Assistive effects of carbon feedstock and etchant on defect healing of carbon nanotubes by thermal process

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[Introduction] Carbon nanotubes (CNTs) have attracted extensive research interest for their extremely unique thermal, electrical, and mechanical properties. Unfortunately, as-synthesized CNTs usually show significantly lower performances than expected due to the formation of defects and amorphous carbon (a-C). Past simulation research has shown that defects of CNTs can be thermally healed by a post-synthesis process[1] and the supply of carbon feedstock such as acetylene (C_2H_2) is effective for healing vacancy defects.[2] Etchant such as water or carbon dioxide (CO_2) was also widely used during the growth process of CNTs to remove a-C. In the present work, we studied defect healing of CNTs by post-synthesis process using C_2H_2[3], CO_2, and the combination of them.

[Experiment] Relatively defective CNTs were synthesized using nanodiamond as growth seeds under low temperature.[3] In the C_2H_2-assisted healing process, CNTs were annealed under 1100 °C at 220 Pa with Ar and C_2H_2 for 0 to 60 min.[3] In the CO_2-assisted healing process, CNTs were treated under 800 to 1100 °C at 65 Pa with Ar and CO_2 for 10 to 60 min. The combination of C_2H_2 and CO_2 was also examined. Defects in CNTs were analyzed by Raman spectroscopy based on the intensity ratio of the G-band to the D-band I_G/I_D with an excitation wavelength λ_{ex} of 633 nm.

[Result and discussion] Firstly, as the C_2H_2-assisted healing process, I_G/I_D of different time and C_2H_2 partial pressure is compared. For 0.088 Pa case, a noticeable increase of the I_G/I_D ratio is observed in the first 20 min and the I_G/I_D ratio reached to 8.9 at 40 min.[3] Secondly, as the CO_2-assisted healing process, Raman spectra in Fig. 1 (a) compare the effect of Ar and 5.85 Pa-CO_2 for annealing at 950 °C for 60 min. Compared with the pristine and Ar treated samples, an obvious decrease of D-band is found and I_G/I_D ratio is increased to around 8, which proves that during annealing process CO_2 also has etching effect and can remove unstable CNTs and a-C. However, the G-band intensity of CNTs significantly reduces more than half even in the Ar case, which shows the low thermal stability of CNTs at 950 °C. Thirdly, as C_2H_2 and CO_2 combination-assisted healing process, Raman spectra in Fig. 1 (b) show the change between pristine CNTs and CNTs that is annealed in 5.85 Pa-CO_2 and 0.052 Pa-C_2H_2. Though I_G/I_D ratio has no obvious change, compared with the Ar case in Fig. 1 (a), a less decrease of the G-band intensity is observed. This indicates that the combination of CO_2 and C_2H_2 should be promising for preserving the quantity of CNTs while increasing the quality of CNTs.

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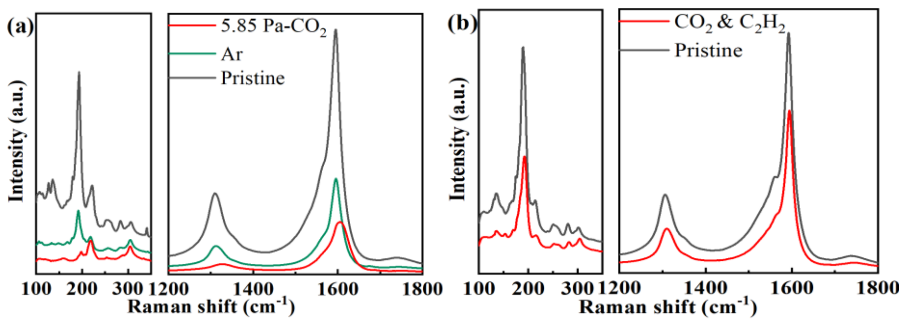

Fig. 1 Raman spectra of (a) the pristine CNTs, CNTs healed in Ar, and CNTs healed in 5.85 Pa-CO_2 for 60 min at 950 °C; (b) the pristine CNTs, and CNTs annealed in 5.85 Pa-CO_2 and 0.052 Pa-C_2H_2 for 60 min at 950 °C.