

The potentials and challenges of electron microscopy in the study of atomic chains[★]

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Abstract. The article is a brief review on the potential of transmission electron microscopy (TEM) in the investigation of atom chains which are the paradigm of a strictly one-dimensional material. After the progress of TEM in the study of new two-dimensional materials, microscopy of free-standing one-dimensional structures is a new challenge with its inherent potentials and difficulties. In-situ experiments in the TEM allowed, for the first time, to generate isolated atomic chains consisting of metals, carbon or boron nitride. Besides having delivered a solid proof for the existence of atomic chains, in-situ TEM studies also enabled us to measure the electrical properties of these fundamental linear structures. While ballistic quantum conductivity is observed in chains of metal atoms, electrical transport in chains of sp^1 -hybridized carbon is limited by resonant states and reflections at the contacts. Although substantial progress has been made in recent TEM studies of atom chains, fundamental questions have to be answered, concerning the structural stability of the chains, bonding states at the contacts, and the suitability for applications in nanotechnology.

1 Introduction

Electron microscopy with atomic resolution has experienced an unexpected stimulus with the emergence of graphene and related self-supporting two-dimensional materials. The availability of aberration correctors after the turn of the millenium came just in time with the rise of two-dimensional materials such as graphene. It became possible, for the first time, to take micrographs of structures with monoatomic thickness without any overlapping atoms in the projection. Image interpretation and contrast analysis are facilitated considerably [1], and electron energy-loss spectroscopy (EELS) with a (sub-) Ångstrom beam spots allows spectra from individual atoms [2,3]. Furthermore, the dynamics of single atoms is getting visible in in-situ experiments. This has been demonstrated in studies where atom displacements and the creation of vacancies are monitored, e.g., in graphene [4–6] or in single-layer boron nitride [7–9].

The logical reduction of dimensions leads us to linear structures. Perfectly one-dimensional materials are chains of atoms; they are self-supporting and only held at their ends (we distinguish atom chains where all atoms are lined up in one row from organic chains with side atoms such as hydrocarbons or polymers that will not be considered here). Stable chains of atoms, in particular electrical conductors, are an important model system in research since they allow studying fundamental solid-state phenomena such as quantum conductivity or Peierls instability. The simplicity of the system (i.e., only a few atoms in a row) facilitates the application of theoretical models. The potential of atom chains in nanotechnology is still vague, but conducting chains would be interesting as few-atom transistors, channels in field effect transistors, or as interconnects in devices.

Although similar arguments as for two-dimensional materials predict thermodynamic instability of one-dimensional structures, a few materials are known to form sufficiently strong bonds in only two opposite directions so that linear arrangements are stable without a support. Elemental carbon is one of these rare examples because it can occur in the sp^1 hybridized bonding configuration [10–12]. Two covalent bonds in opposite direction link each

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atom with its neighbors. The remaining two electrons of the atom are in two orthogonal p -orbitals that can overlap with those of neighboring atoms and form two degenerate π -bands. This allows delocalization of the π -electrons and hence electrical conductivity of the chain. While individual chains of carbon atoms have been undoubtedly identified, not least due to convincing transmission electron microscopy (TEM) observations [13], the existence of a bulk phase of sp^1 carbon, known as carbyne or linear acetylenic carbon, is subject of an ongoing debate [14].

Similar chains are also known from other materials. Boron nitride with its close relationship to graphene has also been observed in a linear modification [15]. Here, alternating boron and nitrogen atoms are linked by covalent bonds, leading to a BN structure similar to sp^1 carbon. However, the electronic structures of carbon and BN chains are different. While sp^1 carbon is metallic or semiconducting, BN has a large bandgap and is insulating. Other quasi-two-dimensional materials like chalcogenides do not have a monoatomic chain-like modification [16]. Not always do atom chains need covalent bonds like in carbon or boron nitride. Linear arrangements of metal atoms have also been made, e.g., by stretching and thinning Au, Ag or Fe nanowires [17–22]. However, these metal chains seem extremely unstable and consist of very few atoms only.

Linear arrangements of carbon, boron/nitrogen, or metal atoms have been created in in-situ experiments in the TEM, allowing a clear identification of the chain-like arrangement of the atoms. Figure 1 shows some examples of TEM images from atomic chains of different materials. Besides TEM, only very few techniques, e.g., Raman spectroscopy, are suitable to identify chain-like structures [23, 24]. The same simplicity in TEM imaging or electron energy-loss spectroscopy (EELS) as in two-dimensional materials should be valid in the study of one-dimensional atomic chains. If the chains are not viewed end-on, there are no overlapping atoms in the beam direction. The imaging of the atoms within a chain, just like the imaging of carbon atoms in graphene, should be easily possible with modern high-resolution instruments. However, several caveats have to be taken into account and will be discussed below.

The possibilities of in-situ electron microscopy, in particular, the availability of specimen stages for electrical probing, make atom chains highly interesting objects for electrical characterization in the electron microscope. The chains can be observed during the measurements, which is an important prerequisite for correlating structure and electrical properties. Performing such measurements on chains seems hardly feasible by scanning tunneling microscopy or related techniques because the objects remain invisible while the measurement is carried out. The first electrical in-situ TEM measurements on metal chains [17] and on carbon chains [25] have already shown very characteristic features and striking differences in the electrical conductivities of different types of atom chains.

2 Electron microscopy studies of atom chains

The first difficulty in TEM studies is the synthesis and preparation of atom-size one-dimensional objects. It has hitherto not been achieved, to our knowledge, to synthesize materials consisting of bulk quantities of atomic chains (the debate about the existence of bulk carbyne [14] will not be picked up here). To date, all TEM studies on individual self-supporting chains have been carried out by creating the chains in-situ in the specimen stage of the microscope. Carbon or boron nitride chains have been obtained by sputtering atoms from nanotubes or graphene-like monolayers [15, 26, 27]. Chains of conducting materials such as metals but also carbon have been made by nano-manipulation in an in-situ electrical probing stage. Retracting an electrode while a current flows through a nanocontact may, under favorable conditions and for a short time, lead to a chain-like bridge at the breaking contact [17] or, in the case of carbon, to the unraveling of atom chains from graphenic material [25, 28]. The integration of piezo-driven tips into specimen holders for TEM like the *Nanofactory* system or some home-made setups [29] allowed these experiments where the generation as well as the electrical characterization of the chains is possible under observation at high spatial resolution.

The first electron microscopy observations of atomic chains have been reported in the late 1990s when metal nanowires were studied with atomic resolution [17]. Gold wires were stretched until rows of 3–4 Au atoms were left between bulk contacts. These chains showed quantum conductivity with a conductance of $G_0 = 2e^2/h$ (e is the elementary charge and h Planck's constant). This has been a very fundamental contribution of in-situ TEM to the understanding of quantum conductivity since it showed the direct relationship between structure and electrical properties as well as the occurrence of ballistic conductivity in atom chains. Similar Au or Ag chains have also been created by electron irradiation [18, 22]. More sophisticated studies showed de-quantization when a larger number of conduction channels were present [19]. Electron beam-induced thinning of Au wires with the formation of atom chains has also been carried out in the scanning transmission (STEM) mode with high-angle annular dark field imaging (HAADF) [21]. Metal chains (Fig. 1c) typically consist of not more than four atoms and remain as bridges, separating the two halves of a breaking nanowire for a very short time. Hence, the metallic chains have to be considered as rather unstable transient structures.

The most exciting and, at the same time, most disputed chain-like material is carbyne (Fig. 1a) which will be discussed in more detail in the following. Although many techniques of characterization have been applied since a long time to prove the existence of the sp^1 -hybridized one-dimensional phase of pure carbon, TEM studies finally showed unambiguous images [13]. It is remarkable that carbon chains have not simply been found on materials specimens; instead, they have been created in-situ by electron irradiation. Electron-beam thinning of carbon nanotubes led to the formation of atom chains at the neck

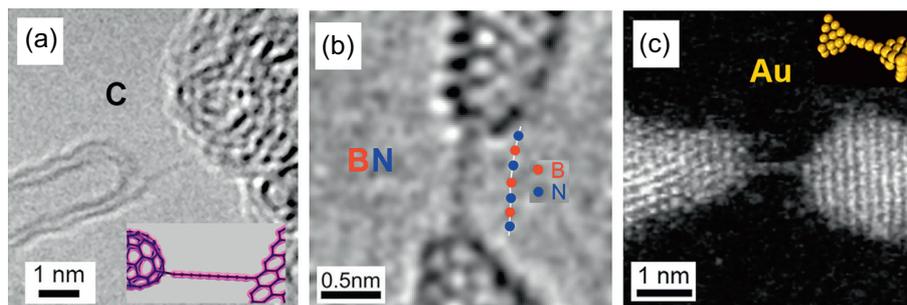


Fig. 1. Examples of TEM images from atom chains. (a) Carbon chain spanning between a double-wall carbon nanotube and disordered graphitic material. (b) Boron nitride chain between two boron nitride ribbons [15]. Only the N atoms are clearly visible. The grain-like contrast stems from noise filtering. (c) Dark field (HAADF-STEM) image of a chain of gold atoms between two gold nanowires (the impression of a double chain is a scan artefact). Figure 1c courtesy R. Arenal [21].

of the shrinking tubes before they break [13,30,31]. Similarly, the electron beam in the TEM can be used for sputtering carbon atoms from graphene layers and so creating chains by thinning the bridge between two neighboring holes [26,27,32–34]. Carbon chains have also been detected on top of graphene layers [35,36]; however, the overlap with the carbon atoms of graphene makes the contrast analysis more difficult. Likewise, carbon chains have been found encapsulated inside carbon nanotubes [24,37]. However, these embedded chains are constituents of more complicated materials and will not be discussed here.

An important subject is the stability of carbon chains. The cohesive energy in a carbon chain is approximately 7.0 eV/atom as derived from density functional theory [38] which is less than the energy of 7.5 eV/atom in graphene. However, it is higher than the energy of partially unsaturated carbon atoms at graphene edges, making the chains energetically more favorable than narrow graphene ribbons [26]. The same stability argument holds for the thinning of carbon nanotubes that are not stable below a diameter of approximately 0.3–0.4 nm [39]. If carbon atoms are left at the neck before breakage, their arrangement in a chain might indeed be the most favorable configuration. It is apparent from in-situ TEM studies that carbon chains have a longer lifetime and are thus more stable than other quasi-one-dimensional carbon structures. However, an unanswered question is the upper limit in the length of a carbon chain. From a theoretical viewpoint, a decreasing stability with increasing length can be expected. Indeed, observations by TEM did not show free-standing chains much longer than 5 nm [25], corresponding to approximately 40 atoms. This is in accordance with the maximum length of 44 atoms reported spectroscopically after a chemical synthesis of sp^1 structures [40]. However, it is expected that the maximum length of a chain depends on the bonding at the ends and the kinetics during their formation.

While ballistic quantum conductivity has been measured in chains of metal atoms [17–19,22], the electrical behavior of carbon chains turned out to be more complex [25,41]. Carbon chains occur either as *cumulene* with solely double bonds or as *polyynes* with alternating single and triple bonds (Fig. 2). Cumulene has delocalized

π -electrons and is metallic while the π -electrons of polyynes are localized on the triple bonds so that polyynes are semiconductors with a strain-dependent bandgap. Due to zero-point vibrations, cumulene is not susceptible to Peierls distortion and constitutes the energetically lowest ground state [42]. In the presence of strain, however, Peierls distortion leads to dimerization and to the opening of a bandgap. The strain-induced metal-semiconductor transition has been confirmed by in-situ TEM measurements of current-voltage characteristics of strained and unstrained carbon chains (Fig. 2) [41]. An indication for the absence of tensile strain in a chain is the curvature of the chain which can be easily seen in a TEM image. Obviously, bent or warped chains cannot be under considerable tensile stress. However, compressive stress with locally elongated bonds cannot be excluded. In contrast to metal chains spanning between contacts of the same metal, the electron transmission in carbon chains is limited by narrow resonant states due to reflections at the contacts. This leads to non-ohmic behavior that depends decisively on the nature of the contacts and limits the transmission far below the quantum conductivity G_0 .

New light on the question of Peierls distortion and dimerization has been shed in the recent work by Lin et al. [43]. By applying the most advanced TEMs and STEMs with sub-Ångström resolution, the atoms in a carbon chain could be clearly resolved, and EEL spectra could be taken with atomic selectivity. The dimerization of carbon atoms within the chains is clearly visible and much more pronounced than expected, in particular at higher temperature of the system. Bond lengths as short as 1.08 Å and as long as 1.51 Å have been measured, whereas single bonds of 1.30 Å and triple bonds of 1.26 Å are expected in polyynes. Such an enormous dimerization cannot be explained with the Peierls model anymore. Strain could play a certain role; however, a convincing model of these surprising observations still has to be found. The EEL spectra of carbon chains [43] show a prominent π^* -peak which is much higher than the σ^* -peak. This is in accordance with the presence of two π -bands (instead of one in the case of graphene). Scans along the chain allow to take EEL spectra from every atom of the chain, though at the expense of noise.

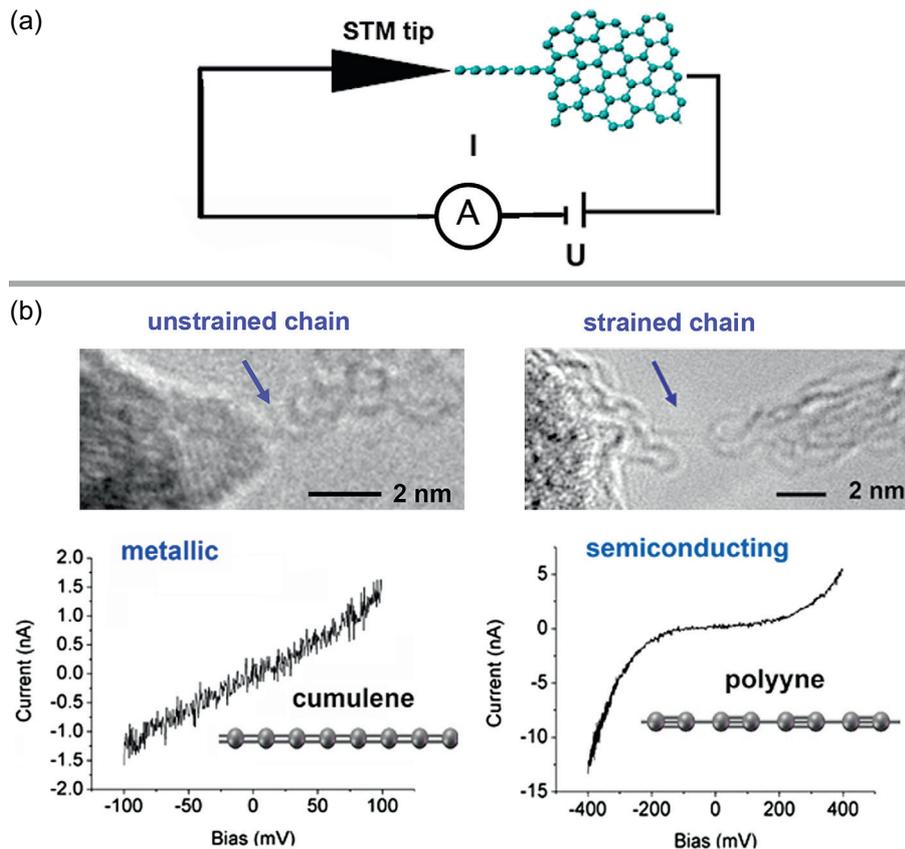


Fig. 2. (a) Generation of carbon chains by extraction from a graphene ribbon and measurement of their electrical properties. (b) Electrical properties of unstrained (left) and strained (right) carbon chains as measured in-situ in the TEM [41]. The warped chain is unstrained and shows ohmic behavior (linear I-V curve) whereas the straight chain is strained and shows semiconducting behavior (S-shaped I-V curve).

The relationship between BN and C chains mirrors the one between their 2D counterparts, *h*-BN and graphene. A combination of high-resolution imaging and energy considerations shows that, in the absence of strain, the structure of these chains is composed of alternating B-N dimers, separated by a distance of 2.7 Å; the B-N bond length is therefore approximately 1.35 Å, which corresponds to the theoretical value and is smaller than the bond length of 1.45 Å found in pristine *h*-BN [15]. This contraction is similar to the one observed for carbon chains and improves the stability of the chains by increasing the bond strength [26]. The formation of BN chains takes place through a combination of atomic displacements due to electron irradiation and structural relaxation, which can be enhanced at higher temperature. Similarly to their carbon counterparts, these chains can exist either suspended or supported by an underlying *h*-BN layer, which dramatically improves their stability. The insulating properties of *h*-BN preclude any kind of in-situ electrical experiment. Electronic structure calculations performed on these species show that they are also insulating with a bandgap close to the one of *h*-BN [15]. Since BN chains are insulators and already have their intrinsic dimerization (B-N pairs), the Peierls theorem is not applicable.

Another important question concerns the mechanical properties of atomic chains. The ultimate strength of carbon chains has been predicted to be of the order 10 nN [38]. However, this will be difficult to measure because 10 nN is right at the lower limit of the sensitivity of *Nanofactory* atomic force microscope (AFM) stages in TEM specimen holders. It has been seen, however, that the rupture of carbon chains during their observation leads to a considerable rebounding of their contacts [41]. This shows, at least qualitatively, that carbon chains are stable mechanically and can withstand considerable forces. More sensitive AFM stages would be needed to corroborate theoretical predictions of the mechanical properties.

An important limitation in TEM studies of atomic chains is their destruction by ballistic atom displacements under energetic electron irradiation. The displacement cross-section for carbon atoms within a carbon chain has not been determined yet, but it can be expected that it is slightly higher than for carbon atoms in graphene [44,45]. With a displacement threshold of 14 eV, which has still to be confirmed experimentally, a carbon atom in a chain would be displaced every 100 s in an electron beam of 200 keV at typical beam intensities for imaging [25]. This is in accordance with the observed lifetimes of chains in

TEM studies at higher voltage. The etching of the structures by impurities in the vacuum chamber of the microscope has not been identified yet but might also play a certain role. A clearly extended lifetime of the chains of several hundred seconds has been observed in the recent work by Lin et al. [43] where an acceleration voltage of 60 kV has been used. The displacement cross-section of sp^1 carbon atoms in the chains appears therefore to be close to sp^2 atoms in graphene. Furthermore, this also indicates that the lifetime of carbon chains could be unlimited, which is a very important argument in the current discussion about the stability of carbon chains.

3 Difficulties and challenges in TEM of atom chains

High-resolution TEM of atom chains is facing several difficulties. It has hitherto only been possible in a few studies to resolve the atoms within a chain [15,31,41]. The necessary point resolution for imaging is the interatomic distance which is 1.30 Å, 1.28 Å and 1.26 Å for single, double and triple bonds, respectively, in carbon chains. Separating the atoms is possible by modern TEMs, whereas the distinction between single, double, and triple bonds would need a precision of 2 pm in the measurement of atom positions. This is beyond the resolution limit of TEMs, in particular since the unavoidable vibration of the chain under the electron beam does not allow fit procedures to determine precise atom positions in the images. The vibration of the chains under the electron beam makes imaging with high resolution generally difficult. This is quite obvious when STEM images are taken [43]. Momentum transfer by the energetic electrons of the beam and charging lead to transverse vibration. In contrast to two-dimensional materials, linear structures have no rigidity in the plane, so the atom positions in the image plane may shift in two orthogonal directions even during short exposure times. It will therefore be necessary to stabilize the chains, e.g., by setting them under mechanical stress that avoids transverse vibration with a large amplitude. Putting them on a substrate stabilizes them mechanically; however, their bonding configuration is altered by cross-links with the substrate.

Since the scattering of the electrons by single atoms, in particular light ones such as carbon, is weak, the image contrast is generally affected by noise. This is visible in the examples in Figure 1. At higher electron energies, e.g., 200 or 300 keV, where the elastic scattering cross-section is low, less contrast is obtained and the images can be so noisy that it is difficult to distinguish the atoms from noise [31]. At low microscope voltages such as 60 kV, the scattering is much stronger and the atom positions can be clearly resolved [43]. Aberration-corrected TEMs or STEMs working at low voltages appear therefore as the ideal instruments to study atom chains in the future. Direct electron detection cameras with higher sensitivity than conventional CCD cameras will allow improving the signal-noise ratio, reducing the exposure times and so

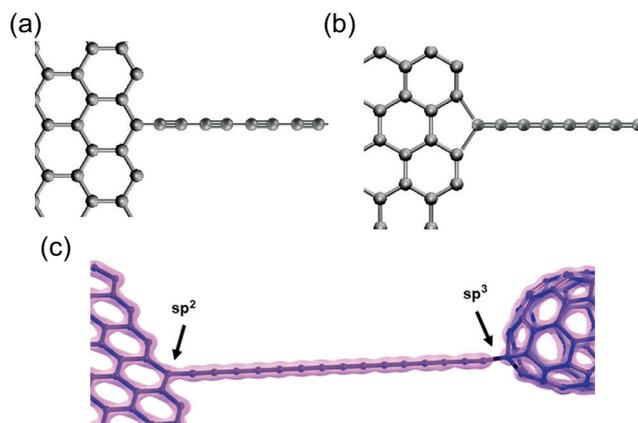


Fig. 3. Simplified structure models of carbon chains with different bonding configurations at the contacts. (a) Single bond to a zigzag edge of graphene, inducing the polyne configuration of the chain. (b) Double bond to two atoms at an armchair edge, leading to cumulene. (c) Calculated electron density at an sp^2 contact to graphene and an sp^3 contact to a cap of a nanotube [41] (Fig. 3c: courtesy A. Botello-Mendez and J.-C. Charlier).

being of further advantage. However, the vibration period of the chains might be shorter than the millisecond timescale and can, most likely, not be overcome with faster cameras.

It is highly important to be able to count the number of atoms and to determine the bonding configuration at the end contacts (Fig. 3). If a single bond prevails at the contact, e.g., between the first atom of a carbon chain and the tip of a zigzag edge of graphene or an open nanotube (Fig. 3a), this imposes a triple bond with the second atom, followed again by a single bond. Polyne would be the only possibility of satisfying such a boundary condition. An even number of atoms in polyne would be necessary to avoid a triple bond at the other end of the chain. Alternatively, the first atom of the chain could be linked by two bonds to different carbon atoms, e.g., at an armchair edge of graphene, leading to a double bond configuration (Fig. 3b). It has not been possible yet to count the number of atoms due to the resolution limit of the microscopes and the stability of the chains. The models in Figure 3 are therefore based on calculations and not on TEM images [41]. The work of Lin et al. [43] has already shown that these important structural configurations can be revealed by TEM, but more detailed work will still have to be done. The influence of temperature on the dimerization appears to be important and needs to be clarified.

Even more challenging would be establishing a relation between the bonding situation and the electrical properties of the chains. If we consider the hybridization of the atom at the contact that forms the bond with the chain, it is apparent that local sp^2 hybridization leaves one electron for retaining a coherent π -electron system with the chain. A sp^3 atom, on the other hand, leads to a missing π -electron and so to a gap in the conducting π -electron channel (Fig. 3c). This has important consequences on

the electrical behavior of the contact. The bonding configuration could be revealed by TEM if the contacts can be imaged with full atomic resolution. While the open edge of a graphene ribbon would lead to a sp^2 contact, the tip of an otherwise perfect carbon nanotube needs a sp^3 -hybridized contact atom. A combination of aberration-corrected microscopes working at low voltages and in-situ probing stages would allow testing these models.

4 Conclusions

Electron microscopy of atom chains is still in its infancy but will certainly contribute more to the understanding of these one-dimensional structures in the future. The main difficulties in the imaging are the short lifetime of the chains due to their sensitivity to electron irradiation and the high flexibility in the plane normal to the chain, leading to wide transverse vibration modes. The same arguments hold for EELS studies. This makes chains much more challenging objects than graphene and other two-dimensional materials. However, in the light of new studies at low microscope voltage and with the most advanced microscopes, imaging and EELS with atomic resolution are now possible, and the bonding configurations can be studied in detail. The enormous dimerization will be a challenge for the theory of linear sp^1 carbon and of atom chains in general. The influence of temperature on the bonding configuration and on the electrical properties will be another field of research. The unique possibility of in-situ TEM to measure the electrical properties while the chains can be observed allows us to attribute the measurements to visible objects. Future TEM studies have to concentrate on the relationship between structural and electrical properties and on stability issues. While chains of metal atoms appear as unstable transient structures, chains of carbon or boron nitride could be stable and potentially interesting for applications in nanodevices. However, only carbon chains are electrical conductors that could be used as semiconducting channels or metallic interconnects. Besides the tuning of the electrical properties, the understanding of the chemical stability of carbon chains will be the milestone that has to be reached before applications can be envisaged. Aberration-corrected electron microscopy at low electron energy and the availability of stable in-situ probing stages will play a major role in the investigation of free-standing atomic chains in the future.

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