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SPIN LOCALIZATION IN ACF DETECTED WITH EPR

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Pure ACF were compared to the ones with adsorbed $C_6H_5NO_2$ molecules, using the EPR technique. If there was a charge transfer between the quasi-graphitic (turbostratic) particles and guest molecules, the hyperfine interaction of electron spin with N or H nuclei could give information about the host-guest interaction. To get unpaired electrons in the vicinity of nitrobenzene molecules we admix some metallic sodium during the distillation process of the nitrobenzene. In effect we observe the EPR signal from unpaired electrons from Na, with splitting of their energy levels due to the interaction with the nuclear spins of nitrogen, hydrogen and sodium. The hyperfine structure of the EPR spectrum disappears after introducing the $C_6H_5NO_2$ + Na mixture into the ACF porous matrix. At the same time the integral intensity of the EPR signal from spins localized within the ACF nanoparticles increases. It indicates that electrons are transferred from sodium-nitrobenzene mixture to the ACF carbon matrix to be localized within the nanoparticles.

INTRODUCTION

Activated Carbon Fibers (ACF) are made up of quasi-graphitic particles of nanometer size. They consist of several graphene layers with spacing different from graphite. Process of activation causes the development of the slit pores – quasi 2D empty voids of approximately 1 nm size between the nanoparticles. Thus ACF have very good adsorption properties with specific surface area up to 3000 m^2/g (Rao, Fung, Dresselhaus & Endo, 1992). The texture of nanoparticles is presented on the Fig 1.

Interactions between the adsorbed molecules and the porous matrix (host-guest interactions) are the reason of changes observed in the system, e.g. it is possible to observe the so-called hexatic phase (Radhakrishnan, Gubbins & Śliwińska-Bartkowiak, 2002). There is also a change of the spacing between the graphene planes of the nanoparticles from 0.38 to 0.34 nm (Drozdowski H.) and, for the most important – the significant change of the ACF electronic properties what allows us to treat the examined system as a matrix of quantum dots (yet disordered) with possibilities to control the electrical transport (Kempiński, Kempiński, Kaszyński & Śliwińska-Bartkowiak, 2006).

SPIN LOCALIZATION IN ACF

Granular Metal model

ACF exhibit peculiar electronic properties resulting from the granular structure. The carbon particles are linked structurally forming the disordered texture. Although connected mechanically, the particles are separated with potential barriers for hopping of charge carriers between them. Thus ACF resemble granular metals in the insulating regime, near the Mott's transition (Fung, Wang, Dresselhaus, Dresselhaus, Pekala & Endo, 1994). For such systems the Coulomb-Gap Variable Range Hopping (CGVRH) model is applied, with the following equation describing the electrical transport:

$$\rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{2}}, \qquad (1)$$

where ρ is the resistivity, ρ_0 – proportionality constant, T – temperature and T_0 – activation energy for hopping (Fung et al., 1994). Such model implies that resistivity increases with lowering of the temperature and system changes from half-metallic to insulating as thermal excitations become too low to allow the charge carriers to move between the ACF's nanoparticles. Following the simple model:

$$\rho = \sigma^{-1} = \left(Ne\upsilon\right)^{-1}, \qquad (2)$$

where σ is the conductivity, N – number of charge carriers in the conducting band, e – electron charge and ν - carriers' mobility, we get that with lowering of the temperature the number of localized spins increases as the conduction electrons become trapped in localized states within the nanoparticles.

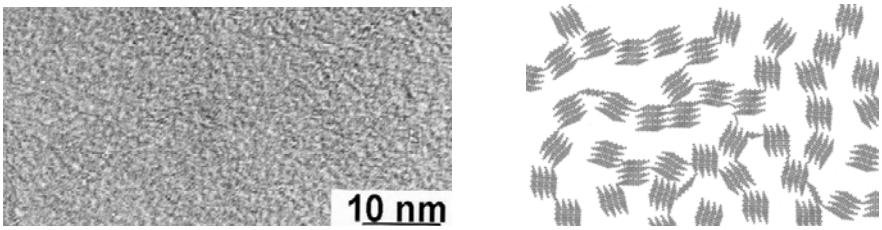

Fig. 1. Texture of ACF nanoparticles. a) TEM image, b) schematic representation of the quasi-graphitic nanoparticles' arrangement.

Electron Paramagnetic Resonance of ACF.

To try to examine the influence of the adsorbed molecules on the electronic properties of ACF, we have performed the Electron Paramagnetic Resonance (EPR) studies on pure ACF samples and with adsorbed $C_6H_5NO_2$ (nitrobenzene) molecules.

Experimental. EPR spectra of ACF were acquired with Radiopan ES/X spectrometer, equipped with Oxford Instruments gas flow helium cryostat, in the temperature range of 4.2–300 K. Fibers were acquired from Osaka Gas Chemicals Co. Ltd, Japan. ACF samples were evacuated at 200 °C by pumping with a turbomolecular pump at 10^{-4} mbar for 1 h in order to get rid of the unwanted molecules adsorbed previously. Introduction of the nitrobenzene molecules were performed without opening the sample to ambient conditions, to ensure the full filling of the pores only with the selected substance.

Pure ACF. Spectra of the ACF samples after purification can be observed only in temperatures below 100 K, where the fibers become insulating and there are localized spins in the system. Fig 2 presents the typical EPR spectrum of the pure ACF at 20 K. It consits of the single, symmetrical lorentzian line, as the nanoparticles' size is far below the skin depth characteristic of graphitic systems (3.2 μm).

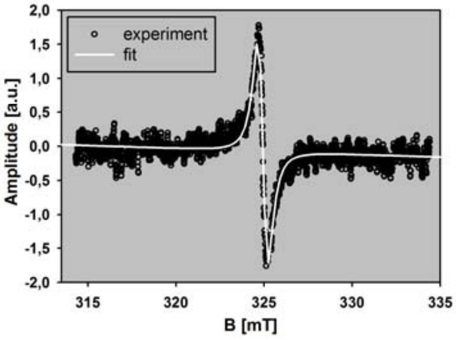

Fig. 2. EPR spectrum of pure ACF at 20 K.

g-factor equals 2.0031, the value commonly observed for carbon structures; lack of anisotropy of the g-factor suggests that spins are delocalized over the whole individual nanoparticles. Peak-to-peak linewidth ranges from 0.3 to 0.5 mT and doesn't change significantly with temperature. Integral intensity of the line increases with lowering of the temperature, but Curie law, expected for the system of localized spins, must be corrected with the term describing the increase of the number of localized spins in the system (Kempiński et al., 2006).

ACF with adsorbed nitrobenzene. Interaction with adsorbed molecules significantly changes the EPR spectrum of ACF. Fig. 3 presents the three-component spectrum, with line (1), similar to the one observed for pure ACF, and two additional broader lines.

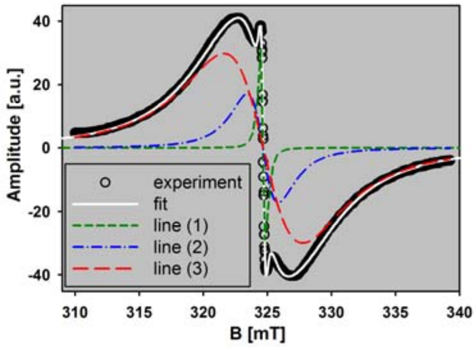

Fig. 3. EPR spectrum of ACF + $C_6H_5NO_2$ at 20 K.

According to (Kempiński, Śliwińska-Bartkowiak & Kempiński, 2004) all the three lines can be ascribed to the ACF nanoparticles from the different fiber regions. Line (1) originates from areas where the adsorbed molecules have no access, line (2) comes from the pore walls and line (3) from the fibers' surface. There is no signal from nitrobenzene, thus we can assume that spins are strongly localized within the nanoparticles and there are only weak host-guest interactions, without formation of chemical bonds.

EPR OF NITROBENZENE

In order to acquire information on the behavior of guest molecules within the ACF pores with EPR, we had to generate some unpaired electrons near the nitrobenzene, as normally the pure substance is EPR silent.

Nitrobenzene with sodium

The easiest way to get unpaired electrons is to admix some metallic sodium during the distillation process of the nitrobenzene. In effect we observe the EPR signal from unpaired electrons from Na with splitting of their energy levels in effect of interaction with nuclear spins of nitrogen, hydrogen and sodium. Fig. 4 presents the experimental result together with the simulation made with WinEPR SimFonia using the following splitting factors for the given nuclei: one Na nucleus with A = 1.01 G, one N nucleus with A = 10 G, two H nuclei with A = 0.92 G, three H nuclei with A = 2.76 G.

Nitrobenzene with sodium adsorbed in ACF

The hyperfine structure of the EPR spectrum disappears after introducing the $C_6H_5NO_2$ + Na mixture into the ACF porous matrix. At the same time the integral intensity of the EPR signal from spins localized within the ACF nanoparticles increases. It indicates that electrons are transferred from sodium-nitrobenzene mixture to the ACF carbon matrix. The other possibility is that due to the selective adsorption Na is separated from nitrobenzene and subsequently the well-known phenomenon of intercalation occurs (entering of the alkali metals in between the graphene planes) (Dresselhaus & Dresselhaus, 2002). Result of this experiment suggests that ACF is a strong electron acceptor and EPR signal in the examined system is of electron origin.

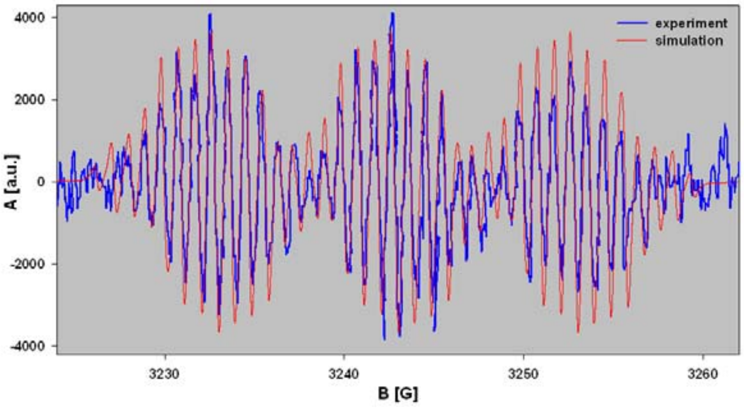

Fig. 4. EPR spectrum of $C_6H_5NO_2$ after admixture of metallic Na.

CONCLUSIONS

Strong localization of electrons in the system of carbon nanoparticles is observed after the lowering of the temperature as well as placing guest molecules into the porous system of ACF. Basic structural units of ACF, the carbon nanoparticles, are very small conducting objects and form separate potential wells. Charge transfer observed in our experiments is another evidence of strong localization of electrons in ACF.

Featured results show possible ways to control the transport of electrons in the systems of quasi-graphitic particles which can be treated as matrices of connected quantum dots with single electron conduction.

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