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Turning refuse plastic into multi-walled carbon nanotube forest

Eugene Oh¹, Jaegeun Lee¹, Seung-Ho Jung², Seungho Cho¹,
Hye-Jin Kim¹, Sung-Hyun Lee¹, Kun-Hong Lee^{1,3}, Kyong-Hwa Song⁴,
Chi-Hoon Choi⁴ and Do Suck Han⁴

¹ Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

² Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA

³ National Center for Nanomaterials Technology (NCNT), Pohang 790-784, Korea

⁴ Central Advanced Research and Engineering Institute, Hyundai Motor Company, Uiwang 437-718, Korea

E-mail: ce20047@postech.ac.kr

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Abstract

A novel and effective method was devised for synthesizing a vertically aligned carbon nanotube (CNT) forest on a substrate using waste plastic obtained from commercially available water bottles. The advantages of the proposed method are the speed of processing and the use of waste as a raw material. A mechanism for the CNT growth was also proposed. The growth rate of the CNT forest was $\sim 2.5 \mu\text{m min}^{-1}$. Transmission electron microscopy images indicated that the outer diameters of the CNTs were 20–30 nm on average. The intensity ratio of the G and D Raman bands was 1.27 for the vertically aligned CNT forest. The Raman spectrum showed that the wall graphitization of the CNTs, synthesized via the proposed method was slightly higher than that of commercially available multi-walled carbon nanotubes (MWCNTs). We expect that the proposed method can be easily adapted to the disposal of other refuse materials and applied to MWCNT production industries.

Keywords: carbon nanotubes, microwave, refuse plastics, recycle

1. Introduction

Plastics are widely used in a variety of fields including food, automotive, medical instrument, environmental and communication technologies. As a result, the quantity of refuse plastics is increasing [1]. The enormous amount of refuse plastics worldwide is buried, incinerated, or dumped into the sea. The natural decomposition of buried refuse plastics occurs over 300–500 years, and the leachate resulting from this process leads to soil pollution [2, 3]. When incinerated, plastics emit toxic gases, such as SO_x , NO_x and dioxins, owing to incomplete combustion, leading to air pollution [3, 4]. Islands of rubbish plastics, called ‘plastic soup’, were recently discovered in the Pacific Ocean which resulted from years of dumping [5]. The amount of drifting ‘plastic soup’ is increasing every year. Therefore, there is

an urgent need for efficient and environmentally friendly methods for treating refuse plastics.

Carbon nanotube (CNT) is a promising material for use in a variety of fields including composites, electronics and molecular filters [6–10]. Existing carbon sources used for CNT synthesis include gaseous acetylene, ethylene, carbon monoxide, methane [11–14], liquid ethanol and xylene [15, 16]. However, a means of synthesizing vertically aligned CNT forests on substrates using solid carbon sources has remained a challenge until now. In a previous report [17], CNT growth was achieved using polyethylene-based used plastics, but the CNTs were not aligned and the reaction time was rather long (2 h).

In this study, we report a novel and eco-friendly method for fabricating vertically aligned CNTs in a very short time (2 min) using polyethylene terephthalate (PET).

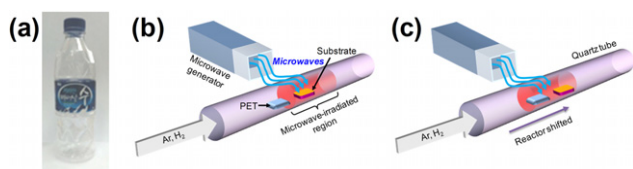


Figure 1. (a) Photograph of a commercially available mineral water bottle used in this work. (b) The substrate was positioned in the microwave-irradiated region of the reactor during plasma generation, leading to the reduction of the catalyst layer. (c) The reactor was shifted to allow continuous decomposition of the PET and growth of the CNT forest on the substrate.

2. Experimental details

A thin layer of Al_2O_3 (10 nm) was deposited on a Si wafer by atomic layer deposition followed by e-beam evaporation of a 1-nm-thick Fe layer. The coated Si wafer was cut into a 1 cm^2 square and placed in a quartz tube with a piece of PET (0.2 g) cut from a commercially available PET bottle (Ppae-eo-nal Su, Haitai Beverage Co., Ltd, figure 1(a)). The diameter and length of the quartz-tube reactor were 2.5 and 30 cm, respectively.

The reactor was evacuated to 1.0 Torr under an argon flow of 500 sccm, and plasma formed inside the reactor upon microwave irradiation. During the plasma formation, the temperature of the substrate was about 700°C , as measured by a dual-laser IR thermometer (Extech Instruments). The microwave power was set to 1000 W. The Si substrate coated with a catalyst layer was positioned in the microwave-irradiated region, and the catalyst was reduced upon exposure to 500 sccm hydrogen flow, as shown in figure 1(b). After the reduction, the reaction proceeded for 2 min, during which time the quartz-tube reactor was shifted so that both the PET piece and the substrate were located in the microwave-irradiated region together as shown in figure 1(c). After the reaction, the microwave power was turned off and the sample was cooled to room temperature.

The morphology of the vertically aligned CNT forest was observed using a field-emission scanning electron microscope (FE-SEM, JEOL JMS-7400F) and a scanning transmission electron microscope (STEM, JEOL JEM-2200FS) equipped with an energy-dispersive x-ray spectrometer (EDS). Raman spectra were excited with the 514.5 nm line of an Ar-ion laser and recorded with a Jobin-Yvon LabRam HR spectrometer.

3. Results and discussion

Figure 2(a) shows a typical FE-SEM image of an as-grown CNT forest grown on a Si wafer using the microwave irradiation system reported earlier [18, 19], and figure 2(b) shows a magnification of the region marked by the square in figure 2(a). The images clearly show that the height of the vertically aligned CNT forest was about $5\ \mu\text{m}$, and the CNTs were uniformly synthesized on the Si wafer. The growth rate of the CNT forest was $2.5\ \mu\text{m min}^{-1}$.

We determined the optimum Ar/ H_2 flow rate by monitoring the heights of the CNTs on the substrate. The Ar

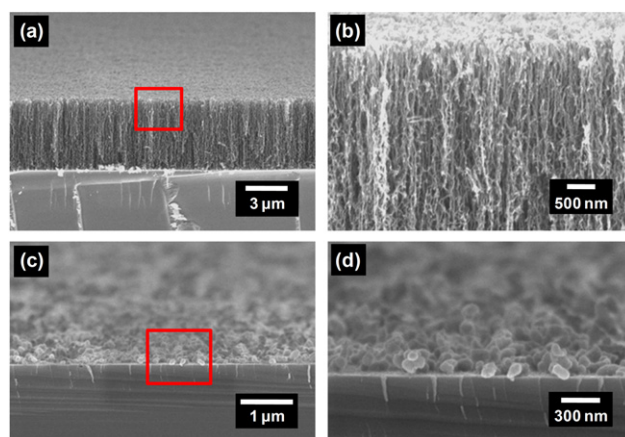


Figure 2. (a) Low-magnification FE-SEM image of CNT forest grown on Si substrate using PET. (b) Enlarged FE-SEM image of the CNTs in the region marked by the square in (a). (c) Control experiment: identical synthesis without the reduction of the catalyst. (d) Enlarged image taken from the region marked by the square in (c).

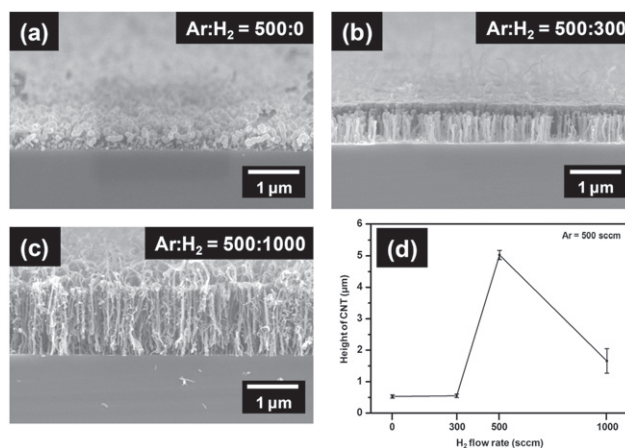


Figure 3. FE-SEM images of CNT forest grown when the Ar flow rate was fixed at 500 sccm and the H_2 flow rate was (a) 0, (b) 300 and (c) 1000 sccm. (d) H_2 flow rate versus height of CNTs.

flow rate was fixed at 500 sccm and the H_2 flow rate was varied from 0 to 1000 sccm. The greatest height of about $5\ \mu\text{m}$ was achieved at a ratio of Ar : $\text{H}_2 = 1 : 1$ as shown in figures 2(a) and 3(d). A relatively low partial pressure of H_2 (0 or 300 sccm) led to the generation of a large number of carbon sources, causing the rapid deactivation of the catalyst used for CNT growth (figures 3(a) and (b)). In contrary, a high partial pressure of H_2 (1000 sccm) brought the formation of a small amount of carbon compounds, reducing the CNT growth rate to $\sim 700\ \text{nm min}^{-1}$ as shown in figure 3(c).

When the microwave irradiation was turned on, an electric field formed in the reactor and Ar atoms became electrically polarized by the electric field. Since the microwave power was sufficient to generate electrical breakdown, avalanching ionization occurred by chains of collisions between the electrons and the gaseous atoms to generate plasma (figure 4(a)) [20]. When the microwaves directly irradiated the Fe thin-film coated substrate, eddy currents were generated on the surface of the Fe thin film

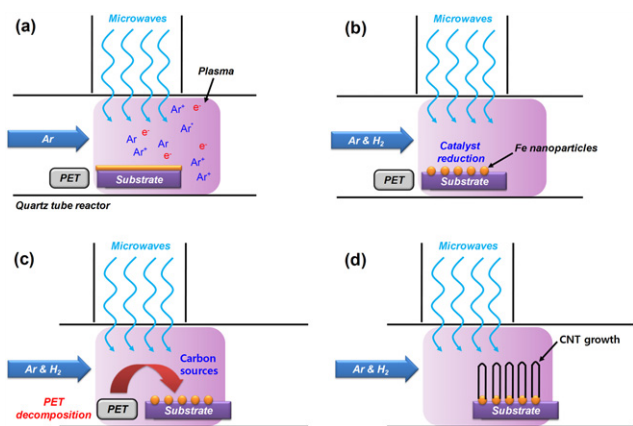


Figure 4. Proposed growth mechanism of CNT forest synthesized using PET. (a) Plasma formed in the quartz-tube reactor within the microwave-irradiated region. (b) The catalyst thin film was converted to Fe nanoparticles, which were then reduced by H₂ gas. (c) The reactor was shifted and the PET piece decomposed in the plasma region. (d) The growth of the CNT forest was induced by the carbon sources originating from the decomposed PET.

[19, 21]. The Fe thin film was subsequently selectively heated while receiving plasma energy. The Fe thin film was finally transformed into Fe nanoparticles, which acted as a catalyst (figure 4(b)). Hydrogen gas was then flowed into the reactor to ensure the complete reduction of the Fe nanoparticles.

Control experiments were carried out to determine whether the reduction of the catalyst was essential for producing CNT forests. When samples were grown without the reduction of the Fe nanoparticles, no CNTs grew on the substrates (figures 2(c) and (d)). From this result, we conclude that the reduction of the catalyst is essential for CNT growth.

After reducing the catalyst, both the PET and the substrate were positioned in the plasma region by shifting the reactor (figure 4(c)). Because PET does not absorb microwaves, the decomposition of the PET piece occurred as a result of the thermal energy of the plasma. According to a previous study, the thermal decomposition of PET produces various aromatic compounds, methane and C₂ hydrocarbons including acetaldehyde, ethylene and ethanol [22]. These carbon sources, especially the C₂ hydrocarbons, dissolved in the catalysts and, when supersaturated, they were extruded to form CNTs, as illustrated in figure 4(d).

Figure 5(a) shows a low-magnification STEM image of a vertically aligned CNT forest grown on a catalyst layer, and figure 5(b) shows a magnification of the area marked by the square in figure 5(a).

The CNTs had an average diameter of 20–30 nm. The upper parts of the inner tubes of some of the CNTs were filled with the catalyst metal, considered to be a result of the capillary force at the start of CNT growth [23]. EDS elemental maps for Fe and C were obtained to identify the composition of the CNT forest. Figure 5(c) shows a high-angle annular dark-field (HAADF) image, and figures 5(d) and (e) present EDS elemental maps of a section of the vertically aligned CNT forest. Although the C atoms are uniformly distributed in the CNT forest (figure 5(d)), the Fe atoms are concentrated at the base of the CNTs (figure 5(e)). Figure 5(f) shows an

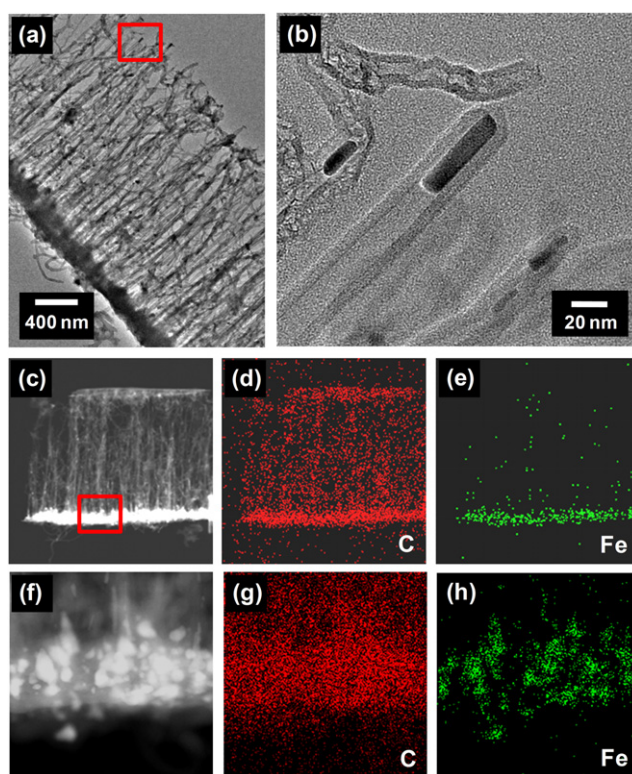


Figure 5. (a) Low-magnification STEM image of CNT forest, and (b) enlarged STEM image taken from the area marked by the square in (a). (c) High-angle annular dark-field (HAADF) image of the CNT forest. (d) and (e) EDS mapping images for C and Fe in the CNT forest, respectively. (f) HAADF image of the base of the CNT forest, taken from the area marked by the square in (c). (g) and (h) EDS mapping images for C and Fe at the base of the CNT forest, respectively.

enlarged HAADF image of the base of the CNT forest, taken from the area marked by the square in figure 5(c). Also, C and Fe EDS elemental mapping images taken from the base layer of the CNT forest are shown in figures 5(g) and (h), respectively. The Fe particles that facilitated the growth of the CNT forest are clearly seen in figures 5(f) and (h). These results suggest that the CNT forest grew by a bottom-growth mechanism.

Figure 6 shows the Raman spectrum of the as-synthesized CNT forest. The intensity ratio of the G and D bands was 1.27 for the vertically aligned CNT forest. The wall graphitization of the CNTs was slightly higher than that of commercially available multi-walled carbon nanotubes (MWCNTs), the G/D ratios of which range from 0.9 to 1.2 [24–26].

4. Conclusions

We have devised a method for growing CNT forests using PET. The advantages of this method are the speed of processing and the low cost of the raw materials. Raman scattering measurements showed that the wall graphitization of the synthesized MWCNTs was slightly higher than that of commercially available MWCNTs. We expect that the proposed method can be easily adapted to the disposal of

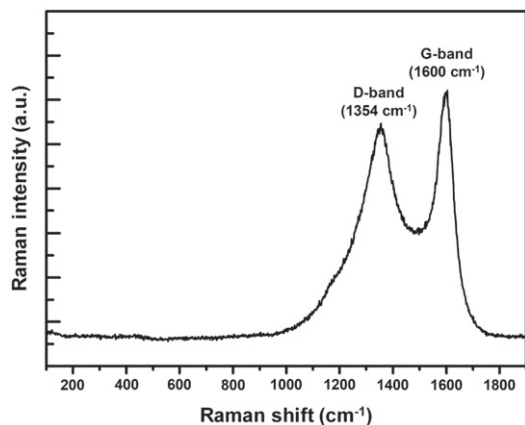


Figure 6. Raman spectrum of vertically aligned CNT forest.

other refuse materials and applied to MWCNT production industries.

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