Pyrolysis of mixed aerosols : a versatile CVD-based process to produce high yields of clean and long aligned carbon nanotubes

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INTRODUCTION

Because of the great interest of carbon nanotubes in nanotechnology, it is important to control their production regarding their quality, quantity and arrangement. Recently, we have demonstrated that pyrolysis of benzene-based aerosols enables to prepare aligned carbon nanotubes (1). The aerosol was generated with an argon-driven atomiser. However, this device does not allow to control independently the production of aerosol and the other functioning parameters.

In this study, the aerosol is generated using an ultrasonic generator, allowing an independent control of the functioning parameters. In this context, aligned and clean multi-wall nanotubes were produced by pyrolysing toluene-based aerosols. High carbon yield (up to 450 % of Fe consumed during the reaction) and high growth rate (up to 55 μm/min) were obtained.

EXPERIMENTAL

The method is based on catalytic decomposition by pyrolysing mixed liquid aerosols containing both the hydrocarbon and the metallic source. The pyrolysis apparatus is similar to the one used in the previous study (1). An ultrasonic aerosol generator (Pyrosol, RBI company) is used to produce aerosols. Experiments were carried out by using solutions of ferrocene (2.5 or 5 wt %) in toluene. Two different ways are involved : either nanotubes are directly prepared and collected inside the reactor, or silicon substrates are placed inside the reactor and nanotubes are grown on them. For samples collected on the reactor walls, pyrolysis temperature was varying from 750 to 900 °C, and duration was 15 min. For samples produced on Si substrates, pyrolysis temperature was 850 °C and duration was varying from 2 to 45 min.

Samples obtained without substrate were collected by scratching the reactor walls and were analysed by SEM, TEM and TGA under air. Samples obtained on Si substrates were analysed by SEM, and enabled to follow the deposition and the growth rates as a function of experiment duration.

RESULTS

Carbon yield was determined as a function of the catalyst weight consumed during the reaction (yield (%) = $((m_{producted} - m_{Fe\ consumed})/m_{Fe\ consumed})*100$) and was followed as a function of the pyrolysis temperature. The carbon yield is increased when the temperature increases up to 850 °C and/or when ferrocene concentration increases. The maximum yield (450%) is obtained for a 5 wt% ferrocene solution in toluene pyrolysed at 850 °C.

Deposition rate was followed on samples obtained on silicon substrates as a function of experiment duration. From 5 min, the deposition rate is stable around 0.8 $mg/cm^2/min$.

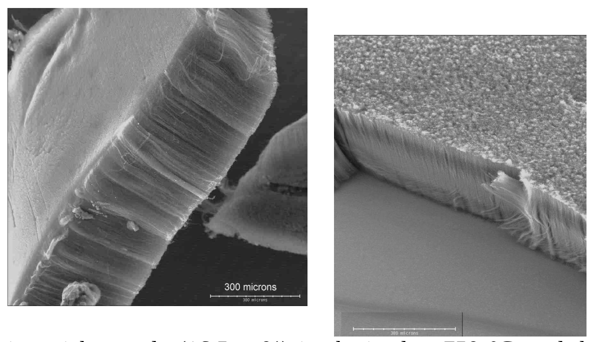
SEM observations (Fig. 1) on samples collected on the reactor walls show carpet-like morphologies which are well defined for samples obtained from 5 wt% ferrocene solution whereas they are looking like chipping for samples obtained from 2.5 wt% ferrocene solution. Nanotubes, distinguished in these carpets or chipping, are aligned. In addition, by-products are almost absent especially for samples obtained at 800 or 850 °C from a 5 wt% ferrocene solution.

Samples obtained on Si substrates are composed of clean nanotubes perpendicularly aligned to the substrate surface (Fig. 1). The growth rate has been followed as a function of the experiment duration. For the first 20 min, the growth rate, in the [40-55] μm/min range, is very high for a CVD-based process, whereas it is slightly lower (30 μm/min) for higher duration.

Figure 1 : SEM observations : left) carpet-like morphology for samples collected on the reactor walls ; right) nanotubes aligned perpendicularly to the Si surface.

TEM observations show partly filled multi-wall carbon nanotubes with almost no by-products. Their diameter are varying in a large range (10-140 nm).

Thermal behaviour under air (from 25 to 800 °C, ramp of 5°C/min) on samples obtained from a 5 wt % ferrocene solution and collected on the reactor walls indicates a weight loss, corresponding to sample oxidation. After thermal treatment, the remaining weight corresponding to iron oxide, allows to calculate the iron content in samples. Thus, the



iron-rich sample (16.5 wt%) is obtained at 750 °C, and the iron-poor sample (2.6 wt %) is obtained at 850 °C which seems to be the cleanest according to SEM observations.

CONCLUSION

Pyrolysis of aerosols generated from an ultrasonic generator is a versatile and continuous process for the production of clean and aligned multi-wall carbon nanotubes. This method enables to get high carbon yield and to grow at high rate (up to 55 μm/min) very long nanotubes (up to 1.6 mm), which is significantly high for a CVD-based process. To the best of our knowledge, such a rapid growth has only been reported by Zhang et al recently (2).

REFERENCES

1. M. Mayne, N. Grobert, M. Terrones, R. Kamalakaran, M. Rühle, H.W. Kroto, D.R.M. Walton, Chem Phys Lett, **338**, 105, (2001)
2. X. Zhang, A. Cao, B. Wei, Y. Li, J. Wei, C. Xu, D. Wu, Chem Phys Lett, **362**, 285, (2002)