Encapsulation mechanism of N$_2$ molecules into the central hollow of carbon nitride multiwalled nanofibers

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Abstract

Nitrogen molecules have been encapsulated into the central hollows of vertically aligned carbon nitride (CN) multiwalled nanofibers by dc plasma-enhanced chemical vapor deposition with C$_2$H$_2$, NH$_3$, and N$_2$ gases on a Ni/TiN/Si(100) substrate at 650 °C. X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectra showed the existence of nitrogen molecules in CN nanofibers. Elemental mapping images with electron energy loss spectroscopy of the CN nanofiber and catalyst metal, and optical emission spectroscopy spectra of the plasma showed the distribution of nitrogen atoms and molecules in the CN nanofiber, catalyst metal, and gaseous precursor, respectively. These studies showed that atomic nitrogen diffused into the catalytic metal particle because of the concentration gradient and then saturated at the bottom of the particle. Saturated nitrogen atom participated in the formation of the CN nanofiber wall but most of nitrogen was trapped in the central hollow of the nanofiber as molecules.

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1. Introduction

Ever since the discovery of carbon nanotubes (CNTs), scientists have been investigating the specific properties of CNTs [1–5] and the possible roles CNTs might play in various kinds of nanotechnologies and molecular electronics [6,7]. In particular, many researchers have investigated the possibility of CNTs being used as energy storage devices such as in hydrogen fuel cells by taking advantage of the high-surface-area of single-walled and multiwalled CNTs [8]. Almost all of their efforts were focused on the interaction between hydrogen and CNTs through physisorption or chemisorption.

Recent studies have revealed that Ar and N$_2$ molecules can also be stored in CNTs [9,10]. The experiments involving Ar introduced Ar gas into CNTs for 48 h at 650 °C under an Ar pressure of 170 MPa. However for those involving N$_2$ storage, nitrogen molecules were trapped directly in the hollow core of the CNTs during the growth procedure. These observations may provide the way for the fabrication of gas storage components using CNTs. However, the encapsulation mechanism of gaseous molecules is, as yet, unclear.

Here, we report an alternative method for storing nitrogen molecules in carbon nitride (CN) multiwalled nanofibers...
(CN-MWNFs) with central hollow using dc plasma-enhanced chemical vapor deposition (PECVD) methods during the growth with a Ni catalytic material and gas mixture of acetylene, ammonia and nitrogen. In addition, we propose the encapsulation mechanism of nitrogen molecules based on the results obtained from the near-edge X-ray absorption fine structure (NEXAFS) and the mapping of the elements using transmission electron microscope (TEM).

2. Experimental

CN-MWNFs with a central hollow were grown using a dc PECVD technique on a 100 nm thick Ni film which was used as a catalytic layer on the base TiN/Si(100) substrate. In order to enhance the adhesion of the catalytic layer, a layer of TiN at a thickness of 100 nm was deposited on the Si(100) substrate. The substrate was loaded into the dc PECVD system which was evacuated to a pressure of \(1 \times 10^{-3}\) Torr. A gas mixture of \(\text{C}_2\text{H}_2\) (10 sccm), \(\text{NH}_3\) (40 sccm), and \(\text{N}_2\) (60 sccm) was used as precursor. The working pressure was 5 Torr. The substrate was heated to 650 \(\text{C}\) using a tungsten filament and the temperature was monitored using a thermocouple. The growth of CN-MWNFs was carried out for 15 min. The structure of the CN-MWNFs and the distribution of the elements in the CN-MWNFs were measured by scanning electron microscope (SEM) (JEOL, JSM6700F) and TEM (JEOL, JEM2100F)/electron energy loss spectrometer (EELS) (Gatan Image Filter 2001). The electronic structure of the CN-MWNFs was analyzed from NEXAFS and X-ray photoelectron spectroscopy (XPS) (VSW 125) data taken at 8A1 beamline of Pohang Accelerator Laboratory. The NEXAFS at \(\text{N} 1s\) absorption edge was measured with an energy resolution of approximately 80 meV. The composition of the plasma in the dc PECVD chamber was monitored by optical emission spectrometer (OES) (SC Technology, PCM402).

3. Results and discussion

Fig. 1(a) shows a typical SEM image of an array of vertically aligned CN-MWNF with an average diameter of 50 nm and length of 10 \(\mu\text{m}\). As can be seen from the TEM images in Fig. 1(b) and (c), the CN-MWNF has a stacked cone arrangement with small angle between the graphite basal planes and the tube axis [11] and a compartmented central hollow, which is similar to that observed in \(\text{CN}_x\) nanotube [12] with Ni catalysts at the tip of the tube.

Fig. 2(a) shows wide scan XPS spectra of as-grown CN-MWNFs and annealed CN-MWNFs at 900 \(\text{C}\). N 1s peaks at 399 eV and 401 eV, a C 1s peak at 284.5 eV and an O 1s peak at 528 eV were observed. The peak at 399 eV reveals the presence of pyridinic nitrogen, while the peak at 401 eV comes from the trivalent nitrogen replacing the carbon in the hexagonal structure [13]. The XPS spectra clearly show that the CN-MWNFs contain nitrogen at temperatures up to 900 \(\text{C}\).

Fig. 2(b) shows NEXAFS spectra at the N 1s absorption edge of the CN-MWNFs taken at several elevated temperatures. Here, N 1s \(\to \pi^*\) excitation peaks marked with arrows a, b and c are at 399.1, 399.8, and 401.1 eV, respectively and the N 1s \(\to \sigma^*\) excitation peak, labeled d, is at 407.1 eV. These peak positions and shapes are close to those of \(\text{CN}_x\) thin films [14] except peak c. As seen in the NEXAFS spectrum, it is noticeable that peak c consists of several peaks, which was not visible on the \(\text{CN}_x\) thin film spectra, and very similar to the N 1s \(\to \pi^*\) excitation peaks of molecular \(\text{N}_2\) in both photon energy and profile. This strongly suggests that molecular nitrogen is present within the CN-MWNFs [15]. These peaks did not change, even after being annealed at temperatures up to 530 \(\text{C}\). If the nitrogen molecules were adsorbed on the surface of the CN-MWNFs, annealing at high temperatures such as 530 \(\text{C}\) would desorb the molecules from the surface [16].

For a more detailed investigation of the profile of peak c, highly resolved spectra were acquired with high-energy resolution as shown in Fig. 2(c). Peak c appears to consist of more than six peaks and did not change in either intensity or shape with annealing at temperatures up to 530 \(\text{C}\) as mentioned earlier. After annealing at 900 \(\text{C}\), the intensity of peak c decreased and broadened out, because of a reaction between the nanofiber wall and molecular nitrogen at such high temperatures.
The as-grown spectrum showed a good fit to the eight components (dotted curves) at 400.9, 401.1, 401.3, 401.5, 401.8, 402.0, 402.2 and 402.6 eV using Gaussian functions, asymmetric Gaussian function and an error function. For N\textsubscript{2} gas, eight peaks appeared corresponding to the eight vibration levels of N\textsubscript{2} gas in N\textsubscript{1s} \rightarrow \pi^* absorption [15].

A specific difference between spectra from gas and the CN-MWNFs is that all peaks of CN-MWNFs are broader and the intensity of the second peak is relatively stronger than that of the gas. It appears that these phenomena are attributed to the existence of small quantities of nitrogen bonded to carbon within the CN-MWNFs. These analyzed results reveal clearly that free nitrogen molecules exist in the CN-MWNFs.

The distribution of nitrogen in the CN-MWNFs was examined by mapping the elements using TEM with a Gatan image filter (GIF). Fig. 3(a)–(d) shows the zero-loss, carbon-mapping and nitrogen-mapping images, and a line profile, taken from the CN-MWNFs. These analyzed results reveal clearly that free nitrogen molecules exist in the CN-MWNFs.

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In order to investigate the mechanism for the encapsulation of the N\textsubscript{2} molecules, the carbon and nitrogen distributions in the Ni catalyst tip were measured using GIF analysis. Fig. 3(e)–(h) shows zero-loss, nickel-mapping, carbon-mapping, and nitrogen-mapping images of the Ni catalyst tip. In Fig. 3(e), the zero-loss image of the Ni tip indicates that the nanofiber showed tip-growth (or top-growth). Fig. 3(f) shows the nickel-mapping image has many areas where the contrast is non-uniform. This indicates that the shape of the Ni particles inside the tip is not symmetric or uniform. The carbon- and nitrogen-mapping images in Fig. 3(g) and (h) shows clearly that carbon and nitrogen are distributed over both the surface and inside of the Ni tip. It seems that the contrast visible in the images is related to the shape of the Ni particles in both cases. These results strongly suggest that carbon and nitrogen diffused into the inside via top surface of Ni and then became segregated during the growth.

According to previous reports, there are three primary supply routes for the carbon source required for the growth of the CNT: surface diffusion [17], bulk diffusion [18], and a combination of both [19]. The catalyst particle melted at
relatively low temperatures due to the effects of the plasma in the CVD process [20] and the effect of the nanoparticle size [21,22]. Thus, carbon diffusion into the melted Ni was enhanced. However, in this experiment, it was also observed that nitrogen, as well as carbon, initially diffused into the bulk Ni during the growth phase. This strongly suggests that the carbon became saturated at the bottom of the Ni tip and formed a wall in the CN-MWNF and that the nitrogen also diffused to the bottom of the catalyst tip through the bulk, became saturated and then trapped in the CN-MWNF in molecule form. However, some of the nitrogen atoms bonded with the carbon atoms and formed a wall in the CN-MWNF.

During nitrogen diffusion into the catalyst tip, nitrogen must be in the atomic phase than the molecular phase. To investigate the source of the atomic nitrogen, the constituents of the plasma in the chamber were measured using OES, as shown in Fig. 4 and analyzed. Fig. 4(b) shows primarily CN radicals present in the plasmas created with C₂H₂ and NH₃. When N₂ gas was then introduced additionally into the chamber, the following various constituents were observed in the plasmas as shown in Fig. 4(a): CN, N₂, N₂⁺, and NH, all of which, are potential sources of atomic nitrogen. It was reported that CN dissociates to form atomic carbon and nitrogen by annealing about 580 °C [16]. Therefore, it appears that from among these components, CN radicals are the most important source of atomic nitrogen during the growth of CN-MWNFs [23]. We confirmed that CN-MWNFs grown with C₂H₂ and NH₃ precursors contained nitrogen molecules in the hollow and the amount of encapsulated nitrogen molecules increased as further nitrogen molecules were added (not shown in here).

Analyzing the results of the elemental mapping of the tip of the nanofiber and the results of the OES analysis, the mechanism of encapsulation of nitrogen in nanofibers was deduced as follows: (1) Precursors dissociated into various radicals including the CN radicals in the plasma. (2) CN radicals became embedded on the top surface of the melted catalyst tip. (3) CN radicals dissociated into atomic carbon and nitrogen, and then diffused into the melted tip. (4) Carbon and nitrogen atoms diffused through to the bottom of the tip via concentration gradient mechanisms and became saturated at the bottom. (5) Saturated carbon and nitrogen atoms participated in the formation of the CN-MWNF wall and a lot of released nitrogen atoms formed molecular nitrogen which then became trapped in the hollow of the CN-MWNF. Fig. 5 shows the suggested schematic of the nitrogen-encapsulation-mechanism during the growth of CN-MWNFs.
Fig. 5. Schematic of the mechanism of nitrogen encapsulation and growth of CN-MWFNs.

4. Conclusion

We have investigated the growth mechanism of CN-MWFNs incorporating nitrogen and the mechanism for the encapsulation of the nitrogen molecules inside the hollow of the CN-MWFNs by using TEM/GIF, NEXAFS, SEM, OES and XPS. Through analysis of these experimental results, it was found that CN radicals in the plasma became embedded on the top surface of the melted Ni catalyst tip and dissociated into atomic phases of C and N, following which the atomic C and N then diffused into the tip. This diffusion mechanism plays a key role in the formation of CN-MWFN walls incorporating nitrogen and in the encapsulation of nitrogen molecules in the hollow of the nanofiber. To the best of our knowledge, the confinement mechanism of nitrogen molecules in the hollow of CN-MWFN has been demonstrated. It is hoped that this research will be able to supply significant information for the growth mechanism of CN$_x$ nanofibers and the encapsulation mechanism of gas molecules in nanofibers.

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