Dirac-Fermi polarons at graphene edges and atomic vacancies: the role of under-coordination and hydrogenation

Xi Zhang, Changqing Sun

School of Electric & Electronic Engineering, Nanyang Technological University, Singapore
zh0005xi@e.ntu.edu.sg

The generation and hydrogen modulation of the massless, magnetic, and mobile Dirac-Fermi polarons (DFPs) surrounding atomic vacancies at graphite surface and at edges of graphene nanoribbons (GNR) are indeed fascinating with mechanisms far from clear. Here we show that an incorporation of the bond order-length-strength (BOLS) correlation into the spin-polarized tight-binding (TB) method with the combination of the density-functional theory calculations have enabled the clarification of the concerns.

We found that: i) the DFPs with high-spin-density at the zigzag-GNR and at the vacancies result from the isolation and polarization of the dangling $\sigma$-bond electrons of identical distance along the edges by the under-coordination-induced local densification and quantum entrapment of the core and bonding electrons; ii) the pseudo-$\pi$-bond formation between the nearest dangling $\sigma$-bond electrons along the armchair-GNR and the reconstructed-zigzag-GNR edges prevents, however, DFPs from being formed at these edges; and, iii) hydrogenation reduces the spin density substantially and turns the asymmetric dumb-bell-like sp$^2$ into the spherical-like p$_z$ charge density of the zigzag-GNR edge and vacancy. A further photoelectron spectroscopic purification has confirmed the origin and consequence of the DFPs generated at graphite surface atomic vacancies.

References

Figures

Figure 1 Comparison of the purified XPS C 1s spectrum of graphite surface with and without vacancy defects showing that bonds near to defects are shorter and stronger than those at the surface. The P, TS, and TD denotes, respectively, the DFPs screened, undercoordination-induced quantum entrapment states of the outermost two atomic layers of surface skin ($z \approx 3.2$) and sites surrounding vacancy defects ($z \approx 2.5$); D and B indicates the bulk position of diamond ($z = 12$) and graphite ($z = 5.335$). The valleys centered at 284.2($z = 5.35$) and 284.4 eV($z = 4$) correspond, respectively, to the removed obvious graphite bulk and surface information. Indicated numbers are the effective z values.
Figure 2 Comparison of the DFT-derived local spin-density contour and the BOLS-TB derived 3D plots of local spin density of occupied states for (a) vacAGNR, (b) H-vacAGNR, (c) ZGNR, (d) H-ZGNR. The Dx (x = a, v, r, z) represents the dangling sp2 electron states indicated using red arrows. The dangling sp2 and the pz electron, contributes to a strong dumbbell-shaped local antiferromagnetism and a weak spherical spin, respectively. The sites of group I show a much higher spin density than group II. Hydrogenation tends more to interact and pair up the dangling sp2 electron than the pz electrons.