

Edge geometry and chemistry effects on the electronic structure of graphene nanostructures

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The electrons moving in the hexagonal bipartite lattice of graphene can be described in terms of massless Dirac fermion in the relativistic quantum mechanics, while it can be understood also on the basis of Clar's aromatic sextet rule in chemistry. When a graphene sheet is cut into nanofragments, the created edge works as the boundary condition, the electronic structure being seriously modified depending on the edge geometry. In the zigzag edges, non-bonding π -electron state (edge state) localized in the vicinity of the edges is created, which gives the electronic, chemical and magnetic activities to graphene edges. In the meantime, electron wave interference takes place in the vicinity of armchair edges, giving rise to the energy stabilization of graphene nanostructures. In addition to the geometry effect, the functional groups bonded to the edge carbon atoms affect the electronic structure in another way. Accordingly, the edge geometry and chemistry details cooperatively work to give a variety of electronic structures to the graphene nanostructures. We investigated the edge geometry and chemistry effects on the electronic structures using STM/STS and noncontact/conductive AFM observations of edges and defects of graphene sheets, with the assistance of DFT calculations. The STM current images of graphene nanostructures embedded in graphene oxide show interesting size and geometry effects; the conductivity becomes larger upon the increase in the size of the nanostructures, and more importantly the zigzag edged nanostructure has higher conductivity than the armchair edged one. The high and low conductive features are well correlated with the migration and localization of Clar's aromatic sextets in the zigzag and armchair edged nanostructures, respectively. These findings experimentally confirm the Clar's aromatic sextet rule, which governs the electronic structure together with their edge geometry effect in the graphene nanostructures. In mono-hydrogenated zigzag edge, STM/STS observations demonstrate the presence of edge state well localized on the edge carbon atoms with the spin splitting of the edge state. In contrast, the partial introduction of di-hydrogenated carbon atoms makes the edge state disappear and instead it brings about the electron wave interference with the $\sqrt{3} \times \sqrt{3}$ superlattice, similar to armchair edges. We found the AFM-tip mechanical force induced switching between the edge state and electron wave interference in graphene defects in which edge carbon atoms

are terminated with oxygen atoms. The switching is reversible between ON and OFF states, the former and the latter of which have the signatures of zigzag edge with the presence of edge state and of armchair edge with the electron wave interference, respectively. This can be explained in terms of the mechanical force induced switching of bonding configurations related to the C-O bondings at the defect periphery.

