STRUCTURAL CHANGES OF DOUBLE WALLED CARBON NANOTUBES BY THERMAL ANNEALING

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Introduction

Recently, a great deal of attention was paid on the synthesis of double-walled carbon nanotubes (DWNTs) by a catalytic chemical vapor deposition (CVD) method because their many physicochemical properties derived from their unique structure such as coaxial structural morphology make them very promising in the fabrication of field emitter and multi-functional filler. The structural stability of DWNTs as compared with those of single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) is a critical factor in companion with the structural perfection, especially when considering application fields. In this study, DWNTs synthesized by a catalytic CVD method were heat treated at various temperatures, from 1500 to 2800^{o}C, in argon atmosphere in order to evaluate the structural stability, and describe the structural changes including diameter variations through a detailed high-resolution TEM observation and Raman studies.

Experimental

The DWNTs utilized in this study were synthesized using a standard catalytic decomposition of methane over iron metal nanoparticles, and were purified followed by acid treatment and air oxidation at 500^{o}C. This severe process decreases significantly the amount of SWNTs due to the higher chemical reactivity of SWNTs with oxygen when compared to DWNTs or MWNTs. Finally, heat treatment under an argon atmosphere was carried out at various temperatures from 1500 to 2400°C for 30 minutes using a graphite-resistance furnace. TEM observations confirmed that high yields of DWNTs (over 95%) in bundle are present before the heat treatment. The TEM used in the present study was a JEOL JEM-2010FEF instrument equipped with an in-column □–type energy-filter. The operating voltage of the TEM was 200 kV. The Raman spectra were obtained using a Kaiser HoloLab 5000 system (excitation wavelength: 532 nm, laser power less than 5 mW).

Result and Discussion

Figure 1 depicts the radial breathing mode (RBM) Raman spectra below 400 cm^{-1} for DWNTs heat treated at various temperatures with a frequency ω_{RBM}, which is inversely related to the tube diameter, d_t [1]. It is noteworthy that tube diameters become larger with increasing the heat treatment temperature, indicating that tubes are transformed into more stable sp^2-like structural forms, that is, larger diameter tubes corresponding to the gentle curvature of graphene sheets. The tube diameters are calculated from the RBM peaks using the equation $\omega_{RBM} = 234/d_t + 10$, where d_t is the tube diameter (nm) and ω_{RBM}, the RBM frequency (cm^{-1}) [2]. There are no significant changes for samples heat-treated at 2100°C except for the disappearance of the peak located at 312 cm^{-1} (0.77 nm), suggesting that highly curved and less stable SWNTs are transformed into more stable graphitic structures via the surface reconstruction

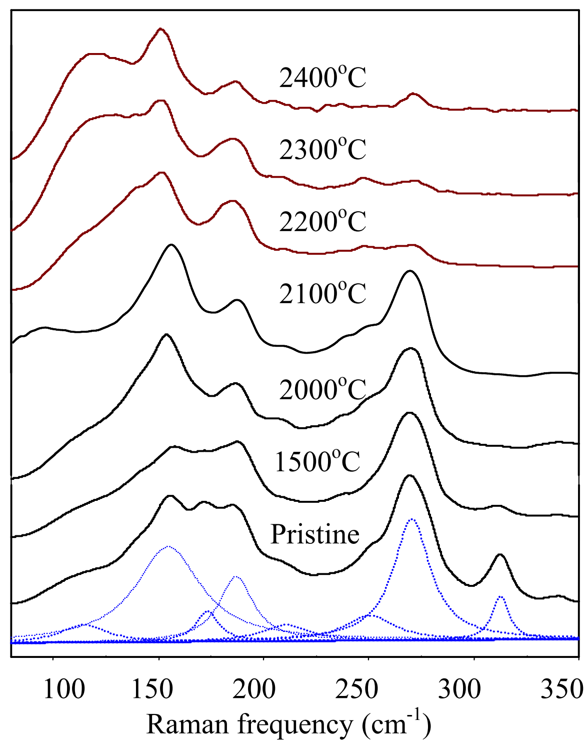

Figure 1. Low frequency Raman spectra of DWNTs (grown by a catalytic CVD method at around 875°C) heat treated at various temperatures from 1500 to 2400°C. The tendency to downshift the RBM frequency with increasing heat treatment temperature indicates the formation of thermally stable large-diameter tubes.

induced thermally [3]. From the applications point of view, the fabrication of high purity DWNTs using heat treatment processes at 2000°C indicate that they could be used as a high-current field emitter, owing to their high structural stability and purity (removal of iron metal particles). This is in contrast with SWNTs, which could be easily damaged when the emitter current exceeds a lower threshold value.

Conclusions

It is natural that each DWNT in a bundle will try to stabilize through a structural transformation when the thermal energy is increased over a critical value, and this transformation occurs from the periphery to the core of a bundle following the temperature gradient. This assumption was confirmed by a detailed HRTEM and Raman scattering study. The abrupt drop in intensity of the RBM peak at 270 cm^{-1} for samples heat treated at 2200°C, indicates the destruction of DWNTs with inner tubes of 0.9 nm diameter and outer tubes of 1.6 nm in diameter. With further increase in heat treatment temperature, two patterns in structural transformation were observed: one is merging into larger DWNTs, and the other is structurally collapsed into MWNTs or flaky carbons.

References

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