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Thorn-like BN nanostructures

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Abstract

Thorn-like BN nanostructures that the nanosize hexagonal BN (h-BN) layers are randomly stacked looking like thorns were synthesized using thermal chemical vapor deposition of B/B_2O_3 under the flow of NH_3 at 1200 °C. They can grow self-assembled forming the microsize lumps, and also deposit as sheathing layers on the pre-grown SiC nanowires with a controlled thickness in the range 20–100 nm. The spreading of the thorn-like BN layers as the sheathing layers results in a significantly enhanced surface area, 2400 m^2/g.

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1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 [1], immense efforts have been devoted to investigate the synthesis, properties, and potential applications of the nanotubular structure which is analogous to graphite. Boron nitride (BN) nanotube is a very attractive material because its physical and chemical properties could complement those of CNT [2–5]. The BN nanotubes have a mechanical strength similar to that of CNTs (elastic modulus ≈ 1.2 TPa) [5]. Unlike CNTs, however, the calculated band structure of single-walled BN nanotubes shows semiconducting properties with the band gap (5.5 eV) which is weakly dependent on the tube diameter and chirality [2,3]. Therefore, they are particularly useful for many applications where high-strength and/or uniform band structure is required. Furthermore, it is expected to use as a potential hydrogen storage medium like CNTs. The high capacity of hydrogen uptake has been measured for the BN nanostructures including the nanotubes [6,7].

Here we synthesized unique thorn-like BN nanostructures by simple thermal chemical vapor deposition (CVD). They can grow self-assembled to form microsize lumps without catalysts, and can also sheath uniformly the pre-grown nanowires in a controlled manner. The morphology and structure of the nanostructures were analyzed by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron energy-loss spectroscopy (EELS), energy-dispersive X-ray fluorescence spectroscopy (EDX). The surface area of these nanostructures has been measured to test a possibility of hydrogen storage medium.

2. Experimental

B pieces (99%, MaTeck) and B_2O_3 powders (98%, Aldrich) were ball-milled separately for 20 h, using a mechanical ball mill system (Spex 8000M). About 0.1 g of ball-milled powders places in a quartz boat inside a quartz

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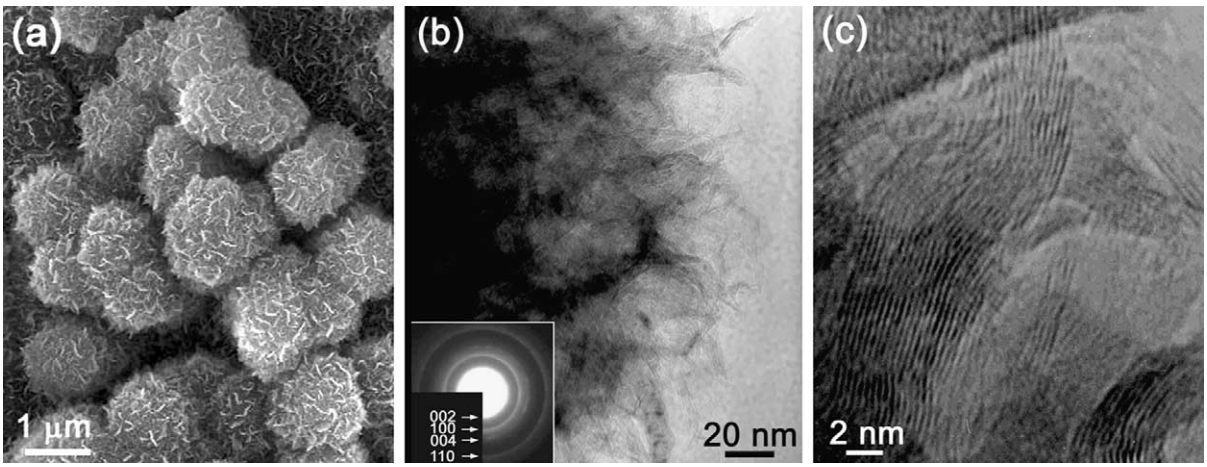

Fig. 1. (a) SEM micrograph showing the micro-size lumps grown on the substrate. (b) TEM image showing the fibrous morphology with its corresponding SAED (inset). (c) Atomic-resolved view showing the high-crystalline curved BN layers.

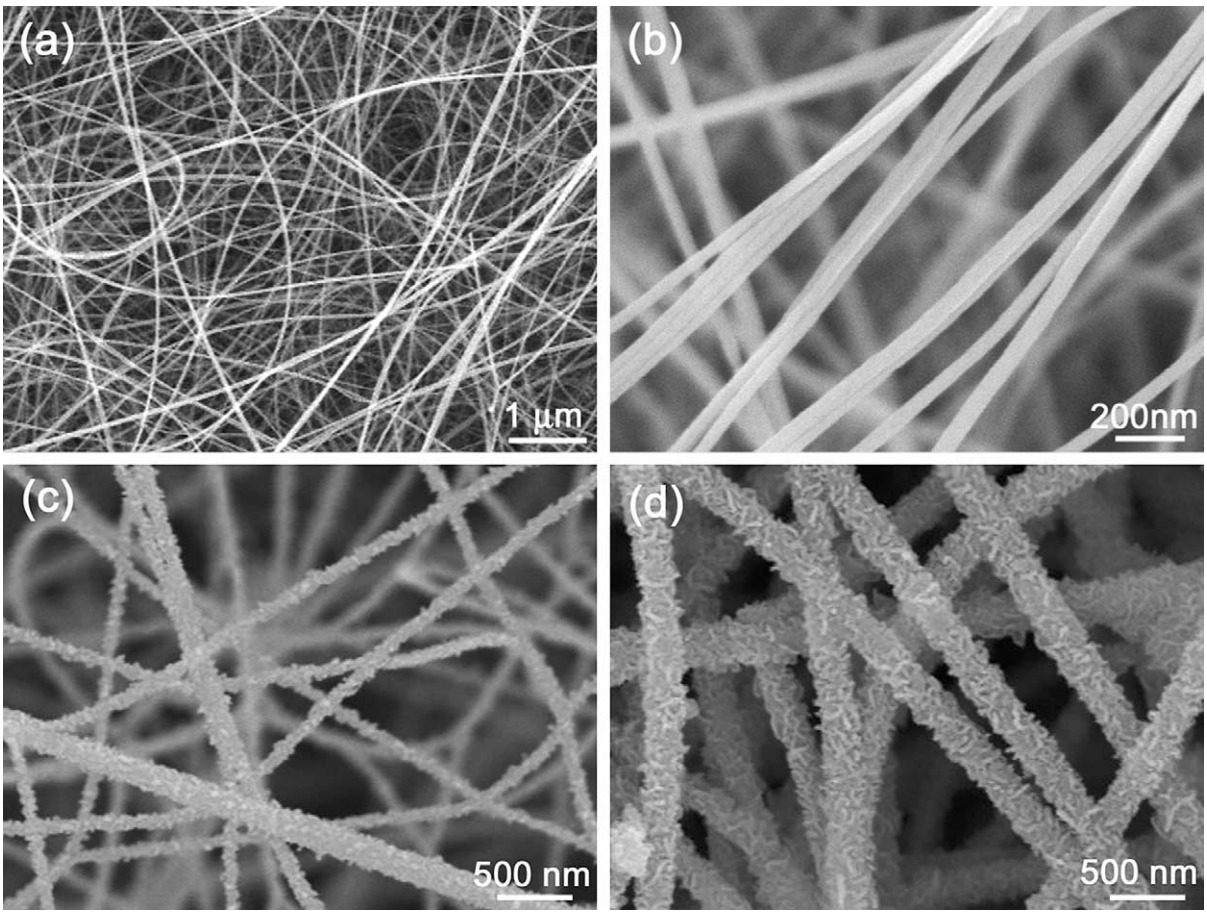

Fig. 2. (a) SEM micrograph showing high-density SiC nanowires grown on the substrates. (b) Magnified image reveals the smooth surface of SiC nanowires. The deposition of BN layers on the SiC nanowires for (c) 20 min and (d) 1 h, increases the diameter and produces a rough surface.

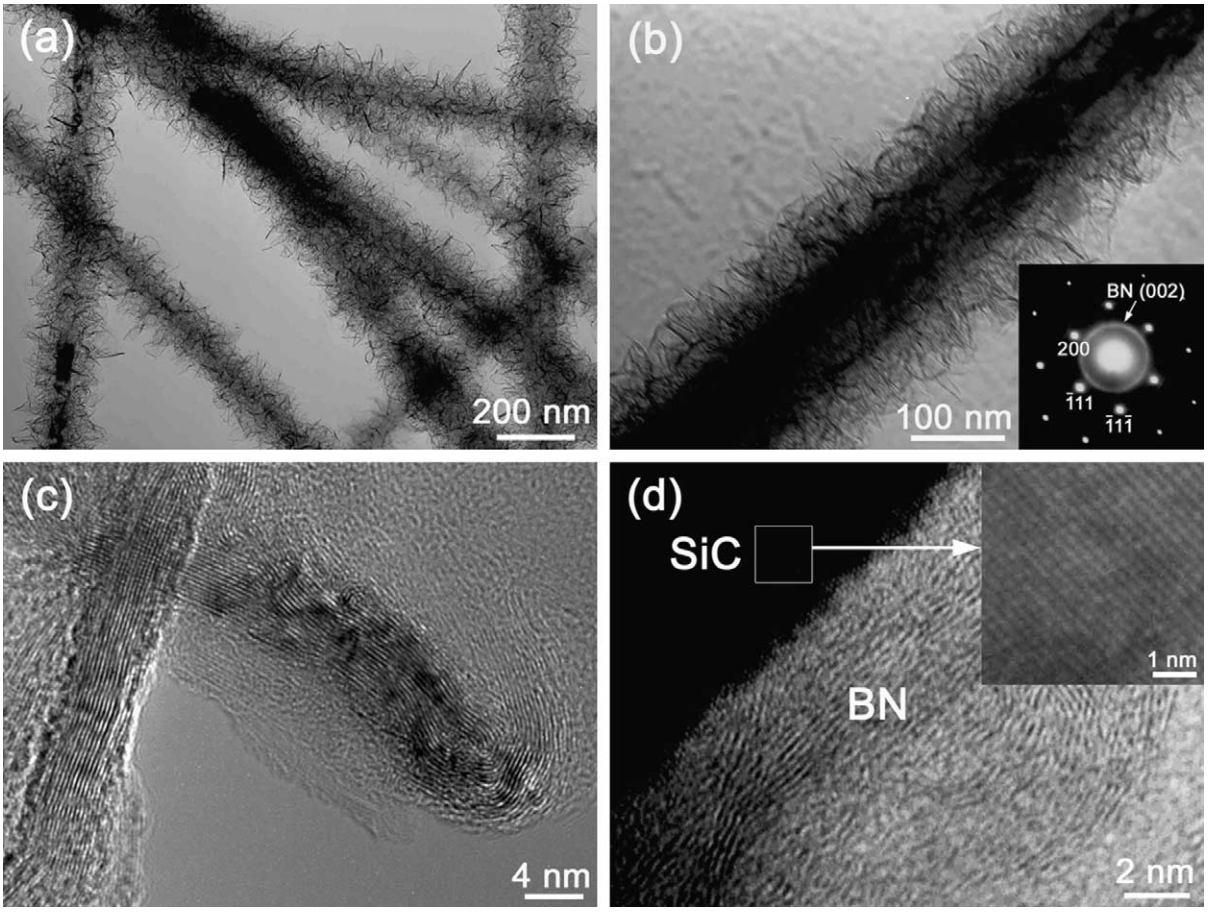

Fig. 3. (a) TEM image showing thorn-like morphology of BN outerlayers. (b) A selected SiC-BN nanostructures with its corresponding SAED (inset). Atomic-resolved image shows highly crystalline BN layers at (c) the edge and (d) the interface with β-SiC nanowire. Inset reveals the single-crystalline β-SiC nanowire.

tube reactor. The SiC nanowires were synthesized on the Si substrates by the procedure described elsewhere [8]. The alumina substrates or the Si substrates deposited with the SiC nanowires covers the source boat. No catalysts deposit on the substrates. The temperature was set at 1200 °C and the growth time was 10 min–1 h. Ammonia (NH_3) gas flows with a rate of 100 sccm. After the reaction, white colored product deposits homogeneously on a large area of the substrate. SEM (Hitachi S-4300), TEM (Jeol JEM-2010), electron diffraction (ED), EDX, and EELS (GATAN GIF-2000) attached to TEM (FEI TECNAI G^2) were used to examine the size, structure, and composition of the products. The surface area and pore size were measured using N_2 adsorption–desorption isotherm at 77 K by Surface Area Analyzer (Micromeritics, ASAP 2010).

3. Results and discussion

The SEM image shows wool-like microsize lumps having an average diameter of 1.2 μm, deposited on the substrates as a film with a thickness of 10 μm [Fig. 1(a)]. These lumps usually stick to each other. TEM image reveals that these microsize lumps are composed of the entangled fibrous layers looking like thorns [Fig. 1(b)]. The inset is its corresponding selected-area ED (SAED) pattern that the circles originate from the random direction of h-BN sheets. The atomic-resolved image clearly depicts that they are composed of highly crystalline h-BN sheets that are curved toward random direction [Fig. 1(c)]. The distance between the h-BN sheets is about 0.33 nm, which is close to that of BN nanotubes.

We performed the synthesis of these thorn-like BN nanostructures on the pre-grown SiC nanowires under the same growth conditions. The SEM image of SiC nanowires before the deposition of BN layers is shown in Fig. 2(a). The high-density SiC nanowires are grown homogeneously with a length of 500 μm on a large area of the Si substrate. Magnified SEM image reveals that they have smooth surface with a diameter of 50 nm (Fig. 2(b)). However,

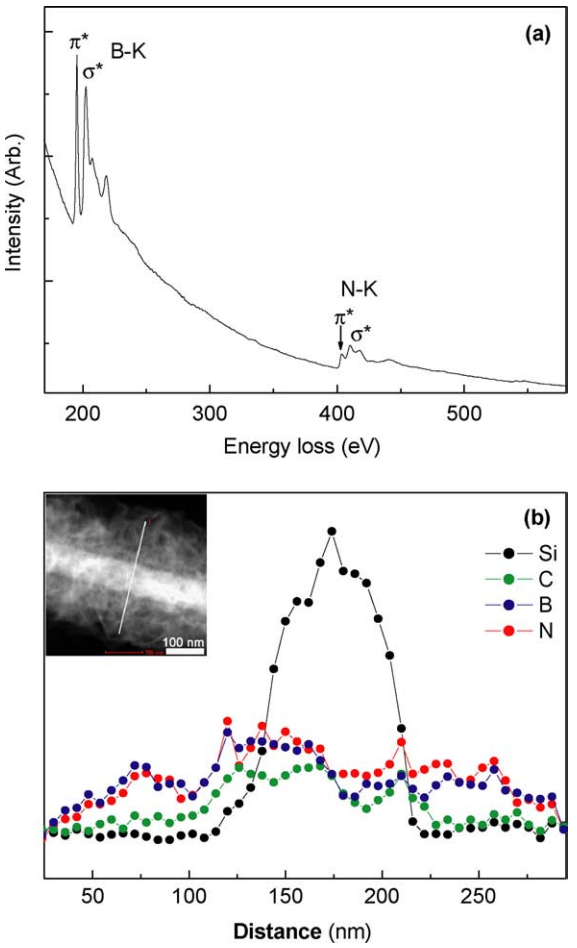

Fig. 4. (a) EELS data for the BN outerlayers, showing two distinct absorption features, one starting at 188 eV and another at 400 eV, corresponding to B-K and N-K, respectively. (b) EDX line scanned profile of SiC–BN nanostructure.

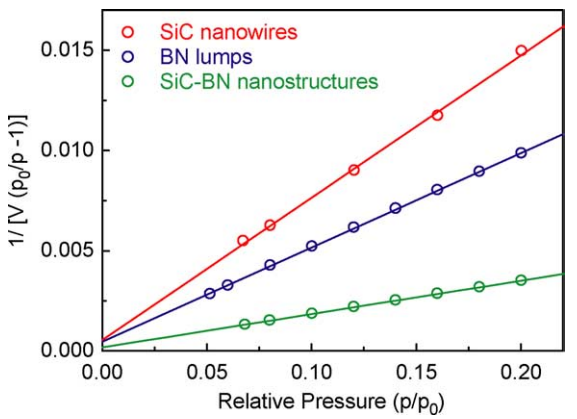

Fig. 5. Adsorption isotherms of BET for BN lumps, SiC nanowires, and BN-SiC nanostructures.

the surface becomes rough after the deposition of BN layers (Fig. 2(c)). The diameter increases to 100 nm when the deposition time is 20 min. As the deposition time becomes longer, the diameter of nanocables increases further. It can reach up to 250 nm at 1 h, as shown in Fig. 2(d).

Fig. 3 shows TEM image for the SiC-BN nanostructures whose SEM image is Fig. 2(c). It reveals that the thorn-like layers surround homogeneously the entire SiC nanowires. The thickness of the outerlayers is about 20 nm. A typical SiC–BN nanostructure is selected in Fig. 3(b). The inset is its corresponding SAED pattern, which is indexed as cubic structure of β-SiC. The growth direction of SiC nanowires is [111]. The brightest circle comes from the randomly oriented [002] direction of h-BN phase. Fig. 3(c) reveals the edge part of the BN layers that are curved and twisted with random direction. Fig. 3(d) clearly shows that the SiC nanowire is surrounded by the BN layers. The inset shows the atomic-resolved image for the single-crystalline SiC core part. The (111) fringes are on average separated by 0.25 nm, which is about the same value of bulk β-SiC, 2.5166 Å (JCPDS Card No. 29-1129).

Fig. 4(a) shows the EELS spectrum for the edge part of the SiC-BN nanostructures, showing two distinct absorption features starting at 188 and 400 eV, corresponding to the known K-shell ionization edges for boron (B-K) and nitrogen (N-K), respectively. A detailed inspection of the near-edge fine structure confirms the sp^2 hybridization state for B, distinguished by the sharply defined π^* and σ^* features. For N-K edge, a defining π^* peak matches to trivalent nitrogens in hexagonal lattices. By subtracting the background, the B/N ratio is determined to be 1 ± 0.1, confirming the highly crystalline BN outerlayers. Fig. 4(b) displays the EDX line-scan profile of Si, C, B, and N elements for a SiC-BN nanostructure whose TEM image is shown in the inset. It confirms the Si and C components at the core region, and B and N components at the outerlayers.

We could control the thickness of outerlayers using the deposition time. The thickness is about 20 nm after 20 min, but increases to 100 nm after 1 h. We also succeed in synthesizing these thorn-like BN nanostructures on the Si_3N_4 nanowires prepared in our laboratory [9]. So we conclude that the deposition of BN outerlayers occurs on any thermal-resistant nanowires at 1200 °C. Bando and coworkers collapsed the BN nanotubes to form the hair-like structured layers using platinum catalyst at 1500 °C, and show the enhanced hydrogen uptake capacity [6]. Rao group reported the production of hair-like BN layers attached to the surface of bamboo-structure nanotubes by the reaction of H_3BO_3 and activated carbons with NH_3 in the presence Fe catalysts at 1300 °C [10]. The morphology of the BN layers of those nanotubes is similar to the present BN layers. The synthesis of uniform BN outerlayers coating the SiC nanowires using one-step route was reported by a number of research groups [11–17]. In contrast, our synthesis uses well-defined pre-grown nanowires and enables to control the thickness of BN layers.

In order to obtain the surface area, we performed the Brunauer, Emmett, and Teller (BET) measurements. The adsorption isotherms were measured to a maximum p/p_0 of 0.20. The BET equation is given by

$$\frac{1}{V(p_0/p-1)} = \frac{1}{cV_m} + \frac{(c-1)p/p_0}{cV_m},$$

where p/p_0 is a relative equilibrium pressure, V is the volume adsorbed, V_m is the volume corresponding to monolayer coverage, and c is a constant. The adsorption isotherms were plotted in the coordinates $1/V(p_0/p-1)$ versus p/p_0, as shown in Fig. 5. Correlation coefficients of the BET plots were 0.98–0.99. The adsorption monolayer volume V_m and c constant were determined from the slope and the intercept of these plots.

The results show that the BN microsize lumps have a specific surface area 90 m^3/g. But the SiC–BN nanostructures have a specific surface area approximately 240 m^2/g in comparison with that of SiC nanowires 60 m^2/g. The deposition of BN outerlayers on the SiC nanowires increases the weight by about 10%, so the surface area of thorn-like BN nanostructure itself is estimated to be 2400 m^2/g. The splitting of the microsize BN lumps into the nanometer thickness outerlayers results in increasing the surface area by a factor of $\sim$30. This surface area overwhelms greatly that of commercial h-BN powders 5 m^2/g (we measured for comparison). Such enhancement is most likely due to the numerous exposed folding edges of nanosize BN layers to the adsorption of gas. The average pore size of these nanostructures is estimated to be about 10 nm by the BET method. Therefore, the deposition of thorn-like BN layers with nanometer thickness would tailor the nanostructures to suit for gas storage applications.

In summary, we synthesized the thorn-like BN nanostructures using the CVD of B/B_2O_3 powder mixture under the NH_3 flow at 1200 °C. These nanostructures can grow self-assembled to form microsize lumps on the substrates without any catalyst. They sheathed the pre-grown SiC nanowires with a controlled thickness in the range 20–100 nm. We confirmed the highly crystalline h-BN structured consisting of B:N components with a ratio of 1:1 by HRTEM, EELS, and EDX. The specific surface area of the microsize lumps is 90 m^2/g, while that of the outerlayers sheathing the nanowires is extremely large as 2400 m^2/g, showing that the spreading of thorn-like BN nanostructures into the nanometer thickness through the nanowire deposition enhances greatly the surface area.

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