Available online at www.sciencedirect.com
ScienceDirect
Diamond & Related Materials 17 (2008) 1482–1488
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Large-scale production of high-quality multi-walled carbon nanotubes: Role of precursor gas and of Fe-catalyst support

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Abstract

The crucial role of precursor gas (PG) and of catalyst support (CS) in the growth of multi-walled C nanotubes (MWCNTs) by iron-catalysed chemical vapour deposition (CVD) is evidenced. This is accomplished by comparing structural and morphological properties of MWCNTs synthesised by the use of different PGs (ethane and isobutane) and CSs (silica and alumina). The results of analyses, carried out on catalysts and C deposits by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy (RS), thermo-gravimetry (TG) and X-ray diffraction (XRD), demonstrate that Al_2O_3-supported catalysts are more efficient than SiO_2-supported ones in decomposing hydrocarbons. The use of i-C_4H_{10} as PG allows reducing Fe-encapsulation and improving yield (Y_C) and selectivity, so as the large-scale production ($Y_C > 900$ wt.%) of high-quality nanotubes can be operated even at moderate reaction temperature (600 °C) after proper calibration of Fe-load (29 wt.%) and catalyst reduction temperature (500 °C).

PACS: 63.22.+m; 68.37.Hk; 68.37.Lp; 81.07.De; 81.16.Hc
Keywords: Carbon nanotubes; MWCNT; Isobutane; Fe catalysts; Raman spectroscopy; Chemical vapour deposition

1. Introduction

Scalability, need of little post-growth processing and direct synthesis on a substrate variety, which allows easily integrating nanotubes (CNTs) into devices, are the most attractive among the manifold advantages of CNT production by CVD technique [1,2]. A wide variety of precursor gases, catalysts and supports can be used. Transition metals, such as Co [3], Ni [4] and Fe [5], seem to be the most active catalysts. Methane [6–8], acetylene [8,9], and benzene [6] are most frequently utilised as precursors. Alumina and silica are often reported as catalyst supports, both as powder-materials and as diffusion-barrier layers onto silicon wafers [9–11].

Many efforts have been devoted to the achievement of a well-controlled growth process with the aim of tailoring the CNT properties on the requirements imposed by the application of interest. Actually, nowadays, the control of CNT diameter is accomplished by adjusting the size of catalytic nanoparticles [12]. However, in view of their use in industrial applications, the crucial task is still represented by the possibility of producing on a large scale well-crystallised CNTs with high purity-degree (i.e. with no amorphous carbon inclusions and no encapsulated catalyst-particles).

Recently, surprisingly high yields and extreme purity-degrees have been achieved in the growth of vertically aligned single-walled C nanotubes (SWCNTs) by point-arc microwave plasma CVD [11]. A very high density of catalytic iron-nanoparticles has been generated by dramatically enhancing the surface-diffusion barrier of catalytic atoms through the use of an ultra thin Fe/Al_2O_3 sandwich-like structure onto Si-substrates [11]. Although the commonly utilised powdered support-

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doi:10.1016/j.diamond.2008.01.060

materials cannot guarantee efficient surface density of catalytic nanoparticles, good-quality MWCNTs with yields acceptable for industrial production have been synthesised by ethane decomposition over alumina-supported iron-catalysts (ICs). As pointed out [7,13], in the most of cases, IC encapsulation seems to constitute still a technical drawback, which may even strongly limit yield to C deposits whenever silica supported catalysts are used [14].

In this work, isobutane, whose use for CNT production, as in our knowledge, has never reported before in literature, is proposed for the first time as a C source and its highly performing behaviour is demonstrated. In particular, the crucial role of precursor gas and of catalyst support in the growth of nanotubes by Fe-catalysed CVD is emphasised. For this purpose, MWCNTs are synthesised by the use of different PGs (E = ethane, B = isobutane) and CSs (S = silica, A = alumina). The results of analyses, carried out on catalysts and C deposits by SEM, HRTEM, RS, TG and XRD, demonstrate that A-supported ICs are more efficient than S-supported ones in hydrocarbon decomposition. The use of B as PG consents to reduce Fe-encapsulation and to improve selectivity. This allows minimising post-growth oxidation processes, necessary for defect removal, but potentially dangerous for CNT integrity. The performances of B as a PG are tested in a wide range of reaction temperatures (400–750 °C) by considering A-supported ICs with diverse iron-loads (10–40 wt.%) pre-treated in H_2 at different temperatures (500–700 °C).

2. Experimental details

Catalysts are prepared by wetting SiO_2 and Al_2O_3 grains (size: 80–150 μm and 75–125 μm, respectively) in an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ with proper Fe concentration. After drying (120 °C) and calcination (750 °C), catalyst precursor is reduced in H_2 flow as indicated in Table 1. Catalyst, placed in a quartz boat inside a quartz tube, is heated in H_2/He flow up to the desired reaction temperature. Then, He is replaced with the PG (C_2H_6 or i-C_4H_{10}). In all the reactions, a 1:1 H_2/hydrocarbon volume ratio and a total flow-rate of 120 sccm are used. Sample codes and synthesis conditions are reported in Table 1. Yield is calculated, in agreement with [10,13], by weighing catalyst after reduction and reaction products after synthesis. After reactions, products are cooled down to RT in He atmosphere. Support and remaining iron particles are removed with (1 M) solutions of NaOH and of HCl, respectively. C deposits are finally washed in distilled water and dried (110 °C).

Table 1
Codes and preparation conditions of investigated samples

Sample code	t_S (h)	m_0 (g)	Y_C (wt.%)
$E_{750}/20S_{650}$	1.75	1.00	35
$E_{750}/20S_{500}$	1.75	1.04	46
$B_{750}/20S_{500}$	1.75	1.00	137
$E_{750}/20A_{500}$	1.75	1.02	283
$B_{750}/20A_{500}$	1.75	1.00	604
$B_{600}/10A_{500}$	2.00	0.50	193
$B_{600}/17A_{500}$	2.00	0.50	828
$B_{600}/29A_{500}$	2.00	0.50	913
$B_{600}/40A_{500}$	2.00	0.50	515
$B_{500}/29A_{700}$	2.00	0.50	299
$B_{600}/29A_{700}$	2.00	0.50	438
$B_{700}/29A_{700}$	2.00	0.50	1434

Sample code is inclusive of information about precursor gas (E = ethane, B = isobutane), Fe-load (wt.%) and support of catalyst (S = silica, A = alumina); first and second subscripts represent synthesis and reduction temperatures, respectively. Time of synthesis (t_S) and catalyst amount utilised (m_0) are reported together with C yield attained (Y_C).

Purified samples are examined by SEM (JEOL JSM 5600LV, 20 kV) in order evaluate the selectivity towards nanotubes achieved under the different synthesis conditions. Morphologies, dimensions and crystalline structure of nanotubes attained are investigated by HRTEM (JEOL JEM 2010, 200 kV, equipped with a Gatan 794 Multi-Scan CCD camera). In order to determine their crystallinity degree, Raman scattering is measured at RT in the 100–3100 cm^{-1} spectral range by using a double monochromator (Jobin Yvon Ramanor U-1000) equipped with a microscope (Olympus BX40, X100 objective unless diversely specified) and a photomultiplier (Hamamatsu R943-02) operating in photon-counting mode. The 514.5 nm line of an Ar^+ laser (Coherent Innova 70) is used for excitation. In order to evaluate purity, ~5 mg of each sample is placed in an alumina pan and analysed by TG (TA Instruments SDTQ600) in the 30–800 °C temperature (T) range at a 20 °C/min scan rate in a 100 cc/min air flux. Further technical details concerning SEM, HRTEM, TG and RS measurements, as well as Raman spectra decomposition, can be found in [14–16].

XRD analysis (Ital Structures APD 2000) of catalyst is carried out using Cu K_α radiation source. The 5–80° 2θ angle range is analysed in step scan mode (step: 0.02°, counting time: 1 s). Temperature programmed reduction (TPR) measurements are carried out in a typical flow apparatus in order to test the reduction profile of catalysts. Catalyst precursors are heated up to 900 °C (rate: 10 °C/min) in an ultra-high purity H_2/Ar mixture (5 vol.% H_2). A thermo conductivity detector (TCD) connected to a PC for data storage and processing monitors hydrogen consumption. The effluent gas is passed through a molecular sieve cold trap and a tube filled with KOH, placed before TCD, in order to remove water and CO_2, respectively.

3. Results and discussion

3.1. Crucial role of precursor gas and catalyst support

The effect of PG (C_2H_6 or i-C_4H_{10}) and CS (SiO_2 and Al_2O_3) on yield and selectivity of MWCNT growth is investigated by studying products of reaction at 750 °C over 20%Fe catalysts reduced at 500 °C. Yields attained are reported in Table 1. The results of SEM, RS and TG analyses on purified samples are illustrated in Figs. 1 and 2.

Regardless the CS nature, the synthesis in B produces higher yields than in E. In addition, as proved by the comparison between SEM micrographs of samples $E_{750}/20S_{500}$ and $B_{750}/20S_{500}$ (Fig. 1), it results are more selective. For a given PG, A-supported Fe-catalysts exhibit higher catalytic activity in hydrocarbon decomposition than the S-supported ones with no loss in