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Cathodoluminescence of boron nitride nanotubes doped by ytterbium

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ABSTRACT

Boron nitride nanotubes (BNNTs) are wide band gap semiconducting material with super thermal and chemical stabilities, which make them an ideal nano-sized host for luminescent ions. In this work, we report an *in situ* synthesis of Ytterbium (Yb) doped BNNTs using a ball milling and annealing approach. Yb doped BNNTs show more red-light emissions in the cathodoluminescent (CL) spectrum in comparison with pure BNNTs. The light emission is due to the insertion of Yb ions into the nanotube wall as the BNNTs serve as a host and contribute directly to the light emission. The cathodoluminescent image demonstrates strong cathodoluminescent emission of whole Yb doped BNNTs.

1. Introduction

Boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) are isostructural with similar mechanical properties [1]. BNNTs have attracted extensive attention because of their special properties such as a stable band gap [2], which determines their optical behaviors. Cathodoluminescent spectroscopy analysis of the single-crystal hexagonal boron nitride (*h*-BN) suggested that *h*-BN had a direct-band gap of 5.76 eV [3], as the conduction band minimum and valence band maximum lay at roughly the same momentum. For BNNTs, theoretical calculation predicted a band gap of 5.5 eV [2] which is independent of the tube chirality and size [4]. However, recent photoluminescent excitation analysis determined a band gap of 5.75 eV for multi-walled BNNTs with a diameter of approximately 100 nm [5] and the band gap becomes smaller when the tube diameter is below 2 nm [6]. Therefore, more experimental investigation should be conducted on controlling band gaps and related optical behaviors. Rare-earth elemental doping is an effective way to adjust light emissions between bands. The cathodoluminescent emission of BNNTs is located in the near ultraviolet (UV) light range. In order to tune the light emission of BNNTs from near UV to visible (Vis) light range, an *in situ* doping process was successfully developed to incorporate different amounts of Eu^{2+} ions into BNNTs' walls during their growth [7]. This work attempts to explore doping Yb into BNNTs and compares the differences in emission spectra between Eu^{2+} and Yb^{2+} ions doped BNNTs.

2. Experimental

The starting materials were amorphous boron powders mixed with 1.0 at% nominal Yb powder. The mixture was milled in a planetary ball mill (Pulverisette 5) within a stainless steel chamber and with several steel balls. The milling was conducted at a rotation speed of 300 rpm for 50 h in NH_3 atmosphere (300 kPa). In this process, a small amount of metal iron and a trace of chromium (from both the milling balls and chamber) were mixed into the milled B and Yb powders, and they actually acted as catalysts helping nanotube growth during the subsequent annealing. The milled sample was loaded into an alumina crucible which was placed into a tube furnace for an annealing treatment to activate nanotube growth [8]. The annealing process was carried out at 1050 °C under a N_2-5%H_2 atmosphere for 2 h. An reducing atmosphere is necessary in order to stabilize the divalent state of the Yb.

Scanning electron microscopy (SEM, Hitachi 4500) was applied to characterize the nanotube morphology. Transmission electron microscopy (TEM, Philips CM300) was employed to examine individual nanotube structure. X-ray energy dispersive spectrometer (EDS) attached to SEM/TEM was used to determine sample chemical contents. Cathodoluminescent (CL) properties were studied using a fibre optic spectrometer (SD2000, Ocean Optics, Inc.) attached to a SEM (Hitachi S2250-N) at room temperature.

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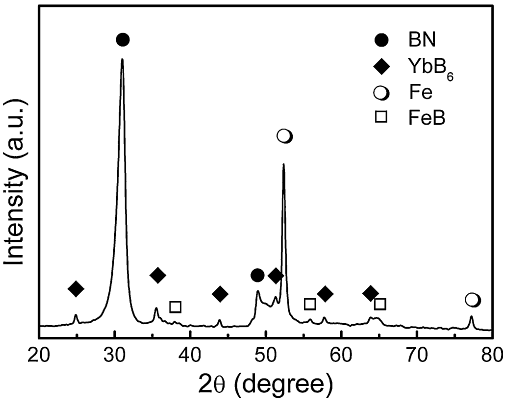

Fig. 1. XRD pattern of ball milled boron sample with the 1.0 at% nominal ytterbium after heating at 1050 °C under N_2-5%H_2 atmosphere for 2 h.

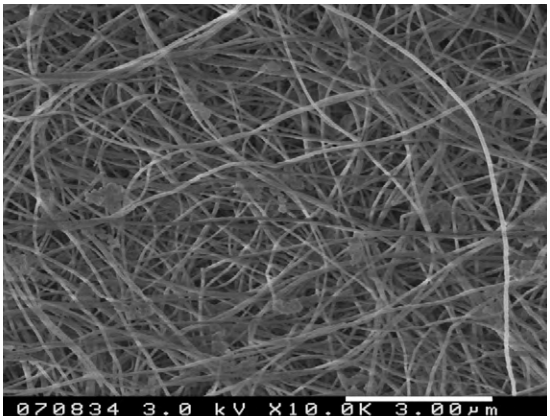

Fig. 2. SEM image of as-synthesized Yb doped BNNTs, scale bar 3.0 μm.

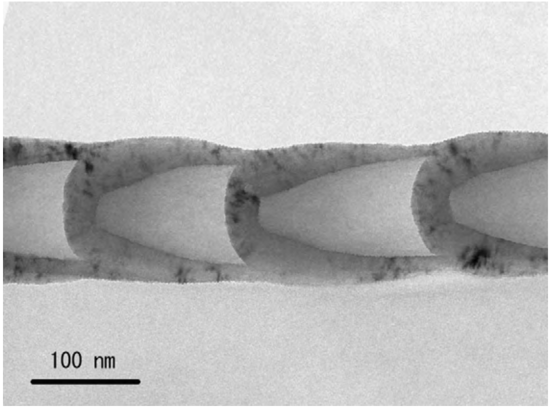

Fig. 3. TEM image displaying a bamboo-like structure of an Yb doped BNNT.

3. Results and discussion

Fig. 1 shows the XRD pattern of the BNNTs synthesized at 1050 °C, which suggests that the sample consists of *h*-BN, Fe, FeB, and YbB_6 phases. The diffraction peak of the (0 0 2) basal planes is relatively broad, indicating the existence of BNNTs or nano-sized BN. Fe can react with B to form FeB phase during the annealing, which may contribute to the formation of bamboo-like BNNTs as reported by Huo [9]. The role of the YbB_6 in the formation of Yb doped BNNTs is just like the EuB_6 in enhancing the formation of Eu doped BNNTs as described in Ref. [7]. The high diffraction intensity of the YbB_6 phase arises from a relatively high atomic scattering factor of Yb atoms in comparison with other elements.

SEM image in Fig. 2 shows the as-synthesized BNNTs with a very high formation yield. Their diameters are from 60 to 180 nm. These tubes have a bamboo-like structure as shown on a typical TEM image in Fig. 3. The B and N ratio is close to 1:1. The average content of the Yb in BNNTs is about 0.2 at% determined by EDS analysis. As the ionic radii of Yb^{2+} ions is less than Eu^{2+} ions which are uniformly distributed within the BNNTs' walls [7], it is rational to deduce that Yb^{2+} ions are also incorporated between the tube walls.

Fig. 4a and b display the SEM and CL images of the Yb doped BNNTs dispersed onto a silicon substrate, respectively. In contrast to the SEM image, the contrast of Yb doped BNNTs is enhanced in CL image, indicating the strong luminescent effect of the Yb doping. In order to find out where the luminescence comes from, the CL spectrum of Yb doped BNNTs was collected and shown in Fig. 5. For pure BNNTs without doping, a strong broad emission peak centred at around 372 nm with two shoulders (~485 and 572 nm) is observed suggesting three broad light emissions. Shoulders have the relative emission intensity of 39% and 23% in comparison with the intensity of the main peak at 372 nm. In contrast, the relative intensities of two shoulder emissions peaked around 487 and 573 nm from Yb doped BNNTs are 56% and 41% to the main peak at around 377 nm. According to the previous light emission spectra of the Yb^{2+} doped $YAlO_3$ [10], a superposition emission in this materials consisted of two strong and broad band emissions (480 and 570 nm) assigned to Yb^{2+} ions. The emission peaks observed in Yb doped BNNTs are very close to these peaks. Such emissions are ascribed to the transitions between $4f^{14}$ and $4f^{13}5d$ configurations of divalent Yb^{2+} ions where the electron in the $4f^{14}$ ground state is excited to the $4f^{13}5d$

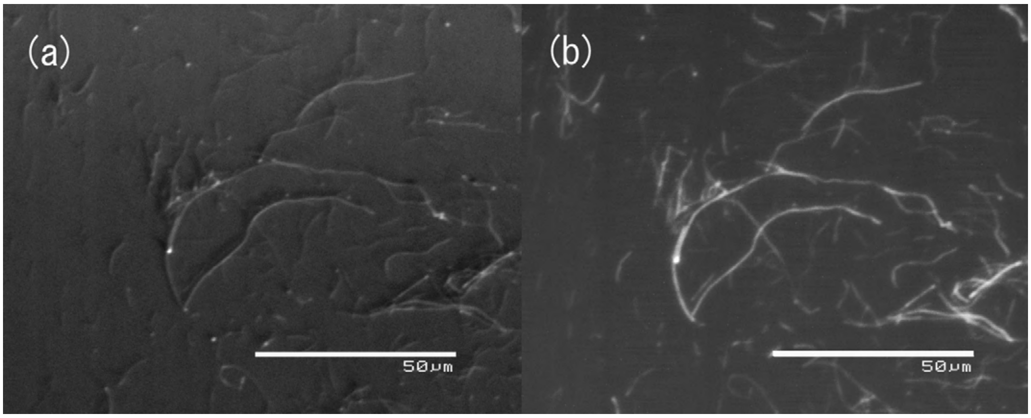

Fig. 4. (a) SEM image of the Yb doped BNNTs; (b) CL image of the same sample, scale bar 50 μm.

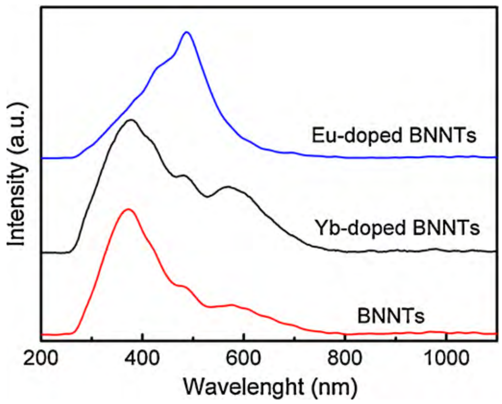

Fig. 5. CL spectra of intrinsic BNNTs and Yb doped BNNTs.

band, which is partially located in the conduction band. The excited electron has a relaxation within the 5d manifold and then leads to the emission occurred at 573 nm. The enhanced peak at 487 nm is assigned to the Yb^{2+} as well. This is because the result is consistent with the previous work in Yb^{2+} doped SiAlON [11] and $YAlO_3$ [10] where it is ascribed to autoionization by which the excited electrons delocalize into the conduction band, recombine with the Yb ground state and thus create the emission of luminescence in this wavelength range. The emission energy strongly depends on sample synthesis condition [11], materials, and measuring temperature. In comparison with the Eu^{2+} doped BNNTs, the light emission of Yb^{2+} doped BNNTs has very broad spectral feature and more red-light component. The latter will make the BNNT more suitable as a nano whitish light that can focus light beam into nano scale, and thus extremely increases the resolution of the light detection.

4. Conclusions

Yb doping improves the light emission from BNNTs. The average Yb content doped into BNNTs is 0.2 at%. CL imaging and spectrum of Yb doped BNNTs indicate a strong and broad light emission closer to the whitish light in comparison with the Eu doped BNNTs. The Yb doped BNNTs could be another choice for nano-sized visible light source.

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