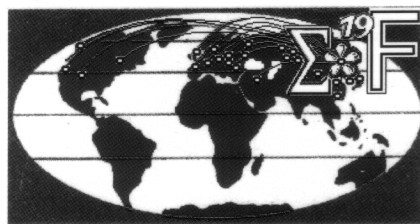


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SYNTHESIS AND SPECTROSCOPY STUDIES OF FLUORINATED ACTIVATED CARBON FIBERS

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Abstracts

The activated carbon fibers (ACF) fluorinated at various temperatures have been synthesized and investigated by techniques of X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (ESR) and X-ray diffraction (XRD). At 150 °C the compound containing nanographenes with edge atoms covalently bound to fluorine has been formed.

Introduction

The activated carbon fibers form a wide class of porous materials with large specific surface ($1000 - 3000 \text{ m}^2 \text{ g}^{-1}$) and find various technological applications. The structure of ACFs is represented by a three-dimensional network of nanosized graphite particles (nanographites), consisting of three to four nanographenes (fig. 1) with the average basal plane size about 2 nanometers. [1, 2]. In nanographite the ratio between inner and surface atoms of carbon is much less than in bulk graphite, that specifies an opportunity of qualitative difference in their physical and chemical properties from those for bulk graphite.

Presence of open edges in nanographenes and nanographites essentially distinguishes them from fullerenes and nanotubes having closed π -electronic system. Presence of nanosize conjugated π -electronic system and the edge π -electronic states allows to consider nanographites as new mesoscopic system with specific properties which distinguish them both from bulk graphite and from fullerenes and nanotubes. Due to the intermediate position between bulk graphite and aromatic molecules nanographites are a potential source of new chemical compounds with unusual electronic and magnetic properties.

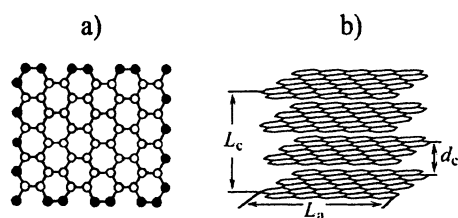


Fig.1. Schematic representation of graphene (a) and nanographite (b). Graphene edge atoms of carbon are painted. L_a and L_c – sizes of Nanographite, d_c – distance between nanographenes

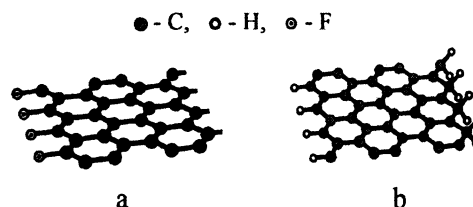


Fig.2. Nanographenes with chemically modified edges: a – fluorinated, b – hydrogenated

At present in various laboratories works searching the ways of controllable chemical bonding of edge atoms of nanographene with atoms of one or two different kinds. According to calculations [3], such compounds can possess new properties. In particular, in nanographenes, in which edge atoms are bound to atoms of hydrogen or fluorine (fig. 2), the magnetic moments of electrons on edge can be ordered.

The important stage on the path of synthesis of magnetic nanographite is the controllable modification of a chemical state of its edge atoms. One of ways of solutions of this problem is the change of their chemical states by bonding with halogens. Previously we synthesized ACFs containing nanographites at which edge atoms of carbon are covalently bound to chlorine [4].

Experimental

In experiments on fluorination the fibers, consisting of nanographite particles which have three to four nanographenes, have been used. The average sizes of nanographite in a basal plane – $L_a \approx 2 \text{ nm}$, average value of interlayer distances – $d_c \approx 0,405 \text{ nm}$.

Table 1.

Sample (No)	Temperature of synthesis (°C)	Time of synthesis (h)	Element concentration (in percentage to carbon)			Binding energies (eV)			
			F	O	Br	C1s	F1s	O1s	Br3d
Purified ACF				< 4		284.3		533.1	
1	100*	80	6	16	< 2	284.7 287.9 289.7	686.9	531.5 532.8	70.2
2	130*	16	≈ 1	9	≈ 1	284.4	687.2	531.4 533.9	69.8
3	150	16	24	< 3	≈ 1	285.0 287.7 290.0	686.4	532.5	70.1
4	300	16	53	≈ 3	< 2	287.0 289.6 291.2	688.1	531.4 534.7	71.5

*- container with reagents was pumped out to ≈ 0.1 Torr before heating.

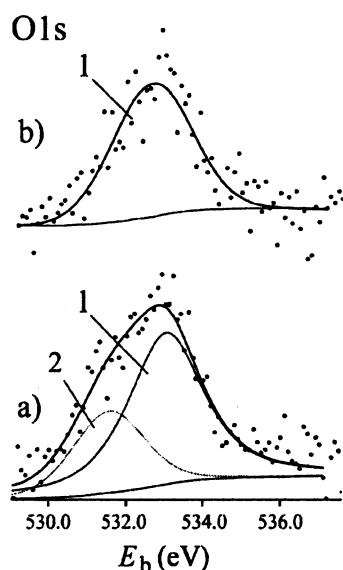


Fig.3. X-ray photoelectron spectra of oxygen 1s-electrons:

- a) – initial ACF,
 b) – ACF purified at 850 °C.
 1 – oxygen of –OH groups,
 2 – oxygen of carbonyl groups

ACF were fluorinated with BrF_3 . BrF_3 was produced in process of thermal decomposition of $\text{Na}[\text{BrF}_4]$. Excess amount of $\text{Na}[\text{BrF}_4]$ and pieces of ACFs were placed into hermetic nickel container. Container with reagents was heated up to different temperature of synthesis (T_{synth}) during long time. The temperature was kept with accuracy about 5 °C. The synthesis temperatures were selected using data on fluorination of different carbon materials [6, 7]. When T_{synth} was below the temperature of thermal decomposition of $\text{Na}[\text{BrF}_4]$ (≈150 °C), the container with reagents was pumped out to ≈ 0.1 Torr before heating. In these synthesis conditions the $\text{Na}[\text{BrF}_4]$ was a fluorination agent. Data on temperature and time of heating are presented in table 1.

X-ray photoelectron spectra of compounds under investigation were measured with standard spectrometer ES-2401 (Russia) using AlK_α radiation. Vacuum in analyzer chamber of spectrometer was kept at $\approx 6 \times 10^{-8}$ Torr. The glove box connected with spectrometer was used with the aim to decrease the contact of the samples with atmosphere water. Photoelectrons binding energies (E_b) were measured accordingly to Fermi level (E_F) position of spectrometer. Effect of possible sample charge during photoemission was not taken into account. The experiment geometry, analyzer transmission function, photo-ionization cross-sections and core electron wave function asymmetries were taken into account at the calculation of chemical element concentrations

using photoelectron spectra. Concentrations of chemical elements relatively to carbon and basic data on binding energies of C1s-, F1s-, O1s- и Br3d-electrons are presented in table 1. The C1s-electron spectra of some samples are presented in Fig. 4.

Large specific surface of ACFs allows to ignore the surface effects in XPS experiment. However, the inhomogeneity of the matrix should be taken into account when XPS data of nanographite particles in ACF are analyzed. In addition to consolidated nanometric graphite particles ACFs include the impurity fraction of aliphatic carbon. Carbon of this fraction also may interact with oxidizer. Special investigation of residual gases mass-spectra in high-vacuum chamber shows that long time heating of ACFs at temperature 800-850 °C at high vacuum condition leads to practically full elimination of “free” aliphatic fraction [4]. Heating of ACF at temperature 800-850 °C leads to decreasing the oxygen content in the sample from ≈10 down to 3-4 %. Types of oxygen

functional groups change also (fig. 3). In the presented experiments only ACFs previously purified by this way were used.

X-ray diffraction data were obtained using spectrometer Bruker D8 (Germany) and presented in fig. 5. ESR spectra were measured using spectrometer Bruker EMX 6.1 (Germany). An example of ESR spectrum of fluorinated ACF synthesized at temperature 150 °C is presented in fig. 6.

Results and discussion

Values of element concentration in the synthesized samples (table 1) show that at $T_{\text{synth.}} < 150$ °C (temperature of Na[BrF₄] decomposition) time is the main factor which determines the degree of nanographite fluorination/oxidation in this synthesis technique and chosen reagents. Relative oxygen content in the samples increases up to 10-20 % and point out its participation in oxidation of nanographite. Meanwhile O1s-electron spectrum becomes similar to oxygen spectrum of ACF which was not preliminary purified. At $T_{\text{synth.}} \geq 150$ °C the temperature determines the degree of nano-graphite fluorination. Oxygen content remains at the rate of 3-4 % (table 1).

Smoothed C1s-electron spectra of purified ACFs and those treated with fluorine are presented in fig. 4. C1s-electron spectrum of purified ACF (fig. 4a) consists of a single asymmetric line which is typical for carbon conducting materials. Signals with low intensities that may be found at high energy side of main carbon line relate to carbon atoms bound with different oxygen-containing functional groups.

In the C1s-electron spectrum of the sample fluorinated at $T_{\text{synth.}} \approx 100$ °C (fig. 4b) the intensities of high binding energy signals increase. This fact indicates that carbon atoms form the bonds with oxygen and fluorine. In the carbon spectrum of the samples fluorinated at ≈ 150 °C (fig. 4c) the intensive signal of carbon covalently bound with fluorine is observed. Integral intensity of this is equal to 25-30% of the carbon signal intensity and approximately corresponds to the percentage of the edge carbon atoms of nano-graphite in the ACFs under investigation.

Spectra of ACF fluorinated at ≈ 300 °C have essentially different characteristics. In this spectra photoelectron signals of all elements are shifted to the high binding energies. This fact points out the sample is charged during a photoemission process. Therefore, conducting properties of the sample are changed. In the C1s-electron spectrum (fig. 4d) the intensive signal of carbon atoms covalently bound to fluorine is observed. Taking into account the fluorine amount (table. 1), the shape of carbon spectra lines and the presence of signals in the carbon spectrum which belong to the $\equiv\text{C}-\text{F}$ and $>\text{CF}_2$ groups, one may conclude that a new compound forms.

Composition of compound and motif of its carbon layers structure are close to polydicarbonmonofluoride (C₂F)_n [6], that consists of undulated layers of sp^3 -hybridized carbon and is not a conductor.

X-ray diffraction spectra of purified and fluorinated ACFs are qualitatively similar and consist of (002), (01) and (11) peaks (fig. 5). Position of the first peak characterizes average interlayer distance in nanographites and its width is determined by average coherence length in the direction perpendicular to nanographenes. Positions and widths of two other peaks are determined by the distance between nanographene sheets and size of nanographite particles in a basal plane, correspondingly. In the samples fluorinated at temperature below 150 °C (fig. 5, curve 2) structure of nanographene does not undergo essential changes. In the samples fluorinated at 150 °C (fig. 5, curve

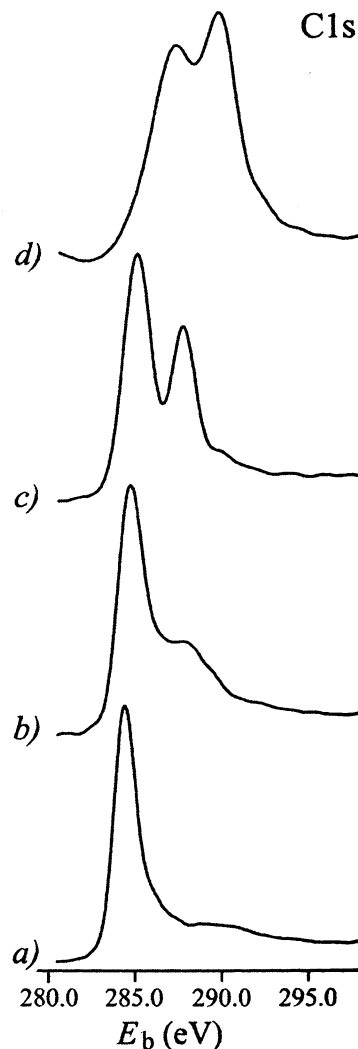


Fig.4. X-ray photoelectron spectra of C1s-electrons:
a – purified ACF; b, c, d – ACF, fluorinated at 100, 150 and 300 °C, correspondingly

3) and at 300 °C (fig. 5, curve 4) nanographene sheets still are present, but in them the average interlayer distance and scattering of these distances is much exceed those in the purified sample (fig. 5, curve 1).

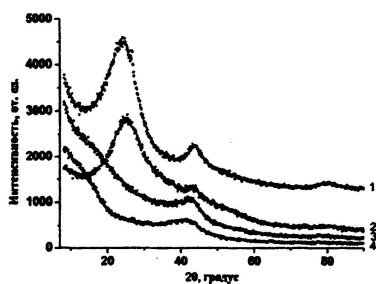


Fig.5. X-ray diffractions spectra of purified (1) and fluorinated (2-4) ACFs. Spectra 2, 3 and 4 belong to the samples, synthesized at 100, 150 and 300 °C, correspondingly

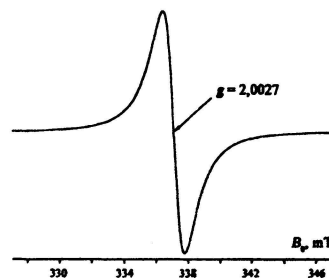


Fig.6. ESR spectrum of ACF, fluorinated at 150 °C

ESR spectra for all investigated samples at room temperature consist of a single symmetric signal of conduction electron spin resonance with $g=2.0027(2)$. The width of the signal for initial not purified sample at room temperature is equal to ≈ 6 mT and decreases at fluorination down to $\approx 1,5$ mT.

Conclusion

The activated carbon fibers fluorinated at various temperatures have been synthesized and investigated by XPS, ESR and XRD techniques. It is established, that at all temperatures of synthesis nanographite particles keep layered structure. For the first time at ≈ 150 °C the compound containing nanographite particles in which edges are decorated by fluorine has been synthesized. According to ESR and XPS data, the specified compound keeps conducting properties. It is possible to estimate approximately the size of nanographite in a basal plane from the ratio of integral intensities of C1s-electron signal of edge carbon atoms chemically bound to fluorine, and other carbon atoms of nanographene (nanographite) not bound to fluorine. Fluorination of ACFs at ≈ 300 °C leads to formation of the compound close on structure to polydicarbonmonofluoride (C_2F)_n.

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