Self-Assembling of Carbon Nanotubes on Carbon Black with Non-Catalytic Chemical Vapor Deposition

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Abstract

We report a unique none-catalytic chemical vapor deposition technique for fabrication of carbon nanotubes (CNTs) on carbon black-CB surface at mild temperature. The topologically heterogeneous structure on carbon surface is a key factor for introducing the decomposition of gas hydrocarbons, and the micro-peripheral crystalline structures are proposed as epitaxial growing sites for self-assembling of the carbon nanotubes.

Introduction

Arc discharge[1], laser ablation[2], and catalytic chemical vapor deposition (CCVD)[3-5] techniques have been developed to produce CNTs. CCVD was evidenced of the greatest potential for mass production of CNTs. In current achievements, growing CNTs on typical materials, such as activated carbon, clay etc., form as bi-functional composites are drawing out great interest. However, previous studies were still employed CCVD for growing CNTs on desired materials. One of the considerable disadvantage of CCVD is the encapsulation of the metallic catalyst within the nanotube during its growth. The existence of metal catalysts may cause a detrimental influence on the practicality of CNTs, especially in electronic conductivity. The other primary problem of the CCVD approach toward the synthesis of CNTs is migration of the nanoscale catalytic metal particles at reaction temperatures, usually during 700~1200^{o}C; this phenomenon makes it difficult to control the positions of the CNT growth sites. Synthesis of CNTs on desired materials by non-catalytic CVD approaches would have the potential to solve two existing problems. In this regard, we have developed a simple non-catalytic CVD method to grow CNTs on carbon black surfaces, which have proved existing unique active sites for self-assembling of CNTs. In this report, multi-walled CNTs (MWCNTs) can be produced at 800 ^{o}C in the flow of C_2H_4/He on carbon black.

Methods

Carbon black-BP2000 was supplied by China Synthesis Rubber Co. and did not proceed with any treatments. In the fabrication of carbon nanotubes on carbon black, the sample were heated to 800^{o}C in He at a flow rate of 40 mL/min, and then switched to C_2H_4/He (3:1) at the same flow rate and maintained at 800^{o}C for 1 hour.

The microstructure of carbon nanotubes on carbon black surfaces were examined by scanning electron microscopy-SEM (JEOL JSM 6400) and the chemical composition of carbon nanotubes was analyzed by Raman spectroscopy (JOBIN-YVON T64000). Transmission electron microscopy-TEM (JEOL TEM-3010) was used to observe the high-resolution images of carbon nanotubes

Results and Discussions

Figure 1a and 1b reveal the SEM images of CNTs grown at 800^{o}C in C_2H_4/He (3:1) for 1 h on carbon black surfaces. In Figure 1 c and 1d, the lower magnification and the close-up image of CNTs with outer diameters of 30-70 nm synthesized on carbon black surface.

Figure 2 are the HRTEM image of MWCNTs on carbon black surface and the Raman spectra of carbon black, CNTs grown on carbon black by synthesized at 800^{o}C in C_2H_4/He (3:1) at a flow rate of 40 mL/min for 1 h.. The HRTEM image demonstrates clearly the 002 fringes (evidenced by XRD measurements, not shown here) in the wall with d_{002}=0.342 nm.

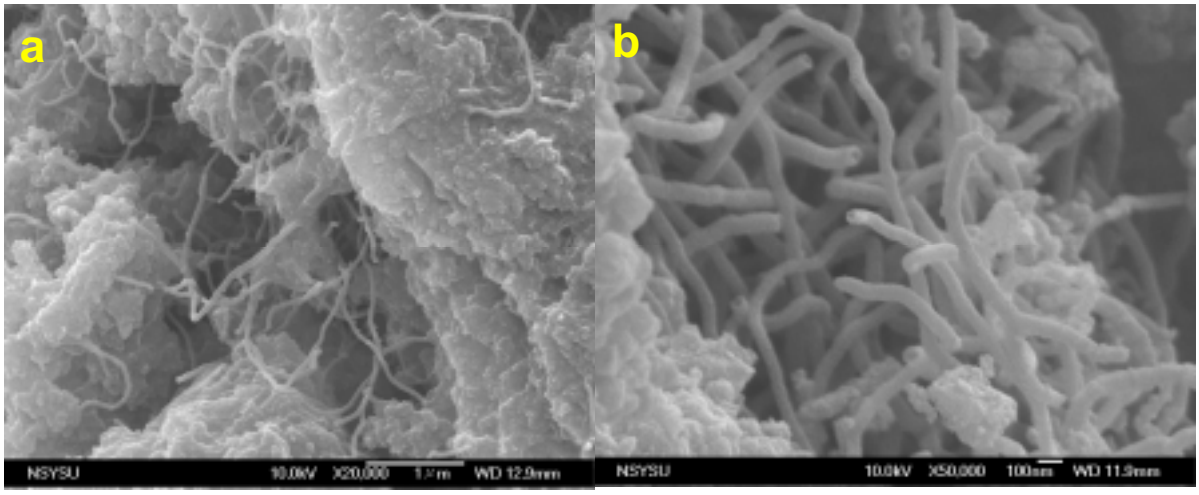

Figure 1 SEM images of MWCNTs on (a) carbon black-BP2000 with a lower magnification and (b) carbon black-BP2000 with a close-up magnification

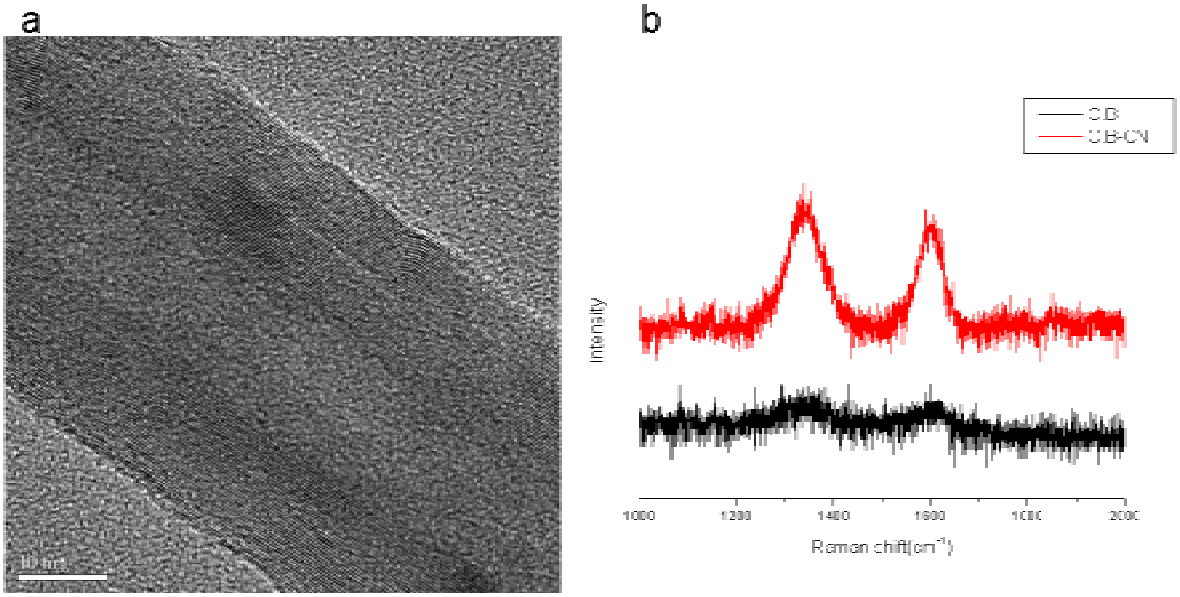

Figure 2 (a) HRTEM image of MWCNTs with outer diameter of 40.6 nm on carbon black-BP2000. (b) Raman spectra of carbon black, CNTs grown on carbon black by synthesized at 800°C in C_2H_4/He (3:1) at a flow rate of 40 mL/min for 1 h.

The HRTEM image indicates that the wall of the MWCNTs has a fairly good crystalinity fabricated on carbon black surface. The Raman spectra are consistent with this result. Before the synthesis of CNTs, the intensities of D-band and G-band of pure carbon blacks are nearly negligibly, when CNTs fabricated on carbon black surface, it is obvious to find a G-band at 1590 cm^{-1} and a D-band at 1341 cm^{-1}, the Raman spectra shown MWCNTs fabricated by CVD method.

Carbon blacks were regarded having distributed micro-crystalline of qusi-graphite structure on surface usually exists a low content of oxygenated functional groups. When carbon blacks were heated in helium to elevated temperature at 800°C or above, most of the oxygenated functional groups were decomposed into CO, CO_2 or H_2O leaving the high energy unsaturated carbon dangling bonds on surface. We proposed these unsaturated carbon dangling bonds would be active sites for cracking the reactant-ethylene into carbon and hydrogen. The cracking carbons diffused and self-assembling on adjacent qusi-graphite structure forming carbon nanotube (CNTs), shown in Fig. 1a (lower magnification) and 1b (close-up magnification).

The mechanism for synthesizing carbon nanotubes on carbon black is disclosed as the self-assembling of the carbon atoms, which cracking by ethylene, on the qusi-graphite structures, these sites acted as crystalline seeds for piling up the CNTs. The preparation of CNTs on carbon blacks would therefore be possible by metal-free CVD process. This technique is easy to produce large-scale carbon nanotube(CNTs)/carbon black (CB) composites in the traditional carbon black manufacturing process. The unique structure of CNT/CB could be potentially applied in electric conductivity, polymer reinforcement and catalyst support.

Conclusions

Herein, we disclose a large-scale self-assembling of multi-walled carbon nanotubes on carbon black at mild temperature. The topologically heterogeneous structure on carbon black surface is the key factor for introducing the decomposition of gas hydrocarbons. The micro-peripheral crystalline structures on carbon black surface are proposed as epitaxial growing sites for self-assembling of carbon nanotubes.

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