Short Communication

The Structure and Content Peculiarities of Carbon Material Obtained under the Polyacrylonitrile Infra-red Heating

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It is first determined by the semiempirical quantum chemical model MNDO for a carbon material (CM) structure based on polyacrylonitrile (PAN) heat-treated that the increase of a content N from 14 to 18 atoms in CM monolayers $C_{46}N_{14}H_{10}$, $C_{44}N_{16}H_{12}$, and $C_{42}N_{18}H_{14}$ and a content H from 12 to 22 atoms in CM monolayers $C_{44}N_{16}H_{12}$ and $C_{44}N_{16}H_{22}$ leads to the decrease of the binding energy (E_B) from 7.40; 7.12 to 6.88 and 6.25 eV, respectively; and to the increase of the differences between the maximum and minimum bond lengths (Δl), between the maximum and minimum valence angles ($\Delta \Theta$), and between the maximum and minimum local charges (Δq) from 0.176 Å; 12.0°, and 0.487 to 0.238 Å; 20.8°, and 0.613, respectively, and promotes the CM structure curvature. Quantum chemical simulation results are confirmed by the element analysis of CM samples and a nanocomposite $FeNi_3/C$. As the IR heating temperature is increased from 30 to 500 °C, concenrations N (C_N) and H (C_H) in the CM and nanocomposite $FeNi_3/C$ are decreased from 27 to 18 and 10 wt % and from 6 to 1 and 0.5 wt %, respectively.

Keywords: Polyacrylonitrile, Simulation, Structure, Heating, Nitrogen, Carbon, Nanocomposite.

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1. INTRODUCTION

In recent years, the cost-effective method using an infrared (IR) heating is used for the creation of functional carbon nanocrystalline materials based on polymers. When the electromagnetic radiation of an IR range with the polymer is interacted, the synergistic effect accelerating polymer transformations based on the self-organization principle is observed [1]. One of the widespread polymers having the broadest range of physical and chemical properties and various applications is polyacrylonitrile (PAN) [2, 3]. The chemical and structural PAN transformations under an IR heating occur, and when the temperature increases, a polyconjugation system is formed. The crystalline and amorphous phases decrease and disappear in the PAN structure, and carbon material (CM) with semiconducting properties is formed (Fig. 1) [1].
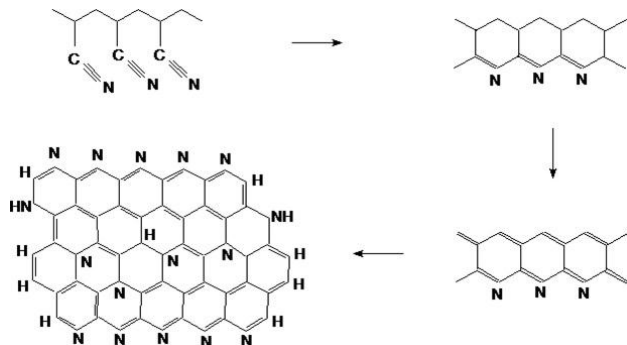

Fig. 1 – Chemical transformations in the PAN structure under an IR heating

Chemical bond hybridization types sp1, sp2 and sp3 for carbon atoms, the nitrogen presence in the CM based on PAN, and the CM modification by metal nanoparticles suggest the appearance of new promising chemical and physical properties such as electrical conductivity, optoelectronic properties, density, adsorption, the work function of the electrons, electromagnetic absorption, and catalytic and sensory properties. These properties are very promising for the low-temperature connection diode and triode structures with thermal molybdenum compensators in power semiconductor devices , for the manufacture of sensors with a high sensitivity to pH and CO_2; fast optical switches; indicators; oxidation catalysts for manufacturing a fuel cell; efficient heat transfer materials; systems with a density equal to 10^{12} bit/sm² for recording an information; cold cathodes with an intense electron emission of ($\sim 10^6$ cm^{-2}), a low threshold voltage (V < 1.5 V/mm), and high emission current density (> 100 mA·cm^{-2}); electrical contacts with a low friction for power plants; effective electromagnetic shielding; robotics actuators changing the shape and size with the power supply [1-8].

However, there is no data on the qualitative and quantitative influence of carbon, nitrogen, hydrogen or metal on the stability and configuration of the CM structure based on PAN. Therefore, the aim is to identify the optimal spatial structure and geometry of a PAN-based CM monolayer obtained by IR heating, the influence of the content for N and H atoms on structuring the CM, and the analysis of the distribution charge-density in the structure.

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2. EXPERIMENTAL

The CM structure simulation is performed by a molecular cluster model and semi-empirical quantum-chemical calculation scheme MNDO (Modified Neglect of Diatomic Overlap modified) using the program package GAUSSIAN 03 [9, 10]. To create the CM, PAN ($M\eta = 1 \cdot 10^5$) synthesized by a redox method is heated by an IR heating set QHC-P610CP. The elemental analysis of samples was carried out by an atomic absorption spectroscopy and pyrolysis chromatography on AAS-30 spectrometer and chromatograph "Carlo Erba", respectively.

3. RESULTS AND DISCUSSION

The simulation of the CM structure for PAN heat-treated carbon material and the investigation of the influence for the N and H content on the CM structure is of interest for the controlled synthesis of the CM with promising physical and chemical properties (Fig. 1) [11, 12]. Four variants for the CM monolayer structures ($C_{46}N_{14}H_{10}$, $C_{44}N_{16}H_{12}$, $C_{44}N_{16}H_{22}$, $C_{42}N_{18}H_{14}$) containing a different number of atoms N and H and constructed in accordance with the covalence of atoms contained in the structures are considered (Table 1). The bond energy

with the use of semi-empirical quantum-chemical calculation scheme MNDO in the structures of variants $1 \div 4$ are calculated by the formula
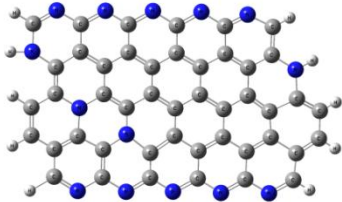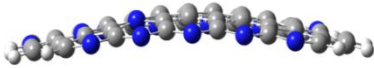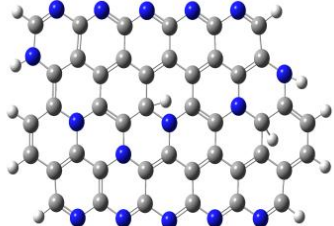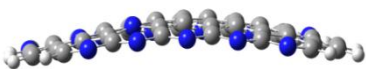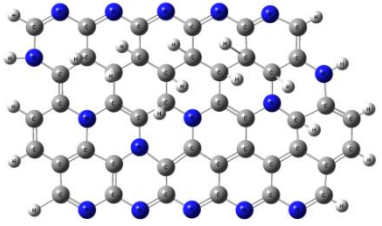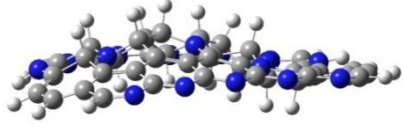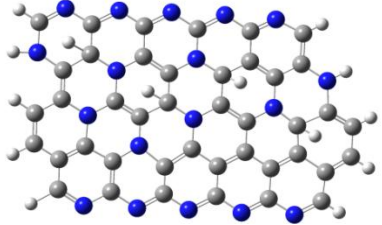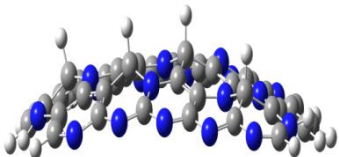
$$E_b = E_f/N_t$$
$$E_f = E_t - N_C E_C - N_N E_N - N_H E_H$$

where E_b is the bond energy; E_f is the energy of the structure formation; N_t is the total number of atoms in the structure; E_t is the total structure energy; N_C is the number of carbon atoms; E_C is the energy of the carbon atom; N_N is the number of nitrogen atoms; E_N is the energy of the nitrogen atom; N_H is the number of hydrogen atoms; E_H is the energy of the hydrogen atom.

As a result of MNDO calculations with the full optimization of the parameters for variants options $1 \div 4$, bond lengths (l), valence angles (Θ), the local charges (q), and the bond energy (E_b) are determined. To define the structure deviation from the flat variant containing only of atoms C, and to determine the curvature of the CM structure, the difference between the maximum and minimum values of the bond length (Δl), valence angle ($\Delta\Theta$), and local charge (Δq) for the structures $C_{46}N_{14}H_{10}$, $C_{44}N_{16}H_{12}$, $C_{44}N_{16}H_{22}$, $C_{42}N_{18}H_{14}$ are calculated (Table 2).
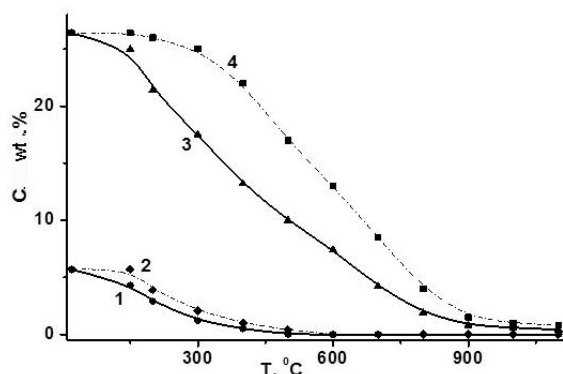
Table 1 – CM structures before and after the optimization using semi-empirical quantum-chemical scheme MNDO
(⬤- atom C; 🔵 - atom N; ⚪ - atom H)

N	Structure	Before the optimization	After the optimization
1	$C_{46}N_{14}H_{10}$		
2	$C_{44}N_{16}H_{12}$		
3	$C_{44}N_{16}H_{22}$		
4	$C_{42}N_{18}H_{14}$		

Table 2 – The difference of bond lengths (Δl), bond angles ($\Delta\Theta$) and local charges (Δq), and the binding energy (Eb) of the CM structure as a function of the chemical CM composition

N	Structure	$\Delta l = l_{max} - l_{min}$, Å	$\Delta\Theta = \Theta_{max} - \Theta_{min}$,°	$\Delta q = q_{max} - q_{min}$, a.u.	E_f, eV	E_b, eV
1	$C_{46}N_{14}H_{10}$	0.176	12.0	0.487	517.95	7.40
2	$C_{44}N_{16}H_{12}$	0.234	15.0	0.607	512.54	7.12
3	$C_{44}N_{16}H_{22}$	0.230	17.0	0.547	512.21	6.25
4	$C_{42}N_{18}H_{14}$	0.238	20.8	0.613	508.91	6.88

It is found that the increase of the N content from 14 to 18 atoms (Table 1; N1, 2, 4) and the hydrogen content (Table 1, N2, 3) from 12 to 22 atoms in the CM structure leads to an increase of changing bond lengths (Δl), valence angles ($\Delta\Theta$), and local charges (Δq) characterizing the difference in energy of the atom electron affinity, and promotes the curvature of the CM structure and the decrease of the bond energy (Table 1, 2). The appearance of local charges in the system contributes to increasing the chemical activity of the CM and adsorption ability and suggests the possibility for sensor properties. Quantum-chemical calculations show that the increase of the content N and H in the CM from 14 and 12 to 18 and 22 atoms decreases E_b structure from 7.40 and 7.12 to 6.88 and 6.25 eV, respectively.

Fig. 2 – The concentrations of the H (1, 2) and N (3, 4) as a function of IR heating temperature in the nanocomposite FeNi$_3$ / C (1, 3) and the carbon material (2, 4)

The results of the quantum-chemical simulation are confirmed by the elemental analysis using the atomic absorption spectroscopy and pyrolysis chromatography of the CM and nanocomposite FeNi$_3$/ C (Fig. 2). The IR heat-ing temperature growth from 30 to 500 °C decreases the concentration of nitrogen (C_N) and hydrogen (C_H) atoms in the carbon material and the nanocomposite FeNi$_3$/ C from 27 to 18 and 10 wt. % (Fig. 2, curves 4 and 3) and from 6 to 1 and 0.5 wt. % (Fig. 2, curves 2, 1), respectively.

The decrease of C_N and C_H in the nanocomposite FeNi$_3$/ C occurs more rapidly than in the carbon material. The incorporation of Fe and Ni in PAN decreases the phase change temperature to 140 °C [1]. This may be due to both the catalytic metal action and the possibility of metal complexation with nitrile polymer groups that significantly changes the way of chemical transformations in PAN under the IR heating [11].

4. CONCLUSIONS

For the first time using quantum-chemical simulation based on the adapted semi-empirical quantum-chemical scheme MNDO for CM structures obtained from PAN heat-treated, it is found that the increase of the nitrogen atom content in the CM from 14 to 18 atoms leads to a decrease of the E_b from 7.40 to 6.88 eV and the increase of Δl, $\Delta\Theta$, Δq from 0.176 Å; 12.0°; 0.487 to 0.238 Å; 20.8°; 0.613, respectively, and facilitates the curvature of the CM structure; the increase of hydrogen atom content in the CM from 12 to 22 atoms leads to the change of E_b, Δl, $\Delta\Theta$, and Δq from 7.12 eV; 0.234 Å; 15.0°; 0.607 to 6.25 eV; 0.230 Å; 17.0°; 0.547, respectively.

The results of the quantum-chemical simulation are confirmed by the elemental analysis using the atomic absorption spectroscopy and pyrolysis chromatography of the CM and nanocomposite FeNi$_3$/ C. The IR heating temperature growth from 30 to 500 °C decreases the C_N and C_H atoms in the carbon material and the nanocomposite FeNi$_3$/ C from 27 to 18 and 10 wt. % and from 6 to 1 and 0.5 wt. %, respectively.

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