

Physics and Chemistry of Graphene and Carbon Allotropes

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Carbon has four electrons in one 2s and three 2p orbitals ($2p_x$, $2p_y$, $2p_z$), which are the players in giving a large variety of carbon-based materials as a consequence of formation of hybrid orbitals. When all the four orbitals form sp^3 hybrid orbitals with four electrons, diamond having a three dimensional (3D) infinite tetrahedral network is created. The presence of a large energy gap of 5.47 eV between the σ -valence and σ^* -conduction bands makes diamond insulating. The formation of sp^2 -hybrid σ -bands from 2s, $2p_x$, and $2p_y$ with three electrons brings about 2D graphene honeycomb lattice. Here the remaining one electron in $2p_z$ orbital participates in the formation of π -bands. The π -valence band and π^* -conduction band touch each other at the Fermi level, giving a zero-gap semiconducting feature. The π -bands have linear wave number dependence. This can be effectively understood on the basis of massless Dirac fermion in relativistic Weyl equation, and consequently graphene has unconventional electronic properties. When graphene sheets are stacked, graphite having a layered structure is created, in which the inter-sheet electronic coupling makes graphite semimetallic. sp -hybridization with two electrons in 2s and $2p_x$ creates a 1D σ -bond chain, and the remaining two electrons in $2p_y$ and $2p_z$ constitute two π -orbitals π_y and π_z , which are orthogonal to each other. In the 1D chain, there are two π -bond conformations; one is alternating π_y/π_z -bond conformation (= C = C = C =), and the other is the one in which both π_y - and π_z -bond coexist in every two C-C bonds (- C \equiv C - C \equiv). The former and the latter are called cumulene and polyynes, respectively. These 1D chain systems are insulating.

In addition to these 1D, 2D and 3D carbon allotropes, there are a wide range of carbon-based materials having disordered structures with a mixture of sp^3 , sp^2 and sp hybrid bonds. Liquid carbon, which is stabilized above 4200 K is explained in terms of the disordered carbon and it is metallic. Quenching the liquid state at low temperature gives amorphous carbon.

When carbon-based materials are cut into nanofragments, the electronic structure is seriously modified. Nanodiamond thus created is subjected to structural reconstruction at its

surface, the surface being an interface between sp^2 and sp^3 electronic structure, which is governed by low-D electronic instability. Decreasing the size of graphene brings us to a change in the aspect from physics to chemistry as we can see polycyclic aromatic hydrocarbon molecules such as anthracene, naphthalene, and benzene in the smallest extreme. In nanographene, which is situated in size between graphene and polycyclic aromatic hydrocarbon molecules, edges created by cutting work to give boundary conditions. As a result, a variety of electronic, magnetic and chemical phenomena are observed depending on the edge geometry, such as the creation of edge state localized at edges and electron wave interference. Cutting a graphene sheet and folding the resulting nanofragment up or rolling it up give fullerenes (C_{60}) and carbon nanotubes. The electronic structure varies depending on their shape which works as the boundary condition, interesting semiconducting and metallic features being created.

Graphite intercalation compounds, in which guest molecules such as electron donor or acceptor are intercalated in the graphitic galleries, are not carbon allotrope but the important carbon-based materials in relation to the electronic structure of graphene. Charge transfer between graphene and guest molecule modifies the electronic structure, giving rise to a large variety of electronic phenomena.

In this lecture, the electronic structures of the carbon-based materials mentioned above are comprehensively discussed.

References:

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