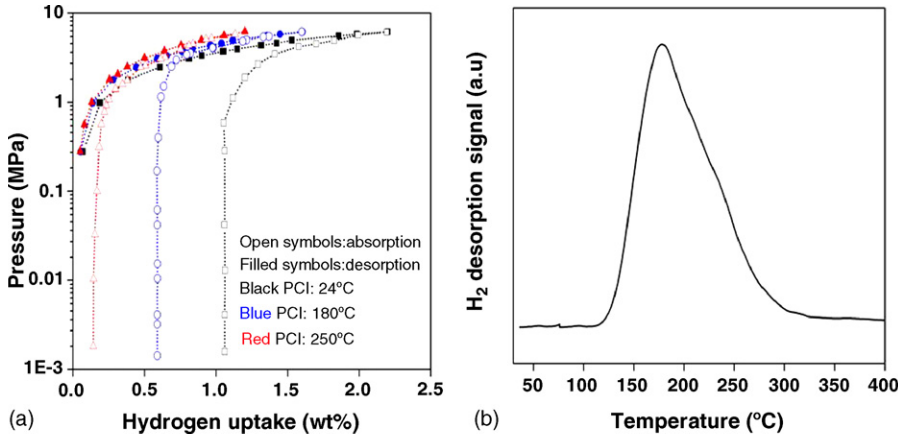

Fig. 4. (a) PCI isotherms of purified BNNT at 24 °C (black curves), 180 °C (blue curves) and 250 °C (red curves). (b) Temperature programmed H_2 desorption profile of hydrogen-pressurized purified BNNT with ramp rate = 10 °C/min, using argon as carrier gas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

purified BNNT was 2.2 wt% at room temperature and 6 MPa. This value is much higher than those of bulk BN and MWNT (not shown in the figure, only ~0.1 and 0.2 wt%, respectively). At 180 and 250 °C, the maximal H_2 uptakes were reduced to 1.6 and 1.2 wt%, respectively. As seen in Fig. 4a the H_2 desorption isotherms of the purified BNNTs do not coincide with the adsorption curves, which strongly suggest the presence of H_2-chemisorption. We have conducted a temperature-programmed desorption (TPD) of hydrogen-pressurized BNNTs (H_2-BNNTs). From TPD measurements, a H_2 desorption peak of chemisorbed hydrogen was observed at ~180 °C for H_2-BNNTs. From the PCI profiles at 24, 180 and 250 °C (Fig. 4a), it is estimated that ~50% of the adsorbed hydrogen on the BNNTs is chemisorbed.

The higher H_2 storage of BNNT can be attributed to its nano-morphology and the presence of heteropolar B–N bonding [20]. The ionic B–N bonding may induce an extra dipole moment and hence stronger adsorption of hydrogen, since the induced dipole moment of hydrogen molecules is sensitive to local electric fields. The binding energy of H_2 on the BN sheet is calculated to be about 90 meV, significantly higher than 60 meV on graphite [20]. The buckling structure in BN nanotubes may induce extra dipole moment so that on BNNTs the calculated binding energy of H_2 can be as high as 110, 85 and 100 meV, respectively, on the top of B_3N_3 hexagon center, boron atom, and nitrogen atom [20]. From first principles [21], it is found that radial deformation on BN nanotubes can modify the H_2 adsorption energy and site. For small defects, hydrogen prefers to adsorb on the boron atom. While for large defects, hydrogen prefers to adsorb on the nitrogen atoms in the high curvature regions. Therefore, from TEM images of Fig. 1, it is surmised that the BNNTs prepared by the present method are defective and some possessed a bamboo shape. And the presence of defects in the BNNTs enhanced its H_2 adsorption.

Table 1 is a compilation of recent H_2 storage performed on various nanostructured materials. The room temperature H_2 storage of our BN nanotube is consistent with that reported in literature [1–9,22]. At present, it seems that the H_2 uptake of BN nanomaterials is limited to 2–3 wt% unless post-synthesis treatment is carried out to modify the BN structure, as in the case of collapsed BN nanotubes, to achieve higher H_2 sorption.

4. Conclusion

In short, an effective B-Ni catalyst was prepared via ball-milling for the synthesis of BN nanotubes. BN nanotubes can be synthesized effectively from the B-Ni catalyst using a mixture of N_2–H_2 gases at 1025 °C. XRD, FTIR and Raman revealed that the nanotubes are of the *h*-BN form. A reproducible room temperature uptake of 2.2 wt% at 6 MPa was achieved and this result was consistent with literature.

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