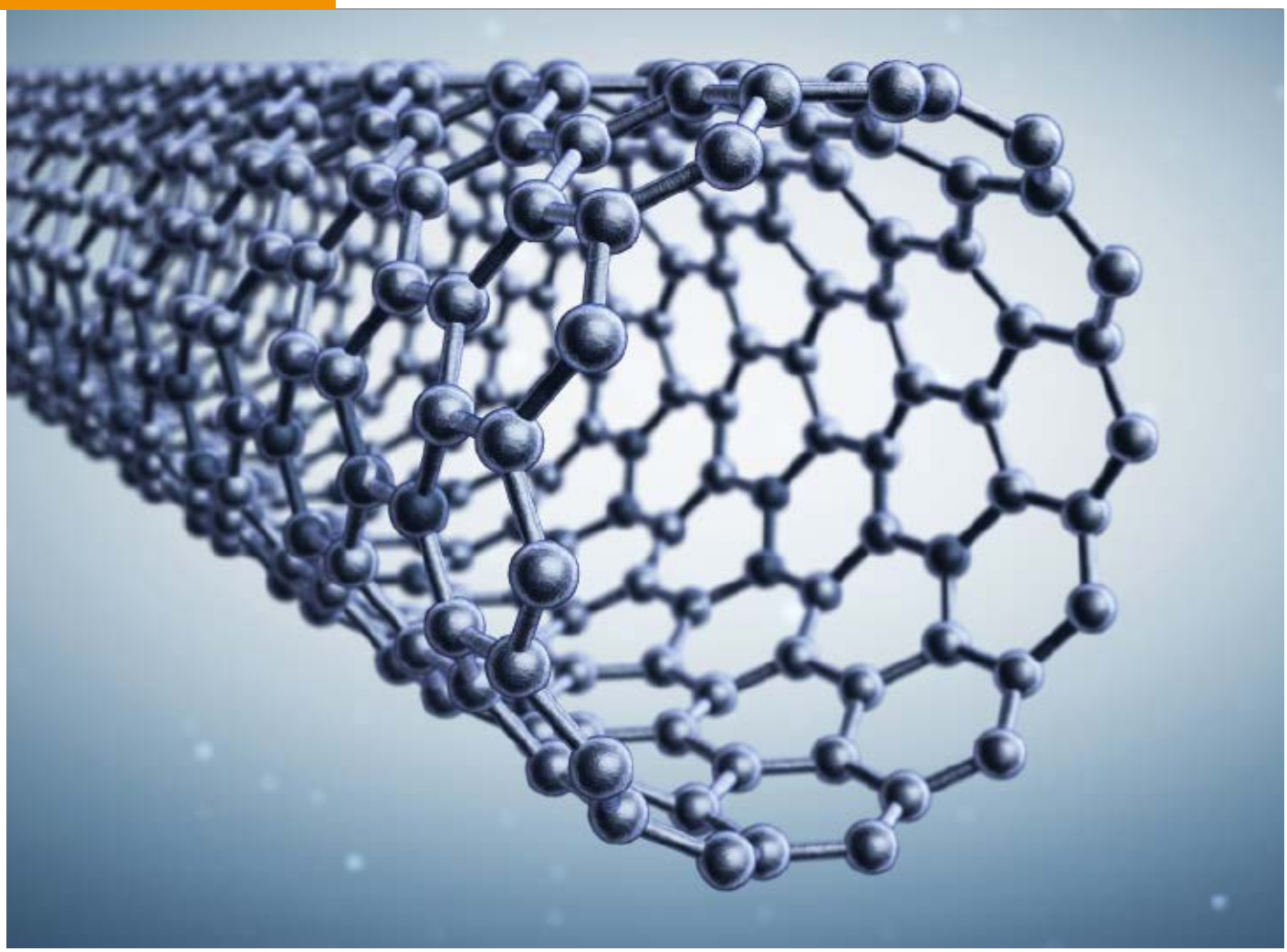

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Atom Chains in the TEM

Experiments with the Thinnest Possible Wires

Florian Banhart

The thinnest electrical conductor we can imagine is a linear chain of atoms. Carbon in the sp^1-hybridization is able to form self-supporting and electrically conductive atom chains. These have been subject of theoretical studies for many years until it recently became possible to create and characterize individual carbon chains in *in situ* electron microscopy experiments. A combination of TEM and STM techniques sheds light on the properties of the ultimate nanowire.

Atom Chains

The progressive miniaturization in nanotechnology calls for smaller and thinner electrical connections. Considerable progress has been achieved through the decades; however, the ultimate nanowire hasn't been made yet. The smallest one-dimensional structure we can imagine is a chain of atoms. If one had a stable, heatproof, tear-resistant, free-standing and, of course, electrically conductive atom chain, this would be the unsurpassable material for wiring at the atomic scale. However, the search for such a species is difficult. Besides alkyl or polymer chains that have side atoms and less favorable properties as conductors, not many candidates are left. Chains of very few metal atoms have been found to be perfect quantum conductors [1] but they are too unstable and with only 3-4 atoms too limited in length to be applicable.

With the rise of carbon as the basis of new low-dimensional materials, a perspective is coming in sight. Besides the well-known two-dimensional and three-dimensional phases graphene resp. graphite (sp^2) and diamond (sp^3), carbon is an element that can also occur in a one-dimensional sp^1 modification [2, 3]. Although the existence of stable bulk sp^1 carbon (*carbyne*) is still discussed, we know from electron microscopy studies that isolated carbon chains exist [4-6]. Highly interesting properties of these monoatomic wires have been predicted in theoretical studies [7, 8]. Two electronic configurations are expected. In cumulene, the atoms always have the same distance and charge is uniformly distributed, leading to metallic conductivity. In polyyne, dimerization occurs, so that alternating long and short (single and triple) bonds prevail and the chain becomes semiconducting. While Peierls distortion favors polyyne, cumulene might be stabilized by zero point vibrations [8]. Due to their strong covalent bonds, carbon chains should have a remarkable ultimate tensile strength of 10 nN [7]. Although the electrical and mechanical properties of carbon chains should be measurable with high precision in dedicated STMs or AFMs, no such results are available yet. This is due

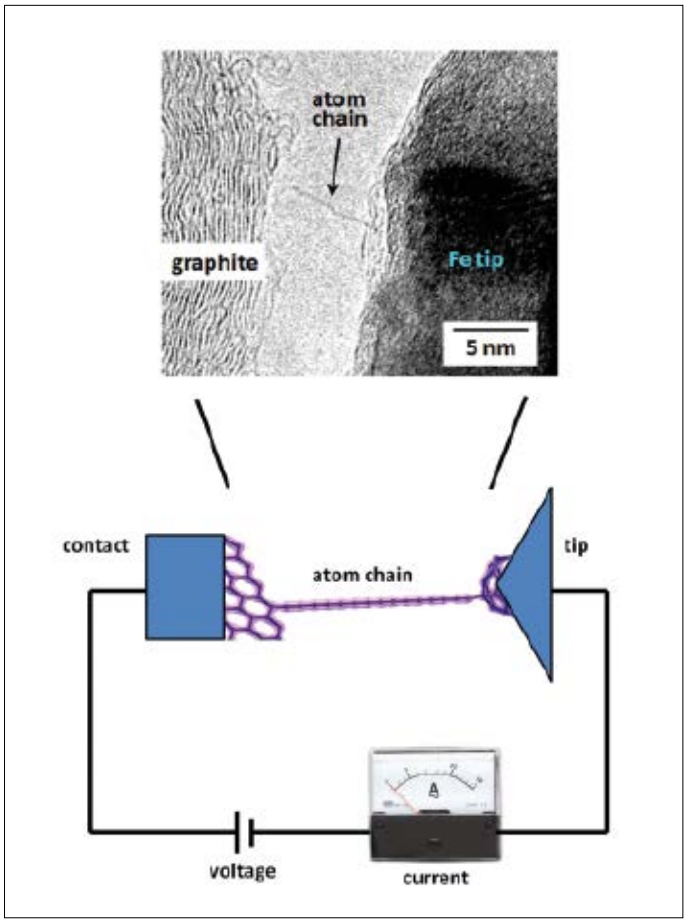

Fig. 1: The principle of the electrical characterization of atomic carbon chains (drawing at the bottom) and a TEM micrograph (top image) showing a carbon chain spanning between a graphitic contact and an iron tip.

to the difficulty of identifying the object as a chain while the measurement is carried out. However, a combined approach of STM resp. AFM with TEM allows us to do the measurement while the chain can be observed. This is an example how the combination of completely different types of microscopy, in this case electron microscopy with scanning tip microscopy, leads to new insights into the properties of nanoobjects.

Making and Characterizing Atom Chains in the TEM

Two ways are known to create free-standing chains of carbon atoms in the electron microscope. Electron irradiation of graphene layers leads to sputtering and the formation of holes. Eventually, free-standing carbon chains remain as bridges between neighboring holes [4-6]. In another approach, carbon chains are made with an STM tip in a TEM specimen stage. The metal tip is first „welded" to graphene by passing an electrical current and then retracted [9]. This can lead to the unraveling of carbon chains from the edges of a graphitic contact as shown in figure 1. In such a way, the TEM serves not only as a tool for identifying the atom chains but also to make them and to measure the electrical properties. This has been done in a series of recent studies.

The unraveling of a chain from the edge of a graphene layer is possible because the chain has fully saturated bonds and is more stable than the unsaturated row of carbon atoms at a graphene edge. The chain is then spanning between the graphitic substrate, which serves as one electrode, and the metal tip

(often covered with a thin graphitic layer) which is the other. To measure the electrical properties, current-voltage curves are taken. Most chains show S-type I/V characteristics which is expected for semiconducting polyyne (fig. 2). In a few chains, however, linear I/V-curves are obtained, indicating the presence of cumulene [10]. In asymmetric contact configurations, a rectifying diode-like characteristics is observed.

The understanding of the electrical behavior isn't possible without extensive calculations based on the Landauer-Büttiker approach of quantum conductivity. The calculations show that strain, which lengthens single more than triple bonds, opens a bandgap which then increases with increasing strain [9]. Under the experimental conditions, where the tip mostly pulls, strain is the common situation. Under unstrained conditions, however, the chain can be metallic. Thus, a metal-semiconductor transition by applying strain is feasible [8, 10]. Another limitation of the electrical conductivity is imposed by the contacts. An infinite carbon chain, where electron transport is ballistic, should have a conductivity of $2G_0 = 4e^2/h$ (G_0 is the quantum conductivity, e the elemenatry charge, and h Planck's constant; the factor 2 is due to the presence of two degenerate p-orbitals in sp^1 carbon). However, the experimentally measured conductivity is much lower. This is due to narrow resonant states and reflections at the contacts. Simulations of the transmission in a 10-atom chain spanning between two graphenic contacts are in good agreement with the measurements [11]. The highest currents measured so far are of the order of several microamperes at 1 V applied bias. This is smaller than the quantum limit but still a remarkably high current in a monoatomic wire.

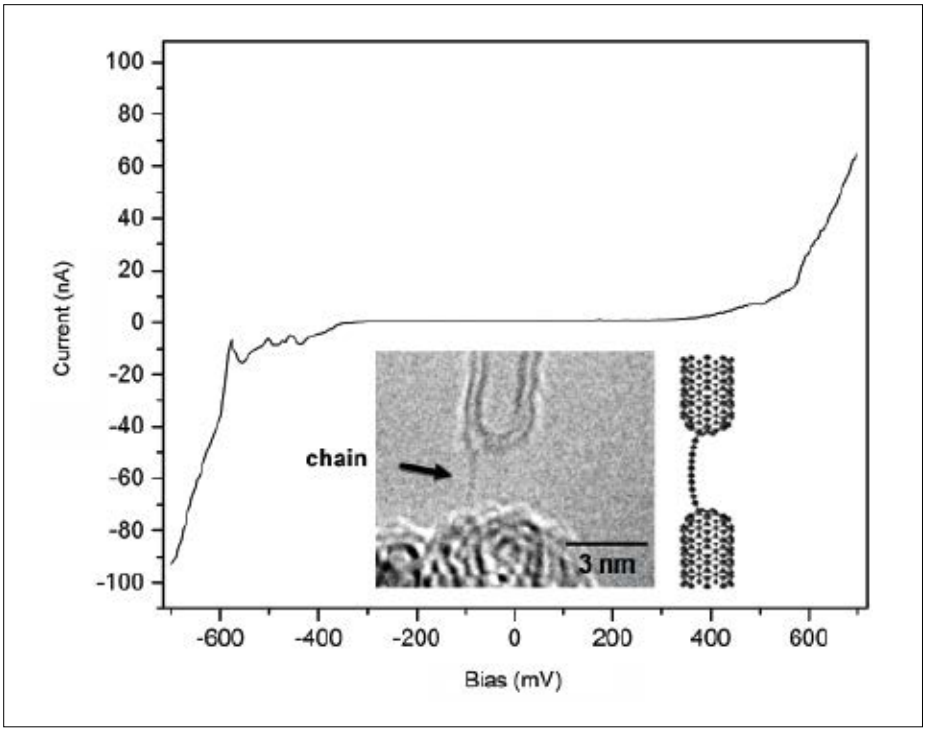

Fig. 2: A carbon chain between two nanotube-like contacts and the corresponding current-voltage curve. The S-shape of the curve shows the semiconducting nature of the carbon chain.

Future Challenges of Microscopy

One of the major drawbacks to date is the lack of atomic resolution during the electrical characterization of carbon chains. However, recent work shows that atomic resolution in imaging as well as in EELS is possible with the most advanced low-voltage TEMs and STEMs [6]. The combination of such a top-level TEM (or STEM) with an improved STM stage would allow us to study the electrical properties of carbon chains as a function of the number of atoms. There are plenty of theoretical predictions that could be verified in such measurements. Furthermore, bonding configurations at the contacts could be revealed.

Another important property of carbon chains is their mechanical stability. The ultimate strength of 10 nN as predicted hasn't been confirmed experimentally yet due to the limited sensitivity of commercial TEM-AFM stages. Since dedicated AFMs can measure much smaller forces, technical progress by developing more advanced stages should be feasible. Nevertheless, the high strength has already been confirmed qualitatively as considerable rebounding of massive contacts during the rupture of a carbon chain is seen [10].

We still don't know whether carbon chains will be applicable in any future device. The chains are highly reactive and a clearly less stable modification of carbon than graphene or diamond. Nevertheless, they are so far the only free-standing one-dimensional and monoatomic conductor of considerable length where experiments on fundamental mechanisms of quantum conductivity can be carried out. With more advanced electron microscopes and specimen stages, important questions of quantum conductivity in realistic systems could be answered.

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[1] References: http://bit.ly/IM-Banhart