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Investigation of thermal properties of carbon nanotubes and carboxyl group-functionalized carbon nanotubes

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Thermal properties characterizations for carbon nanotubes (CNTs), carboxyl group-functionalized carbon nanotubes (FCNT), and graphite were presented in the paper. TGA/DSC and TEM techniques were used for characterization. The features of TGA characteristics transformation for synthesized carbon nanomaterials were investigated. The specific heat capacities of the samples at a constant pressure increased as the temperature increased.

Keywords: graphite, carbon nanotube, carboxylic functionalization, arc discharge method, TEM, TGA, specific heat capacity.

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Introduction

In recent years, there has been growing interest in the investigation and application of graphene-based materials. Since its discovery in 1991 by the famous Japanese scientist S.Iidjima, carbon nanotubes (CNTs) have attracted the attention of researchers due to their unique structure and important properties for applications [1]. The most used synthesis methods for obtaining carbon nanotubes are arc discharge, laser ablation, and chemical vapor deposition. These methods give us the possibility to synthesize different types of carbon nanotubes such as single-walled (SWNT), double-walled (DWNT), and multi-walled (MWNT) [1-3]. Rolling the graphene sheets into a cylindrical shape can tune CNT's bang gap and change the properties from metallic, narrow band gap semiconductors to dielectric. The main reason for this transformation is the effect of rotation angle that depends on their diameters [2]. Their stiffness, large length-to-diameter ratio, and strength make them applicable in optoelectronic devices. The properties of carbon nanotubes can be manipulated by choosing the synthesis method which allows controlling the diameter, chirality, initial materials, and wall length [2].

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) are powerful techniques for the investigation and applications of nanocarbon materials and nanocomposites [4].

In [5] TGA data demonstrated that MWCNTs annealed at 2200 to 2800 °C are more air stable than as-produced MWNTs, diamond, graphite, and annealed diamond. The annealed MWCNTs are similar in stability to annealed graphite. Defect sites along the walls and at the ends of the raw MWCNTs facilitate the thermal oxidative destruction of the nanotubes. Thermal annealing removes these defects, thereby providing MWCNTs with enhanced air stability [5]. In [6] provided recent advances in thermal analysis (mainly, thermogravimetric analysis and differential scanning calorimetry) of carbon nanomaterials.

Nevertheless, optimization of the efficiencies of these materials demands understanding the decomposition mechanisms of CNTs with time and particularly under the influence of heat [7]. The isothermal oxidation of MWCNTs by TGA was investigated in [8] for the experimental temperature range from 573 to 823 K. The oxidation of MWCNTs is controlled by both chemical and diffusion processes, depending on the temperature range. With the help of Chou's model [8], a comparison model of MWCNTs oxidation based on experimental and theoretical results was applied. This model provides an expression for weight loss as a function of time under constant temperature conditions. In [9] TG–DTG data indicated that a high-temperature treatment in an inert atmosphere proved to be an effective way to improve the high-temperature stability of MWNTs in ambient conditions. The possibilities of carbon nanotubes as reinforcement in cementitious materials have been investigated in [10]. The possibilities of creating sensors based on multi-walled carbon nanotubes have been discussed in detail [11,12].

The investigation of gas absorption on the inner and outer walls of carbon nanotubes for gas sensor applications can be performed with the help of TGA analysis. Carboxyl-functionalized MWCNTs (MWCNT-COOH) are efficient nano-platforms to immobilize multiple molecules by covalent bonds, hydrogen bonds, or π-π stacking interactions [13,14]. Sensors made of single-walled carbon nanotubes functionalized with a carboxyl group are sensitive to CO gas [12].

Our previous investigation [15-18] presents carbon nanotube synthesis, functionalization, doping, morphology, structural, and photo-electrical characterizations. The features of negative thermal expansion of sulphur-doped graphene oxide of graphene-based composites at different temperatures were investigated also in [19].

The aim of this paper is the investigation of TGA and DSC data in comparison for different types of carbon materials such as carbon nanotubes (CNTs), and CNTs functionalized with carboxylic groups (FCNT).

I. Experimental details

Sample preparation.

The thermal properties of multi-walled carbon nanotubes, graphite, and FCNT obtained by the electric arc discharge method were investigated.

Carbon nanotubes were initially functionalized in the process of the arc discharge method. The 0.5 g of high-purity carbon nanotubes were mixed with 250 ml of 8 M sulfuric acid in a 500 mL beaker. On a magnetic stirrer with a heater, sulfuric acid was continuously mixed with carbon nanotubes. The process was carried out at 50°C for 3 hours. The resulting compound (functionalized carbon nanotubes) was washed and filtered with distilled water until a neutral medium was removed and dried in a vacuum dryer in a Petri dish.

Characterization.

Transmission electron microscope imaging (TEM) was registered by Hitachi HT 7700 (Japan) TEM microscopy at room temperature. The working parameters are resolution equal to 0.204 nm for 100 kV, magnification range from 200x to 600,000x, accelerator voltage from 40 kV to 120 kV, Stage (Eucentric goniometer stage (70°D tilt).

Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 409 PC/PG setup.

II. Results and discussion

2.1. TEM analysis

The size and shape of initial material such as graphite flakes, morphology, and distribution of CNT and FCNTs nanostructures were investigated using the TEM technique. Figure 1-3 shows the TEM image of carbon materials at low and high magnification.

From the TEM observation, the product is pure and only carbon nanotubes were observed (Fig 2-3).

Graphite

The typical TEM images for graphite flakes with different magnifications x6.0k (Scale bar 1.0μm) and x20.0k (Scale bar 500 nm) are shown in Fig.1. TEM images were collected with an accelerating voltage of 110.0 kV.

The morphology of graphite, consisting of thin stacked flakes of shapes and having well-defined multilayered structures, can be seen in Fig. 1.

CNTs

TEM images for carbon nanotubes obtained by the electric arc method were collected at an accelerating voltage of 110.0 kV and two magnifications such as x20.0k (500 nm) and x40.0k (200 nm). The structural features are shown in Fig. 2 a,b.

From these images, most of the CNTs are nearly good quality and long with a high number density.

FCNTs

TEM images for carboxyl group-functionalized carbon nanotubes (FCNTs) were collected at an accelerating voltage of 120.0 kV and magnifications x10.0k (1.0 μm), x20.0k (500 nm).

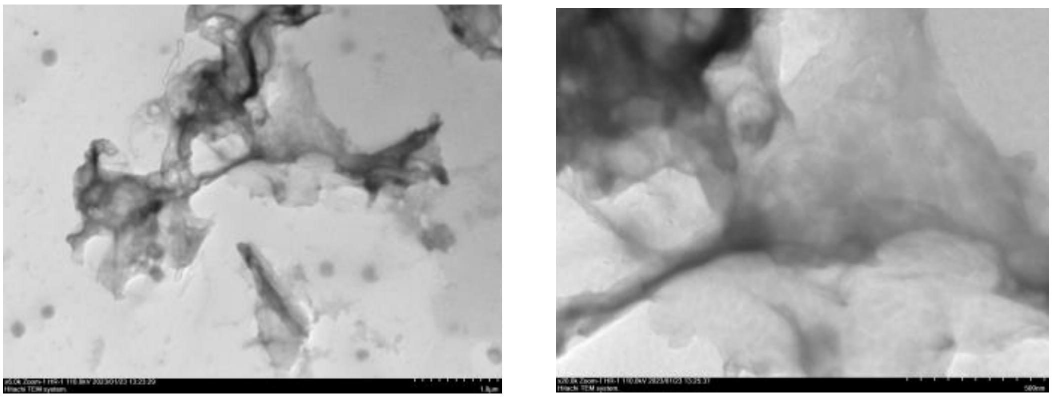
The structural features and transformation of F-CNTs are shown in Figure 3.

TEM images (Fig. 3) verified the tubular morphology of FCNTs, as well as the close to smooth and homogeneous surface [13].

The acid treatment can greatly increase the solubility of MWCNTs by introducing the carboxylic functional group (-COOH) to the side wall and the tip of MWCNTs [20].

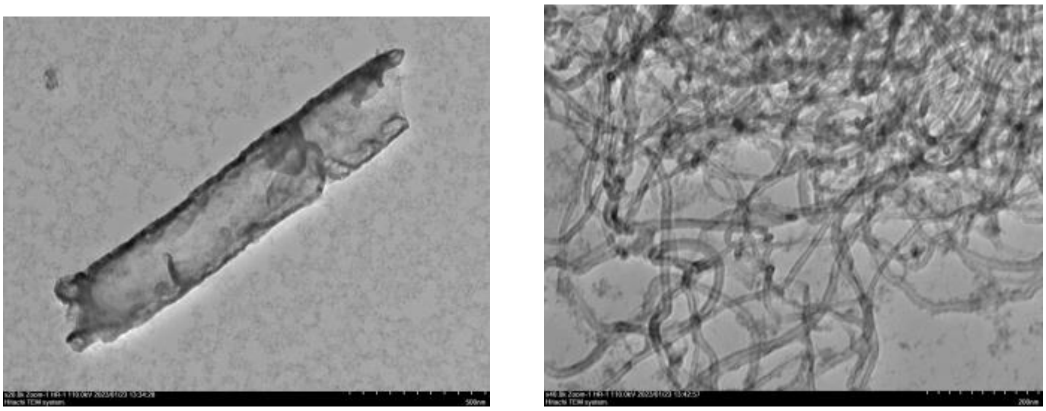
2.2. TGA and specific heat capacity analysis

Thermogravimetric analysis is one of the key methods to investigate the functionalization of carbon nanotube samples. To understand the thermal transformation of the carbon nanotube samples, thermal degradation



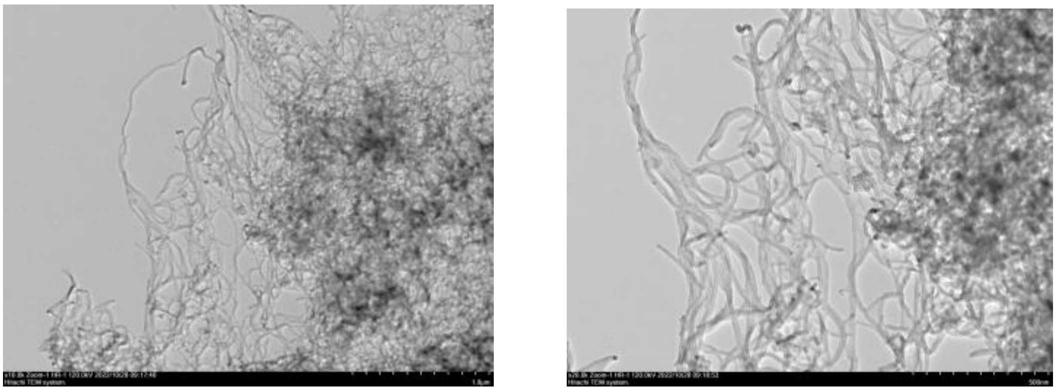
a) b)

Fig.1. TEM images of graphite flakes (a) at low resolution and (b) at high resolution.



a) b)

Fig.2. TEM images of synthesized CNTs (a) at low resolution and (b) at high resolution.



a) b)

Fig.3. TEM image of synthesized FCNTs (a) at low resolution and (b) at high resolution.

experiments were performed in the air atmosphere.

The modification of CNTs with COOH- functional group (FCNT) was identified by TGA.

The TGA weight loss curves of pristine CNTs, FCNT, and graphite were displayed in Fig. 4.

Figure 4 shows the mass losses of the samples as a function of temperature increase. As is seen from the figure, pure graphite is stable up to ~650 °C. The thermal oxidative reaction occurs between 650 and 950 °C destroying all the graphite structure and leaving approximately 7% residual ash mass after thermal degradation. Although carbon nanotubes are made of the graphene layers of graphite, they are not thermally stable at higher temperatures above 500 °C. There is only one-step degradation of the CNT between 500 and 700 °C with a residual ash mass of 10%.

It is expected that after functionalization some oxygen functionalities such as carboxylic groups are added to the CNT structure and the thermal degradation of functionalized CNT proved the continuous mass loss of ~9% up to 500 °C. This is attributed to intermolecular reactions between carboxylic groups and the evaporation of physically adsorbed water molecules from the CNT structures. A sharp mass loss observed between 500 and 700 °C demonstrates the complete destruction of the CNTs with a residual ash mass of ~10% which is similar to the residual mass of the pure CNT degradation result. This data of transformation TGA curves for CNT and

FCNT was in agreement with [21].

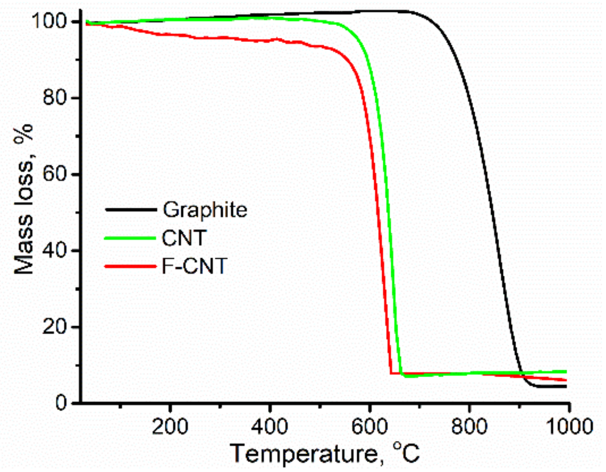


Fig. 4. TGA curves of graphite, carbon nanotubes, and functionalized CNTs.

The temperature dependencies feature of the heat capacity parameter was calculated using DSC data. The heat capacity of the medium at constant pressure was calculated with the help of the following mathematical expressions [22-23]:

$$C_p = \frac{dH(T)}{dT},$$

The integration was carried out by a digital method - the trapezoidal method [22], and the calculations were performed using a program written in the FORTRAN algorithmic language.

Figure 4 shows the temperature dependencies of specific heat capacity Cp=Cp(T) and for CNTs and FCNT samples at constant pressure in comparison with literature data [24-28].

It can be seen that Cp increases gradually with temperature for all materials. The difference in Cp for different carbon materials can be associated with defect surface condition, functionalization, and synthesis method.

As can be seen from Figure 5, the specific heat capacity of the samples at a constant temperature (T) increases as the temperature increases and has a minimum value at certain temperatures.

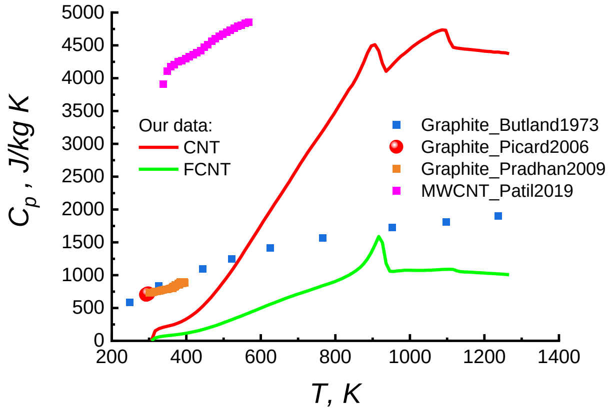


Fig. 5. Temperature dependencies of specific heat capacity parameters of CNTs and FCNT in comparison with literature data.

In Table 1. The maximum values of the specific heat capacities of graphite, CNTs, and FCNTs samples are summarized and shown.

Table 1.

Specific heat capacities data

Sample	C_p, J/kg K	
	T	C_p
CNT	1086.3	4736.3
FCNT	916.3	1588.5

Conclusion

In this study, CNT and FCNT were produced.

The microstructure of the graphite flakes, CNTs, and FCNTs were studied using electron microscopy techniques. The CNTs and FCNTs are characterized by tubular morphology with close to smooth and homogeneous surfaces.

The chemical transformation and thermal properties of synthesized CNTs and FCNTs were confirmed by TGA measurements. Carbon nanotubes are not thermally stable at higher temperatures above 500°C with one-step degradation. The intermolecular reactions between carboxylic groups and the evaporation process of physically adsorbed water molecules lead to mass loss of ~9% up to 500 °C for FCNTs.

From the DSC data processing, the value for specific heat capacities of the obtained carbon nanomaterials was calculated. The specific heat capacities Cp of the samples at a constant temperature increase as the temperature increases. The specific heat capacity takes maximum values at certain values of temperature for CNTs C_p = 4736.3 J/kg K (T = 1086.3 K) and for FCNTs C_p = 1588.5 J/kg K (T = 916.3 K), respectively.

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Дослідження теплових властивостей вуглецевих нанотрубок і карбоксильних груп – функціоналізованих вуглецевих нанотрубок

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У роботі наведено характеристики термічних властивостей вуглецевих нанотрубок (ВНТ), вуглецевих нанотрубок функціоналізованих карбоксильною групою (Ф-ВНТ) і графіту. Для характеризації використано методи TGA/DSC та TEM. Досліджено особливості перетворення ТГА характеристик для синтезованих вуглецевих наноматеріалів. Питома теплоємность зразків при постійному тиску збільшується із підвищенням температури.

Ключові слова: графіт, вуглецева нанотрубка, карбоксильна функціоналізація, метод дугового розряду, ТЕМ, ТГА, питома теплоємність.