INVESTIGATION OF THE EFFECT OF SULPHUR ON THE PROPERTIES OF CARBON NANOTUBES

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However, sulphur has been made use of as a promoter for carbon nanotubes (CNTs) synthesis for many years, a clear understanding of the sulphur effect (essentially, for efficient nanotube production) is still challenging. In this report, we intend to discuss the essential role of sulphur in an Aerosol–assisted chemical vapor deposition (CVD) CNTs synthesis. Though sulphur is not incorporated into the CNTs structure, its presence, however, indirectly affects the yield, nanotube thickness, and even defines a transition between single–, double–, and multi–walled CNTs. Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM), and Raman Spectroscopy analyses were carried out in order to investigate the complex role of sulphur in CNTs synthesis. The effect of sulphur addition as a promoter on the growth of CNTs and attempted to provide insights into the role of sulphur during CNTs formation via catalyst characterization has been investigated.

Keywords: Carbon nanotubes (CNTs), Sulphur, SEM, TEM, Raman Spectroscopy.
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INTRODUCTION

Sulphur and sulphur–containing compounds are widely considered as a material for numerous technologies vital for our civilization: steam methane reforming, water gas shift reaction, and cracking/reforming of hydrocarbons. Ever since then, discovering of carbon nanotubes (CNTs) by the Japanese scientist Sumio Iijima in 1991 [1], these carbon nanostructures and carbon nanomaterials have been the area of great interest and potensial applications in many different fields. High quality carbon nanotubes (CNTs) possess tremendous potential for a variety of a leading applications such as catalyst supports [2], composites [3], drug delivery [4], membranes [5], sensors [6], electrodes [7], capacitors [8], etc. As it is known, CNTs are graphite layers of cylindrical shape, composed of graphitic carbon and rolled into the tubes. In addition, the type of CNTs depends on the orientation of the graphene sheet in the form of a cylinder. This can be expressed in terms of a quantity that defines how the graphene sheet is folded – a quantity called the chirality vector (C_h). The concept of chirality is one of the main factors in determining the electrical properties of CNTs. CNTs have a number of electrical, thermal, and structural properties, and these properties can be changed depending on the physical design of the CNTs. The chirality vector is defined by two integers (n, m) and is expressed as the following formula:

$$C_h = na_1 + ma_2$$

Generally, according to the number of external (outer) walls and atomic structure, CNTs are divided into three types: single–walled (SWCNTs), double–walled (DWCNTs), and multi–walled (MWCNTs).

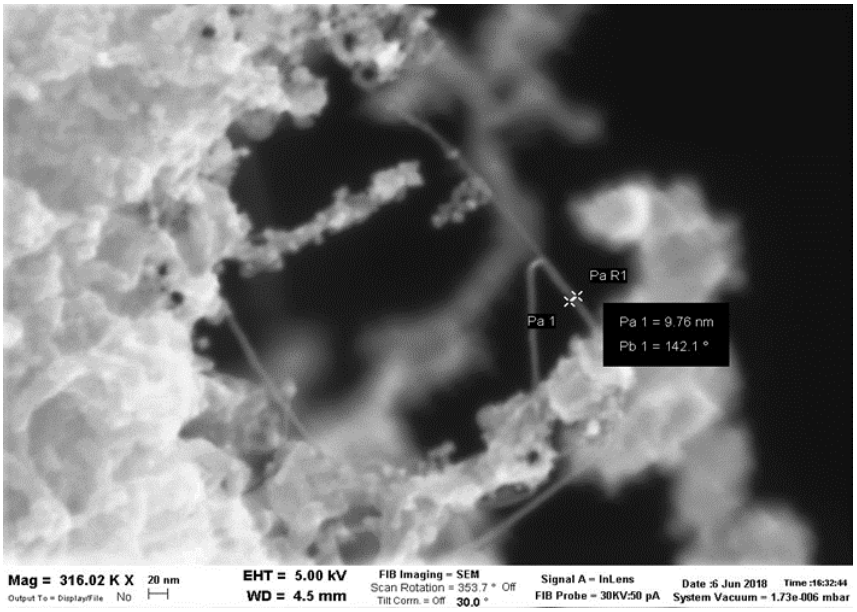

Fig. 1. SEM analysis method of synthesized CNTs using sulphur.

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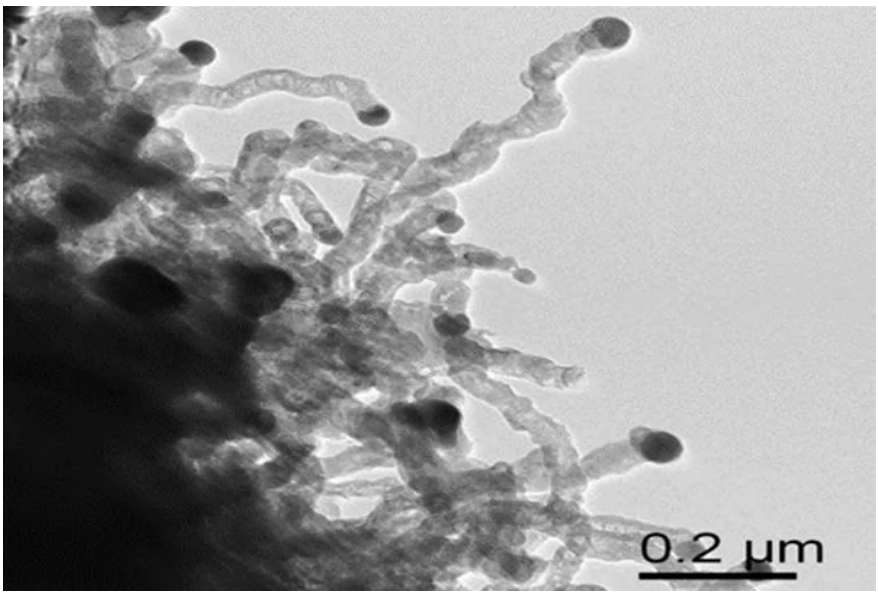

Fig. 2. TEM analysis method of synthesized CNTs using sulphur.

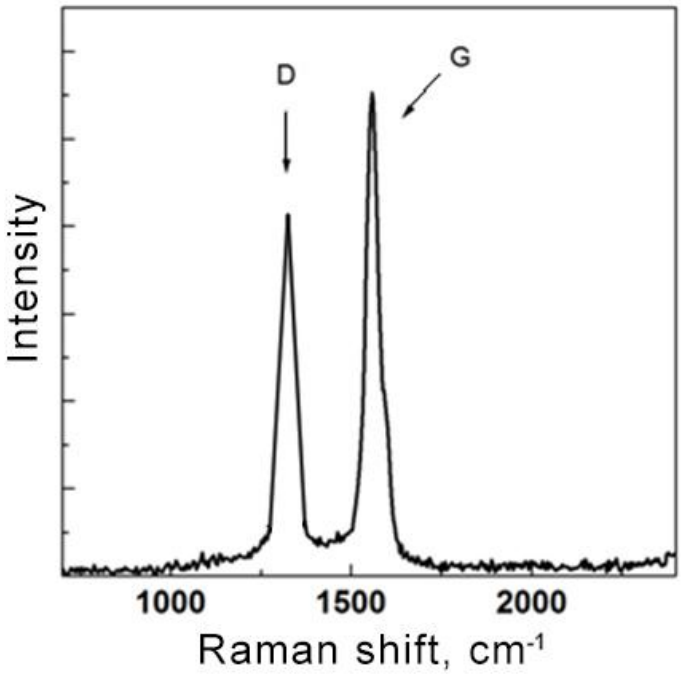

Fig. 3. Raman spectroscopic analyses of synthesized CNTs using sulphur.

However, the leading and most important structures in carbon nanotubes are SWCNTs and MWCNTs. It should be noted that, CNTs have sp^2 – hybridization state as in graphite, and each atom in this compound is combined with three other neighboring atoms. Besides having metallic and semiconducting properties, CNTs also have a strong influence on the electrical, mechanical strength, absorption and many other properties of polymers.

Accordingly, several processes to synthesize CNTs like electric arc–discharge, laser ablation, flame process, chemical vapor deposition (CVD) and others, have been proposed to date. Among these methods, CVD process can be regarded as a most potential candidate. CNTs prepared by this method are added to electric, dielectric, catalyst, polymer materials with the aim of increasing their strength and conductivity, and the obtained nanocomposite material has a number of important properties and advantages. In addition to metal catalysts, the small amount of sulphur (or sulphur–containing compounds) is used as growth promoters.

Elements of the 16^{th} group (chalcogens) like, sulphur (S), selenium (Se), and tellurium (Te), etc., also have been widely proposed as effective promoters. Sulphur is a well–known additive to metals in various fields of science and technology: from metallurgy and steelmaking to the synthesis of carbon nanostructures. S and Se might cause an increase in the diameter and even may lead to a shift in the chiral distribution of CNTs.

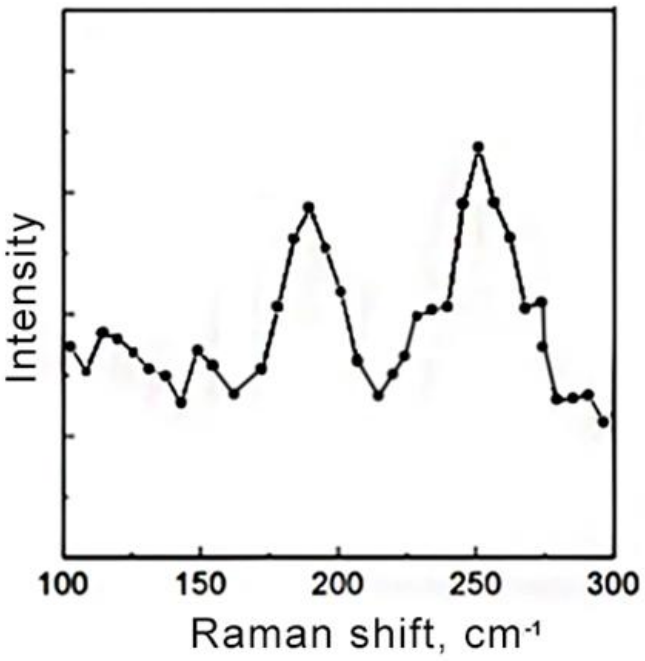

Fig. 4. RBM peaks of synthesized CNTs using sulphur.

However, sulphur is the most widely used promoter for the CNT growth and, therefore, might open a new insight into the mechanisms of the CNT formation. Also, it was determined that the addition of sulphur to the reaction solution dramatically affects the number of walls, morphology and even electrical properties of the synthesized CNTs. In addition, it was determined that a large amount of sulphur in the reagent mixture leads to the formation of amorphous carbon, and a small amount of sulphur leads to the formation of CNTs and other carbon compounds. In previous works [9], many scientists have synthesized CNTs by CVD method using ferrocene ($Fe(C_5H_5)_2$) and sulphur (S_2) as catalyst precursor and growth promoter, respectively, and m–xylene as hydrocarbon source in their investigations. However, in our carried–out works, it was shown that CNTs were synthesized by Aerosol–assisted chemical vapor deposition (AACVD) using ferrocene ($Fe(C_5H_5)_2$) and sulphur as a catalyst precursor and growth promoter, respectively, and xylene (C_8H_{10}) was used as the hydrocarbon feedstock. Using a ferrocene/sulphur/xylene solution with a relative concentration of n = 20 mg/ml, different types of carbon nanotube materials were prepared in the temperature range of $T = 850 - 1000$ ℃ in the AACVD experimental setup.

All these experiments were carried out in order to analyze the influence of sulphur on the growth process of CNTs and their parameters. The results of the experiments show that when sulphur is not included, the final sample is obtained in the form of powder, and after the introduction of sulphur, it is obtained in the form of twisted graphite thin films. For this reason, SEM, TEM, and Raman spectroscopy analysis methods were performed to determine the structure of the synthesized CNTs. When these films are researched by means of the SEM analysis method (Fig. 1), small – sized ($d = 4 - 5\ nm$) CNTs are observed. However, apart from that, TEM analysis method (Fig. 2) were performed to determine the structure of the obtained CNTs. During the TEM analysis, small diameter CNTs were seen among the CNTs with a diameter ranging from 10 to 30 nm. Considering into account all these facts, Raman spectroscopic analyses (Fig. 3) of the obtained samples were performed. As can be seen from this spectrum, in addition to the D (1340 cm^{-1}) and G (1570 cm^{-1}) peaks belonging to graphite, the Radial Breathing Mode (RBM) peak (Fig. 4), X_{RBM} = 180 ÷ 250 cm^{-1}, characteristic of SWCNTs was observed in the wavenumber interval. The frequency of the RBM mode directly depends on the diameter of the CNTs in the form of the following relationship:

$$\omega_{RBM} = \frac{A}{d} + B$$

This also proves the existence of nanotubes with a diameter of d = 1 ÷ 1.3 nm. As for the crystallinity properties of the grown product, here we have used the ratio of the intensities of the D (defect) and G (graphite) peaks. So, as a result of calculations, the ratio of I_D to I_G was equal to 0.42 (I_D/I_G = 0.42).

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