

The atomic and electronic structure of graphene and graphene nanocrystals.

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Graphene, a sheet of one monolayer of carbon atoms that acts as a 2-D “metal” with massless relativistic electrons is of strong scientific and applied interest. In the field of solar cells, sheets of graphene hold promise for transparent contacts to the active light absorbing layers. Also from the viewpoint of future electronic and sensor applications, the electronic structure of graphene nanocrystal quantum dots is very important. Graphene ribbon-nanocrystal-ribbon structures have been employed in field-effect transistor devices. Single-electron transport controlled by electron-electron repulsion is well established.

Despite the enormous interest in the electronic properties of graphene, the *single-particle* electronic structure of extended graphene and graphene quantum dots has not been measured by local (i.e. scanning probe) techniques. In graphene, the C-atoms are connected by strong sp_2 bonds, and additionally with $1/2$ p-p π bond per C-atom. The π band is, therefore, half filled. Wallace in 1947 was the first to draw attention to the extra-ordinary electronic properties of graphene on the basis of a Tight-Binding approach. It became clear that, unlike for other solids, the energy-wave vector dispersion relationship of the electrons and holes is linear (as for photons):, at least sufficiently close to the fundamental K-points in the Brillouin zone. Hence, compared to a photon, the Fermi-velocity of the π -electrons replaces the velocity of light ($v_F = c/300$). The electrons sufficiently close to the K-points mimic relativistic, massless electrons (Dirac electrons). In principle, the electron wave functions and eigen energies of graphene should be obtained by solving the Dirac equation.

The electronic structure of graphene sheets of limited extension in the two-dimensions, i.e. graphene nanocrystals, is a matter of considerable interest. Electrostatic potential barriers are transparent for massless Dirac electrons for a wide region of impinging angles. This rouses the question if the electrons close to the Dirac point can be confined - or not - in a graphene nanocrystal, and if, eventually, the states constitute sharp resonances or broader peaks, related to a chaotic classic electron motion. From a theoretical viewpoint, the Dirac equation has been solved with a position-dependent electron mass (increasing towards the edges), avoiding complete transparency of the edge barrier, leading to typical particle-in-a-2D-box states. On the other hand, the carbon-edges of graphene nanocrystals themselves have their own electronic structure with spatial extension over several unit cells. The edge states depend strongly on the atomic configuration, i.e. a zig-zag or arm-chair carbon termination of the edges. Furthermore, the passivation of the dangling bonds as C-H bonds (as in benzene molecules) might be important. It is obvious that a measurement of the energy and spatial extension of the (electron and hole) states of graphene nanocrystals in relation to their size and their atomic (edge) structure is a major scientific question and challenge. We emphasize that we wish to detect the *single-particle* energy levels, devoid from Coulomb and spin interactions. Furthermore, in order to measure the electronic properties of graphene, interactions between graphene and the underlying substrate should be as small as possible.

We have performed atomic force microscopy (AFM) and scanning tunnelling microscopy/spectroscopy (STM/STS) experiments to measure the atomic configuration and the electronic density-of-states (DOS) of graphene and graphene nanocrystals deposited on Ir(111). Ir only interacts weakly with graphene. We have used a Qplus sensor that allows for non-contact AFM with an ultra-small amplitude, and simultaneously, measurement of the tunnel current. We are able to grow graphene nanocrystals on Ir(111) substrates by chemical vapor deposition in the same UHV

system as in which STM/AFM is performed. The average size of the nanocrystals depends on the experimental conditions, we have grown graphene nanocrystals between 5 and 500 nm with various shapes. We have shown that it is possible to measure the single-particle DOS and map the amplitude of the wavefunction(s) at a given energy. In the case of graphene nanocrystals, this is far from trivial, since a considerable fraction of the current constitutes direct tunnelling between the tip and the Ir(111) substrate. In addition the atomic structure of graphene on Ir(111) has been studied in detail with AFM. Measurements of the atomic termination at the graphene nanocrystal edges are under way. In the lecture, the results will be presented and compared with DFT and tight-binding calculations.

Our final aim is to establish the relationship between the measured single-particle energy level structure and the atomic structure of the graphene nanocrystals including the edges.

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