The role of zigzag and armchair edges in the electronic structure of nanographene

Enoki T.

Chemistry Department, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152-8551, Japan
e-mail: tenoki@chem.titech.ac.jp

The electronic structure of graphene is described in terms of massless Dirac fermion with two Dirac cones (K and K') in the Brillouin zone, giving unconventional features of zero-gap semiconductor. When a graphene sheet is cut, the created edges affect seriously the electronic structure depending on the edge shape (zigzag and armchair edges) as observed with the electron wave interference and the creation of non-bonding π-state (edge state). We investigated the edge-inherent electronic features by STM/STS observations and Raman spectra. Graphene nanostructures were fabricated using graphene oxide with an AFM tip.

STM/STS observations demonstrate that edge states are created in zigzag edges in spite of the absence of such state in armchair edges. In addition, zigzag edges tend to be short and defective whereas armchair edge is long and continuous in general. These findings suggeSt that zigzag edge is less stable in comparison with armchair edge, consistent with Clar's aromatic sextet rule.

The electron wave scattering takes place differently between zigzag and armchair edges, showing different superlattice patterns in STM lattice images. In the vicinity of an armchair edge, a hexagonal pattern was observed together with a fine structure of three-fold symmetry at the individual superlattice spots. At a zigzag edge, the electron wave is subjected to the K-K intravalley scattering without interference, whereas the K-K' intervallery scattering with interference takes place in the scattering event at an armchair edge. The appearance of the hexagonal superlattice is a consequence of electron wave interference. The three-fold symmetric fine structure is understood as the antibonding coupling between the adjacent spots in the hexagonal superlattice.

The Raman G-band shows the edge-shape dependence same to that observed in the STM superlattices. The intervalley scattering at an armchair edge gives specific dependence of the G-band intensity on the polarization direction of the incident laser beam as expressed by $\mathbf{cos}^2\,\Theta$ (Θ; the angle between the polarization and the armchair edge direction). A nanographene ribbon of 8 nm$\times$>1 μm prepared by heat-treatment of graphite step edges shows this angular dependence, being demonstrated to consiSt of pure armchair edges.

Single sheet graphene oxide was found to form a two dimensional regular arrangement of linear wrincles of oxidized lines running along the zigzag direction with an interline spacing of ca.10 nm. This suggests that zigzag edged nanographene ribbons with a width of ca.5 nm are created between the oxidized lines. Nanofabrication by an AFM tip can allow us to create a nanostructure of graphene sheet intentionally.