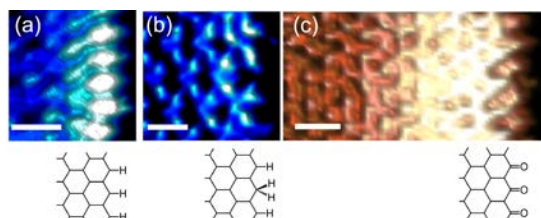


## Chemistry and electronic properties of defects in graphene

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To understand better physical properties of nanomaterials on the atomic and molecular scale, it is crucial to combine theory and experiment. Here we focused on the electronic properties of nanosized two dimensional  $\pi$ -electron network of graphene. The local electronic properties of graphene are crucially dependent on geometrical shape and chemistry of defect sites. According to current understanding, while the zigzag edge of graphene supports the localized  $\pi$ -state (edge state) on its boundary and gives rise to intra-valley scattering of extended electronic states, its armchair counterpart does not possess the edge state and leads to inter-valley scattering of charge carrier. It is therefore appealing to tune electronic and magnetic properties of graphene-based nanostructures via changing geometrical shape of defects in graphene. In a simple structural edge-defect model, each edge site is passivated by a hydrogen atom to saturate the dangling bond and form mono-hydrogenated graphene edges. We prepared atomically well-defined hydrogenated graphene edges contained within nano-sized pits by atomic hydrogen etching of single-vacancies in the topmost graphene layer of graphite. To simulate scanning tunneling microscopy (STM) data, electronic calculations based on density functional theory (DFT) were performed. High-resolution STM characterizations and DFT simulations demonstrate that mono-hydrogenated zigzag edges are preferentially formed in the periphery of the nanoholes [Fig. (a)]. In addition to the conventional mono-hydrogenated zigzag edge, we found a new type of zigzag edge, characterized by disappearance of the edge state and profound interference pattern in a form of electronic superlattice [Fig. (b)]. To understand these two main features we have to take into account chemistry at zigzag edge. Systematic DFT simulations show that the edge state can be removed when every third zigzag-edge site is di-hydrogenated while two others remain mono-hydrogenated. To further explore the effect of the edge chemistry on the electronic properties, oxidized graphene edges were prepared by electrochemical oxidation of graphitic surface. In sharp contrast to the conventional hydrogenated graphene edge [Fig. (a)] in previous reports, newly found oxidized edges (i.e., ketonated zigzag edge) with higher thermodynamic stability exhibited significantly modulated  $\pi$ -states near the Fermi level, which is characterized by (i) spatially extended  $\pi$ -state distribution and (ii) energy-dispersive character with quasi-band gap nature. This modulation can be understood by participation of the oxygen  $\pi$  electron into graphene  $\pi$  electron system and resultant change in the effective boundary condition of the  $\pi$  electron network. These findings open up a way for tuning electronic properties of graphene edges not only by changing the geometrical shape of edges but also by controlling how chemical species are attached to the graphene edge of a given geometry.



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