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New doping process mode to synthesize in situ N-MWNTs in novel coaxial nanostructure

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ABSTRACT

Nitrogen-doped MWNT "N-MWNT" have gained an increasing interest because particularly of their electronic properties allowing their use in specific applications such as catalysis, sensors, nano-electronics and energy storage.

In this investigation, novel coaxial structures consisting of concentric shells of pure carbon MWNT cores with external nitrogen-doped carbon walls (N-MWNT) were produced using a catalytic CVD process, with ethane and ammonia as carbon and nitrogen sources over Fe–Al_2O_3 support. In order to optimize the growth conditions of such N-MWNT nanostructures, we investigate the influence of different key parameters, i.e., ammonia injection moment in two doping process modes "*Instantaneously doping and Mid-doping*", growth temperature (750 and 850 °C) and the presence of H_2 as reducer gas in the reaction environment. A strong correlation between ammonia injection duration (60, 90 and 120 min) and nitrogen content (from 0.4 at.% to 2.2 at.%) incorporated in the nanotube products was observed and different coordination between C and/or O atoms have been described by XPS. These functionalized MWNTs were characterized using HR-TEM, FESEM, XPS, BET, TG analyses and Raman spectroscopy in order to determine their structural characteristics (graphitization and crystallinity) in quantitative and qualitative ways.

1. Introduction

The doping of carbon nanotubes (CNT) with heteroatoms [1] has been frequently used to enhance or tune their physicochemical properties. Thus, it allows modifying the electronic properties of the tubes by replacing carbon by dopant atoms containing additional electrons (donors) or fewer valence electrons (acceptors), similar to the techniques used in the semiconductor industry. Among the dopants, nitrogen has a particular interest in modifying the electronic properties of CNT or other carbonaceous materials [2–4]. The enhancement of other N-CNT properties, including the chemical reactivity [5], the dispersity in a variety of solvents/matrices [6], the structural strength [7] or the thermal conductivity [8] has been also reported. Indeed, extrinsic or intrinsic doping of nanotube surfaces as a functionalization process can lead to localized electronic states in different coordination kinds [9–11]. For this reason, extrinsically doped CNT should be excellent candidates for a new generation of controlled chemically functionalized NT materials for different fields, such as catalysis, sensors, nano-electronics, field emission, Li-ion storage, polymer-CNT composites, etc. [5,6,8,12,13]. The literature survey shows that the N-doping of CNT usually induced lattice deformations, i.e., the formation of regular and irregular compartments that replace or accompany the multi-walled structure [9,12,14,15]. Those defects, e.g., 'bamboo' and/or 'nanobell'-morphologies could translate further into twists and corrugations. In addition, the incorporation of nitrogen was found to be the driving force in the formation of defect sites in the carbon sp^2-network. Therefore, a facile and low-cost synthetic route to create 2D and 3D nanotube junctions (using SWNTs or MWNTs) is inevitably required, as several authors have pointed out [14,16].

In this paper, our aim is to report a scale-able catalytic-CVD synthesis in order to obtain new nanostructure forms of N-MWNT with a high yield, a high purity and crystallinity. We compare the effect of two different doping modes, under two growth temperatures (with and without H_2 as etching gas). We particularly present in this investigation

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Table 1
Different characteristics of the synthesized MWNT in the total (full doping) or partial (mid-doping) presence of NH_3.

	NH_3 (duration)	T (°C)	m_{dep} (g_{NTC}/g_{cat})	S_{BET} (m^2/g)	e_{dop} (nm)
Without doping	150 min	750	4.4	130	0
	180 min	750	5.7	140	0
Mid-doping	60–60 min	750	3.6	198	4
		850	1.8	53	8
		850 (+H_2)	1.2	82	10
	90–90 min	750	4.4	160	3
		850	2.8	24	14
Full doping	120 min	750	2.4	214	–
		850	1.6	80	–
		850 (+H_2)	1.2	87	–

e_{dop}: thickness of waved walls, m_{dep}: weight of N-MWNT/weight of catalyst.

Table 2
Microraman D and G band peak characteristics of the synthesized N-MWNT depending of the doping mode.

		$G_{Position}$	$D_{Position}$	I_D/I_G	N/C (at.%)
Without NH_3 750 °C	150	1598	1331	1.04	0
	180	1598	1328	1.05	0
60/60	750	1587	1333	1.01	0.4
	850	1581	1335	0.86	1.6
	+H_2	1577	1327	0.79	1.2
90/90	750	1580	1324	0.99	0.7
	850	1586	1331	0.87	1.0
120	750	1595	1319	1.1	1.4
	850	1589	1321	1.07	2.0
	+H_2	1598	1331	1.03	2.2

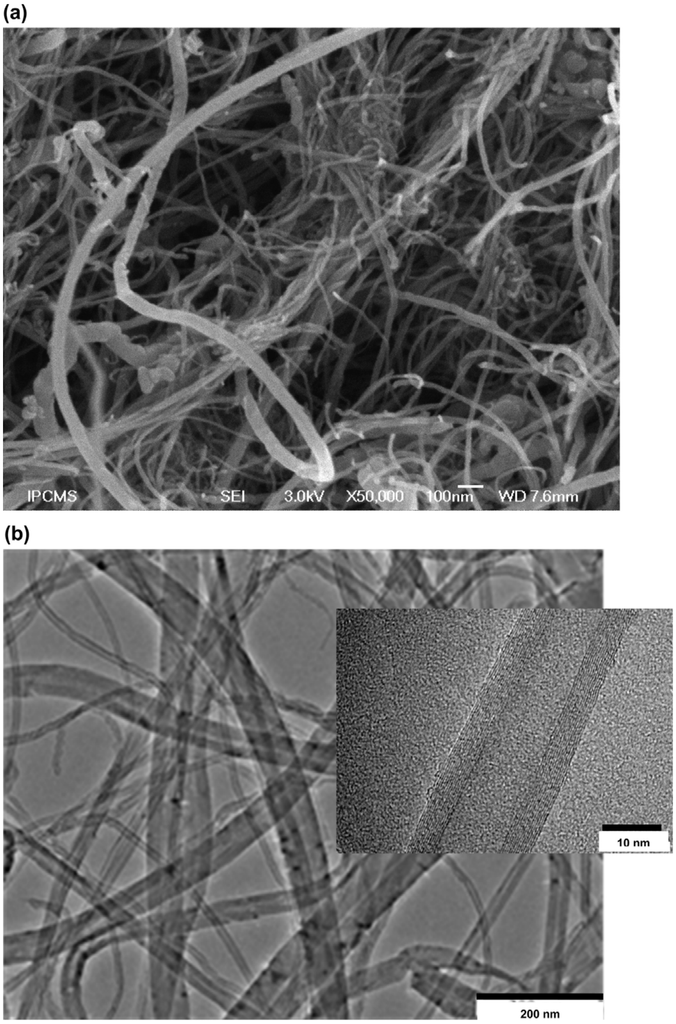

Fig. 1. FESEM (a) and high-resolution TEM (b) micrographs of un-doped MWNT synthesized with catalytic CVD at 850 °C during 2 h.

an original doping process (partial doping or Mid-doping) to introduce in situ functional N groups on the surface of the MWCNT by a classical CVD method: in a first time no NH_3 is present in the reactant, and then NH_3 is introduced during the synthesis.

2. Experimental procedure

MWNT containing substitutionally "doped" nitrogen were synthesized over Fe–Al_2O_3 support as described elsewhere [6,12] using atmospheric pressure catalytic-CVD technique (CCVD) [17,18]. Thus, the N-MWNT synthesis was performed from the decomposition of 50 cm^3/min C_2H_6 and 50 cm^3/min NH_3 at 750 and 850 °C with (or without) 100 cm^3/min of H_2 as etching gas in quartz reactor (with 1000:70:2 mm dimension).

In this investigation, "Continuous or instantaneously" doping was performed in the presence of NH_3 during all the MWNT synthesis duration, while we call "Mid doping" which consists in the synthesis of MWNT firstly without NH_3 followed by a CCVD growth in the presence of NH_3 (the half remaining reaction duration). After, the crude doped products were purified in two steps using basic (NaOH) and acidic treatments (HCl/HNO_3) under reflux in order to remove the alumina support and the residual iron catalyst [12,19].

N-MWNT were characterized using FESEM (JEOL 6700-FEG microscope) and HR-TEM (JEOL 2100F) working under an accelerated voltage of 200 kV with a point-to-point resolution of 0.23 nm in order to control the quality, structure and overall morphology of the produced MWNTs. XPS analyses were performed with a MULTILAB 2000 (THERMO) spectrometer equipped with Al Kα anode ($h\nu$ = 1486.6 eV) during 10 min of acquisition in order to achieve a good signal-to-noise ratio. XPS peak deconvolutions were made with the "Avantage" software from Thermoelectron Company. The C_{1s} photoelectron binding energy was set at 284.6 +/− 0.2 eV relatively to the Fermi level and used as reference for calibrating the other peak positions. XPS was used to examine the chemical composition of functional groups and their concentration in different bonding. Raman spectroscopy was carried out on a Horiba Jobin Yvon LabRAM Aramis confocal spectrometer (with a spot size of 0.4 μm^2 and 1 cm^{-1} resolution) working with a 532 nm wavelength. All spectra show mainly two bands: ~1350 cm^{-1} (D band) and ~1576 cm^{-1} (G band). The G band originates from the Raman active E_{2g} mode explaining the in-plane atomic displacements, otherwise, the origin of D band explains the disorder features. The D/G peak intensity ratio was studied in order to determine the "defective to graphitic" carbon ratio