

# MAGNETISM OF NANOGARPHITE AND ITS MOLECULAR DEVICE APPLICATIONS

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## Introduction

Nanographene or nanographite, featured with flat nano-sized sheet having open edges, is one of the important members of nano-carbon  $\pi$ -electron systems. The presence of open edges makes it entirely different from other members of nano-carbons such as fullerenes or carbon nanotubes which have closed  $\pi$ -electron systems or a minor contribution of edges. Theoretical prediction [1-3] suggests the presence of edge-inherited non-bonding  $\pi$ -electron state (edge state), which gives rise to unconventional nanomagnetism. We have systematically investigated the magnetic properties of nanographite using various kinds of experimental techniques. Single nanographene sheet is prepared by heat-treatment-induced conversion to nanographene from nanodiamond placed on a HOPG substrate by electrophoretic technique. A disordered network of nanographite domains in activated carbon fibers is found to take a spin-glass-like disordered state of edge-state spins in the vicinity of an insulator-to-metal transition. Physisorption of guest molecules into micropore space of the nanographite network brings about magnetic switching effect of edge-state spins, which is easily controlled by reversible adsorption/desorption processes. Edge-state spins can work as a probe for detecting guest-host interaction, with which a huge amount of helium is found to be adsorbed in the micropore of nanographite network. The present paper reports the experimental observations of nanomagnetic phenomena related to the edge-state spins, which impart clues for molecular device applications of nanographite.

## Formation of isolated single nanographene sheet

Nanodiamond particles having a mean size of 5 nm are suspended as colloidal solution in a mixed solvent of acetone and isopropyl alcohol with iodine. Electrophoretic deposition of nanodiamond particles is carried out on a HOPG substrate, where the concentration of nanodiamond particles are varied by changing the electric field applied [4]. The nanodiamond particles deposited on a HOPG substrate are converted to nanographene sheets by heat-treated at 1600°C in Ar atmosphere [5]. Figure 1 shows a typical STM image of an isolated nanographene sheet thus prepared. From the height difference between the nanographene and the substrate, the nanographene is characterized as a single layer nanographene with a mean in-plane size of 10 nm, which is placed epitaxially with respect to the HOPG substrate. The inter-layer distance between the graphene sheet and the substrate is estimated as 0.35-0.37 nm, which is considerably larger than that in pristine bulk graphite (0.335 nm). The elongation of the

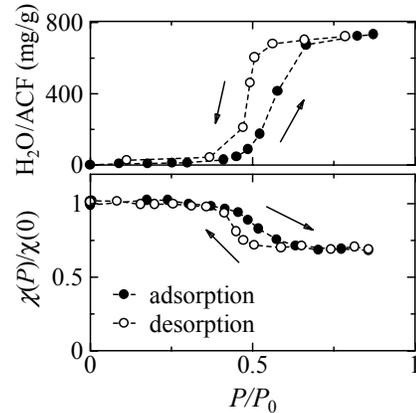
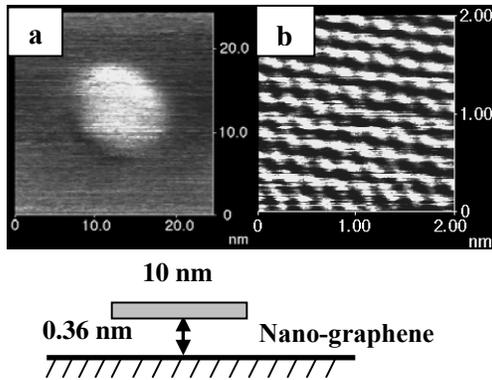


Figure 1.(left) STM images of a single nanographene sheet. (a) nanographene, (b) lattice image of nanographene, (c) schematic view perpendicular to the sheet. Figure 2.(right) Water adsorption isotherm (upper) and magnetic susceptibility (lower) as a function of water vapor pressure for ACFs.  $P_0$  is the saturation vapor pressure.

inter-layer distance suggests that the inter-layer interaction is reduced by 25-50 % from that in pristine bulk graphite. Therefore, the single nanographene sheet prepared from nanodiamond can be a good model system with which theoretical analysis can be made to clarify the presence of edge state and its nanomagnetism, in addition to usefulness for nanomagnetic device applications.

### Magnetic switching phenomenon induced by water adsorption

Activated carbon fibers (ACFs) are featured with a three dimensional (3D) disordered network of nanographite domains, where each nanographite domain consists of a stacking of 3-4 nanographene sheets having a mean in-plane size of 2-3 nm. Around the peripheries of nanographene, localized spins of edge state are experimentally found to exist. ACFs have a huge specific surface area of 2000  $\text{m}^2/\text{g}$  for which micropores surrounded by nanographite domains are responsible. Guest species such as water, bromine, and various kind of organic solvents can be adsorbed in the micropores. According to structural investigation [6], densely accommodated guest molecules squeeze nanographite domains, resulting in a large reduction in the inter-layer distance between nanographene sheets in nano-graphite domains by the effective pressure of guest molecules. Indeed, the inter-layer distance is reduced from 0.38nm to 0.34nm upon the saturation of water molecules in the micropores.

Guest-induced effective pressure plays an important role in the magnetism of nanographite [7]. Figure 2 gives evidence of effect on magnetism upon water physisorption at room temperature. The water adsorption isotherm suggests that no water adsorption takes place in the low vapor pressure range up to  $P/P_0 \sim 0.5$  ( $P_0$ : saturation vapor pressure), at which the amount of adsorbed water takes an upsurge. Above that pressure, it saturates and the micropores become full of water. This ON/OFF change in the isotherm is associated with hydrophobic nature of graphene sheet. The magnetic susceptibility tracks the isotherm with fidelity, as shown in Fig.2(lower panel).

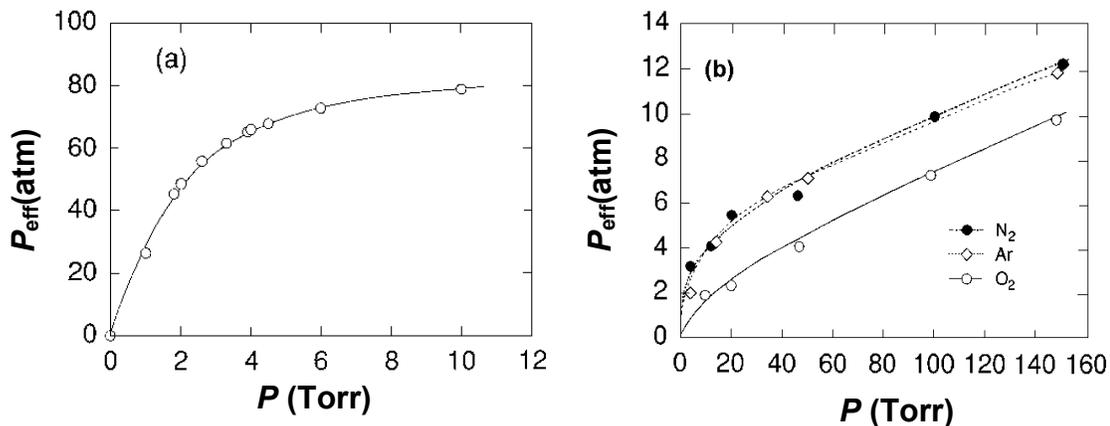


Figure 3. Pressure of guest molecules inside micropores as a function of pressure applied.

Actually, no change occurs in the susceptibility up to the threshold pressure. The susceptibility shows a ca.30% reduction with an adsorption/desorption hysteresis at the threshold, followed by a saturation on the high-pressure side of the threshold.

The correlation between the isotherm and the magnetic susceptibility can be understood on the basis of the structural change induced by the guest adsorption. As we have already discussed, ACFs form a 3D disordered network of nano-graphite domains, where nanographene sheets of each domain have localized magnetic moments of edge state. The introduction of guest water molecules reduces the inter-sheet distance, giving rise to the elevation of inter-sheet electronic interaction. Namely, when no guest species occupy the micropores, the interaction between edge spins on adjacent nano-graphene sheets is weak, making localized magnetic moments be independent from each other as paramagnetic spins. The enhancement of the inter-sheet interaction induced by the guests in micropores brings about the decrease in the magnetic moments of nano-graphite due to antiferromagnetic coupling. Such a change in magnetism induced by water adsorption is considered to be a controllable magnetic switching effect of nanoscopic magnetism, which has never been reported so far.

Similar correlation behavior between the isotherm and the susceptibility emerges in other guest species such as acetone, ethanol, methanol, bromine, etc. When organic guest species are employed, the threshold pressure of the ON/OFF switching is lowered depending on the increase of the contribution of hydrophobic groups in the molecule. This means the switching threshold is varied intentionally. Among the guest species, bromine is particularly interesting, as there are three bromine species accommodated in nanographite; bromine molecules physisorbed in the micropore space, intercalated bromine subjected to charge transfer, and substituted bromine at the edges, the strengths of whose guest-host interactions are elevated in this order. The physisorbed bromine molecules are frozen around 260K from liquid to solid state. In the liquid state, which has a low density, guest bromine molecules squeeze nano-graphite domains, giving the reduction in the magnetic moment, whereas the solidification accompanied by the considerable increase of the density (ca. 30%) or the shrinkage of the guest volume revives the magnetic moments.

## Gas adsorption probed by edge-state spin and huge helium condensation

The edge-state spins are a useful probe in detecting the guest-host interaction [8]. Figure 3 shows the adsorption isotherms for H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, He, Ne, and Ar in ACFs at room temperature. The effective pressure of guest gases inside the micropores is orders of magnitude larger than the pressure of gaseous state in the environment. This means a large condensation of guest gaseous species due to the enhanced gas-nanographite interaction, since accommodated gaseous molecules are surrounded by the surfaces of nanographite domains in every direction. An exceptional feature appears in the case of He; that is, the pressure inside reaches almost 80 atm, which corresponds to about one tenth of the liquid helium density, even when 10 Torr of He is introduced. Here, the condensation rate is over 6000 indeed.

In order to detect the gas-adsorption with the spin-probe, ESR saturation technique is employed with nano-graphite edge-state spins in relation to spin-lattice relaxation process. Figure 4 presents the microwave power dependence of the ESR intensity (saturation curve) taken at room temperature in vacuum and in the atmosphere of 10 Torr He, Ar, O<sub>2</sub>, and N<sub>2</sub>. In vacuum, the ESR signal tends to be easily saturated in the low microwave power range, suggesting that the spin-lattice relaxation rate  $1/T_1$  is considerably small. In contrast, the introduction of gaseous species gives less saturated feature of the saturation curves, as shown in Fig.4. The extreme case occurs in He atmosphere, where no saturation occurs. These experimental findings strongly suggest an important contribution of guest gaseous species to the spin-lattice relaxation mechanism. In a micropore, guest molecules collide with edge-state spin around the peripheries of nano-graphites. The collisional process, which is governed by van der Waals interaction between a guest molecule and a nano-graphite domain, works effectively to accelerate the spin-lattice relaxation rate. In this case, the collision-induced relaxation process is described in the equation;  $1/T_1 = nv\sigma$ , where  $n$ ,  $\sigma$  and  $v$  are the density of molecules, the cross section related to spin-flip process, and the mean velocity of molecules, respectively. A more detailed analytical expression can be obtained on the basis of electric dipole-dipole interaction between gas molecule and nano-graphite [9]. A comparison with the experimental results indicates that the equation well represents the experimental findings, suggesting edge-state spins work as a probe of guest molecules. In other words, edge spins are useful as a gas sensor,

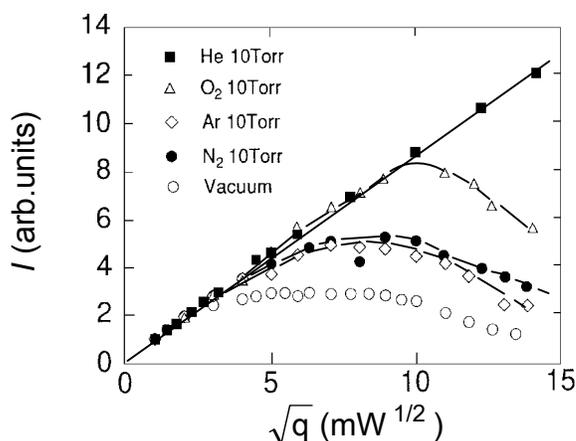


Figure 4. ESR saturation curves in vacuum and in various gas atmosphere.

where electric dipole-dipole-interaction-assisted collisional process plays an essential role. This is the first example, in which the spin-lattice relaxation is governed by electric dipole-dipole interaction.

An important issue, which should be pointed out, is the exceptionally large He condensation in the ACF micropores. Though the origin of this remains unsolved, it suggests the presence of ultra-micropores to which only smallest diameter He atom (0.257nm) can access.

## Conclusions

Nanographite or nanographene is featured with edge-state spins, which impart unconventional nanomagnetism. We successfully prepared an isolated single graphene sheet, which can be applicable for nanomagnetic devices. Microporous carbon consisting of networked nanographite domains shows guest-induced magnetic switching phenomenon. The edge-state spin can work as gas sensing probe. The present works suggest that edge-state spins make nanographite promising in developing molecular devices of spintronics.

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