

Observation of Magnetic Edge State and Dangling Bond State on Nanographene in Activated Carbon Fibers

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Introduction

Graphene has received attention due to its unique properties. When the size of a graphene sheet is reduced to a few nanometers, other interesting phenomena could be expected due to the growing contribution of the edge. The theoretical and experimental studies showed the presence of a localized non-bonding π state (edge-state) in the zigzag shaped edge regions [1]. In investigating the properties of the nanographene, it is particularly important to confirm the presence of edge-states. Here, we pay attention to the activated carbon fibers (ACFs). ACFs are nanoporous carbon consisting of a three dimensional disordered network of nanographite domains, each of which is a stack of 3-4 nanographene sheets with the mean in-plane size of about 2-3nm. ACFs have a high density of edge carbon atoms (the number ratio of edge carbon atoms to the interior carbon atoms is ca. 30/200) due to the small size of nanographene sheets. ACFs are, thus, a good model system for investigating the magnetic edge state.

Experiment

Pristine ACFs were commercially available samples (Kurary Chemicals, FR-20; specific surface areas of 2000 m²/g) prepared by the activation of phenol-based precursor materials. The carbon K-edge NEXAFS was measured at the soft x-ray beam line BL-7A in the Photon Factory in the Institute of Materials Structure Science. The ground powder sample was mounted on a Ta plate and loaded into the chamber maintained in ultrahigh-vacuum (10⁻⁷ Pa). NEXAFS spectra were then obtained by measuring the sample photocurrent.

Results

Figure shows the C K-edge NEXAFS spectra of the ACFs at room temperature and ACFs heated at 1190 K, in addition to the spectrum of HOPG. The NEXAFS spectra were normalized with respect to the value of the edge jump at 340 eV, where the intensity was proportional to the amount of carbon atoms. We can see a tailing on the low energy side of the π^* peak, the presence of an additional peak (p1) being suggested around the Fermi level.

The spectral analysis was carried out for the NEXAFS spectra. First, the peak width of the π^* peak were determined to be 1.5 eV from the spectrum of HOPG. Next, the spectra of the ACFs were fitted with two

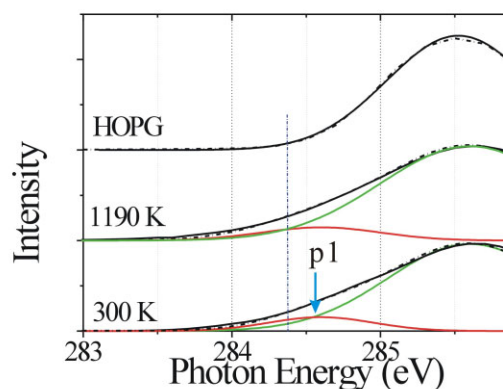


Fig. The pre-edge region of the NEXAFS spectra (line) and convoluted curve fit (dot-dash-line). The deconvolution comprises two Gaussian peaks corresponding to the edge state (p1: red curve) and π^* state (green curve). The vertical dot-dash line indicates the Fermi level of HOPG (284.36 eV)

Gaussian peaks assuming that the energy and peak width of the π^* peak were the same as those of HOPG. The energy and peak width of the additional peak (p1) was estimated as 284.5eV and 0.82 eV, respectively, from the fitting results shown in Figure. The intensity of the p1 peak was 11 % and 9 % of that of the π^* peak for the ACFs and ACFs heated at 1190 K, respectively. The p1 peak survived after heating at 1190 K, although the intensity of the p1 peak slightly decreased.

Usually, the graphene edge is terminated by oxygen-containing functional groups such as carboxyl (-COOH), carbonyl (=CO) groups for the ACFs sample exposed to the air at room temperature. By heating the ACFs above 1190 K in UHV, these groups are completely decomposed. The edge would be terminated by oxygen-free functional groups such as hydrogen. Therefore, the existence of the p1 peak for the ACFs heated at 1190 K confirmed that the p1 peak originates from the intrinsic electronic state of the nanographene close to Fermi level, that is, edge states in the nanographene sheet. We confirmed the existence of the edge state by using ACFs and NEXAFS.

References

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