Synthetic Metals 197 (2014) 159–167

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Properties assessment of multiwalled carbon nanotubes: A comparative study

V. Stefov[a,*], M. Najdoski[a], G. Bogoeva-Gaceva[b], A. Buzarovska[b]

[a] Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, P.O. Box 162, 1001 Skopje, Republic of Macedonia
[b] Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University, Ruger Boskovic 16, 1000 Skopje, Republic of Macedonia

ARTICLE INFO

Article history:
Received 5 March 2014
Received in revised form 21 June 2014
Accepted 11 September 2014

Keywords:
Carbon nanotubes
Co_3O_4
XRPD
Raman
Infrared
Thermal analysis

ABSTRACT

In the last decade the interest in studies of carbon nanotubes (CNTs) from different viewpoints has been constantly increasing. In this work, we have prepared multi walled carbon nanotubes (MWCNTs) by pyrolysis of low density polyethylene (LDPE), using cobalt(II) acetate as a catalyst precursor, and then their systematic structural characterization has been carried out in parallel with the commercial MWCNTs (Nanocyl NC3100). For that purpose, scanning electron microscopy, powder X-ray diffraction, vibrational spectroscopy and thermogravimetry were used. The scanning electron microscopic images (SEM) recorded with different magnification of the synthesized product clearly showed the morphology of the carbon nanotubes. In the diffractogram of the as-prepared MWCNTs, in contrast to the commercial MWCNTs, characteristic peaks for metallic Co were observed besides the typical peaks for graphite. When studying the MWCNTs with Raman spectroscopy, an interesting effect of the laser irradiation on the spectral picture was revealed. In the Raman spectrum of the as-prepared MWCNTs recorded with laser power of 0.111 mW the appearance of the bands from cobalt(II,III) oxide (Co_3O_4) modes clearly demonstrated the oxidation of Co particles from the sample to Co_3O_4. The infrared spectra of the as-prepared and commercial MWCNTs recorded at room temperature (RT) and at liquid nitrogen temperature (LNT) are shown and compared. There is no noticeable temperature effect on the spectra appearance in both the frequency and intensity of bands. The TGA and DTG curves for investigated MWCNTs in air atmosphere are presented and the overall results are summarized. The results of TGA showed that up to 350 °C, the as-prepared MWCNTs are thermally stable in air, and above this temperature the process of thermo-oxidative decomposition proceeds fast and is completed at around 420 °C. The activation energy for the thermal decomposition of the nanotubes is 139 kJ mol^{-1}.

1. Introduction

In the last decade the interest in studies of carbon nanotubes (CNTs) from different viewpoints has been constantly increasing [1]. Carbon nanotubes are nowadays the most promising product for new technologies as one of the stiffest and strongest fibers known with incredible properties [2–5]. They are tube-shaped carbon materials and their discovery is attributed to Sumio Iijima [6,7] even though many other earlier works should also be credited for the experimental evidence suggesting that carbon filaments can be hollow and have a nanometer-size diameter [8]. Carbon nanotubes are members of the fullerene structural family. They are long, thin and have a cylindrical shape and at least one end is a hemisphere. They have a diameter of approximately few nanometers and length of up to several micrometers. Their length-to-diameter ratio is up to 132 000 000:1, which is significantly larger than that of any other material [5]. They can be thought as a sheet of graphite rolled into a cylinder. The graphite layer appears somewhat like a rolled-up wire with a continuous unbroken hexagonal mesh and carbon atoms at the apexes of the hexagons.

There are two main types of nanotubes: single-walled (1 sheet) and multiwalled (2 or more sheets). Single-walled carbon nanotubes (SWCNTs) have a diameter in a nanometer scale and are like a rolled graphene sheet made of just one layer. Their structure consists of a graphene sheet rolled into a tube and capped by half a fullerene. The carbon atoms in a SWCNTs, like those in a fullerene, are sp^2 hybridized. The different types of SWCNTs are defined by their diameter and chirality. Multiwalled carbon nanotubes

* Corresponding author. Tel.: +389 2 3249 942; fax: +389 2 3226 865.
E-mail address: viktorst@pmf.ukim.mk (V. Stefov).

http://dx.doi.org/10.1016/j.synthmet.2014.09.011
0379-6779/

(MWCNTs) have multiple walls. Actually, they are cylinders inside other cylinders. Their shells are closely attached to each other, i.e., there is a small distance between them. The individual shells can be described as SWCNTs.

The fascinating properties of carbon nanotubes fall essentially in three categories:

(a) *Electrical*: semiconducting or metallic behavior;
(b) *Mechanical*: very high tensile strength (100 × steel), high thermal stability and thermal conductivity, and
(c) *Chemical*: extremely high surface area and, in the case of functionalized CNTs, biological interface affinity.

Properties of nanotubes depend in many cases on their detailed structure. They can change depending on the type of the nanotube, i.e., of the nanotube's diameter, length and twisting ability. For instance, chirality of single-walled nanotubes determines their metallic or semi-metallic properties.

Carbon nanotubes are a distinctive class of materials that exhibit unique properties. Since the discovery of carbon nanotubes (CNTs), numerous ideas for applications have arose in a wide variety of scientific subjects, including electronics, opto-electronics, sensors, field emission devices, batteries/fuel cells, fibers, reinforced composites, medicine/biology, catalysis and gas storage [9]. Nowadays, products containing CNTs range from tennis rackets and golf clubs to vehicle fenders, X-ray tubes, and Li ion batteries. Breakthroughs for CNT-based technologies are anticipated in the areas of nanoelectronics, biotechnology, and materials science.

There are few methods of producing carbon nanotubes [10].

1. *Arc method* (plasma arcing) – The first method for producing CNTs and fullerenes in reasonable quantities was the method using electric current across two carbon electrodes in an inert gas atmosphere. Evaporation of one electrode as cations happens, which is followed by deposition at the other electrode.
2. *Laser methods* – CNTs are prepared by laser vaporization of graphite rods with a catalyst mixture (cobalt and nickel) at 1200 °C in an argon atmosphere followed by heat treatment in a vacuum at 1000 °C to remove the fullerenes.
3. *Chemical Vapor Deposition* (CVD) of hydrocarbons over a metal catalyst is a classical method used to produce various carbon materials. Large amount of CNTs can be formed by catalytic CVD of acetylene over cobalt and iron catalysts supported on silica, SiO_2.
4. *Flame pyrolysis* using carbon monoxide as a carbon source for obtaining CNTs with less impurities and high yield.
5. *Bottom-up organic approach* with strategy in two basic areas: synthesis of aromatic macrocyclic templates and development of polymerization reactions to extend these templates into longer CNTs.

The problem with the production of nanotubes using arc discharge and laser vaporization is that they involve evaporating the carbon surface, so there is currently no way to scale up production, making them ineffective for industrial usage.

Recent innovative approaches have been developed for obtaining carbon nanotubes [11–13] and carbon microspheres [14] by thermal treatment of plastic waste. These methodology addresses environmental issues associated with plastic waste since it uses and converts them into technologically important MWCNTs. Out of all these methods, the one of Pol and Thiyagarajan [11] seems as one of the most straightforward and inexpensive.

The initiative for this work started from a study on exploring recent alternative ways of treating plastic waste that led to the first tests employing pyrolysis for obtaining carbon nanotubes from polyethylene. The first results were motivating, so further studies and experiments were designed to study the obtained carbon nanotubes and compare them to ones with already tested purity, diameter and length.

So, in this work, the approach of Pol and Thiyagarajan [11] has been used for obtaining MWCNTs by pyrolysis of low density polyethylene (LDPE) and then their systematic structural characterization has been carried out in parallel with the commercial MWCNTs (Nanocyl NC3100) produced via the catalytic carbon vapour deposition (CCVD) process [15]. Since there is no unified approach for structural characterization and a variety of techniques are used in different laboratories [16–19], we have here tried to demonstrate the information obtained from microscopic, diffractometric, spectroscopic and thermogravimetric techniques in structural characterization of MWCNTs.

2. Experimental

2.1. Samples

Sample of the studied multiwalled carbon nanotubes (MWCNTs) were obtained in our laboratory with pyrolysis of low-density polyethylene waste, carried out in an autoclave, using cobalt(II) acetate as a catalyst precursor, following the procedure introduced by Pol and Thiyagarajan [11]. 2.4 g of polyethylene and 0.6 g of cobalt(II) acetate dihydrate were used as a starting mixture. The pink crystals of the catalyst were put inside the polyethylene bag and it was placed inside an open glass tube (Pyrex-glass). Then the tube was put in an autoclave specially designed for the experiment and a flow of nitrogen was passed through it to enable an inert atmosphere and it was tightly closed. The autoclave was subsequently placed in the center of a furnace, heated at 700 °C for 3 h and allowed to cool gradually after turning off the heating and leaving the furnace door open. After 1 h the autoclave was removed from the furnace and it was allowed for about 1–2 h more to cool gradually to room temperature. Then, the autoclave was carefully opened and the obtained black powder was collected for further analysis. The yield of the product obtained in the experiment was approximately 1.0 g. The yield could be only estimated and not precisely measured since the product was spread throughout the whole autoclave (not only in the tube), due to the extreme conditions inside it during the experiment. It should be mentioned here that if the above procedure is performed without a catalyst, carbon microspheres will be obtained instead of MWCNTs [14].

The other sample of the studied multiwalled carbon nanotubes was a commercial one: Nanocyl NC3100 with 95% carbon purity, with average diameter of 9.5 nm and length of 1.5 μm. These thin multiwall carbon nanotubes have been produced via CCVD process.

2.2. Scanning electron microscopy

The scanning electron microscopy (SEM), type JEOL JSM-6610LV, equipped with detectors of secondary electrons (SE) and backscattered electrons (BSE) was used for recording the SEM images of the obtained CNTs. The SEM images were obtained under acceleration voltage of 30 kV and a spot size of 20 μm at 25 000 and 50 000 magnification.

2.3. X-ray powder diffraction

The X-ray powder diffraction (XRPD) measurements were conducted on a Rigaku Ultima IV powder X-ray diffractometer. Each studied sample was manually dispersed over a silicon sample plate and the data were collected at room temperature on a D/tex detector in the 2θ range from 5 to 80° (scan rate 2° min^{-1}). Cu$K\alpha$ radiation was obtained from a generator set at 40 kV and a current of 40 mA.