

HNO₃ Adsorption Effect on the Magnetism of Nanographite in Activated Carbon Fibers

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1. Introduction

Activated carbon fibers (ACFs) are featured with a network of nanographite domains, and each of them consists of a stack of 3–4 nanographene sheets with a mean size of about 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 calculations and experimental results, a strongly spin-polarized nonbonding π -electron state called edge state exists in a zigzag edge. This gives rise to unconventional nanomagnetic features to the nanographene. Between the nanographite domains, the presence of slit-shaped nanopores in ACFs results in the ability to accommodate large amounts guest molecules which interact with nanographite. Thus the host-guest interaction plays an important role in modifying the electronic and magnetic properties of the host nanographite.

In this research, the HNO₃ adsorption effect on the magnetism of nanographite in activated carbon fibers is investigated.

2. Experimental

Phenol-based ACFs (*Kuraray Chemicals*) with specific surface areas of 2000 m²/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 tube. The concentration of HNO₃ in ACFs is controlled by the mass of ACFs and the volume of HNO₃ gas vaporized from concentrated nitric acid (>97%), 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.

3. Results and Discussion

The susceptibility of pristine ACFs and HNO₃-ACFs can be described in terms of a combination of a temperature-dependent Curie-Weiss term χ_C and a temperature-independent term χ_0 in the whole temperature range and the temperature range below ca.200 K, respectively, as represented by $\chi_{\text{obs}} = \chi_C + \chi_0$ with $\chi_C = C/(T - \Theta)$, where C is the Curie constant, and Θ is the Weiss temperature (Fig.1 (a)). Fig.2 (a) shows that the spin concentration calculated from Curie constant decreases as the concentration of HNO₃ in the ACFs increases. As the strong oxidation ability, HNO₃

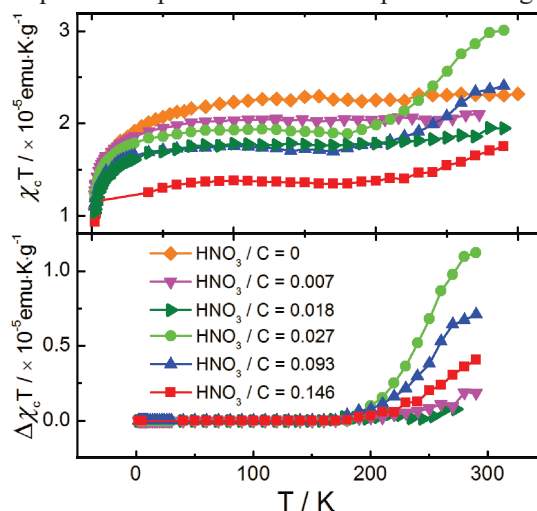


Fig.1. The temperature dependence of the product of $\chi_c T$ for HNO₃-ACFs (a) and the NO decomposition contribution (b).

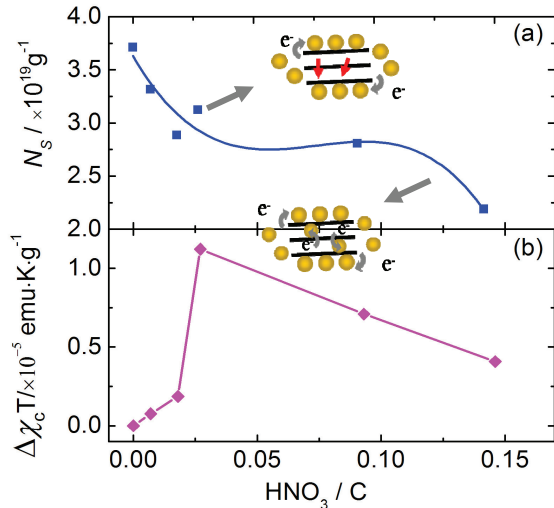


Fig.2 The HNO_3 concentration dependence of the spin concentration (a) and additional magnetic moment ($\Delta\chi_c T$) contribution at 300K (b) in HNO_3 -ACFs

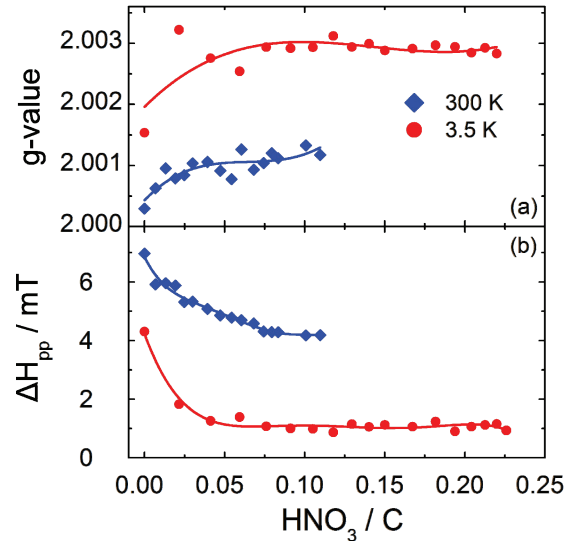


Fig.3 The HNO_3 concentration dependence of g-value (a) and line width (b) obtained from ESR measurement at 3 K and 300K.

molecules are subjected to charge transfer with nanographite domains, and then the edge-state spin density decreases in a manner of two-step process; charge transfer with the exterior nanographene sheets of the nanographite in the first step, and intercalation into the galleries between nanographene sheets of the nanographite in the second step.

Above ~ 200 K, the magnetic moment of HNO_3 -ACFs shows an additional contribution, which grows when the temperature is elevated as shown in Fig.1 (b). The additional contribution is ascribed to the contribution of magnetic NO molecules. Above 231K (the melting point of HNO_3), the decomposition of HNO_3 vapor can be represented by the overall equation $4\text{HNO}_3 \rightleftharpoons 4\text{NO}_2 + 2\text{H}_2\text{O} + 2\text{O}^*$ accompanied with the equilibrium $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$. Therefore, the decomposition reaction of HNO_3 results in the creation of magnetic NO molecules with $S=1/2$, which are condensed into the nanopores surrounded by nanographite domains. The decrease in the magnetic moment upon the lowering of the temperature is brought about by the dimerization reaction, $2\text{NO} \rightleftharpoons (\text{NO})_2$, in which the strong antiferromagnetic exchange interaction between NO molecules is responsible for the stabilization of the singlet spin state in $(\text{NO})_2$ at low temperature. Although HNO_3 decomposition is accompanied with the generation of oxygen, the magnetic O_2 molecules ($S=1$) are not observed in the $\chi_c T$ - T plots. This suggests that the evolved oxygen works to oxidize the edge of nanographene. In Fig.2 (b), the additional magnetic moment contribution at 300K shows a maximal peak at $\text{HNO}_3/\text{C} \sim 0.027$, mainly because the decomposition effect of HNO_3 molecules. When $\text{HNO}_3/\text{C} < 0.027$, NO is the major decomposition products and the amount of NO increases with the acid content. When $\text{HNO}_3/\text{C} > 0.027$, the amount of NO is decreased because the oxidization effect to form NO_2 .

The HNO_3 adsorption into ACFs gives rise to the decrease in linewidth and the increase in the g-value at both 3 K and 300 K as shown in Fig.3. The increase in the g-value reflects the enhancement of spin-orbit coupling caused by the interaction between nanographene and the HNO_3 molecules [1]. The decrease of the ESR linewidth can be attributed to the enlarged distance between edge-state spins due to the reduced spin density upon the increase in HNO_3 in ACFs.

Reference:

[1] Nakajima, M., K. Kawamura, et al. (1988). Journal of the Physical Society of Japan 57(5): 1572-1575.