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Preparation of ultra-large-scale catalysts for catalytic vapour deposition of carbon nanotubes

A. BACHMATIUK[1], R. J. KALEŃCZUK[1], M. H. RÜMMELI[2], T. GEMMING[2], E. BOROWIAK-PALEN[1*]

[1]Centre of Knowledge Based Nanomaterials and Technologies, Institute of Chemical Engineering and Chemical Technology, Szczecin University of Technology, ul. Pułaskiego 10, 70-322 Szczecin, Poland

[2]Leibniz Institute for Solid State and Materials Research, Helmholtzstr. 20, 01069-Dresden, Germany

One of the most important issues in the controlled synthesis of carbon nanotubes is finding a simple way to synthesize the catalyst nanoparticles with a controlled size. The preparation of iron nanoparticles via an organic route has been presented in the paper. The nanoparticles, of the diameter ranging between 9.5 and 31 nm, supported on magnesia, were used as a catalyst in chemical vapour deposition to produce bulk scale carbon nanotubes. Two carbon feedstocks (ethanol and cyclohexane) were examined. In the optimization process, the pyrolysis temperature was varied between 650 °C and 850 °C. In this simple approach, no additional carrier gas was used. Multiwalled carbon nanotubes with a very low diameter distribution (19.5±2.5 nm) were fabricated. Their composition was analysed via X-ray diffraction. The samples were characterized by the resonance Raman spectroscopy and high-resolution transmission electron microscopy.

Key words: *carbon nanotubes; transmission electron microscopy; Raman spectroscopy*

1. Introduction

Since their identification in 1991 [1], carbon nanotubes (CNTs) have been one of the most actively studied materials because of their unique structure and extraordinary physical properties. Many studies have been carried out on their synthesis. Arc discharge [1], laser ablation [2] and catalytic chemical vapour deposition (C-CVD) methods [3, 4], have been developed to synthesize CNTs. The C-CVD method is a promising technique for scaling up the production of CNTs with a relatively low cost. In the C-CVD approach, the structure of carbon materials obtained depends primarily on the catalyst size and carbon source [5, 6]. For instance, it has been shown that the diameter of the nanotubes is determined to an extent by the catalyst particles diameter [7]. Therefore, it is very important to find an efficient way to produce nanosized catalyst

*Corresponding author, e-mail: eborowiak@ps.pl

particles for synthesis of carbon nanotubes. In this study, we focused on two important aspects: the synthesis of ultra-large scale iron oxide catalyst particles with well defined diameters via an organic route (i), and the application of these catalyst particles supported on magnesia for the synthesis of carbon nanotubes in the C-CVD process (ii).

2. Experimental

Monodisperse metal oxide nanocrystals have been synthesized according to the following procedure:

$$\text{Fe chloride} + \text{Na oleate} \longrightarrow \text{Fe oleate complex}$$

$$\text{Fe oleate complex} \xrightarrow[\text{decomposition}]{\text{thermal}} Fe_2O_3 \text{ nanocrystals}$$

In a single experiment, 9 g of the metal-oleate complex and 1.4 g of oleic acid (90%) were dissolved in 50 g of 1-octadecene (90%) at room temperature. The reaction mixture was heated up to 330 °C at a constant heating rate, and then kept at the desired temperature for 0.5 h. After reaching the temperature of 330 °C, a severe reaction occurred and the initial transparent solution became turbid and brownish.

The resulting solution was cooled down to room temperature. Afterwards, 130 cm^3 of ethanol was added to the solution to precipitate the nanocrystals which were separated by the centrifugation and then dried [8]. The diameter distribution of the produced nanocrystals was calculated from their XRD pattern. XRD was measured with a Philips X'Pert PRO.

The prepared catalyst nanoparticles were then placed in a beaker with butanol and magnesia powder. The molar ratios of the support and iron was: MgO:Fe= 60:1. This mixture was dispersed in an ultrasonic bath at room temperature for 1 h. Afterwards, it was dried on a hot plate at 150 °C with the magnetic stirrer for 0.5 h. Subsequently, the product was ground in a ceramic mortar to form a homogeneous powder of the catalyst precursor mix. In the next step, 30 mg of the catalyst mixture was placed in the centre of a horizontal tube furnace. C_2H_5OH or C_6H_{12} vapours were used as the carbon feedstocks during the reaction. In the same step of the synthesis, hematite particles were reduced to iron particles via hydrogen which was produced during the decomposition of the carbon sources. For each experiment, the vapour pressure of C_2H_5OH or C_6H_{12} was the same (50 mbar). Each carbon source was examined at the following temperatures: 650 °C, 750 °C, 850 °C. The dual time of the process was 0.5 h. Figure 1 shows the setup for the C-CVD reactor with ethanol or cyclohexane.

The as-produced material was purified to eliminate the catalyst and support material (MgO). This was achieved by a simple and efficient acid treatment [9]. The product was dissipated in 12 M HCl and ultrasonicated for 0.5 h. Afterwards, the solution was thoroughly washed with distilled water and acetone. Finally, the purified samples were annealed at 600 °C in a dynamic vacuum for 1 h to remove any remaining solvents.

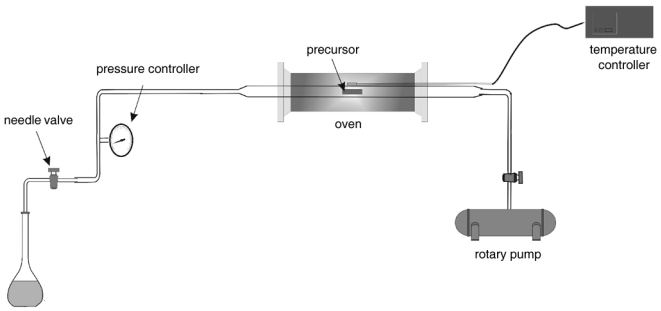

Fig. 1. Schematic setup of the CVD reactor

The morphology of the samples was studied using high-resolution transmission electron microscope (HRTEM) – FEI Tecnai F30. The sample preparation for HR-TEM study has been described elsewhere [10]. The quality of CNTs was determined using a Renishaw InVia Raman Microscope spectrometer.

3. Results and discussion

Figure 2 presents an XRD pattern of the prepared catalyst nanoparticles. The peaks indicated the presence of the hematite phase with a rhombohedral crystal structure. The calculation of the diameter distribution of the nanoparticles was based on the Scherrer equation [11] with help of the X'Pert HighScore Software [12]. In the inset of the Figure 2 the results of these calculations are presented. The crystal sizes range between 9.5 and 31.7 nm.

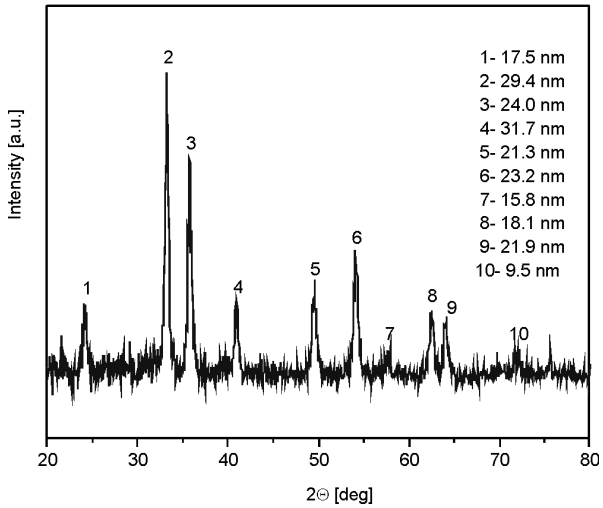

Fig. 2. XRD pattern of hematite nanocrystals

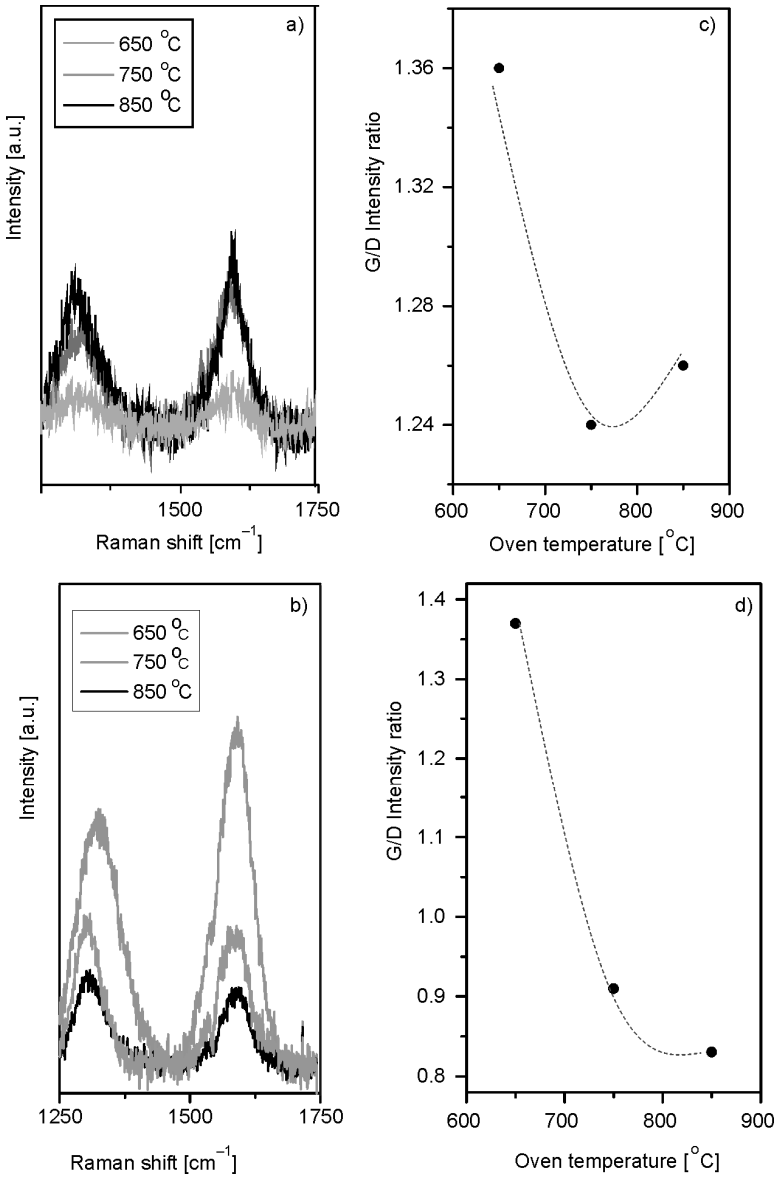

Fig. 3. Raman spectra of CVD synthesized MWCNT: a – ethanol feedstock, b – cyclohexane feedstock, for various oven temperatures and *G*/*D* ratio for various synthesis temperatures: c – ethanol feedstock, d – cyclohexane feedstock

Now we turn to the analysis of the CNT synthesized via the C-CVD technique using the above-described catalysts. Raman spectroscopy is a very efficient tool for the study of CNT. The so-called G-line is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of carbon atoms. This mode is usually centred at ca. 1580 cm^{-1}. The second characteristic mode is observed at ca. 1300 cm^{-1} and is

a typical signature for defective graphitic structures (so called D-line or D-mode) [13]. The comparison of the ratios of these two peak intensities is a measure of the quality of the bulk samples. In addition, there is a third mode, named the radial breathing mode (RBM) which is very sensitive to the diameter of single-wall CNT (SWCNT) and double-wall CNT (DWCNT) [14].

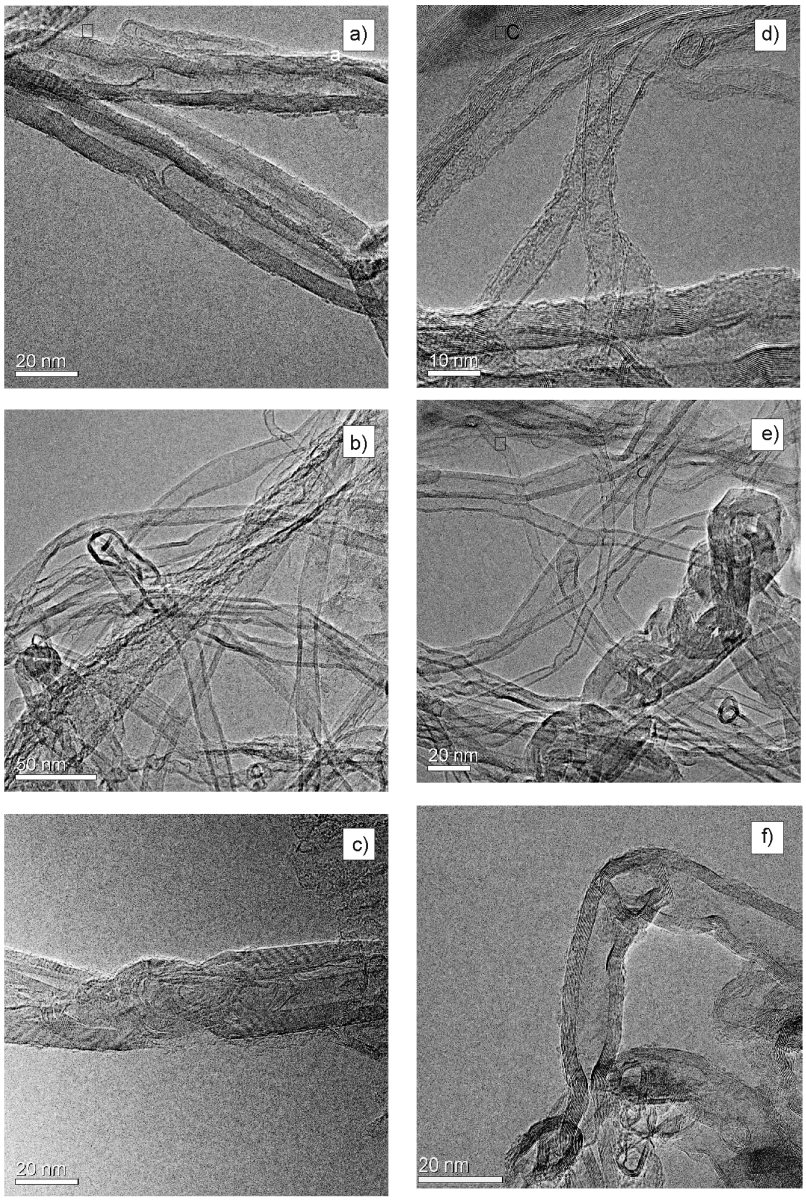

Fig. 4. TEM images of MWCNT synthesized in hotwall CVD at: a) 650 °C, b) 750 °C, c) 850 °C with ethanol as a feedstock, and at: d) 650 °C, e) 750 °C, f) 850 °C with cyclohexane as a feedstock

Raman studies showed that only the D- and G-bands were active in the ethanol feedstock and cyclohexane feedstock samples (Figs 3a, b, respectively). No RBM signal was detected for both series of the samples. Based on this one can rule out the formation of SWCNT or DWCNT in our samples. In order to determine the temperature influence on the quality of the bulk samples of the produced multiwalled CNTs (MWCNTs), the Raman spectra were normalized to the G mode. For the explored temperatures the highest G/D ratio (Figs. 3c, d) is observed at 650 °C which also indicates the highest quality and purity of these samples. The same trend is observed for both carbon feedstocks. This suggests that the prepared catalyst is not particularly sensitive to the carbon source.

Transmission electron microscopy was used to confirm the formation of MWCNTs. Figures 4 a, b, c present TEM images of the samples produced via our C-CVD process with ethanol as the feedstock at 650 °C, 750 °C, 850 °C, respectively. Figures 4 d, e, f present TEM images of the samples produced via C-CVD process with used of cyclohexane at 650 °C, 750 °C, 850 °C, respectively. The analysis of the images shows that the morphology of the materials synthesized with both carbon sources is similar. The MWCNTs formation is observed in all samples. Additionally, some bamboo-like structures with typical compartments in the interior of the multiwalled tubes were observed.

The outer diameters of the tubes were very similar and varied between 17 and 22 nm. The diameter distribution of ca. 5 nm is very low. A further observation shows that the samples are free from catalyst particles, which indicates the efficiency of the purification procedure. There are, however, some minor amorphous carbon deposits on the nanotubes.

4. Conclusions

We have synthesized carbon nanotubes using iron particles (with diameter size between 10 and 30 nm prepared in an organic route) using ethanol and cyclohexane as a carbon sources. The most efficient temperature for MWCNT synthesis was 650 °C were the G/D value was the highest indicating the highest yield and quality of MWCNTs. Finally, in the presented experimental efforts, we successfully produced iron nanoparticles via an organic technique. The resultant nanoparticles are suitable for the synthesis of MWCNTs with a low diameter distribution 19.5 ± 2.5 nm.

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