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Synthesis of Double-Walled Carbon Nanotubes by High-Vacuum Chemical Vapor Deposition from Alcohol

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ABSTRACT

Double-walled carbon nanotubes (DWNTs) were synthesized by high-vacuum chemical vapor deposition (HVCVD) at 875-1000 °C using ethanol and ammonium iron (III) citrate as carbon source and metal catalyst, respectively. Synthesized DWNTs were purified by acid and thermal treatments to remove the metal catalyst and amorphous carbon. Transmission electron microscopy (TEM) and Raman spectroscopy were utilized for characterization of the structure, diameter, crystallinity and purity of DWNTs. By Raman spectroscopy analysis, we found that the optimized synthesis temperature for high quality DWNTs was 900 °C. After purification process, the purity of purified DWNTs was 2.1-fold higher than that of as-grown DWNTs. TEM images revealed the purified synthesized DWNTs at 900 °C with inner and outer diameters of 1.02±0.03 and 1.72±0.05 nm, respectively. These results imply that synthesis temperature and treatment process are key parameters that affect structure, crystallinity and purity of DWNTs.

INTRODUCTION

Carbon nanotubes (CNTs) [1,2] have attracted great attention due to their excellent structural, electronic, thermal and mechanical properties [3]. CNTs have been extensively studied for their potential applications in many fields of nanotechnology. To synthesize CNTs, chemical vapor deposition (CVD) has been considered as a promising method for mass production with controlled diameter, purity, quantity, and orientation. One of the key parameters for CVD method is synthesis temperature. According to previous studies, the synthesis temperature affects the diameter, crystallinity and purity of CNTs [4-7]. The most commonly used carbon source for synthesizing CNTs is hydrocarbon gas. The most obvious danger from hydrocarbon gases is their flammability. Recent studies have demonstrated a simple and safe technique for synthesis of high quality single-walled CNTs (SWNTs) [8-11] and double-walled CNTs (DWNTs) [12-14] using ethanol (C_2H_5OH) as the carbon source. However, there are few studies reporting on the effects of synthesis temperature on structure, crystallinity and purity of DWNTs.

In this work, the effect of synthesis temperature on the synthesis of DWNTs by high vacuum CVD (HVCVD) using alcohol was investigated. The morphology, structure and crystallinity of DWNTs synthesized at different temperatures were characterized.

METHODOLOGY

Synthesis of double-walled carbon nanotubes

DWNTs were synthesized by HVCVD using ethanol (Sigma-Aldrich, 99.9%) as the carbon source. Ammonium iron (III) citrate (Fluka) at the concentration of 3 wt% was mixed with magnesium oxide (MgO, Sigma-Aldrich) nanostructured powders in ethanol by sonication for 30 min. The mixed solution was stirred by Heating ThermoMixer (DITABIS, MHR 13, V 301A4) at the rotation speed of 3000 rounds per minute at 70 °C for 24 h in order to remove the ethanol and was subsequently ground to obtain a fine catalyst powder. The prepared catalyst powder was placed in an alumina (Al_2O_3) crucible and then placed horizontally in the HVCVD. The HVCVD system was evacuated with the turbo pump until a base pressure of

10^{-7} mbar was attained. The temperature was increased to 400 °C to eliminate the humidity in the catalysts until the base pressure was once again attained. The synthesis was carried out at 875-1000 °C. The catalysts were exposed to ethanol vapor, and a needle valve was employed to keep the pressure at ~1 mbar during synthesis for 60 min. Then, the system was cooled down.

The as-grown DWNTs were purified by a four-step process in order to remove the residual iron catalyst, supporting material and amorphous carbon. Firstly, as-grown DWNTs were soaked in 37% hydrochloric (HCl) acid for 12 h, then filtered and washed with distilled water until pH = 7. Secondly, the samples were annealed under air atmosphere at 400 °C for 30 min. Thirdly, the samples were soaked again in 37% of HCl acid for 12 h, then filtered and washed with distilled water until pH = 7. Finally, the samples were annealed under air atmosphere at 500 °C for 30 min.

Characterization techniques

The nanostructure of as-grown and purified DWNTs were characterized by transmission electron microscopy (TEM; JEOL, JEM-2100). Raman spectroscopy (Horiba JobinYvon, LabRAM HR800) was used to determine the purity and crystallinity of as-grown and purified DWNTs with 633 nm (1.96 eV) wavelength light from an Ar laser light source.

RESULTS AND DISCUSSION

Fig. 1 shows the Raman spectra of as-grown DWNTs synthesized at 875-1000 °C. All spectra show the four significant Raman peaks: DWNT-derived Raman breathing modes (RBM) at 237 and 262 cm^{-1}, disordered carbon-derived D-band at 1370 cm^{-1} and graphitic-structure-derived G-band at 1635 cm^{-1}. The peaks at 237 cm^{-1} and 262

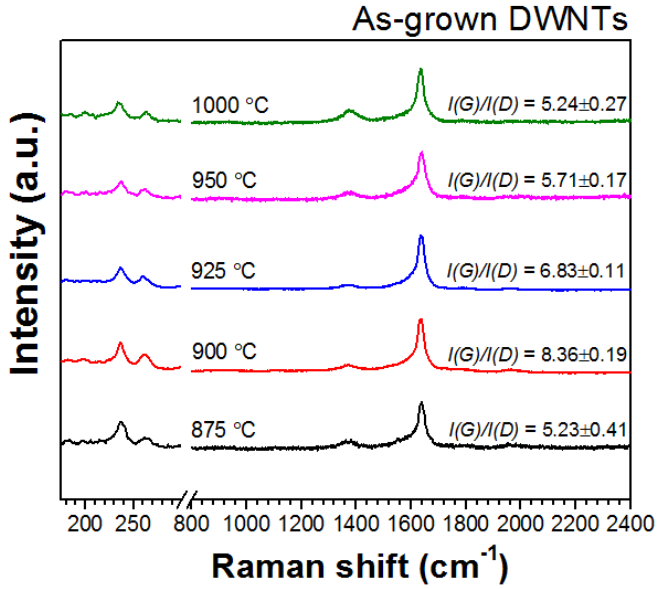

Figure 1 Raman spectra of as-grown DWNTs synthesized at 875-1000 °C

cm^{-1} correspond to the outer and inner tube, respectively. The intensity ratio between the G- and D-bands (*I(G)/I(D)*) is an indication of the crystallinity of DWNTs. The *I(G)/I(D)* ratios of synthesized DWNTs at 875, 900, 925, 950 and 1000 °C were 5.23±0.41, 8.36±0.19, 6.83±0.11, 5.71±0.17 and 5.24±0.27, respectively. These results showed that the

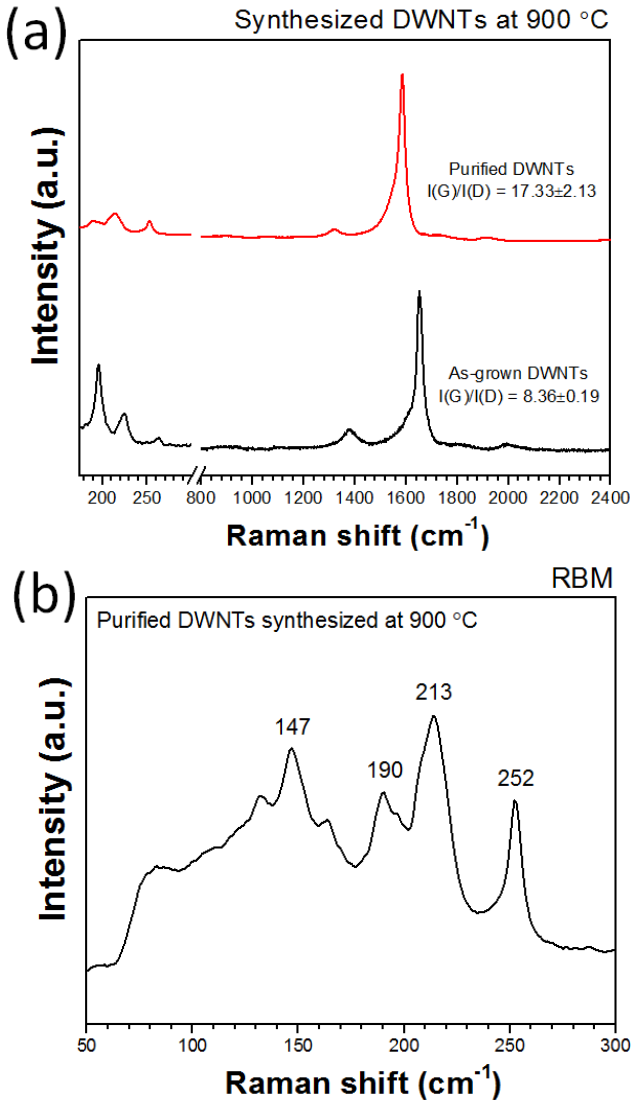

Figure 2 (a) Raman spectra of synthesized DWNTs at 900 °C before and after purification. (b) RBM spectra of purified DWNTs synthesized at 900 °C.

synthesized DWNTs at 900 °C had the highest *I(G)/I(D)* intensity ratio of 8.36±0.19, and 900 °C was the optimum synthesis temperature to obtain the highest purity of as-grown DWNTs.

Next, as-grown DWNTs synthesized at 900 °C were purified by acid and thermal treatments. Fig. 2(a) shows Raman spectra of as-grown and purified DWNTs synthesized at 900 °C. The *I(G)/I(D)* of purified DWNTs was 17.33±2.13, which was 2.07 times higher than that of as-grown DWNTs. The higher *I(G)/I(D)* of the purified DWNTs compared with that of as-grown DWNTs would suggest that the crystallinity of the purified DWNTs was improved due to the removal of disordered carbon structures and impurities. Fig. 2(b) shows RBM spectra of purified DWNTs synthesized at 900 °C. Purified DWNT expresses RBM at 147, 190, 213 and 252 cm^{-1}. The diameter of purified DWNTs can be determined using Eq. 1 where ω_{RBM} and d_t are RBM frequency (cm^{-1}) and tube diameter (nm), respectively [15,16].

$$\omega_{RBM} = 234/d_t + 10 \quad (1)$$

The calculated diameters of purified DWNTs from RBM spectra

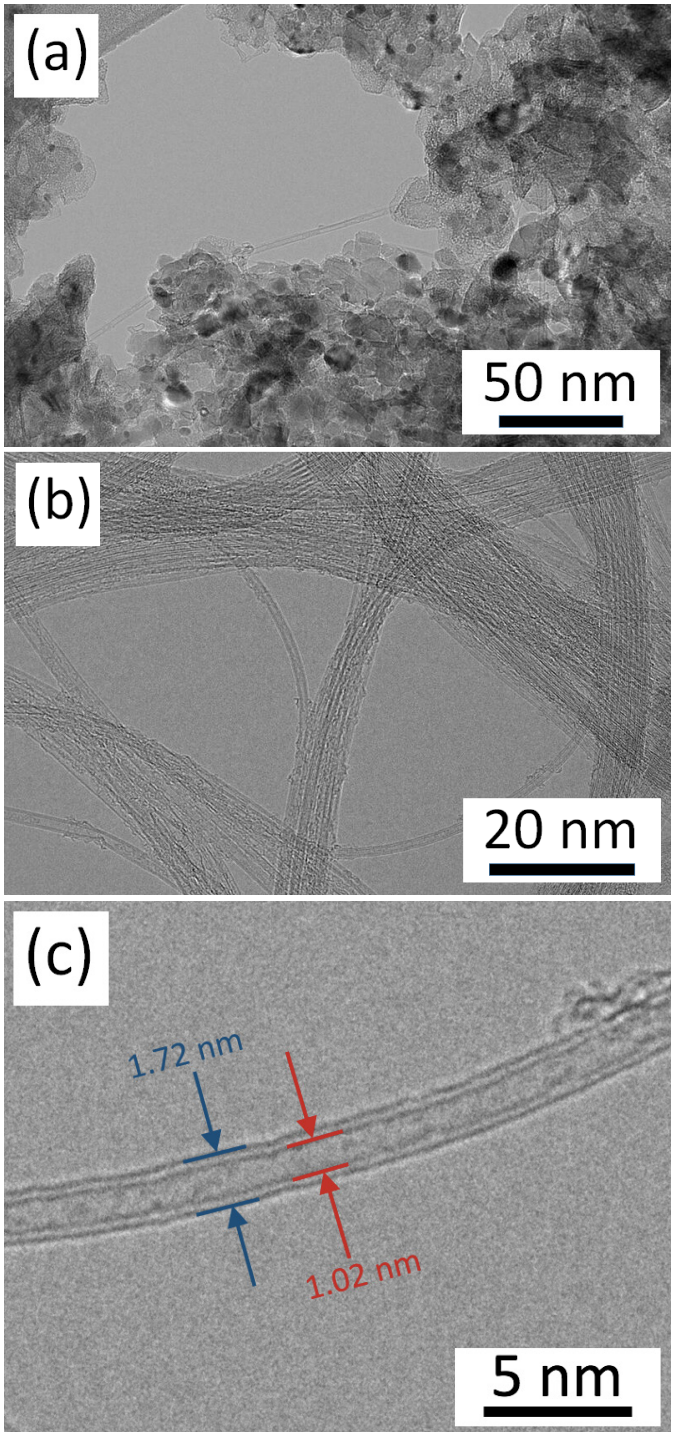

Figure 3 TEM images of (a) as-grown DWNTs, (b) purified DWNT synthesized at 900 °C and (c) high-resolution TEM image of individual purified DWNTs.

at 147, 190, 213 and 252 cm^{-1} were 1.71, 1.30, 1.15 and 0.97 nm, respectively. The interlayer spacing of DWNT ranges from 0.33-0.41 nm [17-19].

Fig. 3 shows TEM images of synthesized DWNTs at 900 °C (a) before and (b) after purification process. After purification, the iron catalysts (small particles with darker contrast) and amorphous carbon were removed. TEM image reveals DWNTs in a bundle structure (Fig 3(b)). The well-aligned DWNTs stick together due to Van der Waals interaction. In Fig. 3(c), a TEM image of individual purified DWNT was taken, with the two graphene layers stacked in parallel on each side. The average diameters of the inner and outer tubes of purified DWNTs were measured as 1.02±0.03 and 1.72±0.05 nm, respectively. Furthermore, the interlayer spacing of isolated purified DWNT is approximately 0.34 nm, which is consistent with the interlayer distance in graphite. The inner and outer diameter and interlayer spacing of DWNTs are in the same range as that observed from the RBM spectra.

CONCLUSION

DWNTs were successfully synthesized by HVCVD at 875-1000 °C using ethanol as a carbon source. Synthesis of DWNTs at 900 °C was found to be optimal for obtaining the highest purity of as-grown-DWNTs. With purification, the *I(G)/I(D)* of DWNTs increased by a factor of approximately 2 over the non-purified DWNTs. We conclude that the synthesis temperature and the purification process directly affect the structure and crystallinity of DWNTs.

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