Electrically-driven dynamics of few-chain $NbSe_3$

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Abstract:

We present an in-situ transmission electron microscopy study of few-chain $NbSe_3$ encapsulated within the hollow core of carbon nanotubes, where the tube/chain system is subjected to applied axial electrical currents. Electromigration and thermal excitation forces result in collective and individual chain dynamics, with concomitant radial deformations of the encapsulating tubes.

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1. Introduction

Low-dimensional materials, when approaching the single-plane or single-chain limit, may display structures and properties very different from those of their bulk counterparts[1–3]. Recently, it was shown that small numbers of chains of 1D van der Waals (vdW) bonded materials, for example $NbSe_3$, can be encapsulated within the hollow core of carbon or boron nitride nanotubes[1]. In the small-chain-number limit inter-chain interactions may be altered, which could lead to ultralow-frictional behavior, where one chain can freely slide/translate past its neighboring ones.

One method of externally driving atomic-scale systems is via electromigration. Electromigration of closed-packed metals, for example iron[4] and copper[5], is well known. Upon the application of an electric field, atoms or small clusters of selected materials become mobile due to the mass-diffusion of atoms under the driving force of electrical wind force[6,7] and/or thermal gradient. This behavior has been exploited to create nanoscale memory devices[4] or nano-pipettes[6].

In this paper we report the electrically-driven dynamics of few-chain $NbSe_3$ encapsulated within the hollow core of multi-wall carbon nanotubes (CNTs). Electromigration and thermal forces can cause the encapsulated chains to move bodily along the axis of the tube. The applied current can also cause the chain pack to dissociate, and one chain may translate past the others, altering the number of chains locally within the chain pack. Both types of behaviors are usually reversible. Our experiments suggest a new atomic-scale translation mechanism (i.e. nanomotor) based on 1D vdW materials.

2. Experimental

Few-chain specimens of $NbSe_3$ are encapsulated within CNTs using a chemical vapor transport method described previously[1]. Briefly, CNTs (from CheapTubes) are oxidized in air at 515 °C for 15 minutes to remove the end-caps before mixing with precursor powders (niobium (Nb) and selenium (Se)) with stoichiometric weight ratios (1Nb:3Se). The mixture is sealed inside a quartz ampoule under vacuum (10^{-3} torr), and kept at 690 °C for 5-7 days. The as-grown materials are then ground and glued onto a copper TEM grid by silver paint. The $NbSe_3$-chain-containg CNTs are subjected to longitudinal electrical biasing using a Nanofactory transmission electron microscope (TEM) holder. Imaging is via a JEOL JEM 2010 TEM operated at 80 keV.[8] A schematic of the experiment is present in Fig. 1. A piezo-actuated tungsten tip electrode is brought into electrical contact with the end of a selected CNT, whose other end is also electrically connected via the silver paint. An electric bias is applied through the nanotube/$NbSe_3$ sample via a Keithley sourcemeter.

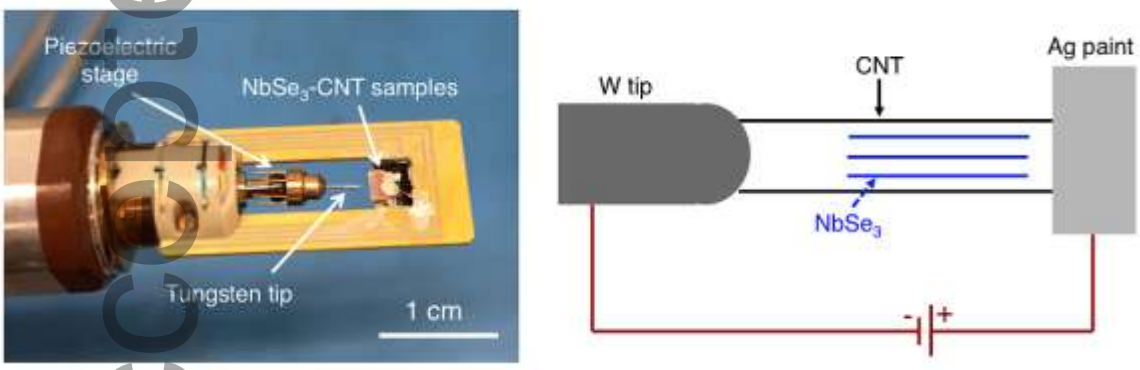

Figure 1. *Setup of the in-situ electrical biasing experiment. (Left) Photograph of the Nanofactory TEM holder. (Right) Schematic of electrical biasing circuit.*

3. Results and Discussion

Fig. 2 illustrates examples of $NbSe_3$ chain dynamics within a CNT, in the presence of applied electrical current (applied voltages range from 0.5 to 2V). The upper images are TEM data, while the lower images are simplified schematics. In Fig. 2a, a two-chain pack of $NbSe_3$ is spontaneously longitudinally severed, and the two segments thereafter can move independently. One segment may move faster than the other, allowing the segments to

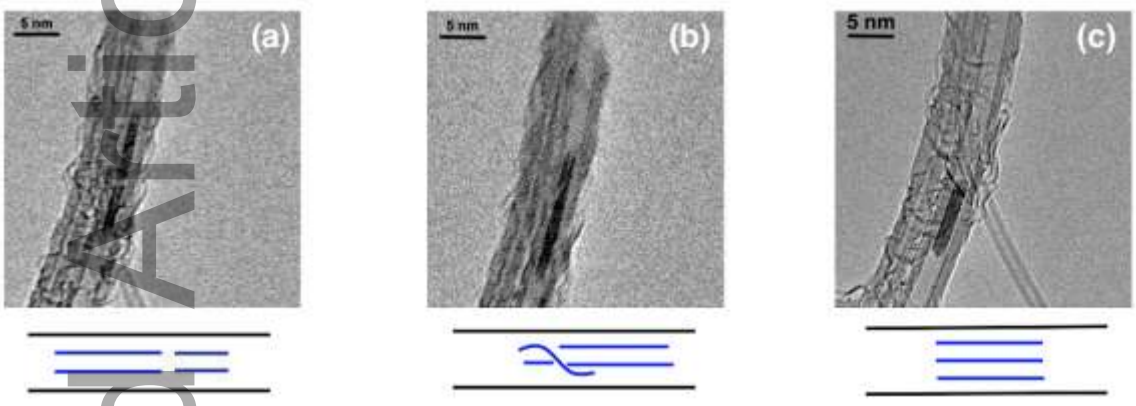

Figure 2. *$NbSe_3$ chain dynamics within a CNT. (a) Two segments of two-chain $NbSe_3$ severed from a longer host two-chain pack. The segments can move independently after separation. (b) A chain in the first segment slides between or over the other two chains. (c) Three chain pack of $NbSe_3$ after the migration. The total lengths of all chains in (a), (b), and (c) are the same (approximately 27 nm). Current flows along the CNT axis. Simplified schematics below each figure show the structures (the black lines represent the CNT while the blue lines represent $NbSe_3$ chains).*

drift farther and farther apart with applied current. Fig. 2b shows how one $NbSe_3$ chain may move independently of other chains in the pack. In this case, a two-chain pack can be transformed into a three-chain pack by addition of a chain, obtained from a nearby segment. (The opposite is also observed, i.e. a three-chain pack can be transformed into a two-chain pack by removal (sliding off) of a single chain). Fig. 2c shows the final three-

chain pack. During the transformation process in going from two to three chains, the total length of all of the $NbSe_3$ chains remains unchanged (~27 nm in this example), which rules out the possibility that the observed two-to-three-chain transformation is simply an imaging artifact caused by rotation of the material with respect to the incident electron beam.

The chain displacements/transformations are driven by a combination of electromigration forces, thermal gradients/agitation, and TEM electron beam irradiation,. One possibility for the chain pack motion, as observed in Fig. 2a, is that the host nanotube is Joule heated and the local temperature is high enough, and electromigration forces strong enough, to deconstruct the $NbSe_3$ chains into individual atoms or small clusters of atoms. Those atoms then migrate along the gaps between the remaining chains and the tube's innermost wall to the front end and reconstruct to form the triple chains.[7] Due to resolution limits of the TEM, and especially the fast dynamics involved, we cannot completely rule out the possibility that foreign atoms, such as carbon atoms from the nanotube, may incorporate into the $NbSe_3$ chains.

A second, more likely, possibility is that electromigration/thermal gradient forces drive the chain packs collectively, as in Fig. 2a, or semi-independently, as in Fig. 2b. Individual intact chains can slide past other chains in the pack, much like the fraying in a multi-strand steel cable just at the breaking point. In the process illustrated in Fig. 2b, one chain in the first segment slithers into the space between or on top of the two chains of the second segment to form a triple chain (Fig. 2c)[9].

These observations imply that interchain interactions are relatively weak in the few-chain limit of $NbSe_3$. Here an individual chain can easily move without disturbing the

surrounding environment. Ultralow friction and sliding behaviors have been reported for other van der Waals materials in various morphologies, such as MoS_2 particles[10], carbon nanotubes[11,12] and graphene[12,13]. In general, several factors are attributed to the enhancement of the ultralow friction (superlubricity) in vdW materials. They are the reduction of number of layers,[14] the decrease of intrinsic defects/impurity concentrations[12], and the downsizing of contact area.[11] The as-synthesized few-chain $NbSe_3$ satisfies all of these criteria, which may in part explain the sliding behaviors of the chains.

An interesting related observation of encapsulated $NbSe_3$ is that the CNT can be radially deformed (necked down) in the encapsulated region. This is illustrated in Fig. 3. Initially only a small segment (5.3 nm long) of the host three-wall CNT is radially deformed, in between the region marked by the two white arrows in Fig. 3a. The inner diameter of the tube (in the projection direction) decreases from 2.40 nm to 1.82 nm, corresponding to 24.1 % radial contraction. When transformed to the double-chain $NbSe_3$ (Fig. 3b) the deformation area in the sheathed nanotube extends to cover the entire length of the encapsulated $NbSe_3$ double chains (20.1 nm). The radial deformation of the carbon nanotube here ranges from 21.0 % at the two ends to 25.2 % in the middle. When changing back to the triple-chain structure (Fig. 3c), the tube becomes deformation-free.

Apparently having a very small number of $NbSe_3$ chains within a CNT effectively enhances the radially inward compressive vdWs forces. We note that in empty CNTs, vdW forces from opposing CNT walls can deform and sometimes fully collapse and flatten a CNT. Partially filling the CNT could lead to symmetry breaking in the internal vdWs forces, increasing the propensity for CNT collapse.

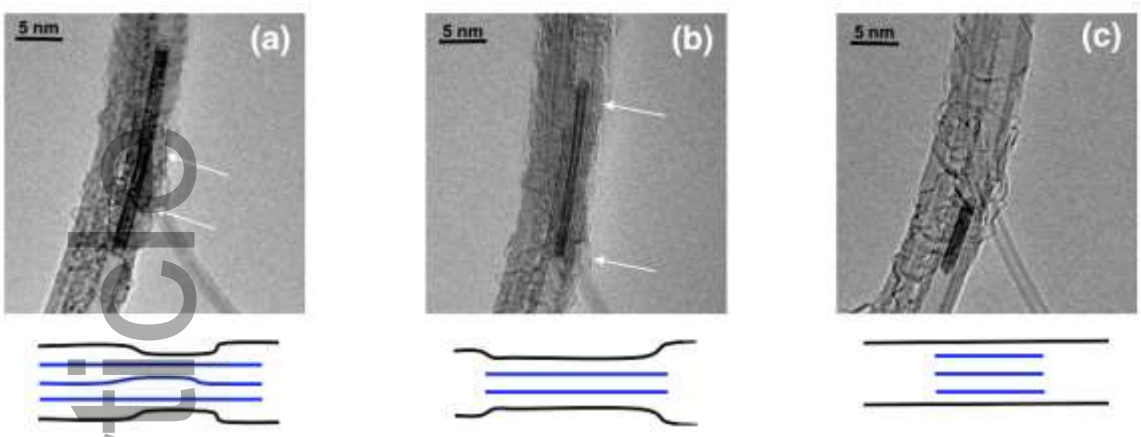

Figure 3. *Deformation of the host CNT. In (a) and (b), a part of the CNT is radially deformed in the region between the two white arrows. In (c), the CNT is deformation-free (having a uniform diameter). Below the TEM images are corresponding simplified schematics of the structures at different stages (the black lines represent the CNT while the blue lines represent $NbSe_3$ chains).*

4. Conclusion

We observe electrically induced structural transformations in few chains of $NbSe_3$ encapsulated in CNTs. Dynamics include breaking of chain packs, reconfiguration of chain number, and deformations of the CNT in the encapsulation region. The chain-like sliding mechanism may open up a new pathway to electrical control the stacking and rotation in vdW materials.

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Axial electrical currents applied to multiwall carbon nanotubes filled with chains of the transition metal trichalcogenide NbSe3 drive the chains to collective or independent chain motion, as revealed by in-situ transmission electron microscopy.