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First-principles Investigation of the Electronic and Transport Properties of Carbon Atom Wires

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Abstract

The last years have witnessed an ever increasing interest in the field of molecular electronics, in which molecules connected with two or more electrodes are used as main building blocks to fabricate the components of integrated circuits. The achievement of high performance interconnects is one of the key step for the realization of such devices. In this context, π-conjugated carbon wires are the most promising candidates to this role due to their structural stability and their experimental feasibility.

In particular we investigated the transport properties of systems where a freestanding π-conjugated carbon chain is contacted with two electrodes in order achieve a two-terminal device. Although some important issues had already been investigated in this field when starting this project, information were very scattered and a well-rounded perspective of the key aspects affecting the electron transport was missing. This thesis represents one attempt to fill this gap first in the case of Ag-chain-Ag systems and then for graphene-chain-graphene devices. Specifically we focused on the role that the chain-electrode junction plays in determining the characteristics of such systems, finding that the contact geometry strongly affect the transport properties.

In fact, for Ag-chain-Ag systems, qualitative different transport properties have been found depending on the adsorption site on the silver surface, while results showed only a weak dependence on the chain length. Moreover we observed that those results can be extended to "tip-like" contacts, mimicking a more realistic electrodic surface. As opposite, linking atoms such as sulfur or silicon strongly influence the conductance. We further demonstrated that the vibrational motion of the atoms has negligible effects on the transport properties for a very large range of temperature. Finally we also critically assessed the reliability of our results using the optical properties of the gas-phase molecules to benchmark the adopted setup.

The results obtained for graphene-chain-graphene devices confirmed that the junction plays a central role in determining the strength of the electrode-chain coupling, and in turn, the conductance. We first analyzed in details the transport properties of single chains connected to ideal electrodes, investigating their geometrical and electronic structure in order to establish a connection with their transport properties. Furthermore, at odds with the above mentioned metal-C-metal systems, we found that "tip-like" junctions here have dramatic effects on the transport properties. More importantly, we investigated the possibility to observe quantum interference, chemical gating and conductance switching behaviors in such systems.

Outline

The thesis is organized as follows.

In chapter 1 we present an overview of the topics of molecular electronics, elucidating the problems arising from the miniaturization of the integrated circuit elements and how they can be replaced by molecular components.

In chapter 2 we focus on the properties of carbon atom wires, reviewing their properties, the methods of synthesis and the state of the art of the fabrication of carbon-wire based devices.

In chapter 3 we introduce the theoretical methods employed throughout this thesis, first reporting the topics of Density Functional Theory (DFT) and then addressing the formalism allowing to compute the transport properties of a system by means of the Non-Equilibrium Green's Function (NEGF) approach.

In Chapter 4 and 5 we show the results obtained for Ag-chain-Ag and graphene-chain-graphene systems, respectively. The content of these chapters has been published in:

- Electron transport in carbon wires in contact with Ag electrodes: a detailed first principles investigation; P. Bonardi, S.Achilli, G. F. Tantardini, R. Martinazzo, *Phys. Chem. Chem. Phys.*, 2015, **17**, 18413

- Electron transport in graphene-based devices; P. Bonardi, S.Achilli, R. Martinazzo, *In preparation*

Finally, in chapter 6 we summarize the results and the main conclusions of this thesis.

Contents

Chapter 1

Molecular Electronics

Molecular electronics investigates the electronic and thermal transport properties of nanosized devices in which individual molecules, or an assembly of them, are used as main building blocks (see fig. 1.1). This field has its origin from the request of new technologies that could complement or partially replace the solid-state electronics. Indeed, the scaling of electronic devices by means of the conventional top-down lithography technique has reached the limit where reliable and reproducible fabrication of sub-20 nm structures is cumbersome and economically unfeasible. Also, at this length scale the conduction properties may become inherently quantum, and transport might occur on a regime which is different from the conventional (diffusive) one operative in present-day devices.

Although further miniaturization of electronic components remain an enormous challenge, it is remarkable that molecules, showing a wide range of physical properties, sizes of the order of few nanometers and the possibility to be synthesized in molar amounts,
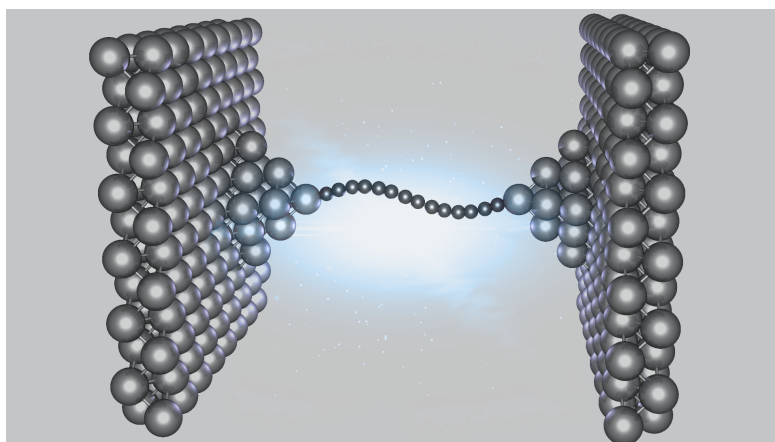

FIGURE 1.1: Molecule contacted to metallic electrodes

have the potential to be used as components of nanoscaled devices. Moreover, recent experimental findings in electron transport through single molecules have strengthened the idea that, beyond silicon technology, the next limit of miniaturization of electronic components is the realization of single-molecule electronics.

Even if it seems difficult that molecular electronics will ever replace the silicon-based one, it could certainly complement it by providing, for instance, new functionalities out of the scope of traditional solid-state devices. In fact many molecules possess rich optical, magnetic, thermoelectric, electromechanical and molecular recognition properties, which may lead to new applications that are not feasible using conventional materials or approaches. Hence, chemistry might play a key role in the design and production of functional molecular-based devices since it is one of the most promising ways to connect the state-of the-art lithography techniques and the molecular-scale dimensions via *e.g.* chemically driven self-assembly techniques.

From a technological point of view, molecular electronics could offer a great variety of advantages, if compared with the silicon-based one. First, the reduced size of molecules (few nanometers at most) could lead to a high packing density of devices, with obvious consequences in device cost, efficiency and power dissipation. Second, molecular wires could reduce the transit time in transistors reducing the time needed for an operation. Finally, changing the composition and the geometry of the device, one can extensively vary its magneto-transport and optical properties in a very simple way.

Of course a number of different physical effects should be taken into account in the miniaturization of electronic devices, including the propagation mechanism of charge carriers along and across a narrow and thin conductor, the quantization of both electrical and thermal conductance as well as the partial loss of electrostatic control of the drain current *vs* the gate voltage.

However, the main challenge concerns the realization of a technology for mass production of single molecule devices, *i.e.* the fabrication of a large number of devices with reliable and reproducible structural and functional characteristics. This, of course, requires the development of methods achieving sub-nanometer precision to produce and handle such devices, in particular techniques allowing to unambiguously identify single molecules contacted with the leads as well as the junction geometry.

Despite these unsettled issues, important and consistent advances have been made in the field in the last years[1]. These advances include: (1) demonstration of simple molecular device functions; (2) development of many different experimental approaches for measuring electron transport in single molecules and theoretical methods for describing the electron transport properties; (3) emergence of new characterization techniques

that help to bridge theories and experiments; (4) realization of devices with functionalities that cannot be achieved in silicon-based electronics, such as molecular sensors or molecular electromechanical or optoelectronic devices.

A variety of techniques have been developed to construct metal-molecule-metal junctions[1], including scanning probe microscopy (SPM), mechanically controllable break junctions (MCBJs), electromigration break junctions (EBJs), and self-assembly of nanostructures. The first three methods have been the most widely used in proof-of-principle experiments of single-molecule electronics, but only the latter seems to have the potential for a mass production of single-molecule devices.

Mechanically-controllable break junction (MCBJ) method is one of the first techniques developed to form atomic-scale metallic constrictions and to examine their electrical and mechanical properties. The working mechanism is depicted in fig. 1.2. A suspended metallic bridge with a notch is fixed on a flexible substrate, which is mounted in a three-points bending mechanism consisting of two pushing rod and one counter-support (or viceversa one pushing rods and two counter-supports). A piezoelectric element is usually used to control the position of the pushing rods relative to the counter-support, allowing the metallic bridge to be elongated, and finally broken, by increasing the bending of the substrate. The elongation can be reduced by pulling back the pushing rod and then reducing the curvature of the surface. Hence this setup allows to mechanically open or close of the gap between the two bridge sections with extremely high accuracy on the gap width. In common applications, the two bridge sections act as electrodes, allowing to record the current flowing through the constriction when contacted, or the tunneling current when kept in close proximity. The possibility of adjusting the nanogap width also allows to deposit and characterize molecules (possibly as few as one molecule) across the break junction. To this aim, considerable displacements of the pushing rod and thus considerable bending of the substrate are necessary. Therefore substrates with a relatively high elastic limit like spring steel or bronze are required. Of course, metallic substrates need to be covered by an electrically insulating material before the junction being fixed on it. MCBJ mechanisms have been developed for various environments including ambient conditions, vacuum, very low temperatures or liquid solutions. The latter is particularly interesting since allows to deposit single (or a few number of) molecules across the break junction by means of self-assembly techniques.

One of the most versatile tools for the fabrication of atomic-size contacts and atomic-thick wires is the scanning tunneling microscope (STM). While in its standard applications a metallic tip is held in close proximity of a conducting substrate in order to record
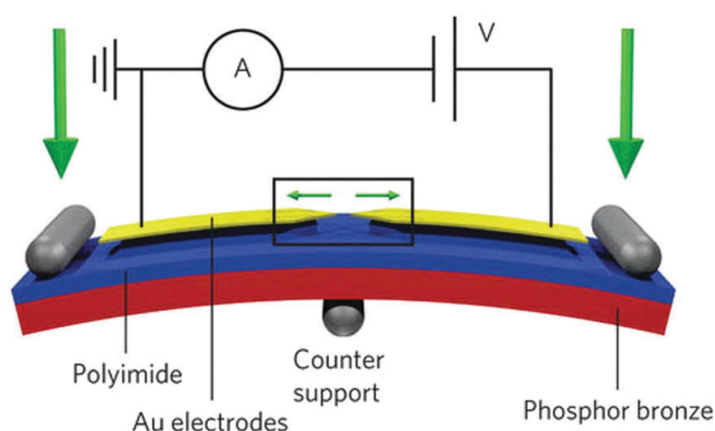
FIGURE 1.2: Schematic illustration of a MCBJ device[2]
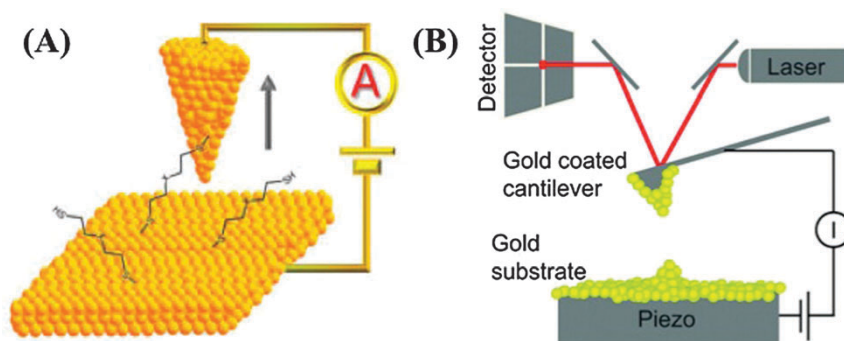
FIGURE 1.3: Schematic representation of (a) the STM break junction setup[3] and (b) a conductive AFM[4].

the tunneling current, the tip can also be indented into the surface and carefully withdrawn until an atomic-size contact forms. The main advantages of this technique are its speed and versatility. Moreover, when the sample is prepared in ultra-high vacuum (UHV) STM also allows one to obtain informations about the topography of the electrodic surfaces before and after the formation of the contact. The main drawbacks are its limited stability with respect to the change of external parameters (*e.g.* the temperature) and the general short lifetime of the contacts, because of the sensitivity of STM to vibrations.

Another scanning probe technique that partially complements STM is the atomic force microscope (AFM). Instead of the tunneling current, AFM uses the distance dependence of the Van der Waals forces between a tip and a surface to gather informations on the surface topography. For the fabrication and characterization of atomic contacts the tips is covered by a thin metallic layer and the procedure is similar to that described for STM, differentiating for the quantities measured, *i.e.* current and force (see fig. 1.3-b).

The force signal can be used to determine the local topography of the junction.

Further developments are the STM- and AFM-based break junction methods, where, upon deposition of molecules on the electrode surface, the transport properties of a single or a small number of molecules are studied by repeatedly approaching and withdrawing the tip from the surface (see fig. 1.3-a).

Another method for preparing and imaging atomic contacts involves the irradiation, *e.g.* with the electron beam of a transmission electron microscope (TEM), of thin metal films deposited onto dewetting substrates. The high energy impact of the beam can locally melt the metal allowing the formation of atomic-sized constrictions. Moreover TEM offers the possibility to simultaneously perform conduction measurements and imaging with atomic precision when this technique is integrated with STM. This combination in principle enables to directly prove the existence of atomic-size wires and the determination of the characteristics of the contacts as well as to establish a correlation between contact size and conductance.

Another common technique is the electromigration. Within this method, a metal wire is prepared on a substrate and then thinned by driving a strong electric current through it in order to achieve atom migration from the shrinking region, while the wire is broken down. Before the wire fails and the current drops drastically, atomic size contacts are formed for a rather short time. The main limit of the this techniques is that it is a single-shot experiment: once an atomic-size contact has been established there are only limited possibilities to come back to a larger contact. Moreover, the control of the final part of the electromigration process is difficult because the transport mechanism changes from diffusive to quantistic. A combination of the electromigration with MCBJ technique overcomes this problem. A wire formed between the electrodes in a MCBJ experiment can be thinned out by electromigration to a narrow constriction with a cross section of few nanometers, then the substrate is bent for completely breaking the wire. This last step is then reversible and repeatable for studying small contacts. This technique is also particularly useful for preparing nanometer-scale gaps between metal electrodes into which individual molecules or other nano-objects can be inserted to measure their electrical properties. However, care has to be taken if the molecule is attached to the device before electromigration is performed, because the heating of the metal during the electromigration process might damage or destroy the molecules.

The methods mentioned so far are all based on a top-down fabrication strategy, where nanogaps are mainly constructed by using standard semiconductor nanofabrication technologies. Another, much less investigated, approach is a bottom-up self-assembly of molecule-metal structures. The general idea is to fabricate a nanogap using lithographic

methods, with dimensions which will be limited by resolution of this technique, and then exploit self-assembly of chemically synthesized metal-molecule-metal structures to bridge the pre-fabricated electrodes. For instance, Dadosh *et al.* have developed a method to synthesize gold nanoparticle dimers linked by single dithiol molecules via a self-assembly process[5]. Then, dimers (Au-molecule-Au) of 30 nm-diameter nanoparticles were deposited onto electrodes with a 40-50 nm separation, and single-molecule conductance was measured.

Usually the first characterization of nanoscale contacts is the measurement of the linear conductance as a function of an external parameter such as the temperature or a magnetic field. The next quantity is the non-linear conductance, *i.e.* the measurement of the current-voltage (*I-V*) characteristics or the differential conductance. Of course, a number of issues has to be taken into accounts when recording the current. First, the correct choice of the bias voltage is difficult because of effects giving rise to nonlinearity happen on varying the voltage scale. Second, sudden voltage spikes and jumps may destroy the sample, therefore abrupt switching actions in the electrical circuit measurements have to be minimized. Moreover an extreme variation of the differential conductance can occur even with small bias changes. Finally the lifetime of the junction is generally of few seconds at most, but often of some milliseconds. This forces one to perform fast measurements, resulting in limited signal to noise ratios and limited statistical informations. Furthermore, atomic and molecular junctions at room temperature reveal intrinsic noise caused by atomic vibrations. Therefore, low-temperature experiments are required.

A wire-shaped molecule that can efficiently transport charge has been actively pursued as it would provide the ideal interconnections for molecular devices. To date, a wide variety of molecular wires have been investigated, mostly based on a carbon backbone structure. Among these, saturated and conjugated carbon chains are the most studied, due to their simplicity and experimental feasibility.

Chains consisting of saturated $C-C$ bonds result to be poorly conducting wires, especially in the long members, as a consequence of the large gaps between their highest occupied molecular orbitals ($HOMO$) and their lowest unoccupied molecular orbitals ($LUMO$). For instance, experiments have shown that the conductance of alkanes decreases exponentially with molecular length, and, together with characteristic current-voltage (I-V) curves and temperature independence, suggests that electron tunneling is the most probable conduction mechanism[6,7].

Although the exponential decay of the conductance with length is similar in most experiments, comparison of the absolute conductance values obtained in different experiments is not straightforward. This is a direct consequence of the difficulty to manipulate

nanodevices. In fact, on one hand, this disagreement is due to the fact that some experiments measure many molecules and others a single molecule. On the other hand, even in the case of single-molecule measurements, conductance values may differ for one or more order of magnitude as a consequence of different molecule-electrode contact geometries. This makes conductance statistics a necessary tool for analyzing transport in molecular devices.

Because of the rapid decrease in tunneling current with distance, conjugated molecules featuring π electron delocalization are better candidates for long-distance charge transport. These molecules feature $HOMO - LUMO$ gaps much smaller if compared to saturated ones and should therefore transport charge more efficiently. However, off-resonant tunneling is still expected to be the predominant conduction mechanism in short molecular wires, while, with increasing length, this is replaced by hopping conduction with only a weak wire length dependence[8]. The electronic and transport properties of π-conjugated carbon chains will be extensively addressed in the next chapter of this thesis.

Device applications would require molecules not only to provide a pathway for the electron transport, but also to be an active element that can perform one or a set of controllable functions in order to create devices with complex functionalities. However, owing to the difficulty of placing a third gate electrode close to a molecule, to date most studies in molecular electronics have focused on two-terminal devices. Nevertheless, such devices can exhibit interesting and important behaviors that could be useful in many applications. Examples include rectification[9], conductance switching effects[10] and negative differential resistance[11].

A rectifier (or diode) is an element of crucial importance in integrated circuits, allowing electric current to flow in one direction and not in the opposite one. The concept of single molecule rectifier was first proposed by Aviram and Ratner[12] in 1974. Their diode consisted of a donor and an acceptor groups connected through a bridge, in general a σ backbone. In this system the electrons first hop from one electrode to the donor unit, then tunnel from the donor to the acceptor unit, and finally hop to the other electrode. At zero applied voltage bias, the $LUMO$ of the acceptor is slightly above the electrode's Fermi energy while the $HOMO$ of the donor is slightly below. Upon application of a voltage bias across the junction, the $LUMO$ (or the $HOMO$) can be aligned to the Fermi energy of the leads or separated, depending on the bias direction. However, this idea has many drawbacks. First, the characteristics of such donor-acceptor diodes are very sensitive to the alignment of the molecular orbitals with each other and with the electrode levels, making difficult their realization in practice. Second, rectification in such
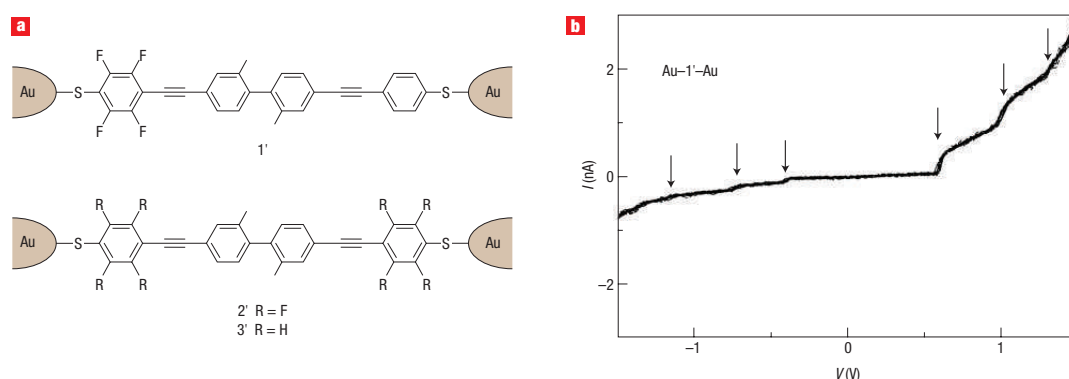
FIGURE 1.4: (a) Molecular diode consisting of single molecule (1') covalently linked to two Au electrodes of a mechanically controllable break junction. Symmetric molecules, 2' and 3', each consisting of two identical conjugated units serves as controls. (b) $I - V$ characteristic for 1' showing rectification behavior, where the arrows point to stepwise increases in the current [13]

diodes requires a σ bridge, which effectively adds a large tunnel barrier between the donor and acceptor groups, resulting in a very large resistance.

To date, the only experimentally realized alternatives to Aviram-Ratner diodes have been devices where one linker group is eliminated or weakened, creating an asymmetrically contacted junction. In such devices the diode behavior is expected to occur as a consequence of different thresholds at positive and negative bias voltage. For instance, direct conductance measurements in a MCBJ experiment on molecule consisting of two weakly coupled conjugated units demonstrated rectification behavior, provided the two units being different – one is fluorized and the other one is not – in order to break the symmetry of the system [13]. When sweeping the bias voltage, the energy levels of both units are shifted with respect to each other. Whenever an unoccupied level become occupied, an additional transport channel opens up and the current increases by a certain amount, giving rise to the steps in the diode-like I-V curve shown in fig. 1.4. More generally, several single-molecule diodes have been realized also in junctions featuring asymmetric molecular backbones that do not contain a pair of donor and acceptor groups [14]. Indeed, diode-like $I - V$ characteristics have been observed by using different molecule-electrode contact geometry on the two junctions [15,16], non-symmetric molecules [17,18] or both [19]. However, symmetry breaking alone is not sufficient to achieve a larger diode effect since the bias voltage largely drops at the molecule-electrode interfaces. Moreover, to date, molecular diodes have shown limited potential for applications due to their low conductance, low rectification ratios, extreme sensitivity to the junction structure and high operating biases (> 1 eV).

A molecular switch is a two-terminal device in which the conductance can be reversibly

switched between conductive and non-conductive states in response to external influences. A number of external stimuli such as electric fields, photochemical processes as well as chemical (*cis-trans* configuration switching, oxidation or reduction of functional groups, bond formation,etc) or mechanical (rotation of a functional group,etc) stimuli can be used to enable molecular switching. Other than turning on and off electronic components, molecular switches can also find applications in molecular memory and logic devices.

One of the largest class of such devices is based on mechanically interlocked bistable complexes, such as catenanes and rotaxanes[20], in which switching behavior can be activated by photochemical, electrochemical or electrical stimuli, making these molecules interesting candidates as molecular switches. Other interesting molecules are oligomeric phenylene ethynylene (OPE) derivatives[21]. A recent study using three different methods – STM, crossed-wire junction and magnetic-bead junction – has revealed reversible switching behavior in these systems with a mechanism based on bias-driven changes in the molecule/electrode hybridization or bond angles[22]

Another class of two-terminal electronic elements is constituted by negative differential resistance (NDR) devices, which feature a region of decreasing current with increasing voltage in the $I - V$ characteristics. They have been extensively investigated due to their potential in the implementation in critical circuit elements such as oscillators, frequency multipliers and low-power memory units. Typical "macroscopic" devices that exhibit NDR are constituted by semiconductor heterostructures in which electrons tunnel through a quantum well formed by two tunnel barriers. The current increases initially when the energy level of one side of the quantum well lines up with an energy level of the quantum well. After reaching a maximum at resonance, the current decreases and gives rise to NDR effect. This effect has also been predicted and demonstrated in a large number of molecular devices. For instance, in a recent MCBJ experiment, Nguyen *et al.*[23] showed that a gap opened in a single layer graphene ribbon along the transport direction give rise to NDR effect (see fig. 1.5).

Although two-terminal devices are certainly interesting and useful, three-terminal field-effect transistor (FET)-like devices are highly desired. Theoretical models have predicted that the conductance of a single molecule can be modulated with a gate electrode in a fashion similar to a conventional FET[25,26]. However the implementation in practice of a three-terminal device needs to ensure that the gate is only electrostatically coupled to the molecule. This would require the gate insulation from the source and drain electrodes. However, parasitic currents caused by various mechanisms (*e. g.*
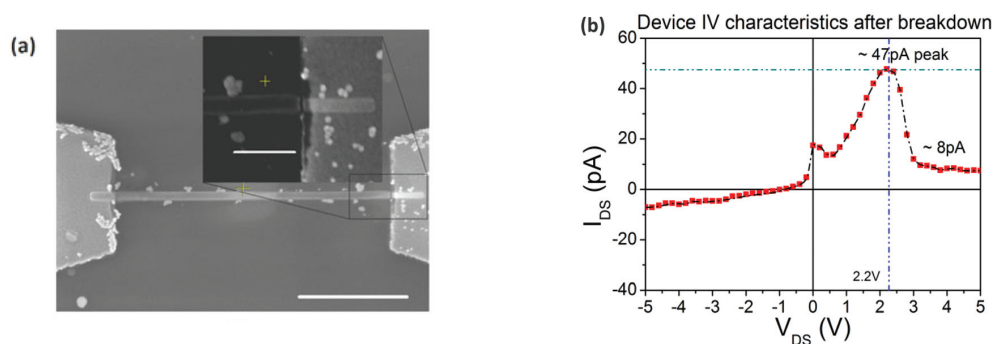
FIGURE 1.5: (a) Scanning electron microscope image of the device after breaking of the nanoribbon (scale bar: 2μm), inset: zoom of the breaking region. (b) Measured $I - V$ characteristics of the device after breaking showing NDR effect[23].
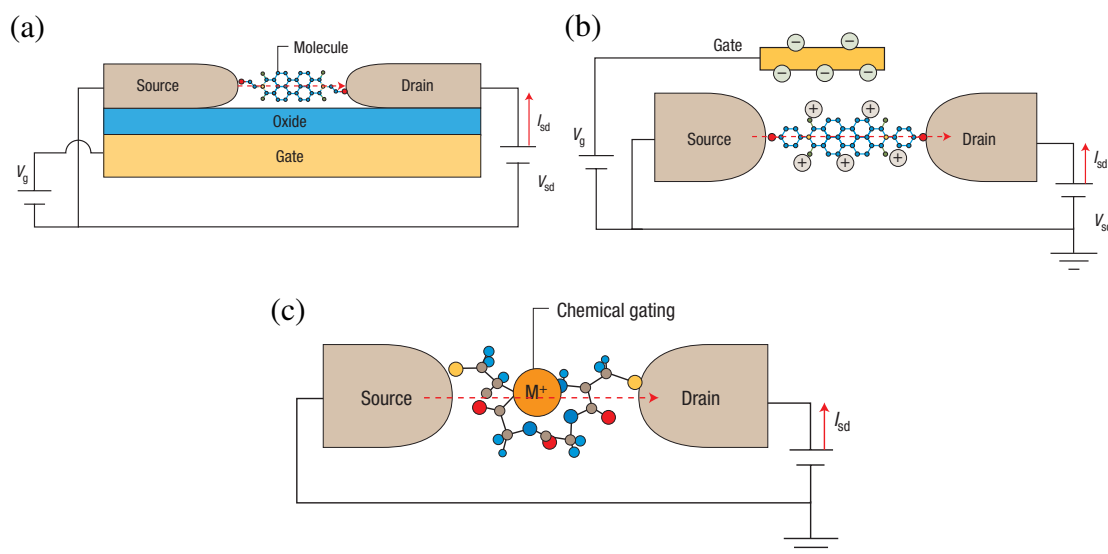

FIGURE 1.6: Schematic picture of back gate (a), electrochemical gate (b) (the counter electrode is not shown) and chemical gate (c)[24]

quantum tunneling) can lead to a current between the gate and the electrodes, overshadowing the molecular characteristics. Hence, the main challenge in fabrication is thus to design a junction geometry, in combination with the right material choice, which reduces as much as possible the gate leakage, but maximizes the electric field reaching the molecule. Essentially three different gate configurations have been proposed and demonstrated in recent years.

The first configuration (fig. 1.6-a) is the back gate approach, which consists of a source and a drain electrodes placed on a solid substrate, such as Si or Al, heavily doped to serve as a gate. A thin oxide layer separates the substrate from the source and drain

electrodes. For example this configuration has been used to demonstrate FET-like behavior in carbon nanotubes[27]. Another approach involves the use of an electrochemical gate (fig. 1.6-b). This is typically achieved in a four-electrode electrochemical setup with counter- and reference electrodes serving alongside the source and drain electrodes (both of which are the working electrodes of the electrochemical cell)[28,29]. By applying a positive voltage on the electrolyte, the negative ions are attracted towards the electrodes, resulting in a higher concentration of positive ions close to the molecule, effectively gating the molecular junction. The last approach is the chemical gate (fig. 1.6-c), where current flowing through the molecule is modulated via a reversible chemical event, such as binding, reaction, doping or complexation of the molecular bridge.

Chapter 2

Carbon Wires

In the last decades the semiconductor industry has been able to improve the performance of electronic systems by making ever-smaller devices. However, this approach soon encountered both scientific and technical limits, paving the way to the search of alternative technologies. The most promising candidates to this aim are carbon-based materials, existing in a large variety of allotropes (see fig. 2.1) with completely different physical and electronic properties. Whereas the most common graphite and diamond have been largely investigated for many years, only the recently discovered allotropes have shown the potential for electronic applications. Particularly the isolation of single-walled carbon nanotubes (CNTs), first reported by Iijima in 1991[31], and, more recently, the discovery of graphene by Novoselov and Geim in 2004[32], gave further impetus in this research area, resulting in rapid progresses in the understanding of their remarkable properties and of their pratical applications. The feasibility of field-effect transistors based on semiconductor nanotubes and graphene nanoribbons have already been demonstrated[33,34], and carbon nanowires could be used as high-performance interconnects, opening the way for the realization of all-carbon electronic devices.

In this context, π- conjugated linear carbon wires are among the most attractive candidates to this role. Despite of their simplicity, the possibility of showing multiple π bonding and the exceptional mechanical properties make these structures ideal conductors, offering exciting prospects for applications in a large number of systems. Hence it is not surprising that the last few years have witnessed an ever increasing interest in such wires and a large number of both theoretical and experimental investigations has addressed the possibility of using these nanowires in light-emitting diodes (LED), photovoltaic devices, transistors, switches, and in general all integrated circuit elements.
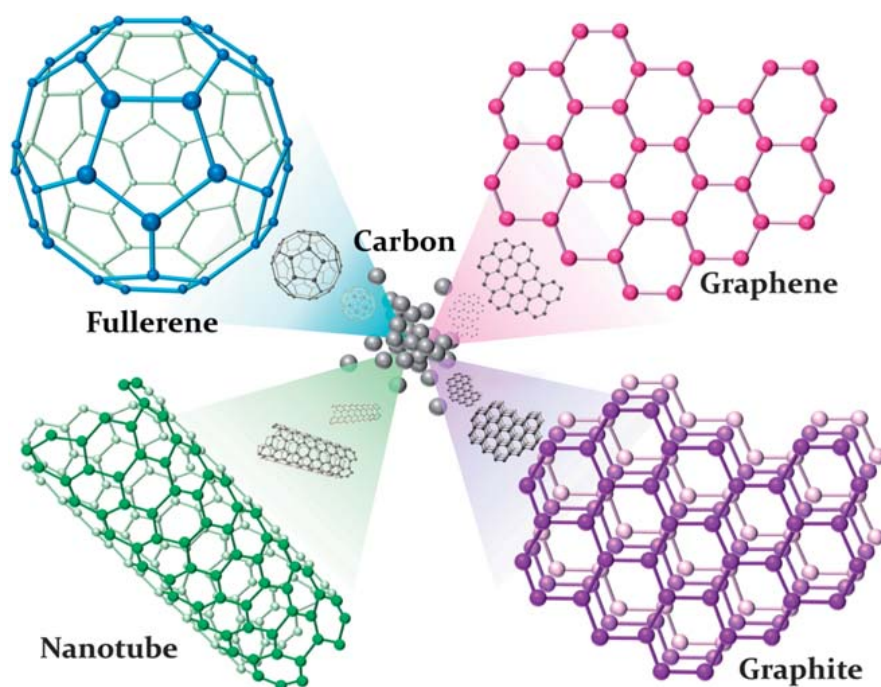
FIGURE 2.1: Carbon allotropes in different structures[30]

One-atom thick wires made of *sp* carbon atoms can either show double bonds through-out the backbone (cumulene, $=C=C=C=C=$), or single-triple bond length alternation (polyyne, $-C\equiv C-C\equiv C-$).

In the ideal infinite chains, polyynes (carbynes) are predicted to be the most stable, since cumulene, as any one-dimensional system, are susceptible to Peierls distortion. According to Peierls' theorem, the electron system of a perfectly one-dimensional crystal is unstable, resulting in the breaking of atomic periodicity in such a way that the elementary period of the chain is doubled. This results in a short-long bond length alternation, opening an electronic bandgap of 0.32 eV at the edge of the Brillouin zone, and stabilizing the structure (the total energy is lowered by 2 meV per atom)[35].

This gap is tunable with an applied strain, since the stretching of the chain determines an increase in the bond length alternation, which is the main factor determining the gap size. Actually, when taking into account the lattice vibrations, carbon chains are predicted to preserve their cumulenic character and to transform into polyyinic under 3% strain[36].

The most basic mechanical property of the carbyne chain is its specific stiffness, which turns out to be $\sim 10^9$ N·m/kg[35], although it still has to be confirmed experimentally.
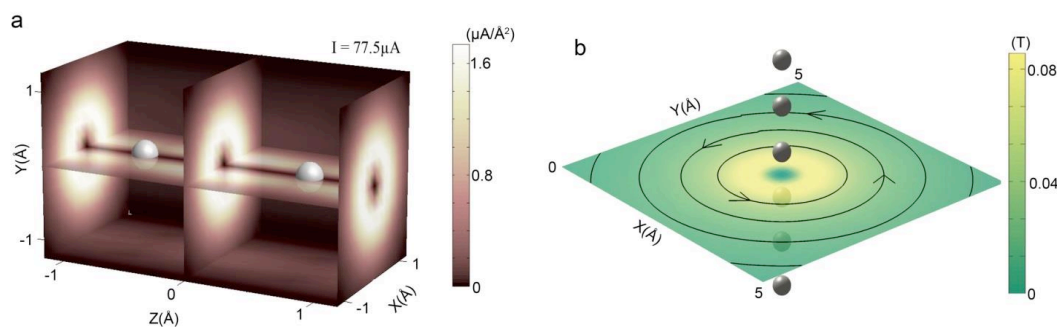
FIGURE 2.2: (a) Current density distributions in the axial plane of carbon chains and in cross-section. (b) The magnetic field induced by the current density of (a). The directions of magnetic vectors correspond to the current flowing from the bottom up. (From ref. [Liu et al.[35]])

This is more than two times higher than the two stiffest known materials - carbon nanotubes and graphene ($4.5 \cdot 10^8$ N·m/kg[37–39]) - and almost three times larger than diamond ($3.5 \cdot 10^8$ N·m/kg[40]).

$$\Phi = \frac{\mu_0}{2\pi}\left(\frac{1}{2} + \ln\frac{R}{r_0}\right) I, \qquad (8)$$

Since the π-electrons of such carbon chains can be considered as a one-dimensional system of free electrons, carbon chains are expected to be highly conductive. As a consequence of their cylindrical symmetry, the distribution of the current density results axially-symmetric with negligible magnitudes on the axis and a bulge at about 1 Å (see fig. 2.2), reflecting the fact that σ bonds are localized between atoms and form the skeleton of the structure, while the delocalized π bonds normal to the axis support the electronic conductance

$$\Phi = \frac{\mu_0}{2\pi}\left(\frac{1}{2} + \ln\frac{R}{r_0}\right) I, \qquad (8)$$

These carbon chains naturally exist in the interstellar environment, especially in diffuse interstellar clouds (*i.e.* low dense, with some hundred of particles per cm^3), dark clouds[41] (highly dense hence opaque to UV radiation), in meteorites[42] and in circumstellar envelopes, which is the richest source. In fact, expanding envelopes of gas and dust that surround carbon-rich, red giant stars contain a wide variety of carbon based molecules formed as by-products of nuclear reactions occurring in the inner region[43]. Another peculiar environment in which polyynes and cumulenes form is Titan's atmosphere. Titan, Saturn's main moon, is the only solar system body, besides the earth, with a substantial atmosphere mainly composed of molecular nitrogen (98%). Methane is the second major constituent with an abundance of about 1.5%, rising to a complex organic chemistry[44] (see fig. 2.3). Several hydrocarbons, such as acetylene, propane and butane, have been detected with an abundance of few ppm in this atmosphere, but, to date, the only polyynic member found is dyacetylene, other than some cyano- (HC_nN) and dicyanopolyynes (NC_nN). However simulations of the reactivity of Titan's atmosphere
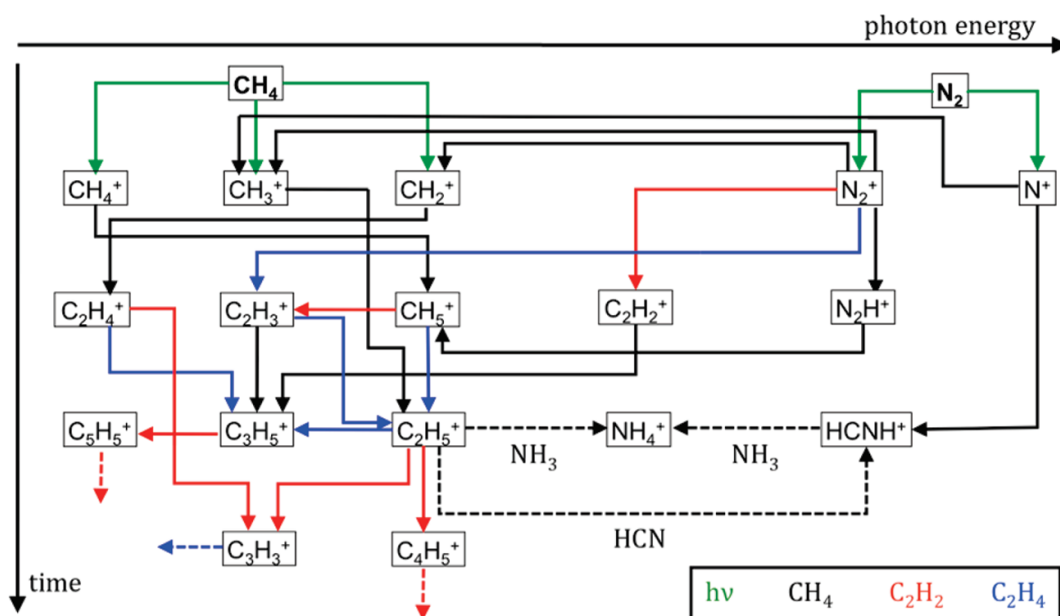
FIGURE 2.3: Chemical flowchart representing the most important reaction taking place in Titan's ionosphere, as resulted from laboratory simulations[45].

have shown that longer chains should also be present, but difficult to detect because of their low concentration and the interference of the polar cyano-derivatives[45]. The understanding of the photochemical processes originating such species is of particular interest in the modeling of planetary atmospheres, since those molecules are supposed to be a link between the gas-phase and the solid-phase visible as haze at high altitudes in Titan's atmosphere as well as in giant planets like Saturn or Uranus[46]. Furthermore, acetylene and longer polyynes are expected to control the relative abundance of atomic hydrogen by competitive mechanisms of molecular dissociation and recombination, in addition to play a key role in the methane photocatalytic reactions.

To date, the synthesis and the characterization in laboratory of carbynes turned out to be very challenging, since these structures are highly unstable and reactive. For this reason carbynes often needs to be stabilized by isolation in rare gas or be chain terminated with suitable functional groups to prevent further reactions. Several routes for their synthesis in gas phase and in solution have been proposed over the years, involving different techniques and a number of procedures (a comprehensive review can be found in ref. [Chalifoux and Tykwinski[47]]).

Already in 1972, Eastmond *et al.*[48] reported the synthesis of mixtures of polyynic chains via Hay coupling, obtaining silicon-capped acetylenic compounds $(Et)_3Si - (C \equiv C)_n - Si(Et)_3$ (Et: ethyl, n=2-16) up to 32 carbon atoms. Since multisteps and very low temperatures are required for such synthesis, laser ablation in solution at room temperature has emerged as a new promising technique for the synthesis of polyynes. Tsuji

et al.[49,50] investigated the laser ablation of graphite and fullerene particles suspended in solutions, finding that hydrogen-terminated polyynes $C_{2n}H_2$ (n=4-8) were produced from graphite particles suspended in benzene, toluene, or hexane solution, while $C_{2n}H_2$ (n=4-6) chains were formed from fullerene in hexane or methanol solution. More recently Cataldo[51,52] also synthesized $C_{2n}H_2$ (n=2-9) polyynes by a submerged electric arc discharge in organic solvents. Earlier studies[53,54] showed the possibility to produce nanostructured carbon films rich in carbynes by depositing pure carbon clusters from a supersonic beam. Furthermore, 8 to 28 carbon atom chains were synthesized with terth-butyl and trifluoromethyl protective group at their ends[55], showing stability at relatively high temperature (130-140 °C), while in other experiments, synthesis of chains up to 44 atoms was claimed[56]. In a most recent study, a novel method for linear carbon chains formation using Pt atoms on a graphene surface has been presented[57], in which Pt atoms act both as nucleation sites and as termination for the chain growth (see fig. 2.4).

Relatively longer gas-phase polyynes (2n=16-26) have also been synthesized in neon matrix and their electronic spectra have been recorded[58,59]. UV absorption spectra are particularly helpful in obtaining absorption cross sections, which can be used to calculate photolysis rates and deduce relative abundances of the member of the series in the interstellar medium. In fact the absence of a permanent dipole moment in such molecule hinders their direct detection with common techniques, such as infrared spectroscopy.

The synthesis of the less stable cumulene has appeared to be much more difficult. Only short chains with two phenyl rings at each end have been synthesized and characterized[60].

Several studies also addressed the possibility that chains close their ends by forming rings. Such ring structures have been observed in carbon vapors produced by laser ablation[61,62] and have been proposed as starting point for the formation of more complex structures such as carbon nanotubes[63] or fullerenes[64].

Although a large number of methods of synthesis has been previously developed, the first experimental indications for the existence of carbon chains in nanostructured materials has been deduced only in 1995 from a study of field emission of electrons from carbon nanotubes. Rinzler *et al.*[65] concluded that the emitting structures were linear chains of carbon atoms pulled out from the open edge of a single-walled nanotube by the force of the electric field, in a process that resembles unraveling the sleeve of a sweater. Early indications came from high-resolution transmission electron microscopy (HRTEM) observation of a carbon chain along the axis of a multi-walled nanotubes
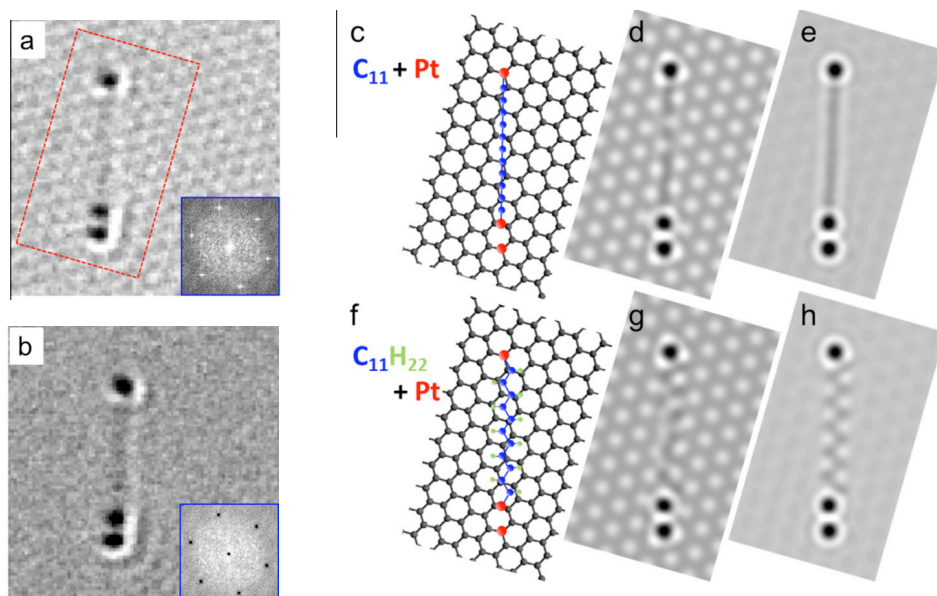
FIGURE 2.4: Experimental and simulated images of Pt-capped carbon chains[57]. (a) Averaged TEM image of straight carbyne; (b) Fourier-filtered image of (a); (c-e) and (f-h) Modeled, simulated, and filtered images of straight carbyne C_{11} and alkane $C_{11}H_{22}$, respectively.
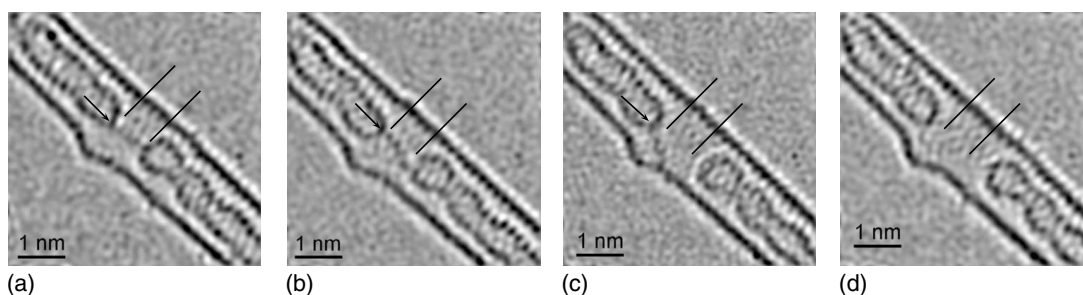

FIGURE 2.5: *In situ* study showing the dynamics of a single carbon chain bridging two single-walled carbon nanotubes[68]. (a) and (b) Single chain bridging two inner nanotubes, with different attachment points, indicated by an arrow. (c) The chain disconnects from the lowest inner tube. (d) The chain disappear and the inner tube sections drift apart. The time elapsed from (a) to (d) is 30 s

with inner diameter of 0.7 nm, produced by arc discharge from a graphite double anode. Calculations on the basis of Wan der Waals interaction demonstrated extremely high thermal stability and high mechanical properties of such chain[66,67]. More recently, carbon chain formation has been observed in double-wall carbon nanotubes where the disintegration of the inner shell lead to short chains in the axial direction bridging the tube fragments[68] (see fig. 2.5).

The first direct observations of the formation of freestanding carbon chains from a graphene nanoribbon have been reported in 2009 by Jin *et al.*[69] and Chuvilin *et al.*[70]

(see fig. 2.6). The procedure has been quite simple: the nanoribbon has been continuously thinned from its open ends by removing the excess of carbon atom row by row by means of controlled energetic electron irradiation inside a transmission electron microscope (TEM), while only one or two rows are left. These chains showed a remarkable stability, with lifetimes of a few seconds before breaking, and lengths up to a few nanometers, even under the irradiation of the energetic electron beams. Chuvilin *et al.* also observed stable planar sp^2-bonded reconstructions of the graphenic bridge when its width was reduced below one nanometer, with pentagon and heptagon rings dominating the constriction. In addition, the authors noticed that amorphous, carbonaceous adsorbates on the graphene sheet also form carbon chains while shrinking under electron irradiation. This variety of conditions in which they are formed suggests that chains are a preferential and stable configuration at a low density of carbon atoms, not limited to graphene only.

However it is worth highlighting that phase contrast images obtained by HRTEM are often difficult to interpret. In fact, despite some efforts, the atoms in chains have not been clearly resolved by TEM although aberration-corrected microscopes should have the necessary resolution power. Other than a contrast problem, related to the weak scattering arising from the carbon atoms of the chain, also its vibration under the electron beam makes atomic resolution difficult. Therefore, the atoms in a chain could not be counted reliably and neither the measurement of the bond length nor the question whether cumulene or polyyne has been observed could find an answer. Moreover, since TEM only gives projections of the chains onto a screen and the chains may be curved or wrapped randomly, neither the chain length could be measured with high accuracy. Recently, some progress has been made in this direction. Casillas *et al.*[71] presented a direct aberration corrected TEM observation of the bond length alternation in C_4 chain, with the central bond measuring 1.5 ± 0.37 $\mathring{A}$ and the outer bonds 1.3 ± 0.37 $\mathring{A}$. In the same study, also cross bonding between two carbon chains has been experimentally observed and confirmed by DFT calculations.

The quality of the devices produced by the above mentioned process strongly depends on a number of experimental parameters, particularly the energy of the electron beam and the temperature. In fact sculpting of graphene can only be done efficiently by knocking out carbon atoms from the graphene lattice, which requires a TEM energy beam above 140 KeV[72] (*vs* ~ 80 KeV used for imaging). Although such method allows the subnanometer precision required to achieve atomic-thick wires, it is also known that such energies are able to amorphisize graphene, yielding a poorly cristalline lattice and significantly modifying its electronic properties. Song *et al.*[73] investigated more in
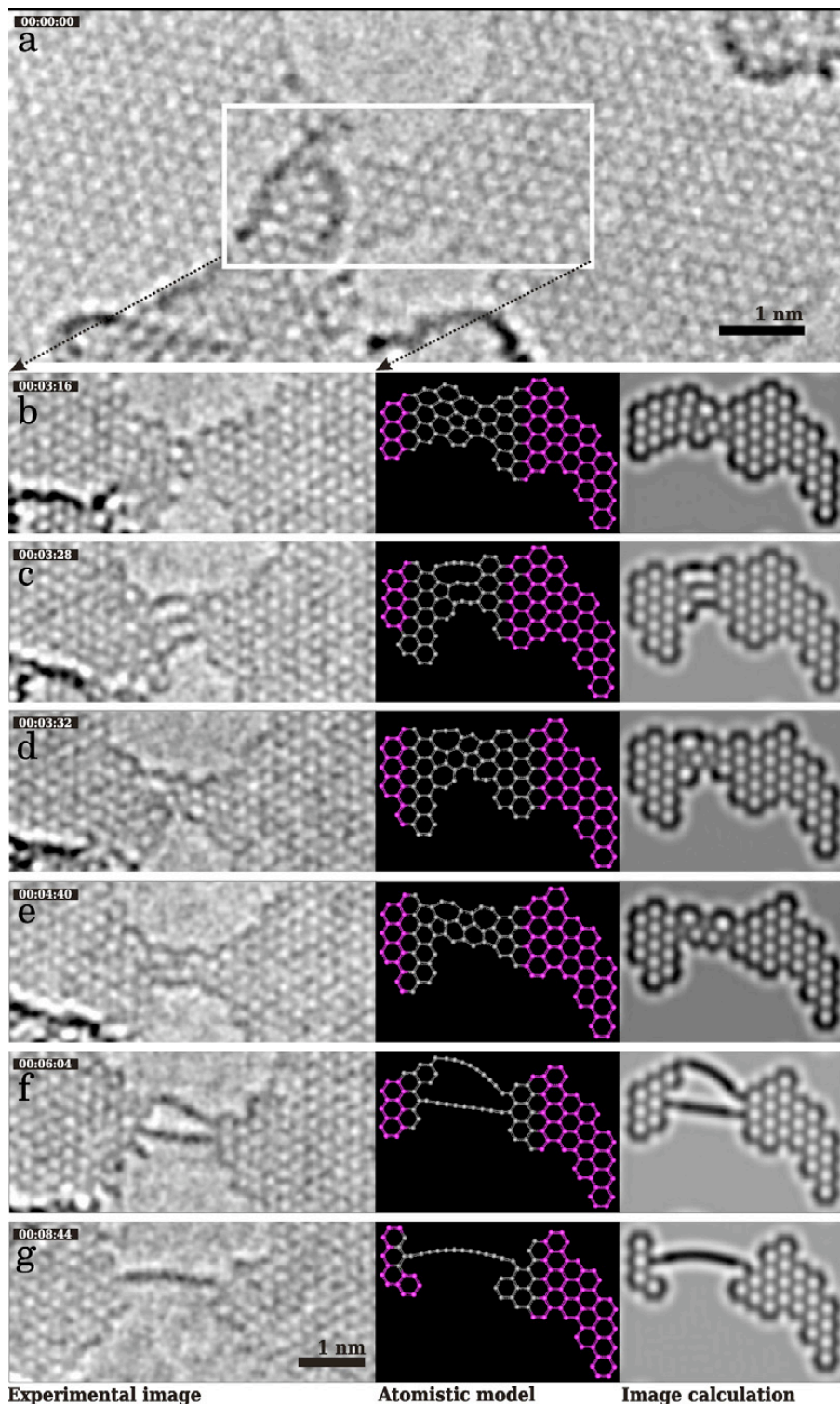
FIGURE 2.6: Transition from a graphene ribbon to a single carbon chains[70]. (a) HRTEM image of the initial graphene ribbon configuration. (b-g) Time evolution of the bridge, in the experimental image (left), atomistic model (center) and corresponding image calculation.

details the processes occurring during the sputtering of carbon atom, finding that this amorphitization surprisingly does not occur at high temperatures (above 600 °C), since self-repair mechanisms mediated by mobile carbon ad-atoms constantly repair the damages caused by the electron beam, keeping graphene in a single-cristalline state during cutting.

The integration of scanning tunneling microscopy tips at the specimen position of TEMs allowed the first electrical characterization of gold wires by Ohnishi *et al.*[74] in 1998. They reported that few-atoms gold chains fabricated *in-situ* showed quantized conductance, with values multiple of $2|e|^2/h$, depending on the number of chain bridging the electrodes.

Only in 2013 two groups first reported electrical transport measures in atomic carbon chains contacted either with gold/graphene[75] or two gold electrodes[76]. In the first case the chain was obtained by unraveling carbon atoms from graphene ribbon by retracting a gold STM tip, while an electrical current flowed through the ribbon and successively through the chain, providing current values in the range 10^{-7} - 10^{-9} A for 1 V of applied bias.

In the second case oligoynes up to 16 carbon atoms and functionalized with anchor groups have been contacted by two gold tips, and both STM break-junction and mechanically-controllable break junction experiments have been carried out, finding similar results. The most promising anchor group turned out to be dihydrobenzothiophene, showing the highest probability of junction formation and electrical conductance much higher than other conductive wires of similar length. However, in this case both the number and the binding characteristics of bridging chains were not determined for certain.

In an earlier work La Torre *et al.*[77] formed and characterized a number of carbon structures connected with Fe/graphene leads. At first graphene flakes were decorated by iron oxide nanoparticle, then these were pinned by a STM tip and reduced by current flowing. Next the tip was retracted unraveling graphene ribbons, nanotube-like structures or single carbon chains (see fig 2.7). The resulting currents were in the order of 10^{-7} A for the first and the second and in the order of 10^{-9} for chains, for an applied bias of $\sim$0.4 eV. However it should be remembered that such experiments were carried out under the electron beam of the TEM, therefore electron irradiation might played a significative role during the formation and characterization of chains. Furthermore, such chains were certainly strained, causing the current to drop by some orders of magnitude, if compared with unstrained wires. In fact increasing strain leads to a decreasing
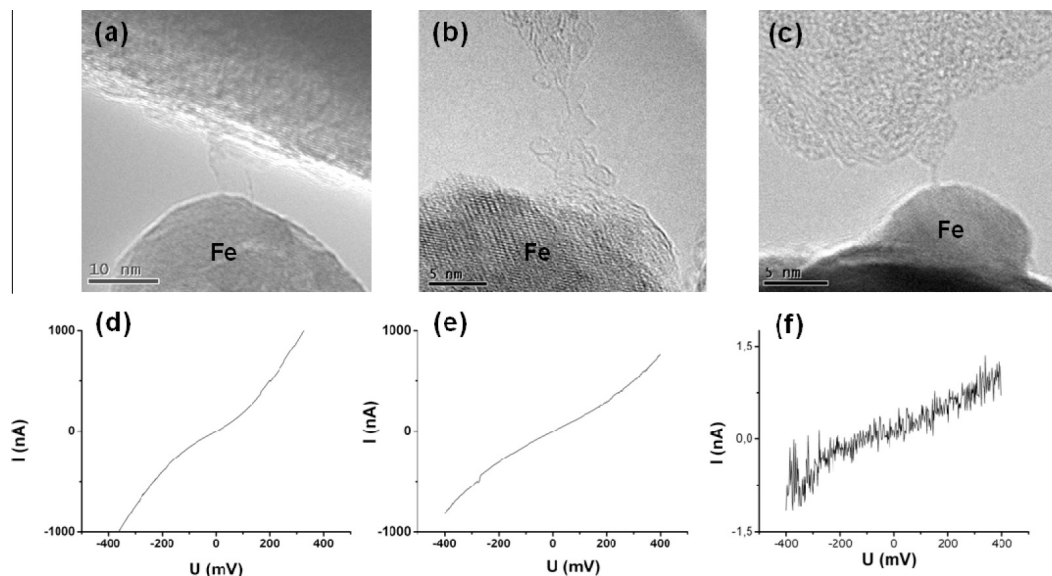
FIGURE 2.7: TEM images and current-voltage characteristics of a graphene nanoribbon (a and d), an irregular nanotube-like structure (b and e) and a monoatomic carbon chain (c and f)[77]

π-electron density over the longer single bonds that, in turn, hinders the electron transfer.

In conclusion, the recent progresses make clear that carbyne represents an exceptional material for applications as conductive wire in molecular devices, nevertheless the production and handling of these atomic-size structures appear very difficult, due to their high instability and the necessity of using techniques with atomic resolution. For this reason many mechanical and electronic properties as well as the influence of the wire-electrode junction on the transport properties, theoretically addressed in many works, are still waiting for experimental confirmations.