

How does the magnetic edge-state vary in the fusion of nanographene sheets?

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Abstract

When a graphene sheet is cut into nanofragments (nanographene), the created edges in nanographene work as a boundary condition to modify the electronic structure depending on the edge geometry [1,2]. In the armchair shaped edges, the electron wave interference takes place, resulting in the aromatic stability of the electronic structures. In contrast, localized nonbonding edge state of π -electron origin is created in the zigzag edges, in which the large spatial electron population at the edges with strong spin polarization causes electronic, magnetic and chemical activities. In the meantime, heat-treatment annealing at high temperatures makes assembled nanographene sheets fused at the expense of edges, ensuing the growth of nanographene sizes. Here the stability and activities of nanographene, for which the edge-geometry dependence in the electronic structure is responsible, are expected to govern the fusion process. In addition, the oxygen-containing functional groups bonded to the edge carbon atoms in the nanographene samples handled in the ambient atmosphere are concerned in the process. We investigated the fusion process of assembled nanographene sheets with a focus on the variation of the electronic and magnetic structure, in which the magnetic edge state plays an important role, using *in-situ* measurements of X-ray photoemission spectroscopy, near-edge X-ray absorption fine structure (NEXAFS), magnetic susceptibility, electrical conductance, together with temperature-programmed desorption (TPD) measurements. The sample is activated carbon fibers (ACFs), whose structure consists of disordered network of nanographene sheets [3,4].

The TPD results indicate that the edges of nanographene sheets are terminated with oxygen-containing functional groups and hydrogen atoms in the pristine sample. Oxygen-containing functional groups such as $-\text{COOH}$, $>\text{C}=\text{O}$, $-\text{OH}$ are almost completely decomposed under heat treatment up to 1300–1500 K, resulting in the formation of edges primarily terminated by hydrogen. The removal of the oxygen-containing groups enhances the conductance owing to the decrease in the energy barriers in the electron transport between nanographene sheets, which is governed by the Coulomb-gap type variable range hopping process. Heat treatment above 1500 K removes also the hydrogen atoms from the edges, promoting the successive fusion of nanographene sheets at the expense of edges. The decrease in the π^* peak width in NEXAFS and the increase in the orbital susceptibility indicate the progress of the fusion reaction, that is, the extension of the π -conjugation. The fusion leads to the random formation of local π/sp^2 bridges between nanographene sheets in the percolative manner and brings about an insulator-to-metal transition at 1500–1600 K, at which the bridge network becomes infinite. The onset of the insulator-to-metal transition is accompanied by the change in the magnetism from the localized spin magnetism to the Pauli paramagnetism, for the former and the latter of which the edge-state spins forming a superparamagnetic structure and π -conduction carriers in the individual nanographene sheet are responsible, respectively. Interestingly spin glass state appears in the vicinity of the insulator-to-metal transition. The intensity of the edge state peak in NEXAFS, which corresponds to the number of the spin-polarized edge states, decreases above 1500 K, demonstrating the successive disappearance of the edges, though the thermal average of the edge-state spin $\langle S \rangle$ estimated from the magnetic susceptibility starts decreasing about 200 K lower than the temperature of the edge state peak change. This disagreement indicates the development of antiferromagnetic short range ordering as a precursor of a spin glass state near the insulator-metal transition, at which the random network of inter-nanographene-sheet antiferromagnetic exchange interactions strengthened with the formation of the π/sp^2 bridges becomes infinite. This is evidenced by the molecular field treatment that gives the estimate of the inter-nanographene-sheet exchange interaction to be -1600 K in the vicinity of the insulator-to-metal transition, which is comparable to the strengths of intra-nanographene sheet exchange interactions. Above 1500-1600 K, the

edge state peak in NEXAFS tends to disappear, demonstrating that the sizes of nanographene sheets grow swiftly at the expense of edges.

References

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