

# Unconventional electronic and magnetic properties of nanographene and its host-guest systems

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The electronic structure of nanographene depends crucially on its edge shape. The periphery of an arbitrary shaped nanographene sheet is described in terms of a combination of zigzag and armchair edges. In zigzag edges, nonbonding  $\pi$ -electron state (edge state) is created in spite of the absence of such state in armchair edges according to theoretical and experimental works [1-3] (Fig.1). Therefore, the zigzag edges are chemically active due to the presence of edge state located at the Fermi level. Furthermore, the localized spins of edge state contribute to make nanographene magnetic. We investigated the magnetic properties of nanographene and nanographite, the latter of which is stacked nanographene sheets, and their guest adsorption effect using nanographene-based nanoporous carbon (activated carbon fibers (ACF)) [4-6].

ACFs consist of a 3D disordered network of nanographite domains, each of which is a stack of 3-4 nanographene sheets with a mean intra-sheet size of ca.3 nm. The magnetism of an individual nanographene sheet is described as ferrimagnetic structure with a net non-zero magnetic moment created by the cooperation of strong ferromagnetic intra-zigzag-edge ( $J_0$ ) and less strong ferromagnetic/antiferromagnetic ( $J_1$ ) inter-zigzag-edge interactions acting between the edge-state spins (Fig.2). Then an individual nanographite domain, in which the edge-state spins of constituent nanographene sheets are coupled with each other by antiferromagnetic inter-nanographene-sheet interaction ( $J_2$  ( $<J_1$ )), behaves as a superparamagnetic particle which is weakly interacting with adjacent domains through inter-domain antiferromagnetic interaction  $J_3$  having a mean strength of -2- -3 K.

The electron transport between nanographite domains is subjected to Coulomb-gap variable range hoppings (Fig.3(d)). According to ESR observations, the spin relaxation is governed by the Korringa mechanism in which the interaction between the edge-state spins and

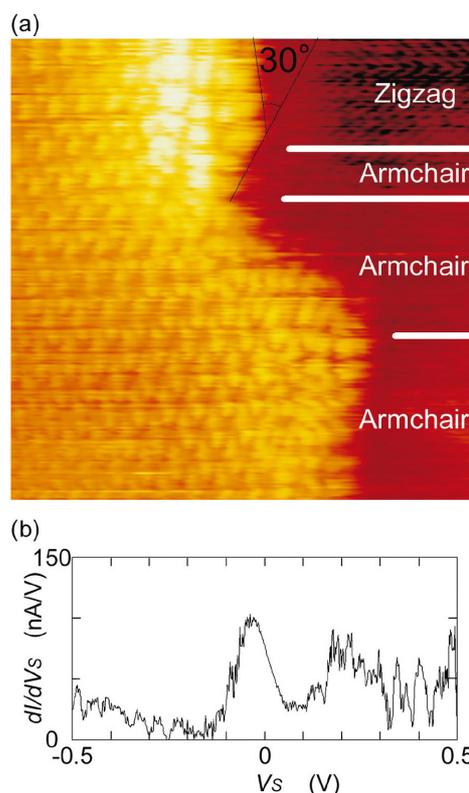


Fig.1. STM lattice image (a) and STS (b) of a graphene edge consisting of zigzag and armchair structures. The bright spots in STM and the sharp peak at  $V_s = 0$  V in STS are assigned to the edge state.

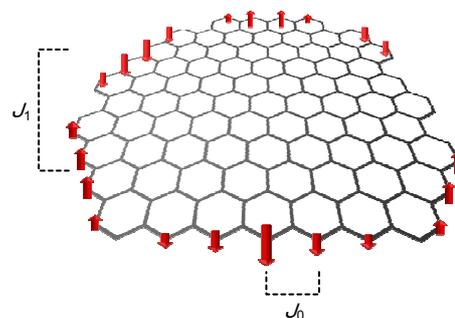


Fig.2. Ferrimagnetic structure of a nanographene sheet.

conduction  $\pi$ -carriers plays an important role (Fig.3(b)). At high temperatures, frequent electron hoppings taking place between the domains create a homogeneous magnetic state of the edge-state spins in the nanographite network. The lowering of the temperature slows down the inter-domain electron hopping process, resulting in the development of an inhomogeneous magnetic state owing to electron localization at low temperatures below ca.20 K. The heat-treatment enhances the inter-domain interaction, bringing about a transition from insulator to metal at a heat-treatment temperature of 1200 °C. In the vicinity of the transition, a spin glass state of the edge-state spins appears, for which a random distribution of exchange interactions  $\sqrt{\langle \Delta J^2 \rangle} / \langle J \rangle \sim 0.8$  is responsible (Fig.4).

Chemically inert guest molecules such as water, organic molecules, rare gas, etc., which are condensed in the nanopores, compress the nanographite domains, resulting in the reduction in the inter-nanographene-sheet distance. The increase in inter-nanographite-domain antiferromagnetic interaction  $J_3$  induced by this mechanical compression works to switch the magnetic state from high spin state to low spin state, as  $J_2$  is sensitive to the change in the inter-nanographene-sheet distance (Fig.5). Charge transfer interaction modifies the magnetism when guest molecules having electron accepting activities such as  $\text{HNO}_3$  are adsorbed.

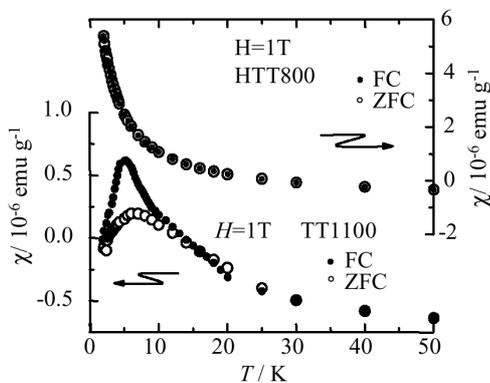


Fig.4. The magnetic susceptibility  $\chi$  of ACFs samples heat-treated at 800 and 1100 °C in zero-field cooling and field (1 T) cooling conditions.

## References

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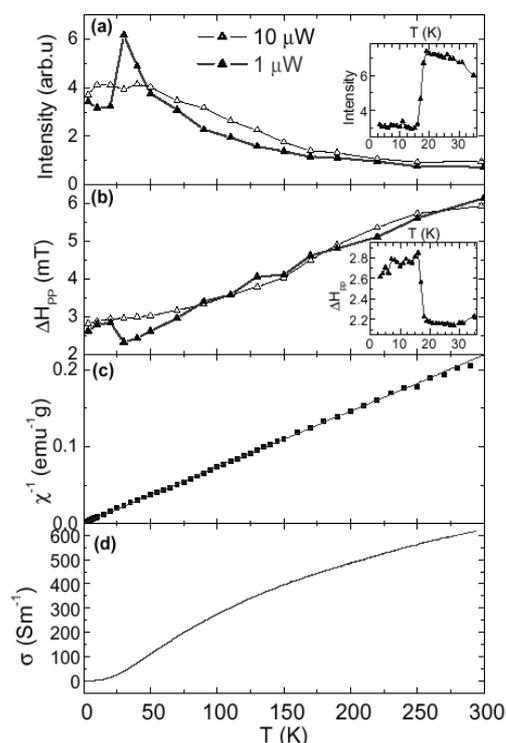


Fig.3. The ESR intensity (a), line width (b), magnetic susceptibility (c) and conductivity (d) as a function of temperature.

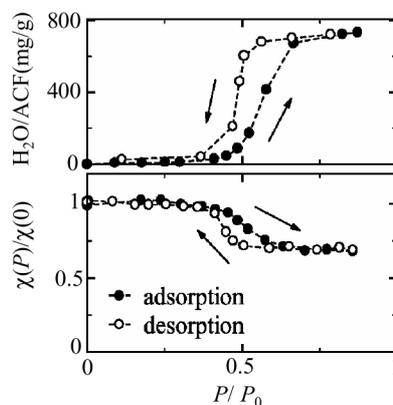


Fig.5. The water adsorption isotherm and susceptibility of ACFs.