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Changes of structure, electronic and magnetic properties of three dimensional disordered network of nanographites at interaction with different molecules

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Abstract. At adsorption of some molecules by nanoporous carbon materials consisting of a three dimensional disordered network of nanographites, the peripheral spin-polarized π -states of nanographites can transform because of interaction with "guest" molecules. In this work the results of investigation of influence of different adsorbed molecules on structure, electronic and magnetic properties of activated carbon fibers and their nanosized constituents are presented.

Introduction

Nanoporous carbons materials consist of a three dimensional disordered network of nanographites [1,2]. This particular structure makes them a good model system for studying nanographites. There are a few reasons for interest of scientists to nanographites. First, due to their intermediate position between the bulk graphite and aromatic molecules, nanographites are the potential source of new chemical substances with unusual electronic and magnetic properties. Second, while the fullerenes and carbon nanotubes are close shaped π -electron conjugated systems [3] which electronic properties are mainly controlled by the quantum size and surface effects, the nanographites represent the edge-open π -electron conjugated system.

Obviously, an arbitrary shaped graphene sheet comprises two kinds of edges: zigzag and armchair type edges. The calculations for the model of graphite ribbons — one dimensional graphite lattices of finite width, show that ribbons with zigzag edges possess edge states with energies close to the Fermi level [4,5]. These edge states correspond to the nonbonding molecular orbital (nonbonding π levels superimposed on the bonding π and antibonding π^* bands). In contrast, edge states are completely absent for ribbons with armchair edges. However, in a general finite graphene sheet consisting of both types of edges, even a few zigzag sites per sequence are shown to lead to non-negligible edge-state effects, resulting in an enhancement in the electronic density of states at the Fermi energy [5]. The theoretical investigations of the stacking effects in the zigzag nanographite sheets show that the edge states are sensitive to the type of the graphene layers stacking [6,7]. In last years, the reality of edge spin-polarized π -electron states was established experimentally [8–10].

In this work, the results of investigation of changes of structure, electronic and magnetic properties of activated carbon fibers (ACFs) at absorption of different molecules are presented.

1. Results and discussion

According to the X-ray data (Fig. 1) nanographites — structural blocks of ACFs, consists of 3–4 nanographene layers with the interlayer distance 0.4 nm. The mean in-plane size of nanographite is ≈ 2 nm. Nanosized pores divide the nanographite domains from each other. The small-angle neutron scat-

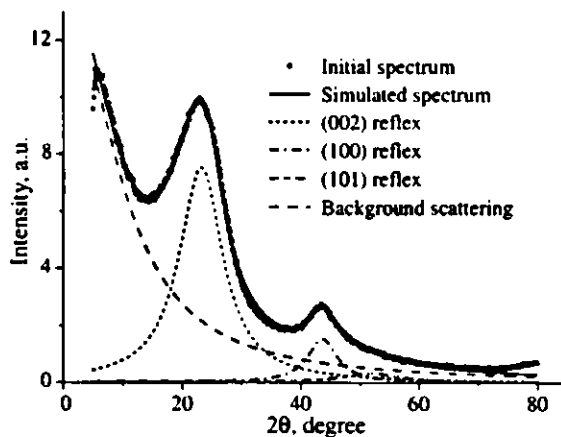


Fig. 1. X-ray diffraction spectrum of ACFs and its representation as the sum of components corresponding to the (002), (100) and (101) reflexes.

tering data shows, that there are two kinds of pores in ACFs: the nanopores with the sizes ≈ 1.2 nm and ≈ 10 nm.

The XPS spectrum of C1s-electrons of ACFs contains intensive peak with the binding energy 284.4 ± 0.1 eV (Fig. 2). The lineshape parameters of this peak are near the same for bulk graphite. Three less intensive peaks with the binding energies 285.9 ± 0.2 , 288.6 ± 0.2 and 290.6 ± 0.3 eV are also observed near this peak. According to the literature data [11] they belong to aliphatic fragments, C-OH bond and $\pi - \pi^*$ excitations, respectively.

The ESR spectrum of ACFs consists of two weakly asymmetrical signals with different linewidth. The values of asymmetry parameter A/B and g -factor, equal for both signals, are 1.15 and 2.0027 ± 0.0001 , respectively. The integral intensity of broad signal does not depend on temperature, while the integral intensity of narrow signal increases at decreasing of temperature. Therefore, the former signal corresponds to the conduction electrons and the latter signal to the localized spins. The concentration N_s of localized spins was found from the magnetic susceptibility data. Thus, by comparing the integral intensities of localized (I_s) and delocalized (I_c) spins, we can estimate the density of states near the Fermi level of nanographites: $D(E_F) = (I_c/I_s) \times (N_s/k_B T)$. Such calculations show that $D(E_F)$ for nanographites is several orders higher than the same value for the bulk graphite.

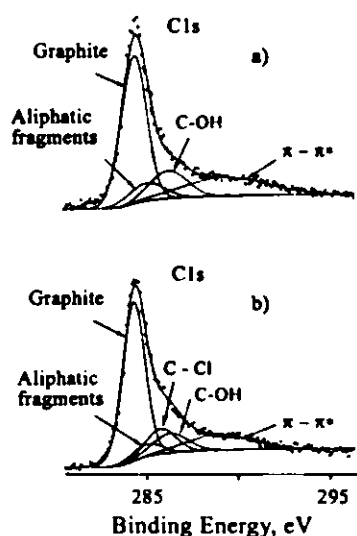


Fig. 2. XPS-spectra of Cl 1s-electrons for initial (a) and chlorinated (b) ACFs.

The absence of linewidth temperature dependence for narrow signal also in non-evacuated sample indicates that the localized spins are in the interlayer space of nanographites. Furthermore, the Curie-Weiss type temperature dependence of the magnetic susceptibility gives evidence that they are present in the nanographites in form of small clusters.

The comparison of integral intensities of ESR signal from conduction electrons in evacuated sample and in the oxygen atmosphere shows that the presence of oxygen molecules increases the number of current carriers near the Fermi level by 25–30%.

At adsorption of halogens by ACFs the intensity and linewidth of conduction electron signal decreases, while their g-factor values increase to 2.0032. Simultaneously, the concentration of localized spins is increased approximately twice (Fig. 3). The XPS data shows (Fig. 2) that at adsorption of these halogens by ACFs the part of nanographite edge carbon atoms forms the covalent bonds with them. We assume that this is the reason for the above-mentioned changes of conduction electron characteristics.

In ACFs with different sorbate the sign and quantity of the (002) X-ray diffraction peak shift, relative to its position in a spectrum of initial fibers, depend on the nature of sorbate. For example, among ACFs with spirits, the sign of this shift changes from the negative to the positive at the transferring from propanol- to isopropanol-containing fibers. In the spectrum of ACFs with water, the (002) peak is located in larger 2θ-angles, than that in a spectrum of a macroscopic graphite. In ACFs with chlorine the sign and quantity of (002) peak displacement is near for its theoretical value for chlorine molecules in nanographite interlayer space. In experiments with some sorbets, a small narrowing of the (100) peak, determining the identity period along nanographene sheets, was also observed. All above-mentioned experimental data can be interpreted as a result of intercalation, at which, simultaneously with increasing of mean distance between graphene sheets, their shift relatively to each other occurs.

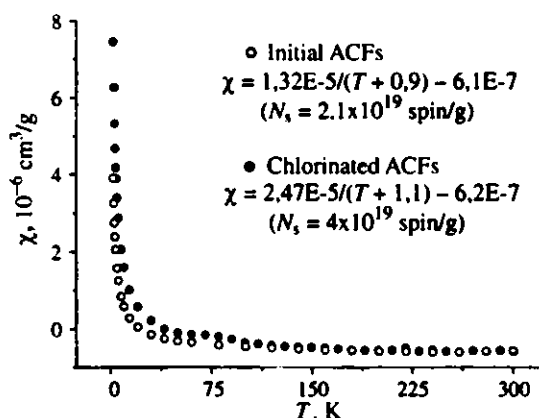


Fig. 3. Temperature dependences of magnetic susceptibility for initial and chlorinated ACFs (the theoretical expressions for approximation curves and localized spin concentrations, N_s , are presented, also).

2. Conclusion

The effect of different molecules adsorption on the structure, electronic and magnetic properties in a nanographite network system is investigated by using ACFs as a host material. We found that the density of electronic states near the Fermi level of nanographites — structural blocks of ACFs, is more, than that in macroscopic graphite. So, in nanographites, with random distribution of armchair and zigzag edges of graphene sheets, stable localized edge π-states, generating peak density of states near the Fermi level, are realized. It was shown that the adsorbed species of different substances are classified into the three groups with respect to the interaction with nanographites: physisorption species, charge transfer species, and covalent bonding species. Only last species destroy the edge π-states of nanographites. However, first two species can displace the Fermi level and change the concentration of delocalized spins.

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