

Magnetic and electronic structures of nanographene and fluorinated nanographene with an interplay of edge-state spins and dangling bond spins

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The magnetic structure of graphene is modified drastically by introducing edges and defects. Here, localized non-bonding edge states of π -electron origin having localized spins are created when a graphene sheet is cut along the zigzag direction, while defects, which are not terminated, have magnetic σ -dangling bond states. We investigated the magnetic and electronic properties of nanographene with a focus of interplay between the edge-state spins and dangling bond spins, using nanoporous activated carbon fibers (ACFs), which are a 3D disordered network of nanographene sheets, and their fluorinated derivatives, by means of NEXAFS, ESR and magnetic susceptibility.

NEXAFS experiments indicate the presence of edge state (peak position 284.5 eV) around the Fermi level in nanographene together with the π^* -conduction band (peak position 285.5 eV). The large negative chemical shift (-1.0 eV) of the NEXAFS peak from the peak of the π^* -conduction band is suggested to be a consequence of large screening effect, which is associated with a large local density of states of the edge state of nonbonding π -electron. ESR result proves that the edge state is magnetic with localized spin. A nanographene sheet, whose periphery is described in terms of a combination of zigzag edges and armchair edges, is found to have ferrimagnetic structure with a net nonzero magnetic moment as a result of cooperation of strong intra-zigzag-edge ferromagnetic interaction and intermediate strength inter-zigzag-edge ferromagnetic/antiferromagnetic interaction. Heat-treatment of the ACFs induces an insulator-to-metal (IM) transition around 1200 °C. This strengthens inter-nanographene exchange interaction in the 3D nanographene network, bringing about a spin glass state in the vicinity of the IM transition.

Fluorination of ACFs proceeds in two step manner; fluorination of the edge carbon atoms first and then that of the carbon atoms in the interior [Figure 1]. The first step taking place up to $F/C \sim 0.4$ works to decrease the magnetic edge-state contribution due to the local destruction of the zigzag edges as evidenced by a monotonical decrease in the spin concentration, while magnetic σ -dangling bond states are created at the carbon site adjacent to the carbon atom attacked by a fluorine atom in the interior of a nanographene sheet in the second step that takes place above $F/C \sim 0.4$ after all the edge carbon atoms are terminated with fluorine atoms. The spin concentration of the dangling bonds starts increasing above $F/C \sim 0.4$, it is maximized when a half of the interior carbon atoms ($F/C \sim 0.8$) are bonded with fluorine atoms and finally it becomes negligible at a saturated fluorine concentration of $F/C \sim 1.2$. This scenario of the fluorination process, which is suggested by the magnetic measurement, is confirmed by the NEXAFS. NEXAFS shows an extra peak assigned to the dangling bonds in the fluorinated ACFs at 284.9 eV above $F/C \sim 0.4$. The small negative shift of -0.6 eV of the peak is a consequence of weak screening effect of the σ -dangling bond states having a small local density of states. The NEXAFS intensity of the σ -dangling bond states tracks the behavior of the concentration of the σ -dangling bond spins with fidelity. A combination of magnetic susceptibility, ESR and NEXAFS experiments demonstrates that the edge-state spins have itinerant nature with a fractional magnetic moment whereas the dangling bond spins are localized in nature with a magnetic moment of $1 \mu_B$ and are free from exchange interaction.

References

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Figure 1

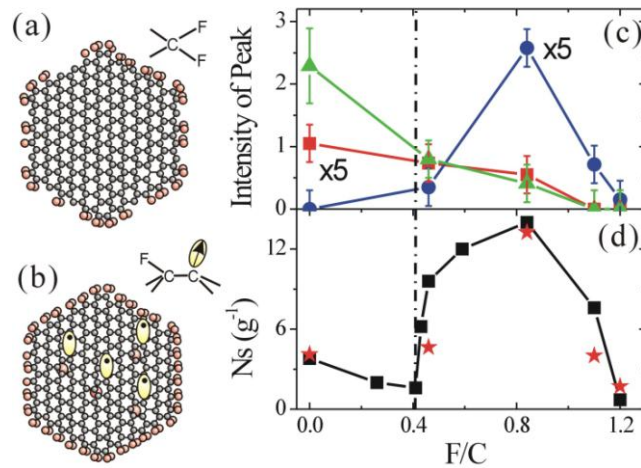


Figure 1. Schematic model of the fluorinated ACFs at (a) $F/C < 0.4$ and (b) $F/C = 0.4 - 0.8$. The edge carbon atoms bonded to two neighboring carbon atoms are terminated by two fluorine atoms (large circles). A σ -dangling bond (ellipsoids with a dot inside) is created at a carbon site bonded to the carbon atom attacked by a fluorine atom in the interior of a nanographene sheet. (c) The intensities of the π -edge state (squares), σ -dangling bond state (circles), and π^* state (triangles) peaks as a function of fluorine concentration, obtained NEXAFS experiments. (d) The total localized spin concentration (squares) as a function of fluorine concentration. The expected total density of magnetic moments in the F-ACF (stars) obtained by multivariable analysis of the NEXAFS spectra with the contributions of the edge state and σ -dangling bond state.