Electronic structures of nanographene with zigzag and armchair edges

Toshiaki Enoki[1], Ken-ichi Sakai[1], Shintato Fujii[1], Kazuyuki Takai[1], Kenichi Sasaki[2], Katsunori Wakabayashi[2], Takeshi Nakanishi[3], and Ken-ichi Fukui[4]
[1]Chem. Department, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551, Japan
[2] International Center for Materials Nanoarchitectonics, NIMS, Namiki, Tsukuba 305-0044, Japan
[3]Nanotube Research Center, AIST, Tsukuba 305-8565, Japan
[4]Dept. of Materials Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
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 into fractions, 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-electron 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 of hydrogen-terminated graphene edges demonstrate that edge states are created in zigzag edges in spite of the absence of such state in armchair edges [1]. 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 energetically stable in comparison with armchair edge, consistent with Clar's aromatic sextet rule. In a finite length zigzag edge embedded between armchair edges, electron confinement is observed in the edge state.

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 [2] (Fig.1), different from the $\sqrt{3}\times\sqrt{3}$ superlattice observed in bulk graphene and also in zigzag edge. At a zigzag edge, the electron wave is subjected to the K-K intra-valley scattering without interference, whereas the K-K' inter-vallery scattering with interference takes place in the scattering event at an armchair edge. Tight binding calculation reproduces the hexagonal superlattice observed in the armchair edge. The three-fold symmetric fine structure is understood as the antibonding coupling between the adjacent spots in the hexagonal superlattice with the mediation of the wave function at the STM tip.

The Raman G-band shows the edge-shape dependence same to that observed in the STM superlattices in relation to the intra-valley/inte-rvalley transition for the scattering at zigzag/armchair edges [3]. The inter-valley scattering at an armchair edge gives specific dependence of the G-band

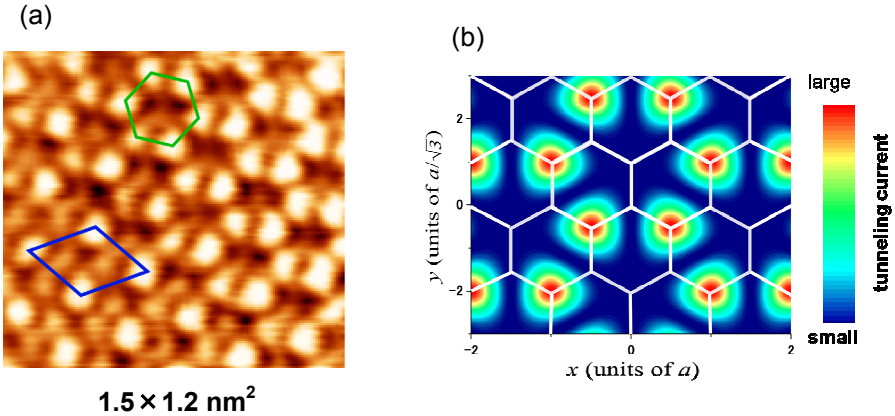

Fig.1.(a) $\sqrt{3}\times\sqrt{3}$ and hexagonal superlattices near an armchair edge. (b) Calculated current image of the hexagonal superlattice.

intensity on the polarization direction of the incident beam as expressed by $\cos^2\Theta$ (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 [4].

Single sheet graphene oxide was found to form a two dimensional arrangement of linear corrugations of oxidized lines running along the zigzag direction with an interline spacing of ca.10 nm [5]

(Fig.2). 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.

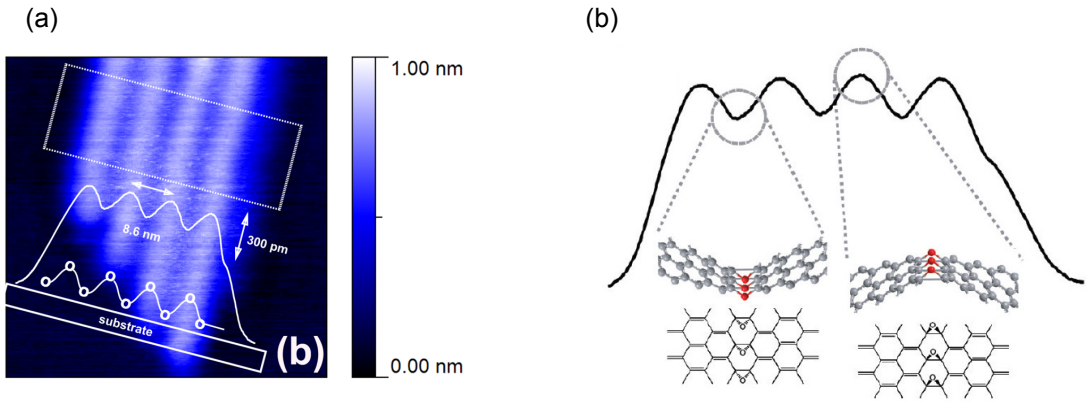

Fig.2.(a) 1D wrinkles in graphene oxide nanohsheet observed by non-contact AFM. (b) schematic model of graphene oxide consisting of zigzag edged nanographene sheets inter-connected through oxygen bridges.

References

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