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New Data on the Formation of SWNTs by the Electrical Arc Method

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Abstract. The formation of single-wall carbon nanotubes (SWNTs) and other carbon nanophases by the electric arc method was investigated by transmission electron microscopy for various conditions while studying the plasma characteristics (temperature profiles, C₂ concentration) by *in-situ* emission spectroscopy. Special attention was brought to the anode type, which has not been a thoroughly studied parameter so far. Related parameters were the dispersion of the catalyst (homogeneous or heterogeneous) and the doping with non catalyst phases. Conditions have been found which are able to produce preferentially either SWNTs, or double-wall nanotubes (DWNTs), or single wall nanocapsules (SWNCs). Focussing on the formation of SWNTs, we also determined arc conditions where web production is increased by up to ~230% compared to standard conditions. Impurities are only catalyst remnants and amorphous – or nearly – carbon, suggesting that acid-based purification procedures could be simplified and less severe, with both higher efficiency and lower harmfulness towards SWNT structure. Investigation of the plasma provided interesting results which emphasise the role of the primary structure of the active carbon moieties generated by the anode vaporisation. The unexpected minimisation of the role of C₂ in the SWNT growth mechanism is one of the results.

INTRODUCTION

Electric arc generated plasma is one of the main methods used to prepare single wall carbon nanotubes (SWNTs) since 1993 [1,2]. Though parameters such as the catalyst type or pressure value have been thoroughly studied since then, others were scarcely investigated, such as the electrode gap or the anode characteristics. Likewise, few studies only have dealt with the subsequent changes in the plasma features induced by the variations in the process conditions, although the related information is likely to be of an utmost importance for the understanding of SWNT and other carbon phase growth mechanisms.

This paper briefly reports some results from our current work in the field. Emphasis is made on the diversity of carbon nanophases which are now able to be synthesised by the electric arc method, and on some relevant features regarding the plasma characteristics. Moreover, we report the discovery that adding a specific non-catalyst Adjuvant to the anode [3] is able to significantly enhance the SWNT formation.

EXPERIMENTAL

The electric arc reactor is vertical. Emission spectroscopy on the plasma is performed in-situ through side windows. Parameters and related value range investigated are: distance between electrodes (1 to 3 mm), current intensity (50 or 80 A), He pressure (40 or 60 kPa), catalyst type (Fe, Gd, Ni/Co, Ni/Y), catalyst dispersion in the anode (homogeneous, heterogeneous), anode composition (graphite + catalyst, or graphite + catalyst + Adjuvant). Heterogeneous dispersion corresponds to standard graphite anode for which a hole is drilled at the center of it, subsequently filled with graphite powder and catalyst, while homogeneous anode are specifically prepared by a pressureless sintering technique for the catalyst being homogeneously dispersed into the anode [4]. Products formed were investigated by transmission electron microscopy.

RESULTS

Using standard anode (hollowed graphite anode filled with graphite + catalyst powder) combined with standard conditions (1 mm, 80 A, 60 kPa), for a Ni/Y catalyst results in regular SWNT formation in both the web and collaret, associated with impurities (catalyst remnants, amorphous carbon, poorly organised polyaromatic carbon, fullerenes, multiwall carbon shells), which all are observations somehow consistent with previous work [5]. However, deviations with respect to the standard conditions promote the prevalent formation of other carbon nanophases. For instance, double-wall carbon nanotubes (DWNTs) can form in the web preferentially to other types of nanotubes by using standard conditions but the catalysts (Ni/Co or Fe) homogeneously dispersed in the anode (Figure 1).

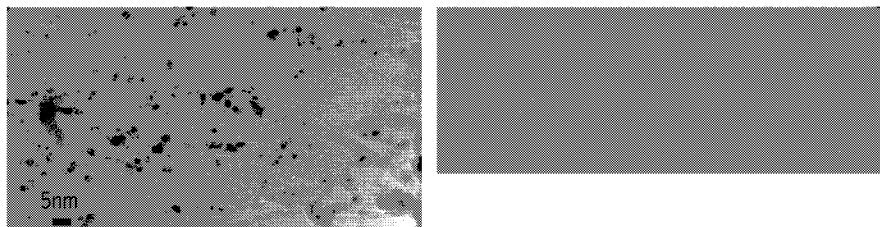


FIGURE 1. (a) TEM image showing DWNTs. Because graphene π electrons are internally satisfied thanks to the interaction between concentric tubes, DWNTs remain isolated or gather into small diameter ropes containing few tubes only. For the same reason, DWNTs appear straighter than SWNTs. (b) HRTEM image of a small rope showing the prevalent occurrence of DWNTs, but regular SWNT (1.4 nm diameter, up right) and MWNTs (3-walls, bottom right) are also present as minor components.

Meanwhile, single-wall nanocapsules (SWNCs) are preferentially formed along with poorly organised polyaromatic carbon in the collaret (and cathode deposit) (Figure 2).

For comparison, same conditions (Ni/Co) but using a standard (heterogeneous) anode result in the absence of web and the moderate formation of SWNTs (and the absence of SWNCs) in the collaret.

One of the most relevant results we have obtained is the possibility to increase the production yield in the web by 230% by adding a specific Adjuvant to the anode [3]. The yield for the collaret also increases, though more moderately, so that the total increase in the production yield of SWNT-containing materials was ~67% (Figure 3).

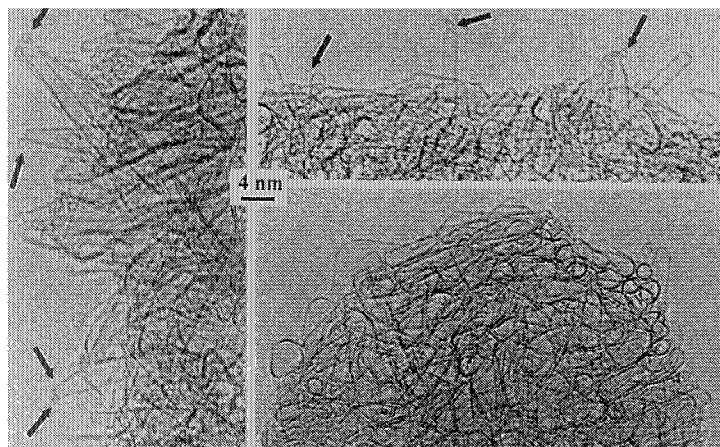


FIGURE 2. HRTEM images showing SWNCs, gathered into pellets for the same reason as SWNTs gather into bundles (van der Waals attraction). SWNCs tend to attract C_{60} molecules at their tips (arrows), revealing both the occurrence of pentagon rings responsible for the closing of the structure and the acceptor character of the C_{60} , attracted by the localised double bonds at the 5-6 ring junctions.

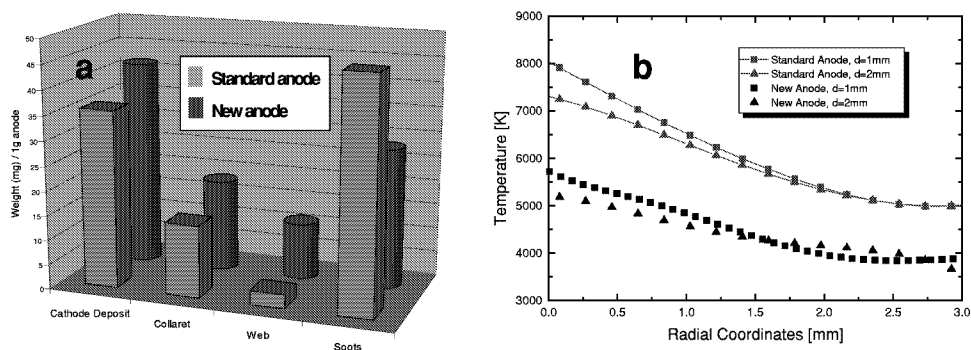


FIGURE 3. (a) Comparison of the difference in the production of (left to right) cathode deposit, collaret, web, and soot with (back) and without (front) adding the Adjuvant in the anode. (b) Whatever the electrode gap (1 or 2 mm), adding the Adjuvant to the anode (bottom plots) lowers the plasma temperature by ~ 2000 K, as a possible favorable condition for the enhancement of SWNT formation.

Although not quantified yet, TEM observations indicate that the SWNT/impurity proportions in the materials is equal or even better than in regularly produced web and collaret. Impurities are merely catalyst remnants, amorphous or poorly organised carbon, and possibly some SWNCs, which presumes that the subsequent purification

procedure could be less detrimental (i.e., less oxidising) to nanotube integrity, since there is no need to remove any well-organised, polyaromatic carbon structure (such as multiwall carbon shells). As these are non optimised results, further improvements in the SWNT yield are expected.

Relationships between the plasma characteristics and the type of carbon nanophase formed are not well understood yet. Plasma temperature depends on the catalyst type, and may vary from about 4000 K from a catalyst to another at the center of the plasma [6]. However, a common feature is that a huge vertical gradient (~ 500 K/mm) rapidly establishes (after ~ 0.5 mm from the center in the radial direction) from the bottom to the top of the plasma, as a probable consequence of convection phenomena (Figure 4a). The zone of actual SWNT formation is beyond the limit of the volume analysable in the radial direction, corresponding to colder areas. Besides, the C_2 concentration

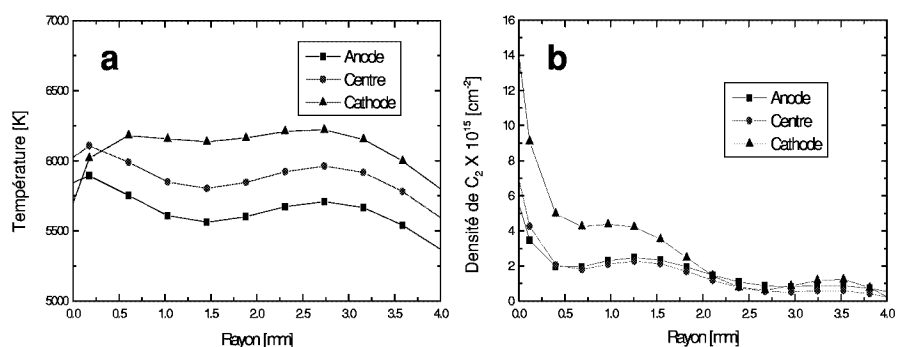


FIGURE 4. Typical temperature (a) and C_2 concentration (b) profiles in the plasma from the anode (square), to the plasma center (dot) and to the cathode (triangle) for standard conditions. Gradients are similar whatever the catalyst, although absolute value may vary.

increases dramatically from the anode to the cathode, and decreases dramatically in the radial direction (Figure 4b). This demonstrates that C_2 moieties are secondary products resulting from the recombination of primary species formed from the anode. On the other hand, it demonstrates that C_2 moieties may be the building blocks for MWNTs, but not for SWNTs.

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