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Raman Characteristics of Multiwall Carbon Nanotubes on Diatomite

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Abstract

In this paper, the diatomite mineral from Mugalzhar field, Aktobe region, has been used as a matrix of catalyst particles to synthesize multiwall carbon nanotubes (MWCNTs) by Catalytic Chemical Vapor Deposition method (CCVD). As a source of carbon was used a propane-butane gas mixture, as a catalyst – Ni particles deposited from $Ni(NO_3)_2$ solution during heat treatment process at 400–500 °C. The CCVD method was conducted at a different temperature: 650 °C, 700 °C, 750 °C, 800 °C. Obtained MWCNTs were studied by Raman spectroscopy. The characteristics such as crystallinity, defectiveness, diameter of MWCNTs synthesized at different experimental conditions were evaluated from the positions and intensity ratios of Raman peaks of the samples. The results of investigations of the properties of the obtained carbon nanotubes show the dependence of MWCNTs characteristics on CCVD method temperature. The observation of changes in all the three peaks – D, G and 2D, of obtained materials exhibit, that MWCNTs synthesized at 800 °C possess high crystallinity, low defectiveness and larger diameters as compared with carbon nanotubes grown at 650 °C, 700 °C, 750 °C.

1. Introduction

Diatomite is a silicon dioxide mineral containing fossilized skeletal remnants of one-cell water plants called diatom algae. Diatomite deposits usually consist of not only diatomaceous membranes, but also contain other sediments, such as clay, inorganic carbonates, iron oxides and fine sand.

Diatomite has a number of significant advantages, such as high specific surface area and easy regeneration. It is also cheap, available in large amounts and has many practical applications. In aqueous solutions, the particles of diatomite have negative charges, so they exhibit a strong attractive force to particles with a positive charge. There are many diatoms around the world, therefore, it can be assumed that in future diatomite will be used in many fields. One of these fields is synthesis of CNTs.

The catalytic chemical vapor deposition method is commonly applied for synthesis of carbon nanotubes due to its several advantages. This method makes it possible to decompose carbon-containing substances on catalytic particles of metallic elements (Fe, Ni, Co). Synthesis with the help of the CVD method is a process that produces high purity solid materials. The catalyst exhibits a great influence on the morphology, characteristics and yield of the carbon material [1, 2].

The preparation of catalysts involves the usage of carriers. These carriers are aluminum oxides, magnesium, silicon, barium, hydroxides, metal salts and zeolites [3]. In the preparation of catalysts, carbon materials are of a great importance. The catalytic chemistry of nickel and species of carbon materials with a wide range of characteristics, made possible the creation of a large number of metal catalysts on carbon carriers [4]. At work [5] a technique for producing a porous carbon material utilized to grow CNTs have been developed.

Chunhua Li et. al [6] have compared nickel catalyst supported by carbon nanotubes (Ni/CNTs) with nickel catalyst supported by diatomite (Ni/SiO_2). It has been found that the quality of CNTs

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prepared with these two catalyst systems is analogous. However, the yield of the former is 1.5 times higher than that of latter.

In 2009, El-Shazly Duraia and his coauthors [7] synthesized single wall carbon nanotubes (SWCNTs) on diatomite by plasma-enhanced chemical vapor deposition, which were characterized by Raman spectroscopy and Scanning Electron Microscope.

Hassan Alijani and coworkers [8] synthesized magnetic MWCNTs using diatomite as catalyst by CVD method. The obtained composite showed superparamagnetic properties and was employed as a sorbent in water purification.

Raman spectroscopy provides unique and useful information about various types of carbon nanostructures. Researchers commonly employ this method to identify quality of carbon nanotubes (CNTs), their purity and concentration of defects. Raman spectroscopy is a non-destructive technique for the detailed determination of structural characteristics of single-wall carbon nanotubes [9]. It also enables to perform comprehensive analysis of multi-wall carbon nanotubes (MWCNTs), which are commonly considered as a set of tubes with a certain range of diameters. Due to a number of ambiguous effects in such complex object, the interpretation of experimental Raman spectra of MWCNT samples is typically based on the data of comprehensive research and the results of previous studies.

Development of new methods for creation of catalytic systems, which allow controlling the structure of carbon particles is an important task leading to the improvement of the existing approaches to the synthesis of CNTs with definite functional properties.

In this work, the diatomite mineral from Mugalzhar field, Aktobe region, Republic of Kazakhstan, was used as a matrix for catalyst particles to synthesize MWCNTs by Catalytic Chemical Vapor Deposition method. The properties of obtained carbon nanotubes were investigated using Raman spectroscopy.

2. Experimental

Carbon nanotubes were synthesized using catalytic chemical vapor deposition method. The typical schematic of the CCVD apparatus is given in [10]. Propane-butane mixture used as a carbon-containing gas, and diatomite was applied as a catalyst carrier. A sample of diatomite was preliminary saturated with an alcoholic solution of nickel nitrate, and then it was dried.

The CCVD system consists of furnace with a 35 mm (diameter) and 450 mm (length) quartz reaction tube. The central part of the reactor can be heated to 1000 °C. The measurement of temperature was made by a chromel-alumel thermocouple. The growth was carried out by catalytic decomposition of a propane-butane gas mixture on a diatomite substrate with a preliminary prepared catalyst.

Propane-butane mixture decomposes into carbon and hydrogen atoms upon entering the reactor. The formation of nickel oxide and its reaction with carbon is shown below.

$$2\left(Ni(NO_3)_2 \cdot 6H_2O\right) \xrightarrow{300\,^{\circ}C} 2NiO + 4NO_2\uparrow + O_2\uparrow + 12H_2O$$

$$2NiO + C \xrightarrow{200-400\,^{\circ}C} 2Ni + CO_2\uparrow$$

Subsequently, the resulting nickel particles catalyze the synthesis of multi-wall carbon nanotubes.

The samples containing carbon nanotubes are characterized by Raman scattering method using the 473 nm laser and Solver Spectrum instrument (NT-MDT) at the National Nanotechnology Laboratory of Open Type of al-Farabi Kazakh National University. The laser beam was directed on the sample using a 100×0.75 NA Mitutoyo lens provided a laser spot of <2 μm. The scattered light was collected in back-reflection geometry via the same lens. All spectra were normalized and the width and intensity of the peaks were studied. The error bars were added for each data reported in the graphs of the paper.

3. Results and discussion

The Raman spectra of MWCNT (Fig. 1) show the four characteristic peaks: D band at about 1360 cm^{-1}, G band at 1580 cm^{-1}, 2D (G') band at 2710 cm^{-1} and D+G band (also assigned as D+D') at about 2930 cm^{-1}. The D band indicates the presence of defects in the MWCNT sample. They are carbon impurities with sp^3 bonding or dangling sp^2 bonds at the edges. The G band is due to sp^2 graphitic nature of the sample and its full width at half maximum (FWHM) can indicate the crystallinity of the sample. The 2D band is associated with the long-range order in a sample mainly along the crystallographic c-axis and also provides information on the number of walls. The 2D peak

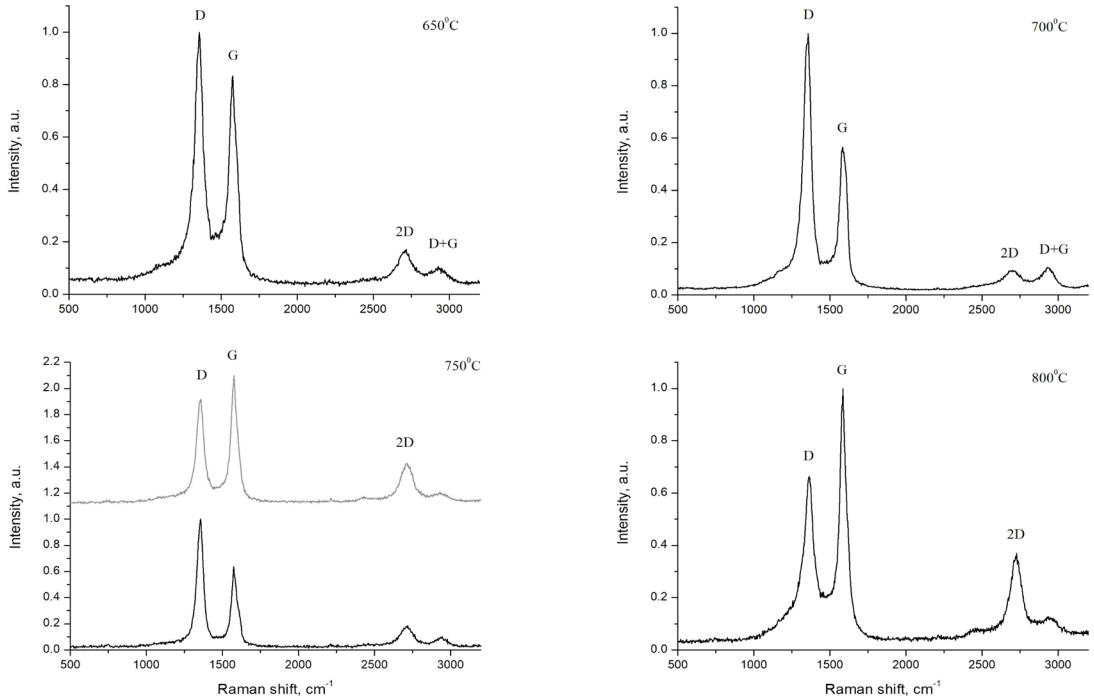

Fig.1. Raman spectra of MWCNTs synthesized on diatomite at different temperatures.

arises from the two-phonon second order scattering process that results in creation of an inelastic phonon [11], no defects are required for its activation. D+G band is combination of phonons with different momenta and thus it requires a defect for its activation [12–13].

Despite some ambiguities in Raman spectra of the samples obtained at higher temperatures, there is a certain correlation between the quality of CNTs and the synthesis temperature. The data from FWHM of the G peak demonstrate that the crystallinity of CNTs increases with increasing the reaction temperature (Fig. 2).

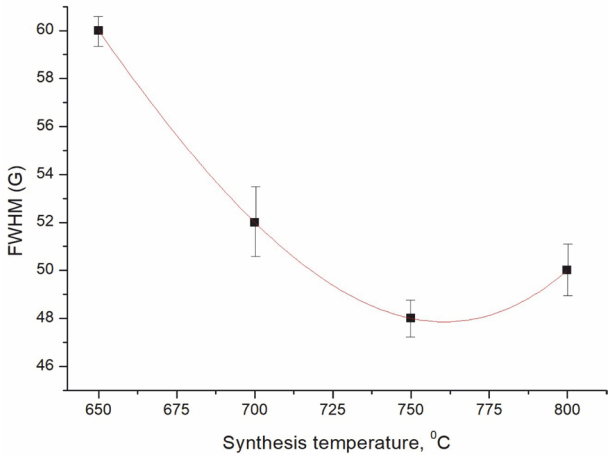

Fig. 2. Dependence of crystallinity of CNT samples on the temperature of synthesis.

The intensities ratio I(G)/I(D) is known to be directly proportional to graphitization of carbon materials. Thus, this value, allows characterizing the disorder level of CNT samples. According to the disorder level of MWCNT, I(G)/I(D) ratio displays 2 types of behavior. The first type of "low" defect density is characterized by decreasing the ratio with increasing defect density. When the amount of defects reaches a certain threshold, a behavior of "high" defect density is observed, at which the ratio I(G)/I(D) begins to increase with rising the defect amount, which can be appeared in the case of more amorphous carbon structures [14]. In Raman spectra of CNTs the intensity ratio I(G)/I(D) for 650 °C is higher than that for 700 °C and then it begins to increase with temperature increase as shown in Fig. 3. Thus, there is a switch point at 700 °C when the "low" defect density regime becomes valid.

It should be noted, that the samples synthesized at 750 °C demonstrate two types of Raman spectra with the I(G)/I(D) ratio of 1.2 and 0.64, respectively. This is explained by the transitional conditions at this temperature that promote formation of non-uniform carbon structures. However, the results demonstrate an obvious tendency of growth of the I(G)/I(D) ratio after 700 °C, which is shown by approximation curve in the plot.

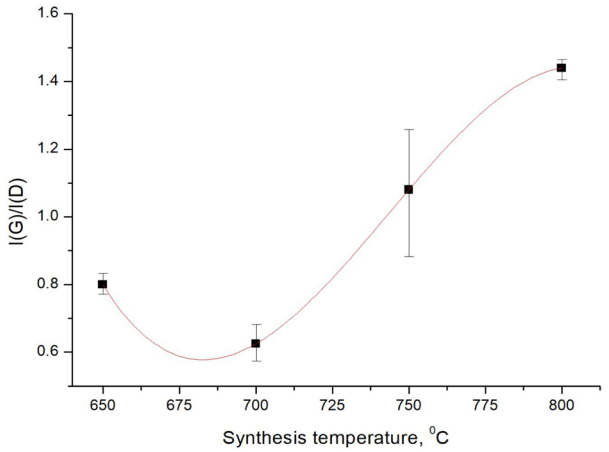

Fig. 3. The evolution of I(G)/I(D) ratio with the synthesis temperature.

Some authors state that the ratio I(G)/I(2D) may represent a more accurate measurement concerning quality or purity of MWCNT [9] and as it was mentioned above, the rise of 2D band indicates the growth of 3D-ordering. The ratio analysis of I(G)/I(2D) (Fig. 4.) showed that a long-range order in our MWCNT samples also increase when synthesis temperature rises, i.e. at a higher temperature, the tubes have a higher length without bundles. Also, there are several reports about dependence of I(G)/I(2D) ratio on the CNT diameter. It was shown that intensity of the 2D band increase when diameter rises [15–18].

Thus, it can be concluded that the increase of reaction temperature leads to the increase of CNTs crystallinity and diameter.

4. Conclusions

Multi-wall carbon nanotubes were synthesized by CCVD method, using diatomite as a catalyst carrier, at 650 °C, 700 °C, 750 °C, 800 °C. The dependence of MWCNT characteristics on an operating temperature of the CVD method was established.

From the intensity of the 2D band on the Raman shifts, it can be concluded, that increasing of the synthesis temperature leads to the formation of nanotubes with higher crystallinity and larger diameters. It was shown, that 800 °C is the optimal studied temperature of the CCVD method to a growth of MWCNTs with the best structural characteristics, high crystallinity, low defect density, a long length, and large diameter.

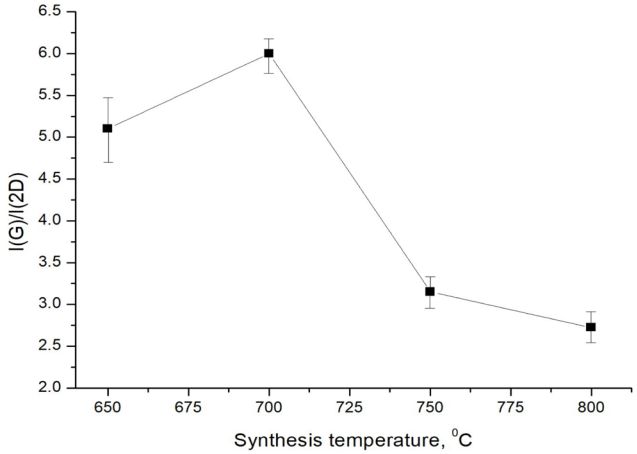

Fig. 4. Ratios of G and 2D Raman peaks intensity for different synthesis temperatures.

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