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Published in:
Nano Letters

DOI:
10.1021/acs.nanolett.7b00969

Published: 14/06/2017

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
Komsa, H. P., Senga, R., Suenaga, K., & Krasheninnikov, A. V. (2017). Structural Distortions and Charge Density Waves in Iodine Chains Encapsulated inside Carbon Nanotubes. Nano Letters, 17(6), 3694-3700. https://doi.org/10.1021/acs.nanolett.7b00969
Structural Distortions and Charge Density Waves in Iodine Chains Encapsulated inside Carbon Nanotubes

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ABSTRACT: Atomic chains are perfect systems for getting fundamental insights into the electron dynamics and coupling between the electronic and ionic degrees of freedom in one-dimensional metals. Depending on the band filling, they can exhibit Peierls instabilities (or charge density waves), where equally spaced chain of atoms with partially filled band is inherently unstable, exhibiting spontaneous distortion of the lattice that further leads to metal–insulator transition in the system. Here, using high-resolution scanning transmission electron microscopy, we directly image the atomic structures of a chain of iodine atoms confined inside carbon nanotubes. In addition to long equidistant chains, the ones consisting of iodine dimers and trimers were also observed, as well as transitions between them. First-principles calculations reproduce the experimentally observed bond lengths and lattice constants, showing that the ionic movement is largely unconstrained in the longitudinal direction, while naturally confined by the nanotube in the lateral directions. Moreover, the trimerized chain bears the hallmarks of a charge density wave. The transition is driven by changes in the charge transfer between the chain and the nanotube and is enabled by the charge compensation and additional screening provided by the nanotube.

KEYWORDS: Atomic chain, carbon nanotube, charge density wave, transmission electron microscope, density functional theory

It was asserted in the early work of Peierls that at low temperature a regular chain structure of a one-dimensional metal with a partly filled band will never be stable because distortion of the lattice with periodicity corresponding to the Fermi-vector opens up a gap that will lower the energy of the electrons in the occupied states. This energy gain competes with the energy cost from the restructuring of the ions, but the former was claimed to always win. When the temperature is raised, thermal excitations over the band gap lead to sizable Fermi-surface nesting and then reflected as a sharp dip in the phonon dispersion. Materials showing charge density waves (CDW) are thought to provide a generalization of this picture in higher dimensions. However, in CDW systems where the origin of the distortion has been carefully examined, the instability has been found to arise from a joint effect of strong electron–phonon coupling and a matching peak in the electronic susceptibility.

To probe one-dimensional metals, atomic chains would be obviously attractive. Atomic chains have been manufactured by the top-down approaches from various chemical elements including gold, carbon, and boron/nitrogen. However, while theoretical calculations predict rich physics in these systems including strain induced changes in the electronic and magnetic properties, so far there is no direct experimental evidence for structural transitions that could be assigned to Peierls or CDW mechanism.

At the same time, it has been demonstrated that encapsulation of atomic chains inside carbon nanotubes (CNT) is a facile approach to stabilize the chains and protect them from contaminants. Specifically, it has been shown that atoms in CsI and I chains do not form chemical bonds.

Received: March 7, 2017
Revised: April 27, 2017
Published: May 26, 2017
with the nanotube walls and that although charge transfer of electrons from the nanotube to the chain leads to electrostatic attraction, the cylindrical symmetry of the interaction leads to rather flat radial potential profile at the center of the tube. Furthermore, for a tube with suitably small inner diameter the chain is sterically confined to the center of the tube. Encapsulation of iodine chains inside carbon nanotubes has been reported.\textsuperscript{20–22} Raman spectroscopy and diffraction experiments point to coexistence of $I_2$, $I_3^-$, and also of longer $I_5^-$ and $I_7^-$ ions.\textsuperscript{23,24} However, direct observation of the exact structure of the iodine chains has remained elusive.

Here, we report on the direct observation of the iodine chains using high-resolution scanning transmission electron microscopy (STEM) that allows unambiguous determination of the chain structure. In addition to chains consisting of $I_1$ and $I_3$ units, long equidistant chains were also found. Moreover, transitions between the equidistant and trimerized chains were observed. Aided by first-principles calculations, we arrive at a model for the phase transition that involves both charge transfer induced charge density wave distortion as well as longitudinal relaxation of the bond lengths.

The double-walled CNTs that we used were prepared by the high-temperature pulsed arc discharge method as in the earlier work.\textsuperscript{25} In order to ensure formation of monatomic chains, the inner diameter of the template must be equal to, or slightly larger than, the ionic diameter of I atom (4.40 Å), and also smaller than 1.3 nm. At larger diameter, formation of double chains was observed.\textsuperscript{22} We here target for double-walled CNTs with less than 1.0 nm inner diameter. The CNTs were exposed to I gas for filling. The CNT-encapsulated 1D I crystals were then dispersed in hexane and dropped on TEM microgrids. For STEM and electron energy loss spectroscopy (EELS) analysis, we used a JEM-2100F equipped with a delta corrector and cold-field emission gun (TC1) at 60 kV combined with a GIF

Figure 1. Atomic structures and transformation in an iodine chain. (a,b) STEM annular dark field (ADF) images of an iodine chain in an equidistant and a trimerized phase, respectively. Both images were taken from the same chain at the same region on the nanotube as seen from markers indicated by the yellow arrows. (c,d) ADF intensity profiles (dotted lines and smoothed in solid lines) and corresponding atomic models for the equidistant and the trimerized chain inside the yellow squares in (a,b), respectively. (e) A typical EELS spectrum for iodine chains inside CNTs, showing pronounced C K-edge and I M$\text{\textsubscript{4,5}}$-edge. To highlight the latter, a 5× enhanced curve is also shown. Inset: EELS chemical map exhibits that the chain is made of iodine atoms only without any impurities.
Quantum spectrometer (Gatan) specialized for low-voltage operation. More than 70% of the nanotubes were found to contain encapsulated iodine chains. Figure 1 shows a typical experimental result, where a single iodine chain is encapsulated in a double-wall CNT with inner diameter of 7.5 Å. The I–I bond lengths appear nearly equidistant (2.9 Å in average but projected) and the length of the chain in the recorded image contains at minimum 30 iodine atoms as shown in Figure 1a. Note that no extra spots nor streak-splitting was found in the corresponding FFT pattern. A typical EELS spectrum measured at the chain is shown in Figure 1e and indicated presence of only I for the chain (see inset) and C for the surrounding CNT. No other chemical species, such as oxygen or alkali metals often present as impurities, has been found.

An intriguing structural transformation was observed in these experiments. After few minutes of observation with the electron beam scanning, the equidistant phase suddenly changed to another phase with a distinct trimerization as shown in Figure 1b. The average I–I bond length of the trimers is 2.6 Å (the trimer size is 5.2 Å) and the gap distances between neighboring trimers are as large as 3.3 Å [see Figure 1d]. Interestingly, when the beam was moved away from the tube to vacuum for a few minutes, the chain returned back to the nearly equidistant phase. Such changes were never observed in the case of the double chains (Figure S1 in SI).

In addition to this structural transformation, we have also found a third configuration in which trimers and dimers coexist in a single chain inside various-sized nanotube templates (Figure 2). This phase was observed close to the ends of the chain, whereas away from the ends the trimer configurations appeared to be the predominant one independent of the nanotube diameter. No pure dimer phase was observed. To quantify the iodine bonding in these different phases (equidistant, dimer, and trimer), we have systematically analyzed the bond lengths. Equidistant chains have an average I–I distance of 2.9 Å as shown in Figure 1c. Note that the distance is measured in projection, but an inclination of the one-dimensional (1D) crystal is small and shows at most a few percent error. In the case of trimers, one can distinguish two categories. On one hand, small diameter tubes yield trimer size of 5.2–5.3 Å (bond length of about 2.6 Å) with the distance between the trimers varying between 2.9–3.3 Å (Figures 1 and 2a). In total, the chain is then slightly contracted when compared to the equidistant chain. On the other hand, larger diameter tubes yield trimer size 5.8–5.9 Å (bond length of about 2.9 Å) with the distance between the trimers varying between 3.5–3.6 Å [Figure 2b–d]. In this case, the average bond length is about 3.1 Å and thus the whole chain has expanded in comparison with the equidistant chain. In the case of dimers, their bond lengths vary between 2.7 to 2.9 Å in most cases, which is in good agreement with the bond length of I2 (2.7 Å). However, in the smaller template [Figure 2a], the dimer size becomes much shorter (2.4 Å), similar to the trimers.

The 2.9 Å bond length found for equidistant chains and for the longer trimerized chain is in good agreement with the bond lengths usually reported for I3− ions and polyiodides in general. In layered chemical compounds, polyiodides may form infinite linear chains of I3− ions, where I–I bond length is again 2.9 Å and weakly bonded together by I3− distances of 4–4.2 Å. In such cases, the distance between trimers can be governed by the surrounding network of cations. In our case, however, there are no cations that would constrain the iodide ions. Therefore, the polyiodides could also be expected to move freely inside the tube. In fact, in several cases the chain was found to lose the atomic resolution presumably due to longitudinal motion of the chains inside the nanotubes [Figures S2 and S3]. In Figure 2b, the images were mostly taken close to the end of the chain. Presumably defects, kinks, impurities, and so forth are fixing the ends spatially which not only helps in imaging but may also fix the bonding configuration similar to what was found in the case of carbyne chains.
To gain insight into iodine bonding and the origin of the observed structural transformations, we carried out density functional theory calculations for I chains encapsulated in CNT. To correctly describe our joint iodine chain/CNT system, HSE06 hybrid functional is used to improve on the atomization energies, geometrical parameters such as bond length alteration, and on the ionization potential of molecule and Fermi-level of CNT. In order to allow both iodine dimer and trimer configurations, the supercell contains 6 I atoms. In the following $L_{z,av}$ corresponds to average I–I bond length within the supercell. CNTs with suitable translational vectors and inner diameters are (5,5), (6,6), and (7,7) armchair nanotubes with diameters of 6.8, 8.1, and 9.5 Å, respectively. The optimized translational vector of 2.45 Å and 8-unit supercell then yield $L_{z,av} = 3.27$ Å. We also consider (10,0) zigzag CNT with a diameter of 7.8 Å. Optimized translational vector of 4.25 Å and 4-unit supercell yield $L_{z,av} = 2.83$ Å. Full computational details are given in the SI.

The energetics of I chains can be described in terms of binding energy of I atoms in the chain, which is defined (per I atom) as $E_b = \frac{1}{n}(E(\text{CNT} + nI) - E(\text{CNT}) - n\mu_I)$, where $\mu_I = E(I) / 3$. $E_b$ for all considered CNTs as a function of average separations between the atoms $L_{z,av}$ that is essentially of strain, is shown in Figure 3a. Two energy minima are found at 2.85 and 3.2 Å. This finding is largely independent of tube chirality and strain. The atomic structures and charge transfer isosurfaces at $L_{z,av} = 2.87$ Å and 3.3 Å are shown in Figure 3e,f and obtained by subtracting from the valence charge density of the joint system the charge densities of the bare chain and the bare CNT at a fixed geometry. At the energy minimum corresponding to the smaller $L_{z,av}$, the chain is equidistant but slightly distorted in a zigzag fashion. In the latter case, the chain consists of trimers. These two structures are in good agreement with the experimental observations both in the bond lengths as well as in the lattice parameter $L_{z,av}$.

In both cases, there is relatively pronounced electron transfer from the CNT to the I chain but no signs of direct chemical bonding. The transition between equidistant zigzag phase and trimerized phase occurs at about $L_{z,av} = 3$ Å and is observed both in the Bader charges of the iodine atoms as well as in the I–I bond lengths as shown in Figure 3b,c. For the zigzag configuration, the bond lengths directly follow the strain, although slightly higher due to the zigzag geometry. The charge transfer is about 0.15 e/atom for all nanotube chiralities and strains, despite rather different Fermi-level positions [Figure 3d]. This lends confidence to our assumption that properties of the chain are disconnected from the strain of the CNT. The trimer configuration yields bond length very close to that of isolated $I_3^-$ (and different from that of isolated $I_3^-$), which is also in agreement with Bader charges of about 0.3 e/atom. Both of these quantities indicate presence of $I_3^-$ anions inside the nanotube. The surrounding nanotube sheath then acts as the cation and electrostatically stabilizes the negatively charged chain.

Although the binding energy is barely negative in the (5,5) tube due to the inner diameter being smaller than the ionic radius of iodine, it interestingly also forces the chain to be straight and consequently shows minor trimerization for any strain. This is in qualitative agreement with the finding that small bond length trimers are observed in small diameter chains, although the calculated energy minimum is at larger $L_{z,av}$.

We also carried out molecular dynamics simulations for the chains inside CNTs. The I atoms showed no correlation with the surrounding C atom positions and consequently also yielded drift of the chain with regard to the nanotube. This explains why the chains are more easily imaged near the fixed ends, whereas away from the ends the atomic resolution may be lost due to longitudinal motion of the atoms. Moreover, due to the vibration and rotation within the tube the zigzag distortion would become unresolvable in STEM and thus we think that the equidistant configuration in fact corresponds to the zigzag distorted structure.

The above considerations hold for an iodine chain inside pristine CNT under ideal conditions. In practice, the nanotube may contain defects, be covered by adsorbates, and is subjected to electron beam in the microscope. All of these can in turn affect the behavior of the iodine chain. Because of the periodic boundary conditions used in our DFT calculations, the tube and the chain lengths needed to match. Because CNT Fermi-level is sensitive to the strain (and chirality) of the tube, the
charge and strain of the chain cannot be controlled separately in these calculations. Therefore, in order to map how the strain and charge affect the structural transformation we carried out calculations for isolated 1 chains with electrostatic energy correction procedure that accounts for the compensating cylindrical charge in the CNT.26

Motivated by the experimentally observed configurations, we calculated total energies for zigzag (equidistant), dimer, and trimer chains under varying strain and charge. From the lowest energy phase we can plot strain—charge phase diagram shown in Figure 4a. All phases are found stable at some combination of charge transfer and strain. For each phase, $L_{z,av}$ yielding minimum energy is denoted by a solid line. Both the zigzag and trimer chains have stable regions at the values of charge expected on the basis of the calculations with CNTs (0.15–0.3 e/atom). At lesser charge transfer, the energy minimum is located within the zigzag region, whereas at larger charge transfer the energy minimum is located at the trimer region. Alternatively, the phase boundary can be crossed by changing the strain. The chain will then transform to a different phase according to the strain-charge phase diagram. If the charge transfer is low for any reason, the dimer chain also can be stable. Because dimers were only observed occasionally or near the ends of the chains [Figure 2b,d], we presume their presence indicates local changes in the charge transfer as governed by, for example, defects or adsorbants.

During the imaging, the charge transfer can be modified due to, for example, emission of secondary electrons, radiolysis of the adsorbants, defect creation, or heating of the sample. Previous investigations on the electron irradiation effects on carbon nanotubes and graphene have indicated that the charging and heating effects should be minor due to their excellent electrical and thermal conductivity.36 Although defect healing is possible, the reversible nature of the transition would evidence against defect creation. Thus, we believe that the leading role is played by the adsorbants: their adsorption to and desorption from the tube and formation of radicals. While some such processes can be observed during the imaging, the exact structure of the adsorbants cannot be determined.

Finally, to verify the presence of Peierls/CDW instability, we examined the electronic structure and phonon dispersion of 1 chains at different band fillings and atomic configurations. To trace the origin of the distortions, we start by considering the band structure of a purely linear iodine chain, as shown in Figure 4b. The Fermi-level crosses both the $\sigma$-band originating from $p_z$ orbitals and the doubly degenerate $\pi$-band ($p_x/p_y$). Upon a fairly small zigzag distortion (in $x$-direction), due the mixing of $p_x$ and $p_y$ bands and consequently breaking the degeneracy of the $\pi$-bands the system may develop a small band gap at the Fermi-level. This configuration persists up to moderately high band filling as was shown in the stability map. Upon pairing and at sufficiently large $L_{z,av}$, the $\pi$-bands flatten out, which leads to half-filled $\sigma$-band and band gap at Fermi-level.26 Thus, the dimer case could be considered as Peierls distorted structure for half filling of the band.

If the linear chain is charged by additional one-third electron per atom, the $\sigma$-band obtains two-thirds filling and the system could undergo Peierls transition, as seen in the trimer band structure and as evident from simple tight binding calculations.26 The calculated phonon spectrum shown in Figure 4c also exhibits a pronounced imaginary frequency mode at $k = \pi/3$, exactly matching with the Fermi nesting vector. The Fermi-nesting condition is naturally fulfilled in 1D system and should lead to peak in the electronic susceptibility, but it did not lead to gap opening at the Fermi-level in the undistorted chain as expected in the classical Peierls picture. In addition, the phonon softening does not display sharp dip at the nesting vector but a smooth valley indicating that it originates from electron—phonon coupling rather than the Kohn anomaly.37 Thus, the instability in this case is akin to that of charge density wave and probably also similar to the 3X lattice distortion observed in the case of metal adsorbed on stepped semiconductor surfaces3,4 or in the case of the mirror twin boundaries of monolayer MoSe$_2$.39

Moreover, the total energy of the system can be minimized by increasing the lattice constant [Figure 4a], bringing it in agreement with the experimental $L_{z,av}$. Concurrently, the band gap opens up. At $L_{z,av} = 3.1$ Å both the structural distortion and the band gap are already rather large (1.5 eV), and the bands...
start to resemble the states of an isolated $\text{I}_3^-$ molecule.\textsuperscript{26} The large band gap is associated with high transition temperature and prevents us from observing the metal−insulator transition just by increasing the temperature. The band gap opening also makes the system less sensitive to the deviations in the charge transfer from the ideal value, temperature effects, and so forth that would otherwise destroy the CDW distortion. Thus, the substantial lattice parameter change makes the system behave distinct from most other systems exhibiting CDW. Although linear iodine chains, consisting of $\text{I}_3^-$ ions and stabilized by surrounding cations, exist in chemical compounds,\textsuperscript{27,28} the structures obtained here are different due to the distinct, homogeneous, and cylindrically symmetric nature of the CNT “cation”. While the time scales in our observation of the transitions are relatively long, the concerted fashion by which the transition takes place simultaneously over a relatively long iodine chain suggests that the system behaves like a chain with delocalized electronic states rather than a group of isolated $\text{I}_3^-$ ions with localized states.

In conclusion, distortions of the atomic structure of iodine atomic chains encapsulated within carbon nanotubes were identified by means of atomically resolved high-resolution STEM and accompanying first-principles calculations. Several different configurations were resolved, and transitions between them were observed during imaging. With the help of first-principles calculations, the transition was understood to involve charge transfer followed by relaxation of lattice parameter. The trimerized chain exhibited electronic structure and phonon dispersion consistent with charge density waves. Our results also indicate that the nanotube sheath performs two important functions. First, it provides an electron reservoir for the charge transfer and concurrently charge compensation, since Coulomb interactions would make a long charged one-dimensional chain unstable. Second, it provides lateral steric confinement to the ions, while still allowing for longitudinal motion. This can be contrasted to the case of metal atoms adsorbed at surface steps where the periodicity is fixed by the substrate,\textsuperscript{3,5} whereas in the case of suspended atomic chains the chain may undergo lateral distortions.\textsuperscript{7,9} It is important to note that the trimerized chain can only be achieved via significant charge transfer from the nanotube; a neutral iodine chain should not undergo such distortion. Thus, our results also hint at the possibility of controlling the atomic structure via the Fermi-level of the nanotube.

\section*{ACKNOWLEDGMENTS}
We thank the Academy of Finland for the support under Project No. 286279 (H.P.K., A.V.K.) and through its Centres of Excellence Programme (2012−2017) under Project No. 251748 (H.P.K.). A.V.K. also acknowledges the financial support of the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST “MISIS” (K2-2015-033). We also thank CSC-IT Center for Science Ltd. for generous grants of computer time. R.S. and K.S. acknowledge support from JST-ACCEL. R.S. thanks JSPS for the support.

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