



Fluorination of single walled carbon nanotubes at low temperature: Towards the reversible fluorine storage into carbon nanotubes

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ABSTRACT

Fluorination of single walled carbon nanotubes was carried out at low temperature in the $-191/25$ °C range under 1 atm pure fluorine gas. In such conditions, the resulting C–F bonding is significantly weaker than for samples fluorinated at 280 °C. If the fluorination is performed at low temperature, fluorine atoms can be then removed from the host structure by moderated heating until 300 °C or by vacuum without strong damage on the tubes. After thermal defluorination, the resulting sample can be refluorinated similarly than the pristine tubes.

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1. Introduction

Single walled carbon nanotubes (SWCNTs) are one of the most attractive new forms of carbon materials because of their possible uses in nanotechnology and more particularly in electronic devices or energy storage [1]. Moreover, many researchers have investigated and still investigate their physical and chemical modification [2–4]. Among those works, fluorination is considered to form fluorotubes (F-SWCNTs) which can be used as fundamental precursors in the wide context of the chemistry of carbon nanotubes [5]. For example, since fluorination can be used to modify the electronic properties of SWCNTs, it is expected to enable fabrication of metal/semi-conductor junctions on a single tube.

Fluorination ways available for carbon functionalization are multiple: catalytic fluorination [6], fluorination by fluorinating agent decomposition [7], fluorination by CF₄ plasma [8] or direct fluorination either static or dynamic [9]. However, most of the experimental works on fluorination of SWCNTs, opened or ended, has been performed using elemental fluorine at elevated temperature via dynamic direct process [10–14] or static one

under pressure [15] or using CF₄ plasma functionalisation [16–21]. Only two deals with room temperature fluorination [22,23], and one on XeF₂ treatment at moderate temperature (100 °C) [24]. Stoichiometry formulas from CF_{0.1} to CF_{0.996} have been obtained, but the tubular structure is maintained only for fluorination level lower than 0.5. In those investigations, it was underlined that fluorine atoms can be attached on the side walls of inner tube (endo-fluorination) or outer tube (exo-fluorination) and that fluorine fixation via a hypothetical accumulation inside the hollow core of a tube was never obtained. The versatility of the C–F bond is exalted in F-SWCNTs because of two main reasons:

- Except fullerenes, SWCNTs are the nanocarbons objects with the highest curvature and the overlapping of fluorine–carbon orbital is the most reduced in the fluorinated nanotube carbon family [25]. This results in a weakening of the covalence of the C–F bonding. The higher the curvature, the lower the covalence is. The weakening of the covalence has been underlined by the increase of the ¹⁹F NMR chemical shift.
- Different fluorine adsorption sites have been proposed: on the outer tube or/and in the inner tube. Fluorination temperature appears as the key parameter to favour the preferential adsorption on one of this site.

Taking into account thermogravimetric analysis and infrared spectroscopy, three groups of fluorine atoms have been underlined

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and related to three modes of fluorine chemisorption: graphite fluoride-like, fluorofullerene-like and internally “adbended” cylindrical sections [26,27]. The fluorine–carbon interaction strongly depends on the fluorination temperature and heating–cooling steps, which could result in C–F bonding changes. Because of this versatility of the C–F bonding in fluorinated SWCNTs and the possible unusual bonding this precursor appears as a promising candidate for reversible fluorine storage. Such storage would be a secure alternative way to confine fluorine than the actual conditioning under pressure.

In this paper, the fluorination of highly purified opened SWCNTs has been performed with elemental fluorine at very low temperatures T_F , from $-191\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$. The resulting samples, denoted as F-SWCNT- (T_F) have been compared to a sample fluorinated at high temperature ($280\text{ }^\circ\text{C}$). Nuclear magnetic resonance (NMR) of ^{19}F nuclei, Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and thermogravimetry analysis (TGA) were carried out in order to investigate the C–F bonding and the stability of fluorine chemisorbed on the nanotube surface. Particular attention was devoted to the possible reversibility of the fluorine addition.

2. Materials and methods

2.1. Starting materials

SWCNTs provided by Helix and grown from chemical vapor deposition were used. The standard steps of the purification process consist of ultrasonication for 3 h in a solution of concentrated hydrochloric acid at $40\text{ }^\circ\text{C}$, the acid bath being then prolonged overnight under stirring. After decantation, the supernatant acid phase is eliminated and water is abundantly added, the later procedure being repeated several times. In the last steps, water is replaced with ethanol and another 20 min sonication is applied in order to disperse the powder prior to filtration, followed by repeated washing (first with a NaHCO_3 aqueous solution). Tubes are finally dried at $120\text{ }^\circ\text{C}$ under primary vacuum. The XPS analysis of the purified sample reveals then around 3–4% of atomic oxygen and no signal arising from residual catalytic particles can be detected up to the detection threshold of the spectrometer. Transmission electron microscopy (TEM) observations show efficient removal of the non-tubular carbons, present in a low proportion in the raw material, and underline the good quality of the used SWCNTs batch. TEM showed open-ended tubes with an average diameter near 2 nm, forming bundles of apparent size of $40 \pm 20\text{ nm}$ most of the time.

2.2. Fluorination conditions

Prior and after fluorination, N_2 flow was passed through the reactor. Fluorination at low temperature was carried out under pure F_2 gas flow, in a nickel reactor connected with a fluorine and nitrogen gas flow (Fig. 1). The reactor can be cooled with nitrogen liquid at the selected reaction temperature. The reaction was carried out with 25–30 mg of pristine SWCNTs during 3 h in the $-191/25\text{ }^\circ\text{C}$ temperature range under 1 atm pure fluorine gas (Solvay Fluor: purity 98–99% (v/v) with HF max. 0.5% (v/v) and other gases, primarily O_2/N_2 at approximately 0.5% (v/v)). After the reaction, the fluorinated SWCNTs were stored and handled under argon at room temperature.

2.3. Physicochemical characterizations

Fluorinated SWCNTs with chemical composition CF_x have x values from 0.18 to 0.42 when the temperature was increased from $-191\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$, respectively. The composition was first

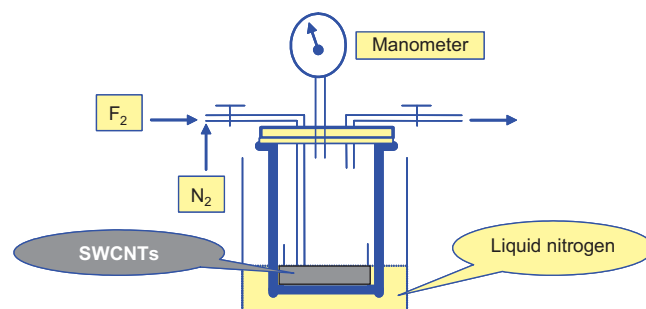


Fig. 1. Reactor used for fluorination at low temperatures.

determined by weight uptake after reaction and then confirmed by TGA analysis (Table 1). The color of these products is still black whatever the operation conditions are. Hereafter, fluorinated SWCNTs are named as F-SWCNT- (T_F) , T_F being the fluorination temperature. Moreover, F-SWCNT-(LT) notation will be used for the samples fluorinated at low temperature, i.e., below $25\text{ }^\circ\text{C}$. In a second time, F-SWCNT- (T_F) samples were treated under dynamic vacuum or by heating under inert gas atmosphere in order to appreciate the reversibility of the fluorine adsorption onto the carbon.

For comparison, the fluorination reaction was also carried out at $280\text{ }^\circ\text{C}$ under fluorine gas flow in a Monel tubular reactor. The composition determined by weight uptake of the black resulting sample was of $\text{CF}_{0.24}$. The reaction temperature was also increased to $520\text{ }^\circ\text{C}$ and the sample exhibited a white color and a chemical composition of $\text{CF}_{1.2}$. Such fluorine content indicates perfluorination and the presence of large amounts of CF_2 and CF_3 groups.

Solid state ^{19}F NMR spectra were recorded at room temperature with a Bruker AVANCE DSX 300 spectrometer with an operating frequency of 282.38 MHz. The experiments were performed without magic angle spinning (MAS). Indeed, spinning could result in heating of the samples. Even moderated, such heating could remove fluorine from the host structure and increase the pressure inside the rotor and open it during spinning. To avoid such a risk and damage in the probe, the samples were put under argon atmosphere of a glove box into an out-gassed glass tube (in order to remove trace of moisture which could react with fluorine to form HF molecules). The external reference was CF_3COOH but the chemical shifts are given with CFCl_3 reference.

Thermal stability measurements were carried out by thermogravimetric analysis (TGA) under dry nitrogen atmosphere with a heating rate of $0.5\text{ }^\circ\text{C min}^{-1}$ from room temperature to $500\text{ }^\circ\text{C}$.

Fourier transform infrared spectroscopy (FT-IR) was performed using SHIMADZU FT-IR-8300 spectrometer; the spectra were recorded using transmission mode in a dried air atmosphere between 400 and 4000 cm^{-1} . Twenty spectra were acquired on pellets made with 2 mg of the material diluted in KBr (200 mg).

Table 1

Operating fluorination conditions and chemical compositions obtained by weight uptake and TGA.

First fluorination					
Reaction temperature ($^\circ\text{C}$)	280	25	-100	-178	-191
Duration (h)	3	3	3	3	3
Composition by weight uptake	$\text{CF}_{0.24}$	$\text{CF}_{0.42}$	$\text{CF}_{0.30}$	$\text{CF}_{0.24}$	$\text{CF}_{0.18}$
Composition by TGA	$\text{CF}_{0.27}$	$\text{CF}_{0.42}$	$\text{CF}_{0.28}$	$\text{CF}_{0.23}$	$\text{CF}_{0.18}$
Second fluorination					
Reaction temperature ($^\circ\text{C}$)		25			-191
Duration (h)		3			3
Composition by weight uptake		$\text{CF}_{0.36}$			$\text{CF}_{0.18}$
Composition by TGA		$\text{CF}_{0.36}$			

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