Torsional instability in the single-chain limit of a transition metal trichalcogenide

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The scientific bounty resulting from the successful isolation of few to single layers of two-dimensional materials suggests that related new physics resides in the few- to single-chain limit of one-dimensional materials. We report the synthesis of the quasi-one-dimensional transition metal trichalcogenide NbSe3 (niobium triselenide) in the few-chain limit, including the realization of isolated single chains. The chains are encapsulated in protective boron nitride nanotube sheaths to prevent oxidation and to facilitate characterization. Transmission electron microscopy reveals static and dynamic structural torsional waves not found in bulk NbSe3 crystals. Electronic structure calculations indicate that charge transfer drives the torsional wave instability. Very little covalent bonding is found between the chains and the nanotube sheath, leading to relatively unhindered longitudinal and torsional dynamics for the encapsulated chains.

The successful isolation of monolayers of van der Waals–bonded quasi-two-dimensional solids such as graphite (1) and the transition metal dichalcogenides (TMDs) (2) has spurred intense experimental and theoretical interest in these low-dimensional materials. Monolayer or few-layer sheets of graphene or TMDs often display electronic, optical, and structural properties that are markedly different from those of the bulk materials. The thin materials have profound underlying physics and far-ranging applications potential (3). Transition metal trichalcogenides (TMTs) such as NbSe3 and TaS3 are closely related van der Waals–bonded quasi-one-dimensional compounds that have been extensively studied in bulk form. These materials can support unusual ground states and collective-mode electronic transport (4). Although some attempts have been made to study thinned TMDs (e.g., NbSe3 samples have been cleaved down to ~200 chains in width (5)), no experimental or theoretical study has examined TMTs in the single- or few-chain limit. It is far more difficult to isolate and manipulate atomic chains than atomic sheets, and atomically thin samples can be highly air-sensitive (6).

We present a facile and effective method to prepare low-number chains of NbSe3 within carbon and boron nitride nanotubes (CNTs and BNNTs). The spatial confinement promotes and stabilizes the growth of sub–unit cell NbSe3 down to triple, double, and even single atomic chains. Encapsulation additionally protects the chains from environmental oxidation and facilitates easy handling and characterization. The chains are mobile within the tubes. Unusual helical torsional waves with regular periodicity are observed, even in the single-chain limit. Computational theoretical calculations show that the electronic band structure of NbSe3 is highly dependent on chain number and orientation, and that the torsional wave instability is driven by charging of the chains. We term this phenomenon a charge-induced torsional wave (CTW).

NbSe3 chains are directly grown via vapor transport inside the hollow cavity of preformed and open-ended multiwall CNTs and BNNTs (7). Related techniques have previously been used to encapsulate foreign species within nanotubes (8–11). Once the synthesis is complete, the samples can be exposed to air and liquids with no apparent degradation of the encapsulated chains.

Figure 1 shows high-resolution transmission electron microscopy (HRTEM) images of NbSe3 chains encapsulated within nanotubes. The structure of numerous (~20) chains encapsulated by a CNT of inner diameter 3.86 nm (Fig. 1A) resembles that of the bulk crystal, with signature one-dimensional (untwisted) chains oriented along the axis of the nanotube. By using nanotubes with smaller inner diameter, fewer parallel NbSe3 chains are isolated, strictly by geometrical constraint, within the cross section of the tube. Shown in Fig. 1, B to D, are triple-, double-, and single-chain NbSe3 encapsulated within CNTs (B) and (C) or BNNTs (D) with successively smaller inner diameters of 2.49 nm, 1.87 nm, and 1.21 nm. This demonstrates that isolated single chains of TMTs can indeed be stabilized. We note that the unit cell of bulk NbSe3 contains six chains (12), so even the three-chain specimen is well below the single–unit cell limit.

Fig. 1. Isolation of one-dimensional TMT materials down to single-chain limit. High-resolution TEM images of (A) ~20 chains, (B) triple chain, (C) double chain, and (D) single chain of prototypical TMT NbSe3 encapsulated within CNTs (1A) to (C)) and a BNNT (D). The simplified cross-sectional schematics show different numbers of chains encapsulated in tubes of different inner diameters; in this representation, the electron beam impinges horizontally, normal to the tube axis. In (A), atoms appear bright (overfocus); in (B) to (D), atoms appear dark (underfocus). The nanotubes serve as nanoreaction chambers to grow the isolated TMT chains and simultaneously protect them from environmental degradation.
Quantitative chemical analysis of encapsulated TMT chains by means of energy-dispersive spectroscopy (fig. S1) yields 75.65 ± 7.37 atomic percent (at %) Se and 24.35 ± 4.26 at % Nb. Although the NbSe₃ chains in the few-chain limit encapsulated within nanotubes have the same stoichiometry as the bulk material, as well as a similar local trigonal-prismatic atomic structure, the chains do not precisely adopt the internal configuration found in bulk crystals. Rather, the chains are twisted, supporting a static helical torsional wave. This is true even for an isolated single chain. For double or triple chains, the strands additionally twist around each other to form double or triple helices, much like double-helix DNA or the strands in a multiwire steel cable. Figure 2A shows an aberration-corrected phase-contrast TEM (AC-TEM) image of a single NbSe₃ chain inside a double-walled CNT. The atomic model and the corresponding TEM simulation by the multislice method are also shown. The experimental image, model, and simulated images confirm the alternating orientations of the chain (i.e., the twisting of the chain). The wavelength of the associated static torsional wave (i.e., the distance for a full 2π rotation) is approximately 41 nm.

Shown in Fig. 2, B and C, are additional TEM images of the spiraling behavior of double- and triple-chain specimens, respectively. For the double chain (here encapsulated within a BNNT), the additional twisting is not strictly periodic; there are regions where the two strands run parallel without spiraling about each other. On the other hand, for triple chains, we invariably find that the three chains are consistently tightly twisted around each other in a triple-helix fashion. Figure 2D shows a typical AC-TEM image of such a triple-chain configuration within a CNT. For triple chains, we find a spiraling node-distance ranging from 1.45 to 1.85 nm within CNTs and 1.90 to 2.30 nm within BNNTs (fig. S2B). (In the simplest interpretation, the full wavelength of the torsional wave in this case is here 6 times the node-node distance, notwithstanding additional complexities of on-chain twisting.)

Stimulation from the TEM imaging electron beam often causes the chains to bodily transport axially along the core of the tube. In addition, the wave itself can propagate along the TMT. For CNTs, charging of the chains, which is key to the torsional wave instability, comes primarily from electron transfer from the CNT to the chain, whereas for BNNTs, the insulating nature of the host tube amplifies charging effects from the TEM beam (either directly from the beam current or indirectly from radiolysis processes of the BN shell or hydrocarbon contaminants nearby) (15, 16) and leads to in situ twisting and untwisting of the chains (as seen in Fig. 2B). To explore the underlying physics of the above systems, we performed first-principles calculations based on pseudopotential density functional theory (DFT) (17). We first investigated the atomic and electronic structure of single-chain NbSe₃ isolated in vacuum. We constructed three initial candidate structures for the chain using the atomic positions of the three different types of chains comprising the bulk solid (18) (fig. S5). The atomic positions for the candidate structures were fully relaxed by minimizing the total energy. All three candidates relaxed into the same atomic structure (Fig. 3A), whose corresponding band structure is shown in Fig. 3B with two bands (Ψ₀ and Ψ₂) crossing the Fermi energy.

We investigated the atomic and electronic structures for the untwisted single-chain NbSe₃ encapsulated inside an (8,8) CNT (indices chosen for convenience) (Fig. 3C). The separately relaxed atomic positions of single-chain NbSe₃ isolated in vacuum, and those of the empty CNT, were used. Further relaxation was not performed. We calculated the binding energy Eₜ of a single-chain NbSe₃ (fig. S6), which is defined as Eₜ = Eₜotot − Eₐₐₓₜotot − Eₐₐₓₜotot, where Eₜotot, Eₐₐₓₜotot, and Eₐₐₓₜotot are the total energies of separated single-chain NbSe₃ and CNT isolated in vacuum, and Eₜotot/CNT is the total energy of the joint system of single-chain NbSe₃ encapsulated inside the CNT. The calculated binding energy of the chain is 1.36 eV per NbSe₃ formula unit (f.u.). This large binding energy accounts for the stability of single-chain NbSe₃ encapsulated inside CNTs. Figure 3D shows the electronic band structure of the chain inside the CNT. Confinement does not alter the states near the Fermi energy appreciably, except for the charge transfer. Charge (0.23 e/f.u.; i.e., 0.08 e per Se atom) is transferred from the CNT to the NbSe₃ chain (fig. S7), driven by the work function difference. We found no appreciable amount of covalent bonding between the chain and CNT (Fig. 3, G and H, and figs. S7E and S8), which explains the high mobility of the chain inside the CNT.

Motivated by the experimentally observed torsional wave in single-chain NbSe₃, we investigated the atomic and electronic structures for the twisted single chain encapsulated inside a CNT with a variable torsional wavelength λ. Figure 3, E and F, shows the atomic and electronic structures of the twisted single chain with λ = 15.7 nm (7). The torsional wave shifts Ψ₀ by π/6λ, whereas Ψ₂ is not affected appreciably. The torsional wave does not change the binding energy and the charge transfer appreciably.
Fig. 3. Calculated atomic and electronic structures of single-chain NbSe₃. (A, C, and E) Atomic structures and (B, D, and F) corresponding electronic band structures of untwisted single-chain NbSe₃ isolated in vacuum [(A) and (B)], untwisted single-chain NbSe₃ encapsulated inside an (8,8) CNT [(C) and (D)], and twisted single-chain NbSe₃ with \( \lambda = 15.7 \) nm within the (8,8) CNT [(E) and (F)]. In the axial views of the atomic structures, blue, red, and white spheres represent Nb, Se, and C atoms, respectively. In the band structures, the Fermi energy is set to zero and marked with a horizontal dashed line. In (D) and (F), the band structures represented by red dots are projected onto the chain and unfolded with respect to the first Brillouin zone of the unit cells of the untwisted chain, where \( Z_{\text{NbSe}_3} \) denotes the zone boundaries for the chain; structures represented by blue dots are projected onto the CNT and unfolded with respect to the first Brillouin zone of the unit cells of the CNT, where \( Z_{\text{CNT}} \) denotes the zone boundaries for the CNT. \( \Gamma \) denotes the center of the Brillouin zone (\( k = 0 \)).

Fig. 4. Charge-induced torsional waves (CTWs) in single-chain NbSe₃. (A) Schematic showing the proposed mechanism of CTW formation in single-chain NbSe₃ inside a CNT. (B) Total energies for neutral and electron-doped single-chain NbSe₃ isolated in vacuum as functions of \( \lambda \). \( E(\infty) \) is set to zero and marked by a horizontal dashed line; \( b_0 = 3.4805 \) Å is the distance between the adjacent Nb atoms. Negative \( \Delta E \) means that a CTW is favored.
and the calculated binding energies are 1.35 to 1.36 eV/f.u. with an electron transfer of 0.23 e/f.u. for all the calculated λs, as for the untwisted chain.

What drives the torsional wave? There are two main contributions. The torsional wave increases the elastic energy by twisting the orbital configuration of the Nb atoms, but this is offset by a reduction in Coulomb energy between negatively charged Se atoms. To quantify these effects, we calculated the elastic energies of a twisted single chain isolated in vacuum as a function of energy difference $E_{\text{DFT-}\text{neutral}}$ for all the calculated $\lambda$s, as for the untwisted chain.

The calculated energy difference $\Delta E_{\text{neutral}}$ of a twisted single chain isolated in vacuum as a function of $\lambda$, defined as $\Delta E_{\text{neutral}}(\lambda) = E_{\text{DFT-\text{neutral}}} - E_{\text{DFT-\text{neutral}}}^{(\lambda)}$, where $E_{\text{DFT-\text{neutral}}}^{(\lambda)}$ is the total energy of the untwisted single chain isolated in vacuum. As shown in Fig. 4, $\Delta E_{\text{neutral}}$ increases as $\lambda$ decreases. We also obtained the energy difference $\Delta E_{\text{DFT-\text{doped}}}$ for an electron-doped single chain isolated in vacuum as a function of $\lambda$ by performing the same calculation with additional electron doping, where we added 0.23 e/f.u. to match the encapsulated situation. For $\lambda > 20$ nm, $\Delta E_{\text{DFT-\text{doped}}}$ is negative and the wave distortion is favorable. Within a device configuration, it should be possible to further control the charge transfer to the TMT chain(s), allowing external control of the torsional wave and thereby its optical and electronic transport properties.

**REFERENCES AND NOTES**

7. See supplementary materials.

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**Data and materials availability:** All data are available in the manuscript or in the supplementary materials.

**SUPPLEMENTARY MATERIALS**

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**SUPPLEMENTARY TEXT**

Figs. S1 to S8

References (17–25)

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