

# NOVEL PHYSISORPTION-INDUCED MAGNETIC SWITCHING PHENOMENON IN ACTIVATED CARBON FIBERS

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## Abstract

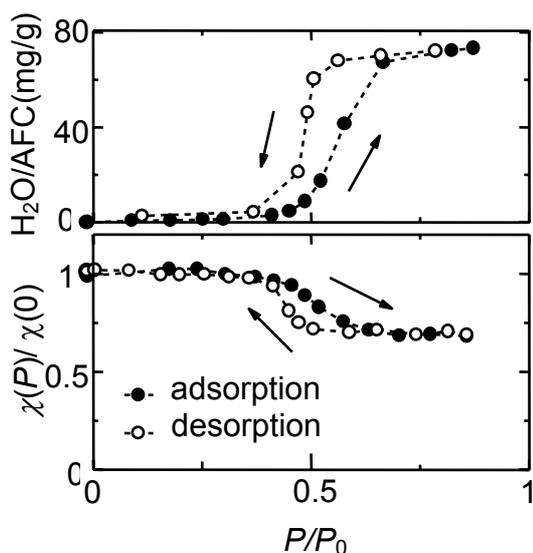
Nanoporous activated carbon fibers consist of a 3D disordered network of nanographite domains, each of which is a stack of 3-4 nanographene sheets with localized edge-state spins of edge origin being around their peripheral region. The physisorption-induced change in the magnetism of edge-state spins is investigated. The magnetism well tracks the isotherms of guest molecular species, showing an unconventional magnetic switching phenomenon from high-spin state to low-spin state with a threshold pressure upon the increase in the vapor pressure. The magnetic switching phenomenon in argon adsorption brings about the development of a magnetically ordered state in the edge-state spin system.

## Introduction

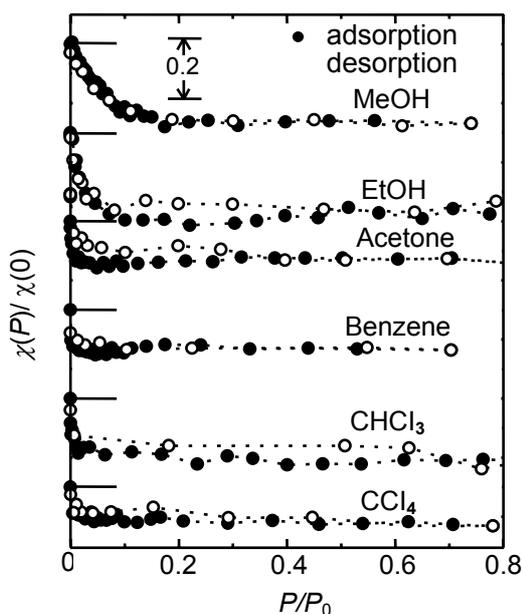
Carbon- $\pi$ -electron-based nanomaterials such as fullerenes and carbon nanotubes have been intensively investigated in this decade as targets of chemistry, physics, materials science and electronics engineering. Nanographene has been recently added to the family of carbon nanomaterials (Enoki and Kobayashi, 2005; Enoki and Takai, 2006). The important feature which distinguishes nanographene from other  $\pi$ -electron-based nanocarbon is the presence of edges in the flat-sheet of nanographene. Indeed, the peripheral shape of arbitrarily shaped nanographene is described in terms of a combination of zigzag and armchair edges. The electronic structure of nanographene depends on the geometry of its edges. Interestingly nanographene has non-bonding  $\pi$ -electron states (edge state) localized around the zigzag edge region in spite of the absence of such edge state in armchair edges. According to experimental (Andersson et al., 1998; Shibayama et al., 2000; Kobayashi et al., 2005; Kobayashi et al., 2006) and theoretical works (Stein et al., 1987; Yoshizawa et al., 1994; Fujita et al., 1996; Kusakabe and Maruyama, 2003), the localized edge-state spins are revealed to show unconventional nanomagnetic features in nanographene, such as spin glass state, magnetic switching phenomenon, edge-state-spin-based gas sensor probe, etc. (Enoki and Kobayashi, 2005; Enoki and Takai, 2006). Among these magnetic features, magnetic switching phenomenon is one of the most important features in characterizing the magnetism of nanographene and nanographite. In this paper, we present the experimentally observed magnetic switch phenomenon of ACFs with water, organic molecules, bromine and argon as guest molecules.

## Magnetic switching phenomenon in the guest adsorption process

Activated carbon fibers (ACFs) have a three-dimensional (3D) disordered network structure of nanographite domains, each of which consists of a stack of 3-4 nanographene sheets with a mean in-plane size of 2-3 nm. The inter-sheet distance (0.38 nm) between the nanographene sheets in the nanographite domain is considerably larger than the inter-sheet distance of bulk graphite (0.335 nm).<sup>11</sup> ACFs have huge specific surface areas ranging 1000-3000 m<sup>2</sup>/g, for which nanopores created between the nanographite domains are responsible. Interestingly, due to the flexible and soft structural features of ACFs, the effective pressure generated by the condensation of guest molecules adsorbed into the nanopores compresses the nanographite domains, resulting in the shortening of the inter-nanographene sheet distance. This affects the magnetism of the ACFs, as shown in Fig.1 for water adsorption (Sato et al. 2003). The increase in the water vapor pressure in the isotherm shows an ON/OFF-type stepwise change with a threshold pressure of  $P/P_0 \sim 0.5$  ( $P_0$ : saturation vapor pressure). This feature of the isotherm is associated with the hydrophobic nature of graphene surface. The pressure larger than  $P/P_0 \sim 0.5$  is required to accommodate water molecules into the nanopores. The magnetic susceptibility faithfully tracks the isotherm, as expressed by a discontinuous drop of 30-40% in the magnetic susceptibility as shown in Fig.1. This change in the magnetic susceptibility can be explained in terms of the compression of the nanographite domains by the water molecules condensed into the nanopores. The reduction of the inter-nanographene-sheet distance generated by the effective pressure induces the wave function overlap between the adjacent nanographene sheets in a nanographite domain. This strengthens the antiferromagnetic interaction between the edge-state spins on the adjacent nanographene sheets, resulting in reduction of the magnetic susceptibility as the consequence of the development of an antiparallel arrangement of the edge-state spins. This is the magnetic switching



**Figure 1.** Comparison between the water adsorption isotherm (upper panel) and the change of magnetic susceptibility (lower panel) upon water adsorption taken at room temperature.  $P_0$  represents the saturation vapor pressure of water at room temperature.



**Figure 2.** The susceptibilities of ACFs under the vapor pressure of various guest molecules.  $P_0$  is the saturation vapor pressure at room temperature. The vertical axis is shifted for each plot for clarity, where the distance between the bars is 0.3 except for the top and bottom plots.

phenomenon.

The magnetic switching phenomenon varies by replacing water molecules with other molecular species (Sato et al. 2006). Figure 2 shows the changes in the magnetic susceptibility in the adsorption/desorption processes of various guest organic molecules. Here is an interesting trend in the behavior of the susceptibility. The threshold pressure of the OH-including molecules is lowered as the weight of OH-group in the molecules decreases ( $H_2O > CH_3OH > C_2H_5OH$ ). The molecules which have no OH-group do not show a clear switching phenomenon except  $CH_3OCH_3$  that is oxygen-including molecule. This behavior suggests an importance of OH-group in a molecule we use as guest species. OH-including molecules tend to avoid the hydrophobic surface of nanographene sheet in the adsorption process. Forced

introduction of these molecules generates a repulsive force between the molecules and graphene surface, giving an effective compression to the nanographite domains. In contrast, molecules with no OH-group do not show a good performance in the compression process since they have attractive force with the graphene surface.

### Magnetic switching phenomenon triggered by phase transition

The phase transition of the molecules condensed in the nanopores also works to give the magnetic switching phenomenon. The typical case is the liquid-solid transition in the bromine molecules condensed in the nanopores, where the bromine molecules have a large density change at the freezing temperature (Takai et al. 2006). Figure 3 shows the magnetic susceptibility as a function of temperature in the bromine adsorbed ACFs at various bromine concentrations. The susceptibility of the pristine ACFs is subjected only to the behavior of the edge-state spins as discussed in previous papers (Takai et al. 2006). The edge-state spin concentration, which is proportional to the product between the susceptibility ( $\chi$ ) and the temperature ( $T$ ) in the temperature range of ca.80-260 K, is lowered as the bromine concentration is elevated. This is caused by the contribution of charge transfer bromine species. Indeed, there are three different types of the bromine species accommodated in the nanopores; charge transfer species, bromine atoms covalently bonded to the edge carbon atoms, and the physisorbed bromine molecular species which are weakly interacting with the nanographene sheets through van der Waals interaction. The edge-state is placed at the Fermi level between the bonding  $\pi$ - and antibonding  $\pi^*$ -bands in the pristine state of ACFs. The charge transfer from the nanographite to the bromine atoms down-shifts the Fermi level, making the edge state be less occupied. This leads to the decrease in the edge-state spin concentration upon the elevation of the bromine concentration.

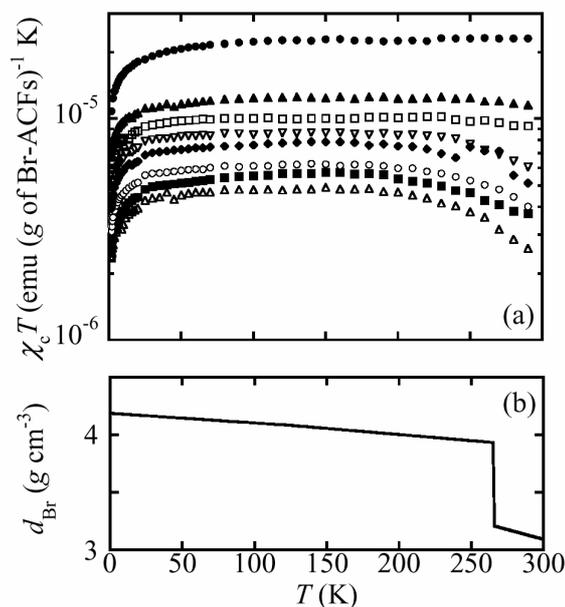
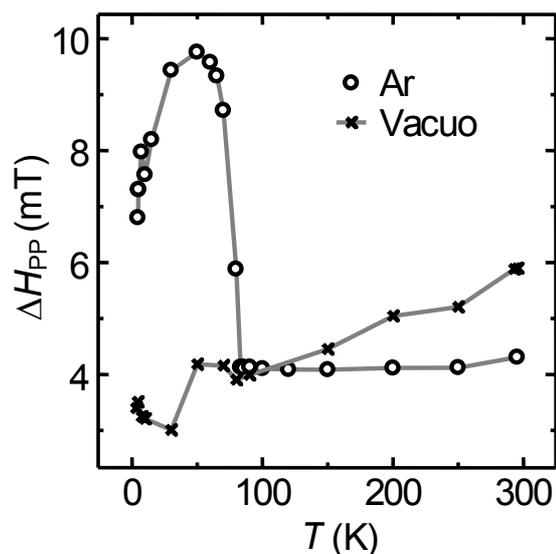


Figure 3. (a)  $\chi T$  vs  $T$  plots for bromine-adsorbed ACFs ( $0 \leq Br/C \leq 0.27$ ).  $\bullet$ ,  $\square$ ,  $\blacktriangle$ ,  $\nabla$ ,  $\blacklozenge$ ,  $\circ$ ,  $\blacksquare$ , and  $\triangle$  denote the data for the non-adsorbed ACFs and bromine-adsorbed ACFs with  $Br/C=0.038, 0.067, 0.083, 0.10, 0.14, 0.16,$  and  $0.27$ , respectively. (b) The temperature dependence of the mass density of bulk bromine.

An interesting feature in the temperature dependence of the susceptibility is the decrease in the value of  $\chi T$  at high temperatures in the high bromine concentration regime above  $Br/C=0.10$ . Actually, the value of  $\chi T$  drops above around 230 K, which is close to the freezing temperature (266 K) of bromine molecules. Here, it should be noted that the bromine molecules in the condensed phases have a large difference (20%) in the densities between the liquid phase ( $3.208 \text{ g/cm}^3$ ) and the solid phase ( $3.932 \text{ g/cm}^3$ ). The liquid phase bromine having a larger specific volume (lower density) can easily squeeze the nanographite domains, inducing the stabilization of the low spin state with a larger inter-nanographene-sheet antiferromagnetic interaction. The abrupt drop in the specific volume in the freezing temperature releases the effective pressure of the condensed bromine molecules. This takes the edge-state spins to the high spins state. Therefore, the magnetic switching phenomenon from the low-spin state to the high-spin state can take place in the liquid-solid transition in the bromine adsorption although only the physisorbed bromine species participate in this phenomenon.

We have one more example for the phase-transition-triggered magnetic switching phenomenon; that is, argon



**Figure 4.** Temperature dependence of the ESR linewidth  $\Delta H_{pp}$  of the non-adsorbed ACFs ( $\times$ ) and the ACFs in Ar atmosphere ( $\circ$ ).

adsorption effect. Argon is chemically inert guest species with no activities in the charge transfer reaction and magnetically silent with no magnetic moment. Accordingly, it can present a good model system of magnetic switching phenomenon. In the present experiment of argon adsorption, the transition from the gas phase to the liquid phase is responsible for the change in the density, which is important in the performance of the magnetic switching phenomenon. The filling rate of the argon into the nanopores gradually increases as the temperature is lowered from room temperature which is considerably higher than the gas-liquid phase transition temperature (87 K), due to the capillary effect in the narrow gap of the nanopores. Then, a discontinuous increase in the filling rate takes place around the transition temperature and the nanopores are completely filled with the condensed argon molecules below the temperature. Figure 4 exhibits the temperature dependence of the ESR linewidth of the edge-state spins. There is no remarkable change in the ESR linewidth in the pristine non-adsorbed ACFs. However, in argon atmosphere, the ESR linewidth shows a discontinuous upsurge at the transition temperature, which is an important indication of the development of the internal field of the edge-state spins in the magnetically ordered state. In addition to this, a muon precession is discovered in the temperature regime below the transition temperature. Eventually, the edge-state spins are in the magnetically ordered state as the consequence of the magnetic switching effect. The stabilization of the magnetically ordered state of the edge-state spins can be explained in terms of the Heisenberg nature of the edge-state spins with an extremely weak magnetic anisotropy. The edge-state spins of Heisenberg type on a 2D nanographene sheets have large fluctuations, which cannot suppress even at low temperatures due to the two-dimensionality. The effective pressure of the condensed argon molecules in the nanopores elevates the inter-nanographene-sheet antiferromagnetic interaction, which enhances the dimensionality to 3D, stabilizing the magnetically ordered state of the edge-state spin system in an individual nanographite domain.

### Summary

ACFs are an attractive model system in investigating the magnetic properties of the localized edge-state spins which appear depending on the shape of the edges of nanographene sheet. The edge-state spins brings about unconventional magnetic features, among which magnetic switching phenomenon is the most important. We investigate this effect with various types of guest molecular species accommodated in the nanopores of ACFs. In the guest physisorption process, the magnetic switching phenomenon is found for water and various organic molecules, where the presence of OH-group in the guest molecules plays an important role in the performance of the magnetic switching effect. The phase transitions which are accompanied by the change in the densities works also in giving the magnetic switching phenomenon. The bromine physisorption generates the switching in the liquid-solid transition. The gas-liquid transition in the argon adsorbed in the nanopores triggers the development of the magnetically ordered state in the edge-state spin system. The magnetic switching phenomenon is a unique magnetic feature which has never been observed so far.

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