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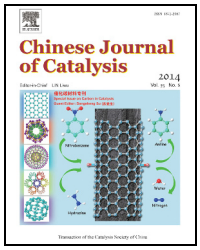

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A selective way to create defects by the thermal treatment of fluorinated double walled carbon nanotubes

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ABSTRACT

Nanoscale defects in the outer tube to preserve the electrical and optical features of the inner tube can be engineered to exploit the intrinsic properties of double walled carbon nanotubes (DWCNTs) for various promising applications. We demonstrated a selective way to make defects in the outer tube by the fluorination of DWCNTs followed by the thermal detachment of the F atoms at 1000 °C in argon. Fluorinated DWCNTs with different amounts of F atoms were prepared by reacting with fluorine gas at 25, 200, and 400 °C that gave the stoichiometry of $CF_{0.20}$, $CF_{0.30}$, and $CF_{0.43}$, respectively. At the three different temperatures used, we observed preservation of the coaxial morphology in the fluorinated DWCNTs. For the DWCNTs fluorinated at 25 and 200 °C, the strong radial breathing modes (RBMs) of the inner tube and weakened RBMs of the outer tube indicated selective fluorine attachment onto the outer tube. However, the disappearance of the RBMs in the Raman spectrum of the DWCNTs fluorinated at 400 °C showed the introduction of F atoms onto both inner and outer tubes. There was no significant change in the morphology and optical properties when the DWCNTs fluorinated at 25 and 200 °C were thermally treated at 1000 °C in argon. However, in the case of the DWCNTs fluorinated at 400 °C, the recovery of strong RBMs from the inner tube and weakened RBMs from the outer tube indicated the selective introduction of substantial defects on the outer tube while preserving the original tubular shape. The thermal detachment of F atoms from fluorinated DWCNTs is an efficient way to make highly defective outer tubes for preserving the electrical conduction and optical activity of the inner tubes.

1. Introduction

In the last decade, the chemical introduction of F atoms onto the walls of single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs) has been used for the nanotubes to improve dispersing ability in an organic solvent, control the electronic structure and tube length, and remove entrapped metal particles [1–8]. Double-walled carbon nanotubes (DWCNTs) consisting of two coaxial tubes have been used as a host carbon material for the fluorination reaction for the followings reasons: (a) better thermal stability and higher accessible surface areas than SWCNTs [9,10]; (b) the inner tubes

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with a small diameter below 1.0 nm have modified optical properties due to a coupling interaction with the outer tube [11–14]; and (c) the remarkable feature of performing a selective outer tube chemistry that leaves the inner tube intact [15–18].

The chemically introduced F atoms in host materials are thermally unstable when the fluorinated carbon materials are subjected to high temperatures [19–21]. Thus, the F atoms would detach from the carbon atoms of the host materials, thereby creating vacancies. In particular, a thermal annealing study of DWCNTs with selectively fluorinated outer tubes prepared by reacting with BrF_3 and Br_2 revealed that the optical properties of the inner tube were unchanged before and after the thermal treatment [16]. Thus, topological defects in the outer tube of DWCNTs can be engineered by the attachment and detachment of F atoms. This defect engineering allows DWCNTs to be utilized in many promising applications such as gas storage materials and electrode materials of supercapacitors and lithium ion batteries where the engineered defects are required for keeping the high electrical conductivity and desirable optical features of the inner tube. However, neither the effects of the high concentration of introduced F atoms (inner and outer tubes form covalent bonds with the F atoms) nor the subsequent thermal defluorination at high temperatures (up to 1000 °C) on the structural and optical properties have been studied systematically. In this study, to elucidate unclarified points in the fluorination and thermal defluorination of DWCNTs in detail, we prepared fluorinated DWCNTs containing different amounts of F atoms by reacting DWCNTs with fluorine gas at 25, 200, and 400 °C. The structural and optical changes of the fluorinated DWCNTs before and after thermal treatment were investigated using Raman, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

2. Experimental

The preparation procedure for synthesizing high purity DWCNTs using catalytic chemical vapor deposition was previously described [22,23]. To obtain high purity DWCNTs, we carried out a purification process (HCl treatment and air oxidation up to 550 °C for 2 h) in order to remove impurities (e.g., SWCNTs and catalytic particles). The fluorinated DWCNTs were prepared by the direct reaction with fluorine gas as follows. Before fluorination, the nanotube sample was vacuum treated at 200 °C for several hours to remove entrapped water. Then, the dried nanotubes were reacted with fluorine gas (1 atm) at 25, 200, or 400 °C for 5 h. Finally, the fluorinated DWCNTs were thermally treated at 1000 °C in Ar to completely detach F atoms. The fluorinated and de-fluorinated DWCNTs were characterized by TEM (JEOL2010FEF), SEM (JEM6335Fs), X-ray photoelectron spectroscopy (XPS, Ulvac-phi model 5600, non-monochromatized Mg-K_α at 1253.6 eV), and Raman spectroscopy (Kaiser Hololab 5000 system, laser excitation at 532 and 633 nm).

3. Results and discussion

SEM and TEM observations showed that our DWCNTs were large bundles in the range of 10–50 nm, with each tube existing in a hexagonal cross-section (Fig. 1(a–c)). It is observed that there was no noticeable change in bundle size and cross-sectional nature when the DWCNTs were fluorinated up to 200 °C (Fig. 1(d–i)). However, when the reaction temperature was increased to 400 °C, we observed a perturbed cross-section nature as well as the formation of disordered carbon atoms attached on the outer tubes of the DWCNTs. The perturbed packing structure in the heavily fluorinated DWCNTs can be explained by a weakened interaction between the outer tubes

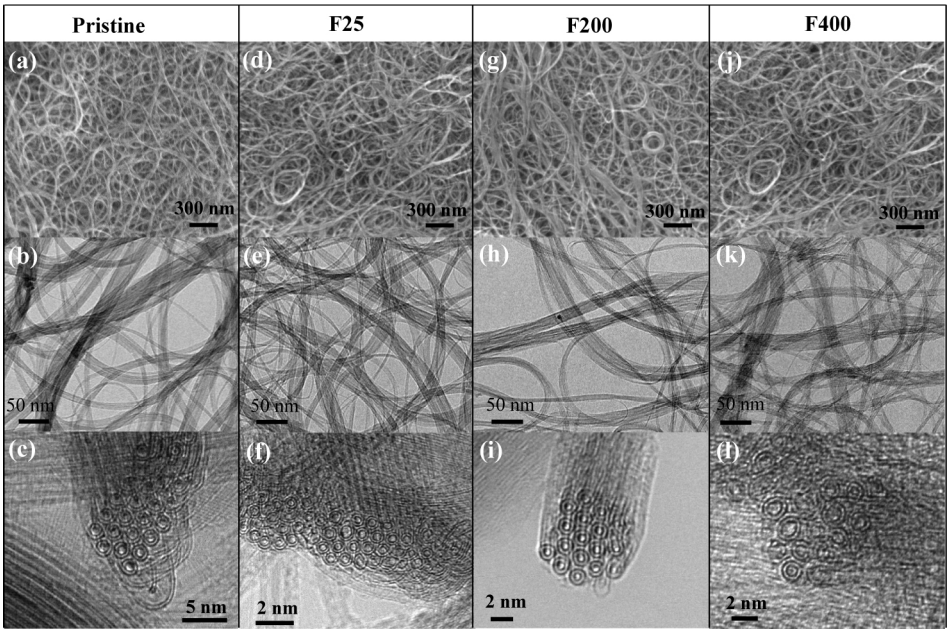

Fig. 1. SEM (a, d, g, j), low resolution TEM (b, e, h, k) and cross-section TEM (e, f, i, l) images of the pristine DWCNTs and the DWCNTs fluorinated at 25 (F25), 200 (F200), and 400 °C (F400). Note that the coaxial structure was preserved after fluorination.