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RAPPORT FINAL DE CONTRAT

PRÉPARATION DE NANOTUBES DE CARBONE ET ADSORPTION DE L'HYDROGENE : ÉTUDE DE FAISABILITÉ

SECTION : PRÉPARATION DE NANOTUBES

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SYNTHESIS OF MULTI-WALLED CARBON NANOTUBES ON OHMICALLY HEATED CARBON PAPER

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ABSTRACT

A new CVD method for growing carbon nanotubes while consuming little energy is presented. In this method, the metal catalyst dispersed on the fibers of a carbon paper is Ohmically heated up to 600-700°C to decompose gases like acetylene, ethylene or carbon monoxide in order to grow carbon nanotubes and/or nanofibers on their carbon fiber support. These nanostructures are from 5 to 25 nm in diameter. The hairy carbon paper thus obtained may find use as high specific area electrode.

INTRODUCTION

Because of their exceptional properties, carbon nanotubes have generated increasing interest in the scientific community. In fact, they are the strongest material known (Young's modulus of 1 to 4 TPa) (1,2), as well as the best conductor of electricity (3) and heat (4). There are many possible applications of nanotubes, ranging from nanoelectronics (5,6) to the reinforcement of materials (7). However, certain applications require the production of nanotubes in significant quantities at reasonable cost (e.g. material reinforcement (7) and hydrogen storage (8,9,10)), while others require a control of the tube parameters during synthesis (e.g. nanoelectronics and flat panel displays (11)).

At the moment, carbon nanotubes can be produced by three different methods: laser ablation, evaporation in an electric arc, and CVD. The first two methods are based on the same principle: local evaporation of a graphite substrate enriched with a metal catalyst in order to obtain a condensation of the vapour in the form of nanotubes. In the CVD technique, a carbon-containing gas is brought into contact with a (hot) metal catalyst; the gas is dissociated, and the carbon feeds the growing nanotubes. The laser and arc methods create single-walled nanotubes (SWNT) in a tangled deposit, and significant energy must be provided to vapourize the graphite; this results in a process which is energetically unfavourable compared to the CVD method. To atomize a mole of carbon, an energy of 717 kJ has to be supplied, while in the CVD approach the decomposition of

a mole of acetylene provides 227 kJ. With the CVD method, it is possible to control the place where the nanotubes are formed (11,12,13), but the problem of amorphous carbon, which is also produced by pyrolytic decomposition of the carbon-containing gas has to be overcome. In addition, the CVD approach normally produces multi-walled nanotubes (MWNT), because of the low operating temperatures which are used.

A new CVD procedure has been conceived. It only heats the surface containing the catalyst and the gas near this surface and allows the growth of nanotubes with a low heating power (about 25 W for 1 cm^2 of carbon paper), without producing amorphous carbon. It may be possible to adapt this new CVD approach to the growth of SWNT.

EXPERIMENTAL

A strip of carbon paper is soaked in a solution of 2 ml of tetraethyl orthosilicate mixed with 2 ml of ethanol, 3 ml of 1.5 M metal nitrate, and 0.5 ml of HF 10%. The metal is the catalyst for the reaction. The addition of HF catalyses the formation of a silicate gel. The carbon paper is dipped into the gel in formation, then it is wiped off and dried for 5 minutes at room temperature. By this method a fine deposit of silicate containing a homogeneous dispersion of metal nitrate is obtained, which will ultimately produce the nanometer-size catalyst particles. The ends of the carbon paper strip are then clamped between two electrodes, and a current (5A at 5V) is passed through the paper in order to Ohmically heat the paper (fig. 1). The carbon paper is first heated to 400 ^{0}C under an argon atmosphere, to decompose the nitrates and obtain the oxidized metal. A reduction process produces the metal, which is supported by the silicate. This reduction is carried out in the presence of hydrogen at a temperature of about 500 ^{0}C for about 2 or 3 minutes. Then the current is adjusted to obtain the desired growth temperature and a gas mixture made up of 90% argon, 5% hydrogen, and 5% of the carbon-containing gas is introduced for 30 minutes. The temperature of the carbon paper is measured pyrometrically.

In this study, three transition metals were used as catalysts (Co, Ni, Fe) and three gases (C_2H_2, C_2H_4, and CO) were used as carbon feedstock. The catalysts were used separately and also mixed in equal parts. The combination of one or two metals has previously been tested by other authors (14,15,16) using the classical CVD technique wherein the substrate is heated in a tubular furnace. In addition, we have also tested CoNiFe, a catalyst consisting in the three metals in equal proportions.

The energy required to separate the carbon atoms of the three carbon-containing gases is different for each of the three gases used. Hence the conditions necessary for the carbon atoms to form nanotubes in the presence of the catalyst will require a specific optimum temperature for each gas. The following optimum temperatures for each gas were determined and used for all experiments: 600 ^{0}C for C_2H_2,, and 700 ^{0}C for C_2H_4 and CO. For higher temperatures there was no nanotube formation. The samples were analyzed by scanning electron microscopy (SEM), field-effect electron microscopy (FEM), and by transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

Figure 2 presents a typical micrograph of nanotubes synthesized by the new method using the pyrolysis of acetylene on Fe at 600°C. The fibers of the carbon paper used as support have a diameter of about 5μm. They are covered by a thin layer of silicate containing Fe particles. Silicate flakes are also observed in between the fibers. The nanotubes grow directly on the silicate, with a metal particle at their base. This is shown in fig. 3a on a FEM micrograph on which the carbon nanotubes are almost transparent allowing the observation of the more opaque metal particle at the base of the nanotube. In addition, in figure 3b we see that there is no metallic particle at the tips of the tubes. The absence of charging indicates that the nanotubes are in electrical contact with their conducting support. Figure 4 shows that there is no amorphous carbon on the tubes or on the support. The diameter of the MWNT varies between 5 and 25 nm and their length is about 10 μm. The nanotubes are of quality comparable to those obtained by classical CVD methods.

We have examined the micrographs obtained by SEM to compare the efficiency of the catalysts for each of the gases. A summary of the results is presented in Table I. Except for Co, which did not produce any carbon nanostructure growth for any of the gases, all the catalysts produced carbon growth with acetylene and ethylene. The density, diameter and length of the tubes are comparable for the two gases. On the other hand, CO produced results only for the FeCo, CoNi and FeCoNi catalysts. We see by analyzing figures 5a and 5b that CoNi is a particularly efficient catalyst, superior to the others tested. Indeed, in this case, the carbon paper is completely covered with a foam of nanotubes. However, it is difficult to make a quantitative comparison between the other catalysts, since the deposits are not perfectly uniform. The best method for comparison would be to weigh the nanotubes which are produced, but this is impossible, given the small weight of the nanotubes compared to that of the carbon paper.

From these results, it seems that all the advantages of the CVD approach are conserved by our new approach. In addition, there are several specific advantages to this approach: (i) the new CVD procedure is easily and quickly implemented, and all the steps (from the synthesis of the catalyst to that of the carbon nanostructure) can be carried out in less than one hour; (ii) only the catalytic sites are directly heated. It avoids deposits of other forms of carbon elsewhere in the reactor; (iii) it is a low power consumption method requiring less than 25 W / cm^2 to produce nanotubes; (iv) finally, the electronic microscopy of the nanotubes is done directly on the carbon paper avoiding manipulations after the synthesis.

In spite of these advantages, the present CVD method using Ohmic heating has also some deficiencies which need to be addressed. Firstly, the temperature is not uniform over the entire surface of the carbon paper. This affects the uniformity of the deposit, since the nanotubes are produced efficiently only when the optimum temperature of the catalyst is used. It is also not possible to exceed 900 ^{0}C with the present experimental procedure. It seems that above this temperature, the structure of the silicate is modified, surrounding the particles of the catalyst, thus preventing their interaction

with the gas. In fact, the samples which were exposed to temperatures above 900 ^{0}C charge up during electronic microscopy, which indicates that the surface is now no longer conducting (fig. 6). The growth of single wall nanotubes requires temperatures of about 1200°C (12). Although these temperatures are easily reachable by the Ohmically heated carbon paper with the present system, succesful growth of SWNT will only occur if the deposition method of the catalyst on the carbon paper is modified.

CONCLUSION

It is possible to grow MWNT by Ohmically heating silicate containing metal catalytic sites spread on carbon paper. Since these nanotubes are in intimate electrical contact with the fibers of the carbon paper they certainly increase the specific area of the carbon paper which may be used as electrode.

The new CVD approach can be improved in many ways, for instance: (i) by better distributing the metal nanoparticles on the carbon paper and hence favoring the formation of smaller nanoparticles; (ii) by changing the present approach wherein a silicate matrix is used to secure the catalytic particles. A direct deposition of metallic clusters onto the carbon fibers might be a solution towards the use of this new CVD approach to obtain SWNT.

Table I

Summary of the production of multi-walled nanotubes (MWNT) or nanofibers (NF) for different combinations of catalyst and carbon-containing gases.

Metal catalyst	C_2H_2 600 ^{0}C	C_2H_4 700 ^{0}C	CO 700 ^{0}C
Fe	MWNT	MWNT	No production
Co	No production	No production	No production
Ni	NF	NF	No production
FeCo	MWNT or NF[a]	MWNT or NF[a]	MWNT or NF[a]
FeNi	MWNT or NF[a]	MWNT or NF[a]	No production
CoNi	MWNT	MWNT	MWNT or NF[a]
FeCoNi	MWNT or NF[a]	MWNT or NF[a]	MWNT or NF[a]

a: remains to be confirmed by TEM

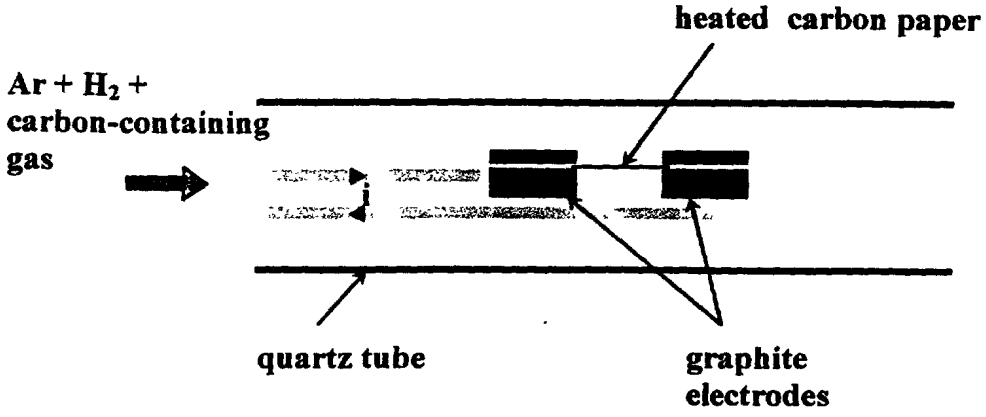

Figure 1: Schematic of the experimental setup

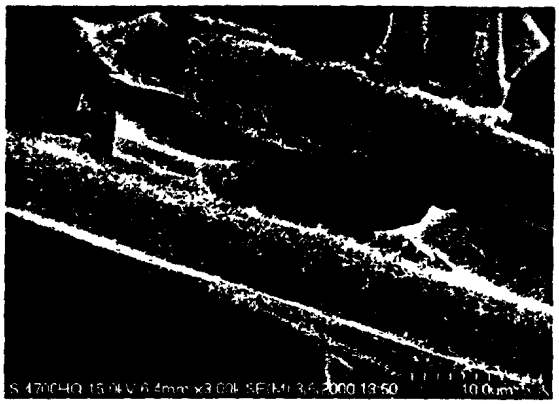

Figure 2: Scanning electron micrograph of carbon nanotubes on carbon paper grown on Fe using acetylene at 600°C

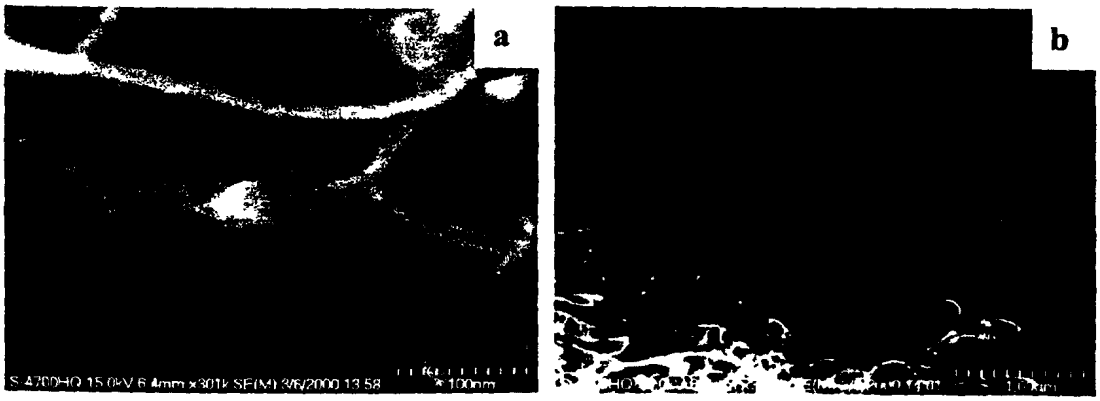

Figure 3a: Field effect electron micrograph of the base of the nanotubes (Fe catalyst/ acetylene/ 600°C)

Figure 3b: Field effect electron micrograph of nanotube tips (Fe catalyst/ acetylene/ 600°C)

Figure 4: Transmission electron micrograph of MWNT grown from acetylene at 600°C on iron in silicate covered carbon fibers

Figure 5a: Scanning electron micrograph of the dense growth of MWNT obtained from ethylene at 700°C on NiCo catalyst in silicate covered carbon fibers

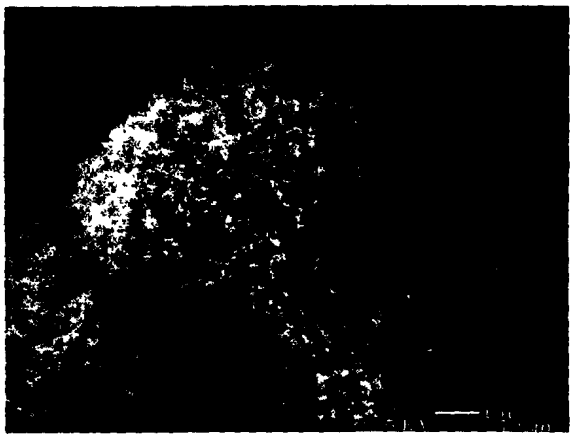

Figure 5b: Enlargement of 5a to show individual MWNT

Figure 6: Scanning electron micrograph of silicate covered carbon paper heated above 900°C

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