Visualization of electronic states along the boundaries of graphite nanoholes

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Introduction. A crystalline matter with topologically non-trivial electronic band structure may support a special kind of electronic state on its boundary. This is so-called *edge state* (in 2D) or *surface state* (in 3D). In graphene nontrivial topology arises from pseudospinorial form of π-electron wavefunction which provides richer structure of edge boundary conditions. This leads, in particular, to a macroscopically degenerated manifold of single particle states (flat band) with nearly zero energy, localized along *zigzag-shaped edges*, while such states are absent at *armchair-shaped edges* of graphene [1-3]. Such enhancement of the density of states (DOS) at Fermi level of graphene can give rise to a number of interesting physical phenomena such as specific edge magnetism [4] and edge state superconductivity [5]. In the context of organic chemistry the appearance of edges state, a non-bonding π-electron orbital, can be seen as geometrical frustration in π-network and accounted for by simple counting rules such as Clar sextet rule or theorem on hexagonal graphs. In last decade several groups reported evidence from scanning tunneling spectroscopy (STS) measurements for presence of the edge state at respectively zigzag- and circular-shaped boundaries of graphite atomic terraces [2,3,6] and pits [7], and zigzag edges of unzipped carbon nanotubes [8]. However, a reproducible *direct visualization* of the edge state wavefunction along well-defined zigzag edges of graphene sheets has not been reported till present moment. Furthermore, with current trend in nanotechnology and nanoscience it is important to study the effect of *finite size geometry* on the electronic properties of graphene edges, as well as to investigate possible ways of controlling electronic and magnetic properties of nanographene via *chemical modification of its edge*. In the present work we used low-bias (30-100 mV) UHV scanning tunneling microscopy (STM) measurements and density functional theory (DFT) calculations to map an electronic wavefunction at the well-defined graphene edges of nanoholes with different types of hydrogen termination created by etching of graphite top layer with atomic hydrogen.

Creation of nanoholes. The key point in achieving well-defined structure of graphene edges in nanoholes was to perform all preparations and measurement procedures strictly under the UHV conditions, avoiding contact with ambient environment. First, we covered graphite surface with atomic vacancies and annealed at 600^0C to remove all possible contaminations. Then, irradiated graphite surface was exposed to atomic hydrogen. The temperature of sample during exposure was $\approx 900^0$C. Compared with previous reports on hydrogen etching of clean graphite basal plane [7], presence of atomic vacancies significantly eased creation of nanoholes, allowing us to use relatively low hydrogen pressures, and influenced the final shape of nanoholes boundaries. Although exact mechanism of nanoholes creation on defective graphite surface is not yet well understood, there are two possible explanations: i) Each atomic vacancy serves as a nucleation center for creation of nanohole; ii) Linearly attached hydrogen “cuts” the graphite surface along the lines connecting different vacancies. The nanoholes produced in the second way will have predominantly zigzag edges, which is consistent with our experimental observations.

Two different types of zigzag edge in nahoholes. The length of studied edges typically ranges from 0.75 nm to 3 nm. We identified two types of nanohole’s edges propagating in the zigzag direction of graphene lattice. The type 1 zigzag (zz1) edge is characterized by spheroidal, and not spherically symmetric, electronic charge distribution in the non-bonding π-orbital on edge carbon atoms. STS measurement at zz1 edge reveals the presence of an edge-state peak in the local density of states (LDOS) at +0.03 eV. This type of edge constitutes about 80% of all the observed zigzag edges in graphene nanoholes.

The type 2 zigzag (zz2) edge constitutes around 20% of the observed edges and is characterized by honeycomb-like superperiodic pattern previously reported only for armchair edges. Furthermore, there are no features of non-bonding π-state at this type of edge. Both features can be explained if we assume periodical arrangement of two mono-hydrogenated and one di-hydrogenated carbon atoms at the edge. The latter leads to elimination of every third p_z orbital and introduces two additional carbon sites from different sublattice at the edge. The total sublattice imbalance is therefore zero and the situation is same to the case of armchair edge. We did, however, find deviations from ideal

periodicity of this structure observed as a mismatch between the honeycomb lattices at certain points along the zz2 edge.

Effect of finite sized geometry on the electronic structure of zigzag edge. The important difference between graphene nanoholes and nanoribbons is the presence (absence) of edge corner structure in the former (latter). When two zz1 edges are connected by 120^0 corner, our atomically-resolved STM imaging mostly does not reveal the presence of edge localized state in the nanohole's corner. This is in good agreement with recent tight-binding (TB) model predictions [9]. However, the similar absence of edge state in 60^0 corner of zz1 edges looks surprising and deviates from the results obtained within TB calculations scheme. To understand the origin of this discrepancy, we employed DFT calculations to determine the LDOS in a relaxed structure of 60^0 corner, where two carbon atoms in the corner are not saturated by atomic hydrogen. The presence of two dangling bonds results in structural reconstruction in the corner and reduces the amplitude of the edge state wavefunction in the 60^0 corner.

We have also found a circular-like superperiodic pattern in the vicinity of zz1 edge originating from non-uniform distribution of charge density along C-C bonds. Our DFT calculations suggest that such pattern can be due to the mixture of the edge state and $\sqrt{3} \times \sqrt{3}R30^0$ superstructure. The latter originates from the intervalley scattering taking place at the ends of short zigzag edges in nanoholes. This is different from the case of infinitely long graphene nanoribbon model where intravalley scattering does not favor the formation of superstructure.

We have not experimentally detected significant effects of finite size geometry on zz2 edge. However, the deviations from ideal periodicity mentioned above suggest a possible connection between edge length and thermodynamically stable arrangement of mono – and di-hydrogenated carbon sites along the edge.

Armchair edges of nanoholes. The electronic structure near the *straight* armchair edge of nanoholes represents wave-like superperiodic pattern, with bias-independent charge oscillations linearly decaying away from the edge. The appearance of the continuous wave-like superstructure indicates the presence of non-negligible charge density of π-electron between carbon sites and therefore deviates from description of graphene honeycomb lattice within TB scheme. Previously, such patterns were considered to be specific to electronic scattering at armchair edges of monolayer graphene as a consequence of localization of the DOS along the C-C bonds [10]. However, our data obtained on multi-layer graphene system suggests that this is a general property of graphene sheets regardless of the number of layers. In contrast, the electronic structure near *disordered* armchair edges can be seen as a combination of rhombic and honeycomb superperiodic patterns, in agreement with previous reports on edges of graphite nanopits [11]. The rhombic-honeycomb pattern can be therefore seen as a partial destruction of wave-like patterns at defective armchair edge.

Conclusions. To summarize, we succeeded in detailed visualization of electronic states along the boundaries of graphene nanoholes with well-defined edges. The obtained knowledge will be useful in realization of future electronic devices based on periodical arrangement of nanoholes in graphene (quantum antidots), and may open way towards realization of magnetic nanographene which requires existence of highly hydrogenated zigzag edges [4].

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Figures

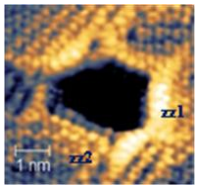

Fig.1. STM image (U=100 mV) of one of the graphite nanoholes observed in the experiment. Two types of zigzag edge discussed in the text are marked by zz1 and zz2.