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Study of parameters important for the growth of single wall carbon nanotubes

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Abstract

We report on the production of single wall carbon nanotubes (SWNTs) using a continuous wave (cw) 10.6 μm CO_2-laser. A wide range of experimental parameters such as the catalyst composition, the gas-atmosphere, the gas-pressure, the gas-flow, the laser-mode (continuous or pulsed) as well as the temperature environment and their influence on the formation of SWNTs has been investigated. Characterization of the produced SWNT material by various techniques shows the importance of two parameters: the metal in the target rod and the temperature environment for the evaporated carbon and metal species acting as feedstock for the formation of SWNTs. These results will help to develop a controlled and efficient method for the production of SWNTs.

Keywords: Carbon nanotubes; Laser ablation; Characterization; Growth

1. Introduction

Single wall carbon nanotubes (SWNTs) currently are paving the way for revolutionary advancements in various areas of technologies ranging from fuel cells [1] up to electronic devices [2]. Here, many of the potential applications are depending on the specifics of SWNTs, like their diameters and chiralities. Therefore, the availability of "tailored" samples in large amounts certainly would boost the further progress in these innovative fields. However, the production of SWNTs in a controlled way and in large amounts currently represents a major challenge to solve. Today, one way which allows the production of SWNTs by systematically varying the experimental parameters, is the laser ablation method. Using this technique certainly will give information about the possibilities for a controlled growth and a future up-scaled production.

In this article we report on the study of parameters important for the controlled growth of SWNTs using a continuous wave cw-CO_2 laser technique [3]. The effects of catalyst composition, type of gas, gas pressure, gas flow, laser power, and the effects of the laser operating mode on the formation of SWNTs have been investigated. All changes of sample characteristics can be related to two parameters: The used metal in the target rod, and the temperature environment necessary for the assembling of SWNTs. These two parameters play a key role in the whole production process.

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2. Experimental

SWNTs were produced employing a CO_2-laser operating in continuous wave (cw) mode at a wavelength of 10.6 μm [3]. The laser beam is guided into a stainless steel chamber where it is focussed with a spot size of ~1 mm onto the lateral side of a graphite/bi-metal composite target rod (Fig. 1). The evaporation chamber is evacuated and filled from its bottom side with inert gas. Under best conditions, up to 200 mg of the target material gets evaporated. The experiments were performed under the following conditions:

(a) Metal composition of the graphite target (in at%): Single metals: Ni (2), Co (2), Y (0.5), Fe (2); bi-metallic mixtures: Ni/Y (4.2/1), (2/0.5), (1/0.25), (0.6/0.6), (0.5/0.13); Ni/Co (4.2/1), (2/2), (2/0.5), (1/0.25), (0.6/0.6), (0.5/0.13); Ni/Fe (4.2/1), (2/0.5), (0.6/0.6); Co/Y (2/0.5), Ni/La (2/0.5).

(b) Gas, pressure and flow-rate: argon, nitrogen at 50, 100, 200, 300, 400 and 500 Torr. Flow-rates: 1, 0.6, 0 l/min. Helium at 400 Torr at a flow-rate of 9 l/min.

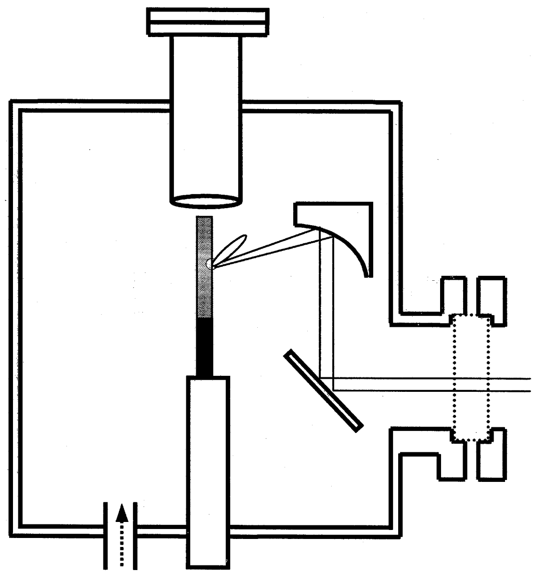

Fig. 1. Evaporation chamber: The laser is focused onto the target rod, which gets heated during the evaporation. Different grey tones represent different temperature zones.

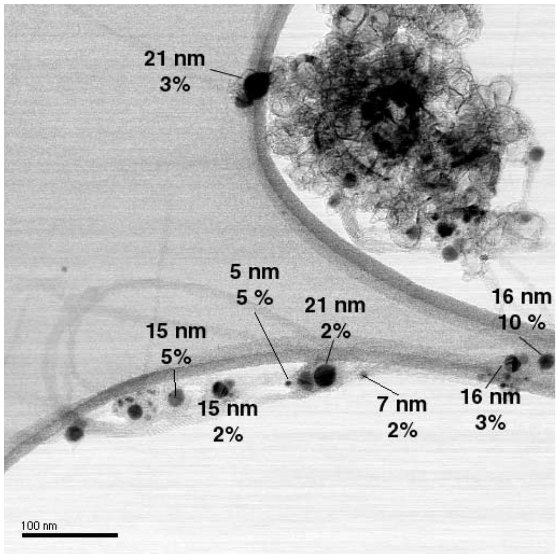

Fig. 2. TEM image of the Ni/Y sample showing bundles of SWNTs and catalytic nanoparticles whose size and Y content is indicated.

(c) Laser power density and cw versus pulsed mode: 12, 9, and 6 kW/cm^2 in pulsed mode at a frequency of 2 kHz (not Q-switched).

The as-produced carbonaceous materials have been investigated using scanning and transmission electron microscopy, (SEM and TEM, respectively) (Fig. 2). More images can be found in [3,4]. The overall metal content has been determined by inductively coupled plasma spectroscopy (ICPS). Individual metallic nanoparticles have been characterized by energy dispersive spectroscopy (EDS) and energy electron loss spectroscopy (EELS).

3. Results and discussion

3.1. Laser–target interaction

The first step in the laser experiments is the interaction of the laser beam with the (metal-) graphite target. Here, the appropriate laser conditions play an important role. Working under cw mode conditions and with power densities of 12 kW/cm^2, evaporation rates of 200 mg/h and high quality SWNT material using Ni/Y/graphite targets can be achieved. Lowering the power density to 9 kW/cm^2, leads to evaporation rates of 90 mg/h without a change of the sample quality. In both cases a heating of the rod can be observed (ranging gradually from 3000°C in the focal spot to 1200°C in a distance of 1 cm around the laser interaction point, see Fig. 1). However, under pulsed mode conditions at power densities of 6 kW/cm^2, no heating of the target is observed and the evaporation rate falls as low as 4 mg/h. Under these conditions, the produced soot material is dominated by amorphous carbon. These experiments clearly show that working under cw conditions, one part of the laser energy continuously is dissipated as heat into the target, which then acts as a local furnace. The rest of the incoming energy is used for the evaporation of the target material. Under pulsed conditions the time scale for heating the target is too short and all the laser energy is used for the evaporation process. Furthermore, one can see from the outcome of the cw and pulsed experiments that the assembling of carbonaceous fragments into SWNTs is directly connected to a temperature environment of sufficient high thermal energy which experience the evaporated species. Beside the laser parameters, the metals in the target rod also have an effect on the laser–target interaction, especially on the evaporation rate. However, the influence of the metals is much more important in the next step of the production process, i.e. the gas phase.

3.2. Gas phase interactions

The gas phase is the part of the experiments where SWNTs are formed. Here, carbon and metal interactions are from great importance, and parameters like type of metal and its concentration, gas, pressure and flow, as well as the temperature environment are crucial factors.

3.2.1. Effect of target composition

Without metals, no SWNTs are formed [4]. The same results are observed with rods containing Y and Fe. However, adding metals like Ni and Co to the pure graphite target, a powdery soot is obtained containing a few and in most cases only isolated SWNTs. Using graphite/bi-metal targets, high amounts of SWNTs organized in bundles are found (Fig. 2). Highest yields are achieved with Ni/Y (4.2/1) (2/0.5) and Ni/Co (2/2). Lower amounts belong to the lowest bi-metal concentrations. The metals can be found in the produced samples as nanoparticles with diameters of 5–25 nm embedded in amorphous carbon. A global ICPS analysis shows that the produced soot contain roughly the same metal composition than was used in the target rod: 2.6/2.3 wt% for the Ni/Co sample with starting composition 2.8/2.8 wt%, and 19.6/6.6 wt% for the Ni/Y sample with starting composition 17.6/6.6 wt%. This points to a quite homogeneous evaporation process for carbon and metals. Using the Ni/Y sample, EELS studies on individual particles in the vicinity of the SWNTs (Fig. 2) confirm that these are pure metals and EDS measurements reveal an average Y content of 9 ± 3 wt% which roughly corresponds to the eutectic point at 10 wt% in the Ni/Y phase diagram. It becomes clear that the presence of certain metals is absolutely necessary for forming SWNTs. Probably there is an optimum metal and metal-graphite composition, and as well an optimum nanoparticle size between 5 and 25 nm. Whatever the interaction between carbon fragments and the metals might be, at this size scale, some physical or chemical properties of the metals, like solidification temperature, diffusion coefficients, segregation dynamics, and segregation induced stress [5], may promote a favorable interaction with the carbon fragments in the gas phase.

3.2.2. Effect of gas, pressure and flow

No difference in the sample quality using argon and nitrogen can be observed. Both gases allow the formation of high yields of SWNTs between 200 and 400 Torr, whereas below 100 Torr the formation of amorphous carbon is favored. Using helium, no SWNTs have been formed under the conditions employed. Changing the flow conditions does not lead to differences in the quality and quantity of the produced SWNTs material. These results are strongly connected to the temperature environment experienced by the species in the gas phase. Here, the use of different gases can strongly influence the cooling rates and, in the case of helium, lead to a rapid lowering of the thermal energy necessary for forming SWNTs [6]. Therefore, the optimum pressure range for helium lies above the values found for argon and nitrogen. On the other hand, flow rates certainly have an influence on the temperature; however, in our experiments they are far too small to induce significant changes in the ambient temperature.

4. Conclusions

There are essentially two parameters, which play a key role in the formation process of SWNTs: The kind of metal and its concentration in the target rod, as well as the temperature environment for the evaporated carbon and metal species. This has to be kept sufficiently high at around 1200°C and can be controlled by the laser power and mode, the gas, pressure and flow.

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