

Magnetism in HNO₃ Adsorbed Nanographene-based Nanoporous Carbon and the Residue Compounds

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1. Introduction

Nanographene — nano scaled piece tailored by cutting graphene sheet — can be recognized as a unique nanocarbon system with open π -electron conjugated structure, in contrast with fullerenes and carbon nanotubes that have closed conjugated configuration. Different from the graphite and graphene, it's theoretically and experimentally demonstrated that at the Dirac point (positioned at the Fermi level in neutral nanographene sheet) where the bonding π - and antibonding π^* -bands intersect, a localized nonbonding edge state is presented on the zigzag edge, however the armchair edge has no such state. The edge state having a large local density of states in the zigzag edge region is electronically and chemically active. Furthermore, the edge state is strongly spin polarized with localized spins populated around the zigzag edge region, and it gives rise to the unconventional magnetism of the nanographene sheet.

Here, the magnetism of nanographene interacting with nitric acid having strong oxidizability will be presented, by using nanoporous activated carbon fibers (ACFs) consisting of 3D disordered network of nanographite domains, each of which consists of 3-4 nanographene sheets with a mean size of 2-3 nm stacking.

2. Experimental

Phenol-based ACFs with specific surface areas of about 2000 m²/g was employed for studying the effect of HNO₃ adsorption. The bundle of ACFs was packed vertically into a glass tube and evacuated to 10⁻⁶ Torr for at 200 °C for 72 h, in order to remove adsorbed foreign gaseous species. The vaporized HNO₃ gas from the fuming nitric acid solution with a volume fraction higher than 97% was purified by the freeze-pump-thaw method prior to the adsorption process. For all the nitric acid adsorbed samples (HNO₃-ACFs) the amount of the nitric acid could be controlled by varying the adsorption temperature and duration. The static magnetic susceptibility was measured by the SQUID magnetometer at 1 T (or 2 T) between 2 and 300 K with about 20 mg HNO₃-ACFs vacuum-sealed in a Pyrex tube. ESR measurements were performed for typically 2 mg samples sealed in a quartz sample tube in the temperature range between 3.5 and 300 K. Besides, the residue compounds were made by desorbing as-prepared samples at room temperature and 200 °C.

3. Results and Discussion

The observed magnetic susceptibility of the pristine ACFs and HNO₃-ACFs can be described in terms of a combination of one temperature-dependent Curie–Weiss term χ_s and one temperature-independent term χ_0 , as represented by $\chi_{\text{obs}} = \chi_s + \chi_0$ with $\chi_s = C/(T - \theta)$, where C is the Curie constant, and θ is the Weiss temperature, and the results are shown in the Fig.1 (a). In contrast to that of pristine ACFs, the susceptibility of HNO₃-ACFs deviates from a simple combination of these two terms at high temperatures above ca. 170 K. The discussion consists of two different temperature regimes based on the magnetic behaviors which are shown in Fig.1.

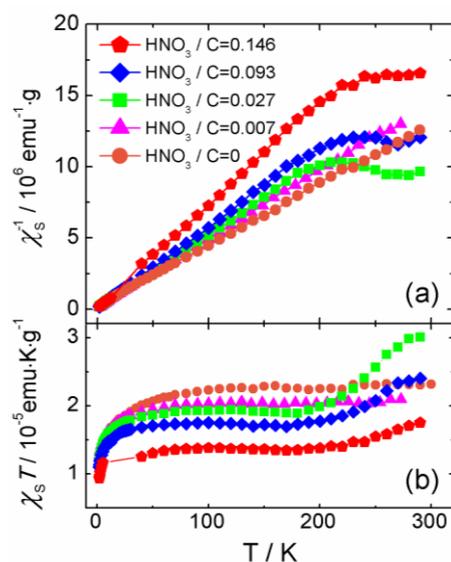


Fig.1 The temperature dependence of (a) χ^{-1} and (b) χT for the ACFs and HNO₃-ACFs.

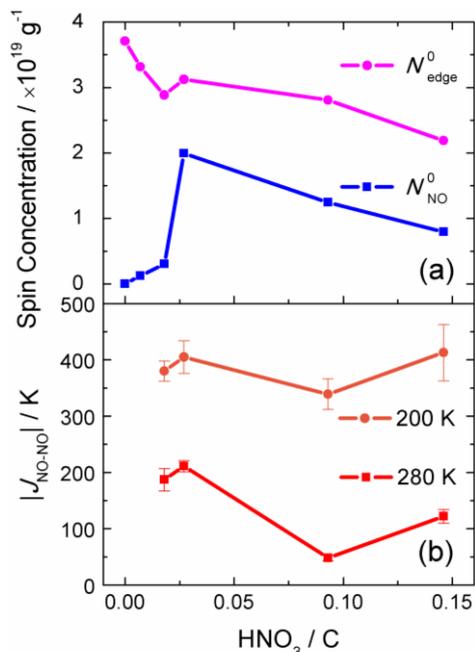


Fig.2 The concentrations of the edge-state spins and the NO spins at 300 K (a), and the strength of the exchange interaction between NO spins (b) as a function of HNO₃/C ratio.

and 2NO₂ ⇌ 2NO + O₂). The decrease in the magnetic moment upon the lowering of the temperature is brought about by the dimerization reaction, 2NO ⇌ (NO)₂, which induces the triplet-singlet transition, and the strong antiferromagnetic exchange interaction between NO molecules is responsible for the stabilization of the singlet spin state in (NO)₂ at low temperatures, which is estimated in Fig.2(b). 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. In Fig.2(a), when HNO₃/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 HNO₃ molecules. However when HNO₃/C > 0.027, the creation of NO is depressed because most of the edge active sites becomes inactive due to the reaction with HNO₃ and the HNO₃ molecules are accommodated into the galleries of nanographite domains.

3.3 Residue compounds

The release of NO molecules are still found in the residue sample of HNO₃-ACFs which is desorbed at room temperature, however NO is not observed in the desorbed HNO₃-ACFs at 200 °C. This phenomenon suggests that the NO molecules are stable enough to accommodate in the nanopores at room temperature.

The HNO₃ adsorption into ACFs gives rise to the decreased ESR linewidth, exchange narrowing being operated, meanwhile the sharp decrease in ΔH_{pp} is still observed in the residue sample treated at 200 °C (Fig.3(b)) in spite of the absence of NO, suggesting the some nitrogen-containing functional groups remaining bonded to the edge carbon atoms, which increases the concentration of conduction carriers that mediate the exchange interaction, resulting in the enhanced exchange interaction.

3.1 Charge transfer - Regime below 170 K

The concentration of edge-state spins calculated from the Curie constant decreases as the concentration of HNO₃ in the ACFs increases (Fig.2(a)). Due to the strong oxidation ability of HNO₃, charge transfer takes place from nanographite domains to HNO₃ molecules, resulting in the decrease in the edge-state spin density in a two-step manner; charge transfer with the exterior nanographene sheets of the nanographite in the lower HNO₃ concentration region, and then intercalation of HNO₃ into the galleries between nanographene sheets of the nanographite domain takes place when HNO₃/C > 0.027.

3.2 Magnetic NO species - Regime above 170 K

As shown in Fig.1 (b), for each sample, the additional spin contribution in the χ_s(T)T product appearing above 170 K increases and tends to be saturated as the temperature is elevated. This additional contribution is ascribed to the paramagnetic NO molecules with S=1/2 that are created in the decomposition reaction of HNO₃ (4HNO₃ ⇌ 4NO₂ + 2H₂O + O₂

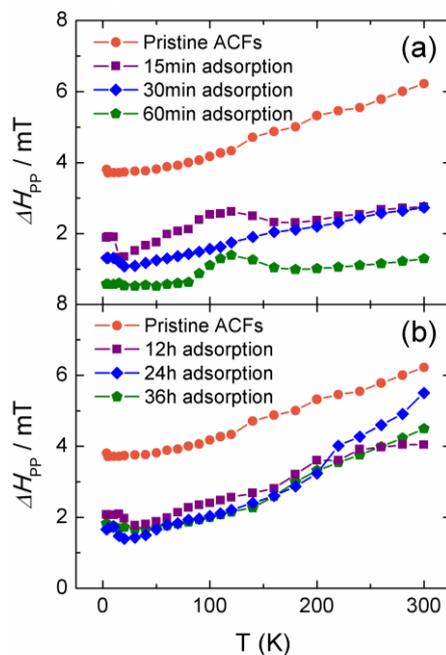


Fig.3 The temperature dependence of ΔH_{pp} for the HNO₃-ACFs residue compounds evacuated at room temperature (a) and 200 °C (b).