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Featured Letter

Synthesis of $BC_{1.61}N_{0.76}$ micro-nano structures from natural rubber latex with visible-light emission property

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ABSTRACT

A novel route to the synthesis of boron carbonitride ($BC_{1.61}N_{0.76}$) micro-nano structures called nanosheet-decorated submicrowires is demonstrated for the first time, by annealing amorphous boron powder, natural rubber latex and ferric chloride ($FeCl_3$) at 1200 °C in flowing ammonia atmosphere. The microwires have diameters of about 200–500 nm, while the nanosheets have an average thickness of less than 20 nm. The nanosheets are mostly separated with a bending and crumpling morphology. This micro-nano structure shows good visible-light emission property at 501.2 and 592.6 nm. A combination growth mechanism of vapor-liquid-solid (VLS) and vapor-solid (VS) model is proposed to be responsible for the formation of this $BC_{1.61}N_{0.76}$ micro-nano structure.

1. Introduction

Boron carbonitride (B-C-N) material attracts intensive attentions because its electronic structure can be tailored by simply changing the composition rather than geometrical structure [1,2], which is superior to the carbon and boron nitride (BN) counterparts. Moreover, B-C-N material has better oxidation resistance and chemical stability in comparison with graphite, making it applicable in electronic devices [3], hydrogen storage [4], supercapacitors [5] and electron field-emission [6]. To date, many efforts have been devoted to the synthesis of B-C-N nanotubes (BCNNTs) such as arc-discharge [7], laser ablation [8], pyrolysis [9], chemical vapor deposition (CVD) [4,10–12] and substitution reaction [13]. Meanwhile, triggered by the discovery of graphene, two-dimensional (2D) B-C-N nanosheets (BCNNSs) and nanoflakes have also become a hot research area [14–16]. However, toxic precursors such as B_2H_2, B_2H_6, BCl_3, BF_3 and BH_3–trimethylamine were usually employed, and B-C-N products often encountered the phase-separation of BN and C. In addition, BN micro-nano composite structures were reported to exhibit appealing properties and have potential applications in lasing, field-emission displays, composite materials and nanodevices [17–19]. As an analog of BN, B-C-N micro-nano composite structures are believed to have similar or even better properties. However, B-C-N micro-nano structures have not been reported so far.

Herein, we report a novel route to the synthesis of $BC_{1.61}N_{0.76}$ micro-nano structures called nanosheet-decorated submicrowires, by annealing simple raw materials of amorphous boron (B) powder, natural rubber latex (NRL) and ferric chloride ($FeCl_3$) in NH_3 flow. The NRL is produced in Hainan province locally, which is low-cost and has good operability. The main component is shown in Table S1. The $BC_{1.61}N_{0.76}$ micro-nano structures have a relatively uniform distribution of B, C and N elements. The photoluminescence (PL) property and growth mechanism are also investigated.

2. Experimental

B powders and $FeCl_3{\cdot}6H_2O$ with a weight ratio of 1:1.35 were dissolved in absolute ethyl alcohol. Different contents of NRL were then added under stirring (the weight ratios of B: NRL = 1: 50, 25, 12.5). After dried naturally, solidified gels were obtained with different contents of NRL. About 1.5 g gel was loaded into an alumina boat which was heated in a tube furnace to 1200 °C under 50 mL·min^{-1} NH_3 flow and maintained for 3 h. The boat was covered with a commercial stainless steel (3 0 4) foil for trapping the intermediate gases. After runs, white-gray products were obtained in the boats and characterized. The experimental details and relevant characterization can be found in Electronic Supplementary Information.

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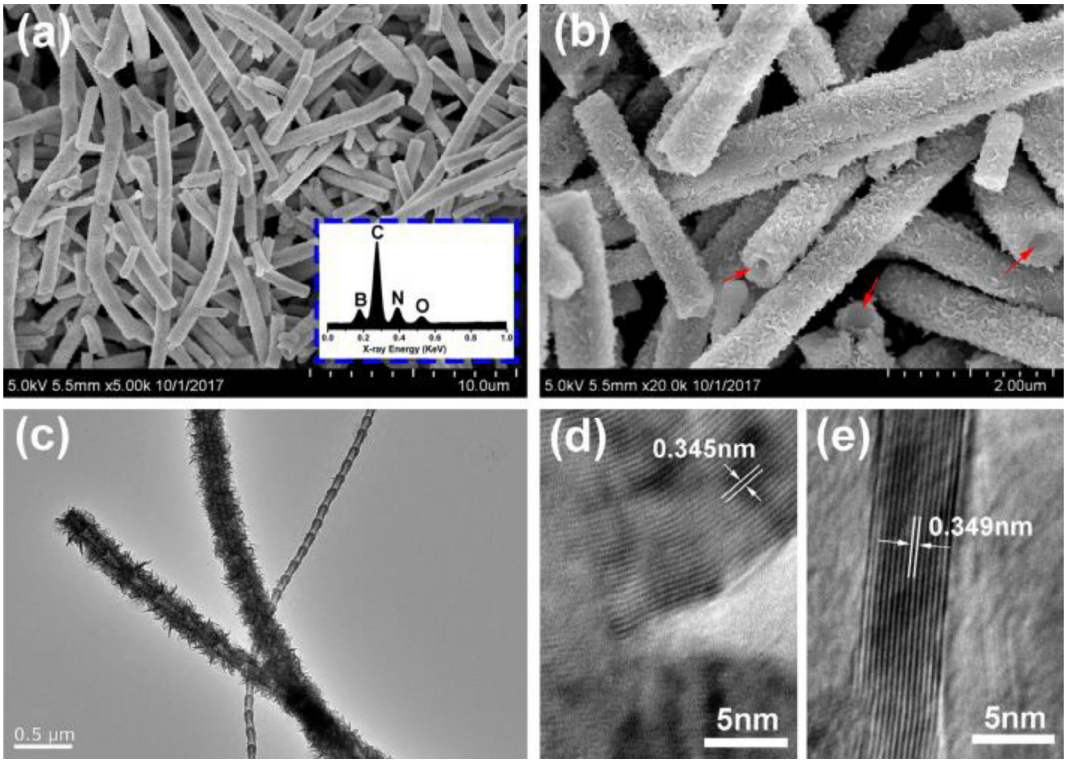

Fig. 1. (a) and (b) SEM images of the B-C-N micro-nano structures synthesized at B:NRL = 1:50. (c) The corresponding TEM image. (d) HRTEM image of the joint between the compartment and walls of a bamboo-like nanotube. (e) HRTEM image of a nanosheet.

3. Results and discussion

Fig. 1a shows the SEM image of the product synthesized at B: NRL = 1: 50, revealing that the product consists of one-dimensional (1D) structures with length of several to tens microns. No particles can be found in the product. The enlarged SEM image (Fig. 1b) reveals that these 1D structures have a micro-nano composite structure, namely nanosheet-decorated submicrowires. The diameters of the submicrowires are 200–500 nm and the thicknesses of the nanosheets are estimated to be less than 20 nm. The micro-nano structures have a hollow core (indicated by arrows), hinting the growth of nanosheets on the bamboo-like nanotube, which will be discussed later in this study. The inset EDS result in Fig. 1a indicates the dominating composition of B, C, N with a small amount of O of the product. O signal should be attributed to the slight surface oxidation or oxygen adsorption of the micro-nano composite structure. Elemental mapping images successfully identify the presence of Fe catalyst in addition to the B, C, N and O elements in these micro-nano structures (Fig. S1), revealing the vapor-liquid-solid (VLS) growth mechanism that will be discussed later. With the decrease of NRL content, the amounts of nanosheet tend to reduce and even disappear when B:NRL = 1: 12.5, and the diameters become more and more uneven (Fig. S2). TEM characterization (Fig. 1c) further confirms that these micro-nano structures synthesized at B:NRL = 1:50 have a bamboo-like nanotube core and nanosheets are grown from the nanotubes. The nanosheets are bending and scrolling with taped edge morphology. From the high-resolution TEM (HRTEM) images of the joint between the compartment and walls of a bamboo-like nanotube (Fig. 1d) and a nanosheet (Fig. 1e), highly ordered lattice fringes can be observed. The interlayer spacings of the nanotube wall and nanosheet are about 0.345 nm and 0.349 nm, respectively, corresponding to the (0 0 2) planes of *h*-BCN (JCPDS No. 35-1292).

XPS spectra of the micro-nano structures are shown in Fig. 2. The survey scan reveals the presence of B, N, C and O elements (Fig. 2a), which is in agreement with EDS result. The B 1 s spectra can be divided into three components (Fig. 2b), and the peaks at 189.9 eV, 190.5 eV and 191.4 eV are corresponded to B-C, B-N and B-O bonds [10,19,20], respectively. Fig. 2c shows the C 1 s spectra with four fitted peaks at 284.03 eV, 284.8 eV, 286.2 eV and 288.9 eV, which can be assigned to C-B, C-C, C-N and C-O bonds, respectively. The N 1 s spectra depicted in Fig. 2d can be deconvoluted into two peaks locating at 397.8 eV and 398.6 eV, which are related to N-B and N-C bonds, respectively. Fig. 2e shows the O 1 s signals that can be divided into two peaks at 533.2 eV and 531.7 eV, which may correspond to O-C and O-B bonds, respectively [21]. The relative quantification analysis offers a B: C: N atomic ratio of 1: 1.61: 0.76. Therefore, from EDS, HRTEM and XPS results, it can be concluded that the synthesized B-C-N micro-nano structures have a composition of $BC_{1.61}N_{0.76}$. Fig. 3 shows the room-temperature PL property of the $BC_{1.61}N_{0.76}$ micro-nano structures. Two visible-light emission bands are observed. The emission band at 501.2 nm is related to the carbon and oxygen impurity [21], while the strong emission band at 592.6 nm is ascribed to the carbon-rich composition nature of the $BC_{1.61}N_{0.76}$ micro-nano structures, which is similar to that of BC_2N compound [22].

Based on the results described above, the formation process of $BC_{1.61}N_{0.76}$ micro-nano structures can be depicted as follows, which is very similar to that of the BN micro-nano structure [19]. At first, $FeCl_3$ reacts with B powder to generate BCl_3 vapor and Fe droplets at experimental temperature (e.g. 1200 °C). NRL is also pyrolyzed to generate carbon species. B, C and N