

Experiments on C nanotubes synthesis by Fe-assisted ethane decomposition

M.G. Donato^a, G. Messina^a, C. Milone^b, A. Pistone^b, S. Santangelo^{a,*}

^a *INFM, Dipartimento di Meccanica e Materiali, Facoltà di Ingegneria, Università "Mediterranea", Località Feo di Vito, 89060 Reggio Calabria, Italy*

^b *Dipartimento di Chimica Industriale e Ingegneria dei Materiali, Facoltà di Ingegneria, Università di Messina, Contrada di Dio, 98166 Messina, Italy*

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Abstract

We performed experiments on the synthesis of carbon nanotubes (CNTs) by iron-catalyzed chemical vapor deposition (CVD) in $C_2H_6+H_2$ atmosphere. We varied flow-rates of reactant gases (ethane: 30–120 sccm, hydrogen: 0–120 sccm), as well as their ratio, in order to study the evolution of the growth kinetics. We used scanning electron microscopy, high-resolution transmission electron microscopy and Raman spectroscopy to investigate the morphologies, dimensions and crystalline structure of the samples. Our results demonstrate the crucial role played by H_2 in the enhancement of C diffusion-rate and in the consequent development of ordered and smooth graphene layers. A faster growth-rate is achieved by the increase of C_2H_6 flow-rate. However, if H_2 flow-rate is not adequately enhanced, the improvement is only apparent. The excess of C supplied gives rise to deposition of amorphous carbon onto the CNT walls, and to the co-production of different nanostructures. A substantial agreement is found with results reported for CVD growth of CNTs by the use of different catalysts, reactants and gas-flowing setups.

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1. Introduction

Thanks to their unique physical properties, CNTs possess great potentialities in a large variety of advanced applications (an extensive review on this field can be found in [1,2]). Among the manifold techniques successfully utilized for their preparation [1,2] the catalytic CVD is increasingly preferred for large-scale CNT production. It allows selectively synthesizing single- (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) by properly choosing the carbon precursor [3]. Light hydrocarbons, such as methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4) and ethane (C_2H_6), are often used as C source for MWCNT preparation over different transition-metal catalysts (Fe, Co, Ni or related alloys) [4–8]. Reactive gases, such as ammonia (NH_3) and hydrogen (H_2), are sometimes added in order to preserve the metal catalytic-activity [4–8]. Their presence in the growth atmosphere results in removal of amorphous carbon (AC), re-

sponsible for metal passivation upon high C supply [4–6], with consequent improvement of surface- and bulk-diffusion.

At a given synthesis temperature, the competition between AC formation and catalyst-activity preservation by H_2 (or NH_3) is ruled by the gas flow-rates and their ratio. Different growth regimes are achieved depending on which of them ultimately prevails. According Juang et al. [4,5], the growth of CNTs is hampered in case of low C supply-rate and high C diffusion-rate, as well as in the opposite case. In the former growth regime (“C-Supply on catalyst surface Limited”) CNTs exhibit a spaghetti-like morphology or a curly structure. In the latter (“C Diffusion-rate Limited”) the excess of C atoms deposit in amorphous phase on metal and nanotubes. The optimal condition for steady growth of high-quality nanotubes is obtained when the C supply-rate equals the C diffusion-rate.

In this paper, experiments on the CNTs synthesis by Fe-catalyzed CVD in ethane + hydrogen atmosphere are carried out, and the evolution of the growth kinetics, produced by the variation of C_2H_6 (30–120 sccm) and H_2 (0–120 sccm) flow-rates and their ratio, is investigated. A wide variety of different morphologies are obtained, ranging from high-quality CNTs

* Corresponding author. Tel.: +39 0965 875305; fax: +39 0965 875201.

E-mail address: saveria.santangelo@unirc.it (S. Santangelo).

with no AC inclusion to highly-defective tubular structures coated by a thick AC deposit. The results of the growth experiments are compared with those obtained [4–6] by the use of different catalysts, reactants and gas-flowing setups. From the discussion a substantial agreement emerges.

2. Experimental procedure

In order to perform experiments on the synthesis of CNTs by iron-catalyzed decomposition of ethane (Table 1), we prepared catalysts by wetting SiO₂ particles (Merck, size: 80–150 μm) in an aqueous solution of Fe(NO₃)₃·9H₂O (Fe at 20 wt.%). The wet solid was dried at 100 °C and calcined in air at 450 °C for 2 h in order to obtain the oxidic form of the catalyst precursor. The catalyst precursor (1.00±0.01 g, unless otherwise specified) was placed in a ceramic boat inside a quartz tube (diameter 50 mm, length 700 mm), located in a horizontal electrical furnace, and flushed for 30 min in flowing pure hydrogen at room temperature and finally reduced at 650 °C for 10 min. After such a pre-treatment, we replaced the H₂ flow with a C₂H₆+H₂ mixture. In order to investigate their influence on yield of growth process and morphology of deposits, we varied flow-rates of reactant gases, as well as their ratio. The total pressure was 2 atm in all the experiments.

Carbon yield (Table 2) was calculated, in agreement with [8], as 100 (M–M₀)/M₀, where M is the mass of all the materials (reaction products + catalyst) after synthesis and M₀ is the mass of the catalyst after H₂ pre-treatment. In order to get more insight into the growth problem, the C transformation efficiency was also evaluated, giving the fraction of the overall C supplied during reaction that is transformed to deposits.

After yield evaluation, the silica support was removed by a solution of KOH (1 M) at 105 °C and the resulting material, washed with distilled water, was treated with a solution of HCl (1 M) in order to remove the remaining iron particles [3,8], and subsequently washed with distilled water and dried at 200 °C.

We used scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy (RS) to investigate the morphologies, dimensions and crystalline structure of the purified samples. SEM and HRTEM analyses were conducted respectively on a

Table 1
Growth experiments carried out for 1.75 h at 750 °C in various gas-flowing setups

Experiment	Sample	C ₂ H ₆ (sccm)	H ₂ (sccm)	C ₂ H ₆ /H ₂ flow ratio
1 High C supply-rate and no or small H ₂ addition	1.a	120	0	1/0
	1.b	120	30	4/1
	1.c	90	30	3/1
2 Low C supply-rate	2.a	30	90	1/3
	3.a	50	50	1
3 Fixed mixing ratio	3.b	60	60	1
	3.c	75	75	1
	3.d*	120	120	1

*2.07 grams of catalyst were used, so as the C supply-rate (relative to the catalyst-mass) resulted to be approximately the same as in the preparation of sample 3.b.

Table 2
Results of experiments described in Table 1

Experiment	Selectivity towards CNTs	Sample	Yield (wt. %)	CTE* (wt. %)	CNT morphology
1	Very low	1.a	82.0	6.1	Highly-defective with very thick external AC coating and large outer diameter
		1.b	61.7	4.5	Constituted by undulated graphene sheets with thick external AC layer
		1.c	67.7	6.6	
2	Optimal	2.a	20.7	6.1	AC free, consisting of sequence of very smooth graphene layers
3	Decreasing with increasing yield	3.a	18.7	3.3	Large diameter due to very thick external AC layer
		3.b	34.7	5.1	Thin AC layer on tube walls
		3.c	36.5	4.3	Thick AC tube-coating
		3.d	37.7	5.7	Curly, almost AC free

*CTE (standing for “carbon transformation efficiency”) is the relative amount of C supplied that is transformed to deposits.

20 kV JEOL JSM 5600LV instrument and on a 200 kV JEOL JEM 2010 analytical electron microscope (LaB₆ electron gun) equipped with a Gatan 794 Multi-Scan CCD camera for digital imaging. Raman scattering induced by 2.41 eV excitation was measured by using a Jobin Yvon Ramanor U-1000 double monochromator operating in micro-Raman configuration. By the use of a X100 objective, the laser spot was focused to a diameter of approximately 1 μm. Further technical details concerning SEM, HRTEM and RS measurements, as well as Raman spectra decomposition and interpretation can be found in Refs. [9,10].

3. Results of experiments and discussion

Various gas-flowing setups were examined in the three experiments performed (Table 1). Results correspondingly obtained are briefly summarized in Table 2. The selectivity towards nanotubes was evaluated by SEM analysis (Fig. 1). The examination of CNT morphology by HRTEM revealed that in all the experiments MWCNTs formed (top of Fig. 2). We observed the presence of some Fe-nanoparticles encapsulated within the tubes. No one of these particles was located at the tip of the tube, indicating that a “base-growth” mechanism occurred. It is believed that the metal-particles are sucked inside the tube channel during CNT precipitation as an effect of the surface tension at the growing-nanotube/catalyst interface [11]. As discussed elsewhere [9], their relative amount diminishes with increasing the flow-rate of the C source. By varying flow-rates of reactant gases and their ratio, we obtained a large variety of different morphologies, ranging from high-quality CNTs,

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