Adsorption of Nitric Acid in Nanoporous Nanographite Network and the Role of Graphene Edges

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1. Introduction

The structure of activated carbon fibers (ACFs) features a disordered 3D network of nanographite domains, each of which consists of a loose stacking of 3 to 4 nanographene sheets with a mean in-plane size of 2 to 3 nm. Different from the nanotubes and fullerene, nanographene possesses a two-dimensional extended electronic structure of π-electrons with open edges. According to theoretical predictions and experimental results, a strongly spin-polarized nonbonding π-electron state called edge state exists in the zigzag edge, which gives rise to unconventional nanomagnetic features to the nanographene. Besides ACFs is an excellent adsorbent with a huge specific surface area (~1000-3000 m^2/g) due to nanosized interstitial spaces (nanopores) distributed between the nanographite domains. The presence of nanopores in ACFs allows large amounts of various kinds of guest molecules to be accommodated, where the interaction between the adsorbed molecules and the nanographites plays an important role in modifying the electronic and magnetic properties of not only the host nanographite but also the guest species.

In this presentation, we will show the HNO_3 adsorption effect on the magnetism of nanographite in ACFs, and discuss the role played by graphene edges in this host-guest interaction system.

2. Experimental

Phenol-based ACFs (*Kuraray Chemicals*) with specific surface areas of 2000 m^2/g were heat-treated at 473 K for 24 h in vacuum of 10^{-6} Torr to remove adsorbed foreign gaseous species, and were then sealed in a Pyrex or Quartz tube. The concentration of HNO_3 in ACFs is controlled by varying the ratio of the mass of ACFs to the volume of HNO_3 gas vaporized from concentrated nitric acid (>97%, *Wako Pure Chemical Industries, Ltd.*), which was purified by the freeze-pump-thaw method prior to the adsorption process. Magnetic susceptibility measurements were carried out using a SQUID magnetometer (*Quantum Design MPMS5*) in the field of 1 T between 2 and 300 K with about 20 mg of each sample. ESR measurements were performed with a conventional X-band ESR spectrometer (*JEOL JES-TE200*) for typically 2 mg samples sealed in a quartz sample tube in the temperature range between 3.5 and 300 K. Besides, the residue samples of HNO_3–ACFs were made by desorbing as-prepared HNO_3-ACFs samples at room temperature and 200 $^{\circ}$C.

3. Results and Discussion

The observed magnetic susceptibility of the pristine ACFs and HNO_3–ACFs can be described in terms of a combination of a temperature-dependent Curie–Weiss term χ_s and a temperature-independent term χ_0, as represented by $\chi_{obs} = \chi_s + \chi_0$ with $\chi_s = C/(T - \Theta)$, where C is the Curie constant, and Θ is the Weiss temperature (Fig.1 (a)). Fig.2 shows that the concentration of edge-state spins calculated from the Curie constant decreases as the concentration of HNO_3 in the ACFs increases. Due to the strong oxidation ability, charge transfer takes place from nanographite domains to HNO_3 molecules, resulting in the decrease in the
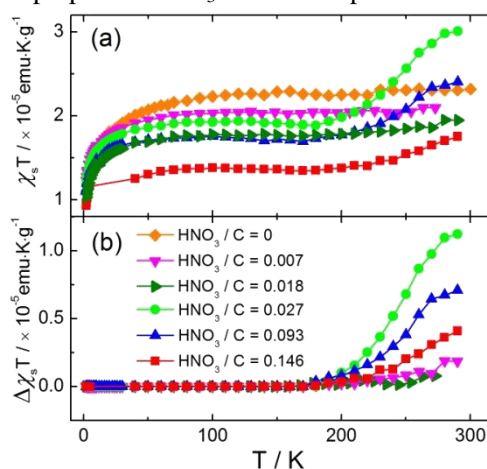

Fig.1. The temperature dependence of the product of $\chi_s T$ for HNO_3-ACFs (a) and the NO decomposition contribution (b).
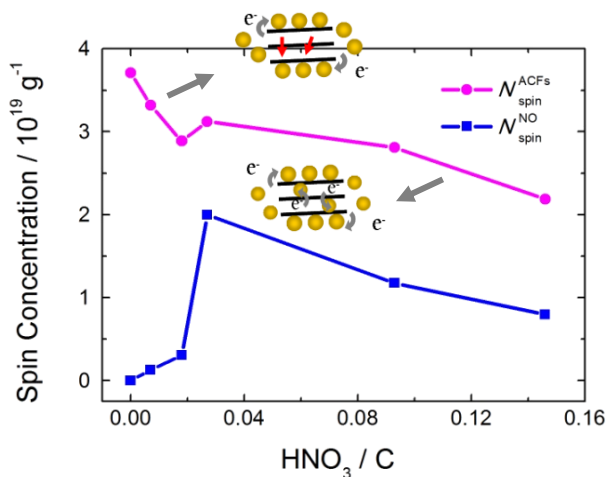
Fig.2 The HNO$_3$ concentration dependence of the spin concentration and additional magnetic moment ($\Delta\chi_s T$) contribution at 300K in HNO$_3$-ACFs
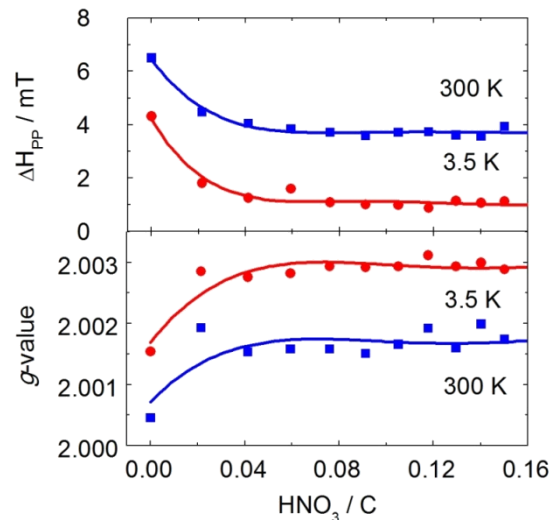

Fig.3 The HNO$_3$ concentration dependence of line width and g-value obtained from ESR measurement at 3.5 K and 300K.

edge-state spin density in a two-step manner; charge transfer with the exterior nanographene sheets of the nanographite in the lower HNO$_3$ concentration region, and then intercalation of HNO$_3$ into the galleries between nanographene sheets of the nanographite domain takes place above HNO$_3$/C ~ 0.027.

As shown in Fig.1 (b), the contribution of an additional magnetic moment appears above ~200 K for all HNO$_3$–ACFs and it becomes enhanced as the temperature elevates. This additional contribution is ascribed to the paramagnetic NO molecules with S=1/2 that are created in the decomposition reaction of HNO$_3$ (4HNO$_3$⇔4NO$_2$+2H$_2$O+O$_2$ and 2NO$_2$⇔2NO+O$_2$) and the oxidization reaction (C+4HNO$_3$⇔ CO$_2$+4NO$_2$+2H$_2$O). The decrease in the magnetic moment upon the lowering of the temperature is brought about by the dimerization reaction, 2NO⇔(NO)$_2$, in which the strong antiferromagnetic exchange interaction between NO molecules is responsible for the stabilization of the singlet spin state in (NO)$_2$ at low temperatures. The dimerization of NO molecules is understood to originate from the combined effect of the enhanced potential in the nanopore environment and the enhanced chemical activity of nanographene edges. It should be noted that the magnetic O$_2$ molecules (S=1) are not observed in the $\chi_s T$-T plots, although HNO$_3$ decomposition is accompanied with the generation of oxygen. This suggests that the volatile O$_2$ molecules are easily desorbed above ca.200 K as evidenced in the behavior of ESR spectrum. In Fig.2, the spin concentration of the released NO shows a maximal peak at HNO$_3$/C~0.027. When HNO$_3$/C<0.027, enough number of the active edge carbon sites which are in charge of the creation of NO are available for the decomposition of HNO$_3$ molecules. However when HNO$_3$/C>0.027, most of the edge active sites becomes inactive due to the reaction with HNO$_3$ and the HNO$_3$ molecules are accommodated into the galleries of stacked nanographene sheets in the interior of nanographite domains. This reduces the creation of magnetic NO molecules. The release of NO molecules are still found in the residue sample of HNO$_3$–ACFs which is desorbed at room temperature, however NO is not observed in the desorbed HNO$_3$–ACFs at 200 ^{o}C. This phenomenon suggests that the NO molecules are stable enough to accommodate in the nanopores at room temperature.

The HNO$_3$ adsorption into ACFs gives rise to the decrease in the ESR linewidth and the increase in the g-value at both 3.5 K and 300 K as shown in Fig.3. The sharp decrease in ΔH$_{PP}$ is still observed in the residue sample treated at 200 ^{o}C, in which no NO molecules are present, suggesting the enhancement of exchange narrowing effect. This indicates that the charge transfer with NO-containing functional groups still bonded to the edge carbon atoms in the residue sample increases the concentration of conduction carriers that mediate the exchange interaction, resulting in the enhanced exchange interaction.