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Study of nitrogen-doped carbon nanomaterials by bomb calorimetry

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ABSTRACT

Nitrogen-doped carbon nanotubes (N-doped CNTs) and nitrogen-doped carbon nanoflakes (N-doped CNFs), which are promising materials for energy storage devices, were investigated by adiabatic bomb calorimetry method to determine their enthalpies of combustion ($\Delta_c H^0_{298}$) and of formation ($\Delta_f H^0_{298}$). All materials were characterized by elemental analysis, transmission and scanning electron microscopy, X-ray photoelectron, Raman spectroscopy as well as thermal analysis. The relationships between composition, nitrogen content and structure were studied. All $\Delta_f H^0_{298}$ values of the N-doped CNTs and CNFs were found to be negative and to decrease with the increase in nitrogen content. The value of $\Delta_f H^0_{298}$ of the N-doped CNTs changed from −(0.79 ± 0.01) to −(74.08 ± 0.15) kJ/mol with the increase in nitrogen content from 1.54 to 2.52 wt. % and that of N-doped CNFs changed from −(59.49 ± 0.30) to −(126.84 ± 1.16) kJ/mol with the increase in nitrogen content from 7.07 to 11.25 wt. %. The enthalpy of formation of carbon nanoflakes was −(29.78 ± 0.58) kJ/mol which is higher than that for N-doped CNFs.

1. Introduction

Nitrogen-doped carbon nanomaterials (CNMs) are interesting due to their unique physico-chemical properties [1,2] which enable their applications in different areas such as supercapacitors [3,4], Li ion batteries [5], catalyst supports [6–8] etc. It has been observed that the nitrogen content in such CNMs may vary in a wide range. For example in nitrogen-doped carbon nanotubes (N-doped CNTs) the nitrogen content is typically from about 1 to 4% [9–11] up to about 20% [12] whereas nitrogen-doped carbon nanoflakes (N-doped CNFs) may contain up to 10% of nitrogen depending on synthesis conditions and nitrogen precursors [4]. Nitrogen content in carbon nanomaterials affects their characteristics, such as the specific surface area, pore size distribution [4], etc.

The most important fundamental parameters and bulk characteristics of carbon nanomaterials are the heat of combustion and the standard enthalpy of formation [13]. Earlier these values were determined for diamond (1.89 ± 0.05 kJ/mol) [14], single-wall carbon nanotubes (7 ± 1 kJ/mol) [15], cylindrical multiwalled carbon nanotubes (8.60 ± 0.52 kJ/mol) [13], herringbone multiwalled carbon nanotubes (21.70 ± 1.32 kJ/mol) [13] and carbon nanofibers (16.56 ± 2.76 kJ/mol) [13], whose values differ from the those of the enthalpy of formation of molecular forms of carbon such as fullerenes. For example, enthalpy of formation of fullerene was found to be 2288.5 ± 16.2 kJ/mol for C_{60} [16] whereas 2554.0 ± 57.6 kJ/mol for C_{70} [17].

The heat of combustion and the enthalpy of formation of carbon nanomaterials are very sensitive to the presence of functional groups on their surface. With the increase in the content of carboxylic groups on the surface of multiwalled CNTs, the values of enthalpies of formation will decrease and become negative [13,18]. The similar trend was observed for carboxylated nanodiamonds, where the enthalpy of formation decreased from −(14.0 ± 6.8) to −(50.4 ± 11.4) kJ/mol with the increase of carboxylic groups content on nanodiamond surface from 0.48 up to 1.4 (COOH groups)/nm^2 [19]. Particle size and structure of carbon nanomaterials also affect the enthalpy of formation. The enthalpy of formation of onion-like carbons was established to increase with the particle size and synthesis temperature and decrease when functional groups presented in their structure, with the enthalpy of formation being positive or negative [20]. In the case of multiwalled CNTs strong dependence of the enthalpy of formation upon the structure, internal diameter, length and number of layers was found [21].

This work dedicates to the relationship between the heat of

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combustion and/or the standard enthalpy of formation of nitrogen-doped carbon nanotubes and nanoflakes, and their structure, nitrogen content and degree of defectiveness using bomb calorimetry.

2. Experimental

2.1. Synthesis

N-doped CNTs were synthesized at two different temperatures of 650 and 750 °C for the same duration of 5 h by pyrolytic decomposition of acetonitrile in the presence of Co–Mo/MgO catalyst which was placed in a quartz tube reactor with the diameter of 55 mm. The reactor was heated up to synthesis temperature with the flow of nitrogen (99.999%, Logika Ltd., 200 ml/min). Then the nitrogen flow was increased to 500 ml/min and acetonitrile (99.8%, Sigma–Aldrich) was injected into the stream.

Synthesis of carbon nanoflakes and N-doped CNFs was detailed in Ref. [22]. In a typical synthesis, magnesium oxide template with the specific surface area of 140 m^2/g, synthesized under decomposition of magnesium oxalate, was placed in the quartz tube reactor, and heated up to 900 °C in a nitrogen gas atmosphere (200 ml/min flow rate) for 1 h. Then the nitrogen flow was increased up to 1000 ml/min. Hexane was used as a precursor for CNF synthesis. Three types of organic compounds – acetonitrile, pyridine (99.8%, Reachim) and *n*-butylamine (99.5%, Reachim) were used as nitrogen containing precursors. The duration of synthesis was 0.3–1.5 h.

All as-synthesized materials were purified from the oxide impurities by boiling in HCl (99.8%, Fluka) solution. They were then washed using distilled water and dried at 120 °C for 24 h. All amorphous impurities were removed by annealing at 400 °C in air atmosphere for 4 h. Designation of the samples and synthesis parameters are given in Table 1.

2.2. Characterization

Morphology and microstructure of the samples were characterized using JEOL JSM-6390LA scanning electron microscope operating at 25 kV and transmission electron microscope JEOL 2100F operating at 200 kV. For transmission electron microscopy (TEM) investigation the small amount of sample was dispersed in ethanol using ultrasonic bath and a droplet of the suspension was placed on the polymer covered copper grid.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed using Netzsch STA 449 PC LUXX thermal analyzer with a heating rate of 5 °C/min under ambient condition.

Brunauer–Emmett–Teller (BET) specific surface area was determined using AUTOSORB-1C/MS/TPR sorption analyzer.

The chemical composition of the surface and the nature of chemical bonds were studied using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS) with a monochromatic Al Kα source (hν = 1486.6 eV, 150 W). The XPS elemental content was calculated based on the peak areas using Kratos sensitivity factors. High resolution N1s XPS spectra after Shirley background subtraction were deconvoluted into eight Gauss-Lawrence (70:30) components at the fixed binding energies of 398.3, 399.5, 400.1, 401.1, 402.5, 404.4, 405.5 and 407.2 eV which corresponded to different nitrogen containing groups (see further). For 2.52N–CNT sample the additional component was used for overlapped $Mo3p_{3/2}$ line. The content of each nitrogen containing group was proportional to the area of the corresponded component in N1s XPS spectrum. O1s XPS spectra indicated different oxygen species including metal oxides (MgO, MoO_3) as well as poorly resolved components of carbon and nitrogen bonded oxygen atoms resulted from the oxidation and contamination of the surface of studied samples.

The amounts of C, H and N in the samples were measured using Elementar Vario MicroCube elemental analyzer. Hitch of 1–2 mg of material was placed onto Sn boat to be burn at 1150 °C in the flow of oxygen (99.7%, Logika Ltd.). CO_2, H_2O and N_2 were analyzed by TCD detector. For each material the analysis was repeated 3–4 times.

Raman spectra were registered using LabRam HR800 UV microscope-spectrometer using 5 mW argon laser excitation (514.5 nm) and 50× Olympus lens. For each Raman experiment the spectrum was obtained at least in three points and then they were averaged.

The determination of the heat of combustion was performed using an e2k isothermal bomb calorimeter. The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (DDS CAL2k). Its specific energy of combustion was (26.456 ± 0.006) kJ/g. Graphite was used as a reference point and its energy of combustion measured using the present isothermal bomb calorimeter was found to be equal to (32.81 ± 0.03) kJ/g that was in good agreement with the reference value of (32.79 ± 0.13) kJ/g [23]. The measurement procedure was similar to the one used for carbon nanotubes described earlier [13]. Pellet of carbon or N-doped carbon nanomaterials (~0.4 g) was pressed with benzoic acid as an internal standard at a ratio of 1:3 and placed onto a bomb of calorimeter followed by filling of 30 bar of oxygen (99.7%, Logika Ltd.). In the case of N-doped CNMs 1 ml of water was added into the calorimetric bomb for thermodynamic equilibrium establishment. The amount of solution of nitric acid obtained was determined by acidimetric titration with alkali in the presence of phenolphthalein. Under the condition of bomb calorimetric experiments nitric acid was quantitatively allocated. The reaction gas products were analyzed on Agilent Technologies 6890N gas chromatograph equipped by 5 m HayeSep column filled with Porapaq R and TCD detector. In all cases only CO_2 was found as a product of full CNM burning. For each material the experiment was repeated at least 5 times to determine the statistical error that includes statistic deviation, errors in deviation of elemental compositions, errors in the determination of enthalpy of formation CO_2 and instrument error of bomb calorimeter [24].

Table 1
Synthesis parameters of carbon and N-doped carbon nanomaterials.

Sample	Precursor	T (°C)	Duration of synthesis (h)
1.54N–CNT[a]	Acetonitrile	750	5
2.52N–CNT	Acetonitrile	650	5
CNF	Benzene	900	0.3
7.07N–CNF	*n*-Butylamine	900	0.5
7.68N–CNF	Pyridine	900	0.5
11.05N–CNF	Acetonitrile	900	0.5
11.25N–CNF	Acetonitrile	900	1.5

[a] The number before N letter denotes the nitrogen content according to elemental analysis data (see farther).

3. Results and discussion

Fig. 1 shows scanning electron microscopy (SEM) and TEM images of the synthesized materials. Fig. 1a and c respectively show bundled 1.54N–CNT and 2.52N–CNT at low magnification. The N-doped CNTs reveal a bamboo-like structure with multiple jumpers between internal walls (Fig. 1b and 1d). Typically the internal channels were found to be thicker than those in undoped CNTs but the number of carbon layers was smaller in this case. Images of undoped CNFs are shown in Fig. 1e and 1f. CNFs doped with different amount of N are shown in Fig. 1g–n. It is clearly seen that