NANO LETTERS

2007
Vol. 7, No. 6
1532−1535

Polymorphic Structures of Iodine and Their Phase Transition in Confined Nanospace

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Received February 7, 2007; Revised Manuscript Received April 19, 2007

ABSTRACT

Atomic chains and crystal of iodine were successfully generated in a controlled manner inside single-walled carbon nanotubes (SWNTs). The structure is strongly dependent on the diameter of SWNTs; the single, double, and triple helical structures became quite stable when the diameter of SWNTs matches the certain size. More than three chains of iodine are not very stable, and they often crystallize inside the carbon nanotube when the diameter is larger than 1.45 nm. The crystallization or phase transition in a confined nanospace is thus directly observed, and there is indeed a critical size of the hollow nanospace for the stable formation of the atomic chains of iodine.

Atomic wire, a linear chain of atoms, is the ultimate quantum object. Structures and properties of atomic wires are predicted to be completely different from bulk materials. Much effort has been devoted so far to realize a single atomic chain for many kinds of materials. Linear gold atomic chains were successfully generated with transmission electron microscopy (TEM), and the quantization of conductance was verified by in situ transport measurements.[1,2] Fabrication techniques of these atomic wires with a controlled number of chains and length have not been well established except for the case of gold atomic chains.[3] We intend to use single-walled carbon nanotubes (SWNTs) as sheaths for the atomic chain in this experiment. SWNTs have an ideal one-dimensional hollow space of 0.4−3.0 nm[4,5] in diameter and of up to a few millimeters in length. One can therefore expect that the length and the number of atomic chains can be controlled by changing the diameter and the length of the nanotube sheaths. Also the atomic wires formed inside a carbon nanotube should be well isolated and may be stabilized and last longer.

In this Letter, we report the formation of atomic chains and crystals of iodine in the hollow space of SWNTs. Iodine is unlikely to be intercalated into a graphite gap (0.335 nm spacing); however, it can be considerably stable inside the SWNT, since it has a larger space. Iodine is a typical p-type dopant of SWNTs and indeed effective for the positive charge transfer into SWNTs.[6,7] If the iodine atoms can be stabilized inside the SWNTs due to the massive interaction with the SWNTs, one can expect polymorphic structures of iodine inside the narrow space of SWNTs with various diameters. One of the previous experiments of doping a SWNT with iodine reported stable two atomic chains of iodine in SWNTs.[8] However the polymorphic structures have never been studied at the atomic level. By means of high-resolution transmission electron microscopy (HR-TEM), we have made a systematic study of the structures of iodine generated in SWNTs with various diameters and demonstrate the realization of iodine atomic chains in various numbers and a new iodine crystal structure. This is the first report to show the polymorphic structures of iodine with the various numbers of atomic chains.

Iodine was introduced into the SWNT by heating a mixture of SWNT bulk powder and iodine in an evacuated glass tube at 150 °C for 24 h. In this experiment, two types of SWNTs were used as host sheaths of iodine atomic chains with a wide distribution of diameters: high-pressure carbon monoxide conversion (HiPCO) SWNTs with diameters of 0.6−1.3 nm (mean diameter of 1.0 nm) are commercial available (95% in purity), SWNTs with diameters of 1.2−1.6 nm are prepared by an arc discharge method with YNi_2 as catalyst and subsequently purified.[9] The excess iodine remaining on the SWNT surface was removed by washing several times with ethanol until the solvent became colorless. Thus obtained iodine-inserted SWNTs were dispersed in ethanol

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10.1021/nl070313t CCC: $37.00
Published on Web 05/04/2007

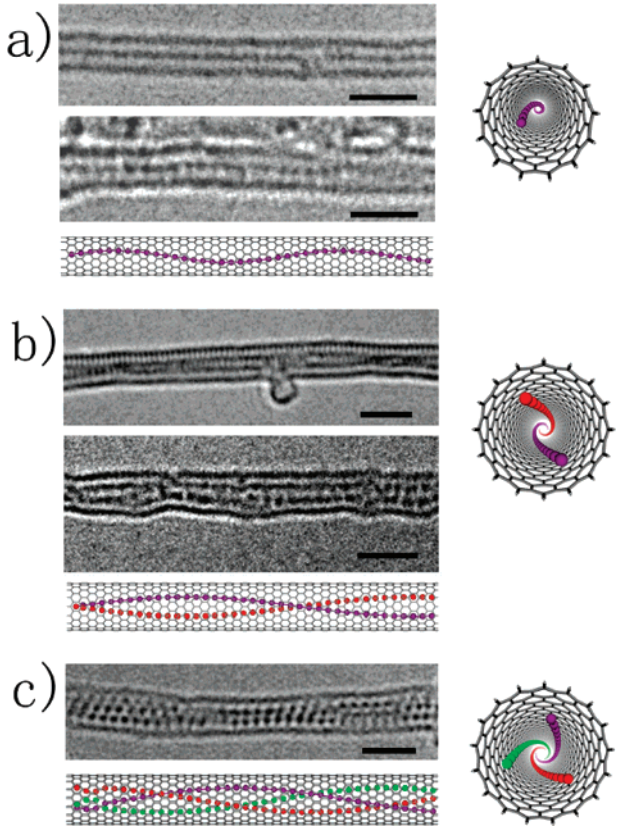

Figure 1. HR-TEM images (taken by JEOL 2100F) of the atomic chains of iodine sheathed with SWNTs and their schematic illustrations. (a) A single iodine chain in a thinner SWNT with diameter of 1.05 ± 0.05 nm and the structure model (side view and top view). (b) A double iodine chain in a SWNT with diameter of 1.30 ± 0.05 nm and the structure model (side view and top view). (c) A triple iodine chain in a SWNT with diameter of about 1.40 ± 0.05 nm and the structure model (side view and top view).

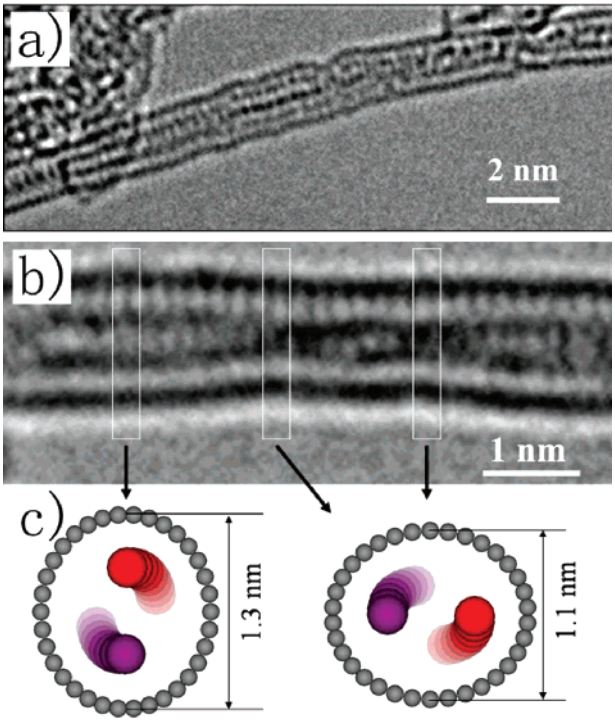

Figure 2. The elliptical distortion of SWNT induced by the repulsive force between atomic chains. (a) Diameter variation from 1.25 ± 0.05 nm to 1.50 ± 0.05 nm of a SWNT encapsulating a triple iodine chain. (b) Diameter variation from 1.10 ± 0.05 nm to 1.30 ± 0.05 nm of a SWNT encapsulating a double iodine chain. (c) The repulsive interaction leads to the elliptical distortion of the SWNT. When the two atomic chains of iodine are nearly parallel in projection to the electron beam, the projected diameter appears largest (1.30 ± 0.05 nm), while when the two atomic chains of the iodine plane overlap, the projected diameter appears smallest (1.10 ± 0.05 nm).

by ultrasonic treatment, and a droplet of the suspension was deposited on a TEM holey carbon grid. The sample was characterized by field emission TEMs (JEOL, JEM-2100F, and JEM-2010F with a postspecimen aberration corrector, both operated at 120 kV). During the HR-TEM observations, we employed optimized conditions to visualize the ions entrapped inside SWNTs.[10]

Figure 1 shows the typical HR-TEM images of the atomic chains of iodine sheathed with SWNTs and their schematic illustrations. The number of atomic chains in the host SWNTs strongly depends on the diameter of SWNT. In those HR-TEM images, dark spots are attributed to the iodine atoms which are aligned along the tube axis between the outer two parallel dark lines corresponding to the SWNT walls. It should be noted that direct measurement of the distance between two parallel dark lines (apparent diameter) exhibits a systematic deviation (∼0.1 nm) from the true diameter.[11] All the diameters of the SWNTs shown below are calibrated. Figure 1a shows HR-TEM images of a single iodine chain in a thinner SWNT with diameter of about 1.05 ± 0.05 nm. The iodine atomic chain stays near the middle of the hollow. The structure model is also shown in the side and top view. This is the first realization of a single atomic chain of iodine. The iodine chains inside SWNTs are not immobile, they occasionally move inside the tube during the observation and could be blocked at a defect or maybe some contamination of SWNT. (See Figure S1 and Movie 1 in Supporting Information). Figure 1b shows HR-TEM images of slightly thicker SWNTs (1.30 ± 0.05 nm in diameter) containing two helical chains of iodine atoms. The spacing of the two inner atomic chains can be estimated as large as 0.49 nm in the projection along the incident electron beam direction. The helical pitch of the iodine atomic chains is not constant, and more than two different helical pitchs are often found in a SWNT (see Figure S2 in Supporting Information). We do not find any positive correlation between the helical structure of iodine atomic chains and the nanotube helicity, in contrast to the previous theoretical prediction (Figure S2).[8] Figure 1c shows a HR-TEM image of a triple chain of iodine atoms encapsulated in a larger SWNT with diameter of 1.40 ± 0.05 nm, together with the structure model, indicating a helical structure in three dimensions. We have not succeeded in producing four or more atomic chains.

In most cases, the structure of the host SWNT appears to vary in axial direction as seen in the HR-TEM images. In Figure 2, the apparent diameter measured by a ruler in the projected HR-TEM images is not uniform, showing considerable variations from 1.25 ± 0.05 nm to 1.50 ± 0.05 nm (Figure 2a) and 1.10 ± 0.05 nm to 1.30 ± 0.05 nm (Figure

2b). This variation suggests that the host SWNTs elliptically distort in accordance with the helical structures of the guest atomic chains of iodine. According to the previous Raman spectroscopy studies, the iodine atoms inside SWNTs are negatively charged by forming I_3^- or I_5^- species.[7] This charge transfer, typically 0.2−0.3 eV per iodine atom, should provide a repulsive force exerted among the adjacent atomic chains of iodine in SWNT. The repulsive interaction leads to the elliptical distortion of the SWNT, as shown in Figure 2c. When the two atomic chains of iodine are nearly parallel in projection to the electron beam, the projected diameter appears largest (1.3 nm), while when the two atomic chains of the iodine plane overlap, the projected diameter appears smallest (1.1 nm) in the case of the double helical structure (Figure 2b). Such elliptical distortions have been predicted theoretically[12] and observed experimentally[13] in SWNTs involving some other inorganic crystals. This experiment is however the first proof that rigid atomic chains and their repulsive force can indeed deform the host SWNTs.

The critical diameter for the atomic chain formation was found around 1.45 nm. Another crystalline phase of iodine is found in a SWNT with a larger diameter. Most interestingly, a phase transition between the atomic chains and the crystalline phase can be occasionally observed "in situ" inside the SWNT around the critical diameter. In Figure 3, a series of HR-TEM images shows an example of the phase transitions of the atomic chains of iodine encapsulated in a SWNT of 1.45 ± 0.05 nm diameter. Since there is no apparent defocus difference along the tube, the inclination of SWNT with respect to the electron beam would be negligible. In the sequence of the HR-TEM images (Figure 3a−k), at least three different phases appear (and disappear) in turn inside the SWNT. The phases are denoted as I, II, and III. Phase I involves the three helical atomic chains of iodine which has already been discussed above and occasionally comes out during the observation (Figure 3c,d,f). Phases II and III are both crystalline but differ from each other. Both structures are based on the iodine dimer (I_2 molecule). The structure of phase II can be regarded as the known orthorhombic structure[14] but highly distorted. The atomic arrangement of phase III is completely different from the known crystalline structure of iodine in bulk (orthorhombic) and is really a new crystalline phase, since it could not be derived from rotation of orthorhombic iodine crystal or iodine chains. (See Supporting Information Figure S3 and Figure S4 for more detail.) The periodicities of the dark spots, which are corresponding to iodine dimers parallel to the electron beam, in axial direction and across direction are measured as 0.72 and 0.65 nm, respectively. When the electron beam irradiates continuously, one structure often alters into one of the other ones (Figure 3a−k). The phase transition is reversible, implying that the energy difference between three structures is quite subtle. Phase III seems the most stable phase inside the SWNT of 1.45 ± 0.05 nm in diameter, since it survives for longest time during the HR-TEM observation, compared with the other two phases.

When the diameter of the host SWNT continues to increase, one would expect to see the crystalline iodine

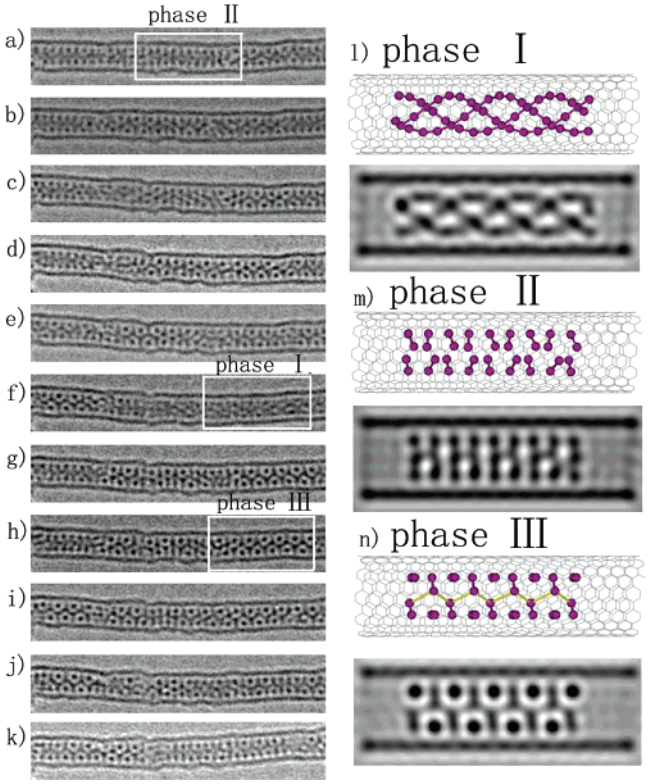

Figure 3. The phase transition of iodine from the atomic chains to crystalline structures during the HR-TEM observation taken by JEOL 2100F. (a−k) Sequential HR-TEM image of iodine structures inside a SWNT of 1.45 ± 0.05 nm in diameter. The images were recorded every 2 s. The three different structures appear during the observation (denoted as phase I, II, and III). Phase I represents the helical atomic chains (l), while phase II indicates a crystalline structure (m). The atomic arrangement of phase III derived from the HR-TEM images implies a new structure generated inside a SWNT (n). These phases appear repeatedly during the observation. See also movie 2 in Supporting Information.

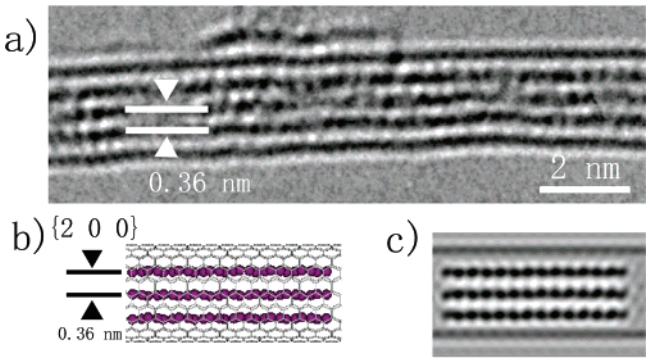

Figure 4. Crystalline iodine confined in a 1.55 ± 0.05 nm SWNT. (a) HR-TEM image taken by a JEOL 2010F with a Cs corrector. (b) Schematic model based on the orthorhombic iodine (bulk crystal) encapsulated in a SWNT with the ⟨010⟩ direction parallel to the tube axis and the ⟨001⟩ direction parallel to the electron beam. (c) The corresponding simulated image.

identical with the buck orthorhombic iodine crystal. Shown in Figure 4a is a HR-TEM image of the crystalline iodine in a SWNT with 1.55 ± 0.05 nm in diameter. The average intervals of the parallel lines inside the SWNT are about 0.36 nm, close to the 0.359 nm {200} *d*-spacing of the orthorhombic iodine.[14] The HR-TEM image is agreement

with the simulated image (Figure 4c) based on the schematic model, in which the orthorhombic ⟨010⟩ direction is parallel to the SWNT axis and the ⟨001⟩ direction is parallel to the electron beam.

In general, materials confined in nanospace could exhibit different structures and properties, such as coordination and bond length, compared with their bulk counterpart.[15] In this study, the exotic structures of iodine are clearly verified in carbon nanospaces and the structure of iodine is strongly dependent on the diameter of the size of the nanospace; a slight change in the diameter of the host SWNT will result in a totally different structure of the guest iodine. It also demonstrates a new usage of SWNT as a nanoscale sheath to realize the atomic chains inside, which may be unable to stand alone. This method may therefore be applicable to achieve other atomic chains rather than iodine. Measurements on physical properties of such atomic chains would be of great interest since the atomic chains in SWNTs could survive longer because of the sheath.

Acknowledgment. The authors from Peking University acknowledge the financial support from the NSFC, NKBRP (2001CB6105), and MOST (2006CB0N0701). The work of electron microscopy is supported by NEDO and the CREST project.

Supporting Information Available: Figures showing the movement of a single iodine chain, the helical pitch of the iodine atomic chains, iodine crystals confined in SWNTs with different diameters, and image simulations with different SWNT diameters and videos of phase transition. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL070313T