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Synthesis of carbon nanotubes from liquid hydrocarbons using a spray-pyrolysis method

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Multiwalled carbon nanotubes have been prepared using catalytic decomposition of solutions of ferrocene in liquid hydrocarbons: n-hexane, benzene and xylenes. The solutions were injected into the reaction furnace using Ar as carrier gas. The experimental investigations were effectuated in a home-made experimental setup using the spray-pyrolysis method, a liquid carbon source based variant of chemical vapor deposition (CVD). The reaction products were analyzed by TEM. The possible role of the hexagonal carbon-cluster based growth mechanism of carbon nanotubes is discussed.

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1. Introduction

Since their discovery by Iijima, carbon nanotubes (CNTs) have been studied intensively for more then 15 years [1]. CNTs are useful because they have remarkable physical properties, in particular their mechanical and electrical properties are promising [2]. Due to their outstanding physical properties, CNTs have important applications, for example: i) in nanoelectronics [3], ii) in field emission based devices [4], iii) in composite materials [5]. For their applications it is crucial to develop techniques for large-scale production of high quality CNTs. The spray-pyrolysis method - a variant of the CVD method - used in our experiments, is suitable for industrial scale-up. Beside this method the DC arc discharge [6] and the laser ablation [7] are also significant in the synthesis of CNTs. In recent years, based on data from different publications, the importance of CNTs in biological applications can be predicted, as the carbon itself has a high affinity with the human body. So CNTs are ideally suited for applications related to DNA and other molecular identification materials [8].

There is a lot of research data referring to the growth mechanism of CNTs: i) the walls of CNTs grow consecutively [9], ii) the CNTs are formed by the folding of graphene layers [10], iii) the walls of CNTs grow simultaneously [11]. Also the ideas of Baker and Kanzow concerning the growth mechanism are interesting [12, 13]. The theory of Kanzow is able to explain the growth of single- as well as that of multiwalled CNTs (MWCNTs). In the last few years some results have been published regarding the role of hexagonal carbon-clusters in the growth mechanism of MWCNTs, using benzene as carbon source [14, 15, 16]. We reported in our previous papers the preparation of carbon nanotubes by spray pyrolisis [17,18] and injection chemical vapour deposition [19]. It seems that our latest experimental data also support the role of hexagonal carbon-clusters in the growth mechanism of MWCNTs.

2. Experiment

2.1 Experimental setup

Our home-made experimental setup - including the sprayer - used for spray-pyrolysis of ferrocene dissolved in liquid hydrocarbons is described in detail in our earlier published works [20,21].

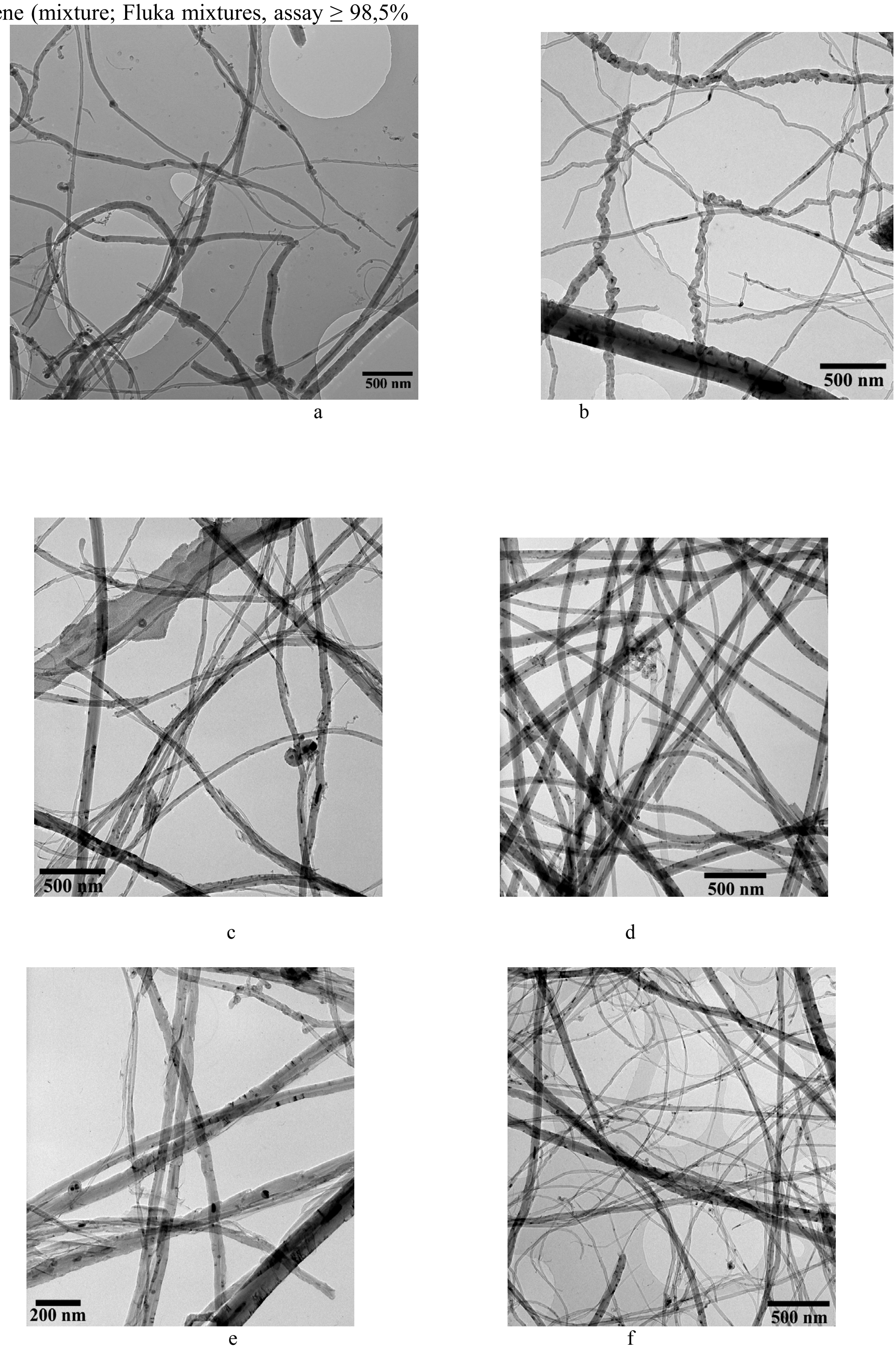
2.2 Experimental procedure

The solution of ferrocene in liquid hydrocarbon and the Ar carrier gas are introduced in the sprayer at the desired flow-rate. The solution is sprayed into the quartz reactor, set to a given temperature, in which the carbon source material is pyrolysed and transformed in CNTs. Characteristic experimental parameters are: the flow-rate of solution 1 ml/min; the flow-rate of Ar carrier gas 500 l/h; the temperature of the quartz reactor 875 °C; the catalyst concentration 2 g ferrocene in 100 ml liquid hydrocarbon. These experimental parameters were established and optimized in our earlier experiments.

In the present paper we have examined the influence of the nature of carbon source regarding the quantity of the final product which contains the CNTs.

3. Results

In the present work we have studied the influence of the following carbon sources: n-hexane (Riedel-de Haën, for high-performance liquid chromatography, assay ≥ 97%), benzene (CHIMACTIV SRL Bucuresti, for analysis), xylene (mixture; Fluka mixtures, assay ≥ 98,5%), orto-xylene (Merck, assay ≥ 90%, for synthesis), meta-xylene (Fluka, assay ≥ 99%, for synthesis), para-xylene (Merck, assay ≥ 99%, for synthesis). We used ferrocene (Fluka, assay ≥ 98% Fe, purum) as catalyst. The obtained experimental results are included in *Table 1*.



Fi. 1. TEM image of CNTs obtained using a) n-hexane, b) benzene, c) o-xylene, d) m-xylene, e) p-xylene, f) xylene-mixture.

Table 1. Experimental data.

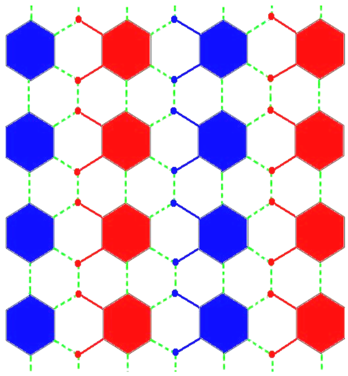
Sample	The carbon source and it's quantity	The catalyst and it's quantity	The quantity of the final product
S166	50 ml n-hexane	1 g ferrocene	0.2720 g
S178	50 ml benzene	1 g ferrocene	0.6820 g
S175	50 ml o-xylene	1 g ferrocene	1.0735 g
S176	50 ml m-xylene	1 g ferrocene	0.8544 g
S177	50 ml p-xylene	1 g ferrocene	1.1958 g
S180	50 ml xylene mixture	1 g ferrocene	0.8722 g

The data included in Table 1. were confirmed by several experiments. These results were obtained by our last experimental investigations.

The quality of the obtained CNTs were examined by transmission electron microscope (TEM). In Figure 1. one can see the TEM image of the samples included in Table 1.

4. Discussions

After a careful study of the data included in Table 1., we can observe, that there are two significant changes in the quantity of the final product. The first is when we use benzene instead of n-hexane (in which case the hexagonal carbon-clusters appear, but a part of benzene nucleous are dissociated) and the second is when we use xylenes instead of benzene, (in this case the hexagonal carbon-clusters are binded with the aid of two carbon atoms existing in two methyl-groups). These results can probably be explained if we accept the ideas of Y. Yang et al. [15] referring to the hexagonal carbon-cluster-based growth mechanism of CNTs. According to these ideas, the graphene planes forming the nanotubes can be constructed with C_6 clusters contained in aromatic compounds. In addition, the formation of the graphene planes is promoted by the two carbon atoms which exist in two methyl groups in the xylene-molecules. We present this formation of graphene planes in Fig. 2.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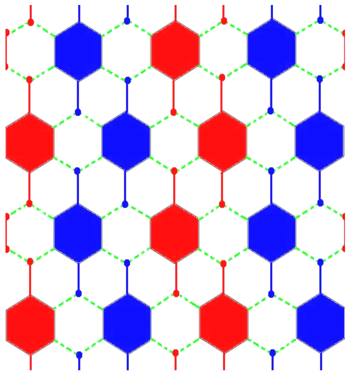
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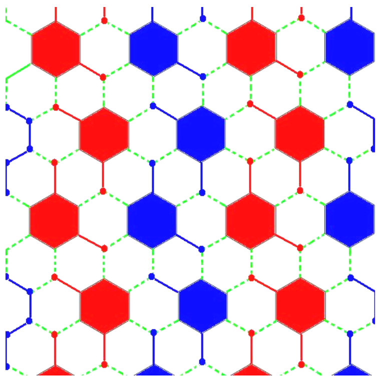
c

Fig. 2. Formation of graphene planes in case of a) o-xylene, b) p-xylene, c) m-xylene.

5. Conclusions

Using n-hexane, benzene, o-xylene, m-xylene, p-xylene and xylene-mixtures as carbon source, the best results in synthesis of MWCNTs were obtained in the case of xylenes. The differences in quantities of final products in case of isomers are not as significant as in the cases when we used benzene instead of n-hexane or xylenes instead of benzene. The TEM images of the xylene-isomers also can be considered very similar. The obtained results can be regarded as an experimental proof of the ideas of hexagonal carbon-cluster growth mechanism which were suggested in [14, 15, 16].

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