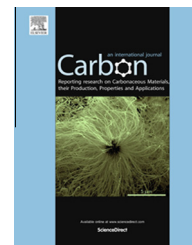


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Improvement of carbon nanotube stability by high temperature oxygen/chlorine gas treatment

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ABSTRACT

Carbon nanotubes are interesting for applications in numerous fields. Nevertheless the as-produced samples prepared from bulk synthesis methods contain impurities and remain entangled if neither mechanical nor chemical treatment is applied. Such treatments are known to damage the carbon nanotube structure and to reduce their stability which induces drastic diminution of their properties. We have developed a purification method based on the use of a gas-phase treatment under an oxygen/chlorine mixture at high temperature (around 1000 °C). We were able to efficiently remove metal-based impurities from catalyst residue without damaging carbon nanotubes. We show that their stability is improved thanks to the presence of chlorine-containing functional groups at the carbon nanotube surface. Under the used conditions, the functionalization level remains low preserving the SWCNT structure and efficiently protects SWCNTs from combustion by oxygen.

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1. Introduction

Carbon nanotubes (CNTs) have a huge potential of application in many fields [1–6]. However, as-produced samples prepared by processes such as arc-discharge, laser-ablation, chemical vapor deposition, contain both carbonaceous and particles of transition-metal catalyst impurities. Post-synthesis treatments are thus required in order to obtain high-purity and high-stability CNT samples. Oxidation of CNTs is a widely used treatment for various objectives. Chemical modification of the CNT surface could be achieved, by oxidative attack using either pure acid or acid mixtures such as nitric acid and/or sulfuric acid [7–13] or gas phase oxidation [14,15]. Dispersability of CNTs can be advantageously increased thanks to the presence of oxygen-containing groups at their surface

[16]. Oxidation has been successfully used for CNT purification including both selective elimination of carbonaceous impurities and catalyst residue [17–21]. The oxidative atmosphere has several roles: (i) a selective attack and elimination of the low-stability carbonaceous species (amorphous carbon); (ii) weakening the carbon multi-shell particles usually protecting the metal impurities via an etching process; (iii) oxidation of the metal particles. The subsequent removal of these latter by solubilization in acids is all the more efficient since the metal oxidation yield is high. Nevertheless, CNTs themselves are known to be particularly sensitive to oxidative atmospheres [22–24]. Dry and/or wet oxidation has to be performed with carefully optimized experimental parameters depending also on the nanotube source. Even under rather mild oxidation conditions, CNT walls can be attacked by

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inducing formation of defects and holes. Shortening of CNTs can also be observed [25–28]. Regarding purification processes, even if the final quality of the CNTs (concentration of CNTs and amount of sidewall defects) can attain more than 99%, the purification yield consequent upon the attack and the consumption of the CNTs is often disappointing [29]. A subsequent high temperature annealing of the samples is required in order to remove the functions that have been grafted at their surface by the previous chemical treatments, to cure the created defects and to restore the crystallinity of the CNTs.

Besides, the problem of low-stability CNTs under oxidizing gases inducing their pre-combustion lies with the metal particles present in the CNT samples [30–33]. Development of alternative treatments that allow to access to high purification yield without damaging the CNTs is therefore of important interest. Chlorine has been recently successfully applied to CNT purification. Under pure chlorine at an elevated temperature, metal impurities can be selectively removed from the samples without damaging the CNTs [34,35]. The obtained low-metal-containing CNT samples are expected to be less sensitive to oxygen. We report here on a gas-phase purification treatment combining the use of oxygen added to chlorine subsequent to the use of pure chlorine. The samples were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Under these conditions, CNTs could sustain oxidation treatments at temperatures close to 1000 °C. The results show that both the efficiency of metal removal and the stability of the SWCNTs are improved. Interestingly, the treated CNTs show a thermal stability gradually increased with the increase of oxygen content under chlorine. A possible protective effect of the CNTs by chlorine is discussed.

2. Experimental

2.1. Sample preparation

SWCNTs were produced using a homemade arc-discharge reactor [24]. The used catalysts were nickel and yttrium, in an atomic ratio Ni/Y of 4.2/1 as it is typically used [36]. The catalyst content in the catalyst-graphite mixture was intentionally reduced below 10 wt.% in order to obtain a starting raw SWCNT sample with low-metal impurities. The raw as-produced sample is referred to as R-SWCNT.

R-SWCNT was purified by a chlorine-based purification procedure described elsewhere [34]. The treatment consisted in heating the raw SWCNT powder (200 mg) under pure chlorine at 950 °C for 2 h. A washing with a low concentration hydrochloric acid (4 N) solution was performed afterwards overnight at room temperature in order to solubilize the possible remaining metal chlorides. This treatment involving pure chlorine is referred to as T_{Cl}. After filtration, washing with pure water and drying, this sample treated using pure chlorine at 950 °C for 2 h is named Cl-1-SWCNT. A treatment under pure chlorine was done at 950 °C during 4 h, the treated sample is named Cl-2-SWCNT. A series of treatments was performed by adding a chosen flux of oxygen (F1, F2 and F3)

in chlorine for the second hour of treatment at 950 °C (the total duration being of 2 h): F1 = 0.45, F2 = 2.00 and F3 = 4.10 mL/min. The process under chlorine/oxygen mixture is named T_{ClOx}. For T_{Cl} and T_{ClOx}, the chlorine flux was maintained at around 100 mL/min. The temperature and the chlorine flux have been chosen, based on previous experiments, in order to minimize CNT oxidation and maximize metal removal. The obtained purified samples by the T_{ClOx} process are referred to as: ClOx-F1-SWCNT, ClOx-F2-SWCNT and ClOx-F3-SWCNT, for F1, F2 and F3 oxygen fluxes, respectively.

2.2. Characterization techniques

The thermogravimetric analyses (TGA) were performed in a Setaram Setsys evolution 1750 Thermal Gravimetric Analyser. The temperature is increased from room temperature to 1000 °C at 3 °C/min under dry air (flux: 10 mL/min). The remaining weights correspond to the metallic residues that have been oxidized, i.e. NiO and Y₂O₃.

Raman spectra were collected at room temperature (300 K) with a LabRAM HR 800 micro-Raman spectrometer. We have used two incident lights: 514.5 and 632.8 nm focused on the samples with a ×50 microscope objective. Typical power densities on the samples' surface were not higher than 0.25 mW/μm² in order to avoid over-heating and damaging of the SWCNTs. For analysis, a small amount (around 1 mg) was dispersed in ethanol using a low-power sonication bath (to avoid any introduction of defects) during 5 min. Three spectra were at least recorded on different zones for the same sample.

The main Raman features are the following. The Radial Breathing Modes (RBM) have a frequency ω_{RBM} ranging from 160 to 195 cm⁻¹. The corresponding SWCNT diameters d_t can be deduced from:

$$\omega_{\text{RBM}} = A/d_t + B \quad (1)$$

where the parameters A and B are determined experimentally as $A = 234 \text{ nm} \cdot \text{cm}^{-1}$ and $B = 10 \text{ cm}^{-1}$. The D band is located at higher frequency, in the 1320–1350 cm⁻¹ range. Its intensity increases upon any addition of defects in the SWCNT structure [37,38]. The G band, in the 1500–1600 cm⁻¹ range, corresponds to the C=C bond vibrations of nanotubes. Based on the Kataura plot [39], for semi-conducting SWCNTs, the G band is well fitted with three Lorentzian curves corresponding to three main components: the G⁻, G⁺ and G* bands. The G* band is visible as a shoulder at around 1610–1620 cm⁻¹ and is associated with defective structure [40]. For metallic SWCNTs, the well-known Breit–Wigner–Fano (BWF) curve is added as a low-frequency component [41]; the G band is thus fitted with a BWF curve around 1540 cm⁻¹ and two Lorentzian curves as G⁻ and G⁺ components. In all cases, the D band is fitted with a Lorentzian curve. The D/G⁺ intensity ratio $I_{\text{D}}/I_{\text{G}^+}$ is used to follow structural modifications of SWCNTs upon chemical treatments. For sake of clarity, the intensity of the spectra shown in the figures has been normalized with respect to the maximum of the G band. The value given for $I_{\text{D}}/I_{\text{G}^+}$ are an average obtained from the data recorded for the same sample and error bars are given on the figure.

Transmission Electron Microscopy (TEM) observations were carried out using a Philips CM 20 apparatus at an

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