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RPPR Final Report
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Major Goals: We propose to explore one-dimensional (1D) van der Waals nanomaterial - tellurium (Te) - and to isolate and realize a single atomic chain of Te. Although thousands of publications in van der Waals 2D materials including graphene, MoS₂ and phosphorene in the past decade, we are not aware of any single experimental work on 1D van der Waals nano-materials such as Te or selenium (Se) in the recent wave of 2D research. Using liquid solution synthesis, we are able to form a 2D form of tellurium which we call it tellurene. Tellurene, which, unlike graphene, can have an inherent and direct bandgap (0.35-2.0 eV layer dependent) and, unlike MoS₂ or other transition-metal dichalcogenides (TMDs) with strong d-orbital coupling, can have carrier mobility on the order of 10⁴ cm²/Vs, unlike phosphorene, is very stable in ambient. We are uniquely qualified to explore the isolation of a single Te atomic chain structure as the limit of all nano-materials because we are the first in the world to successfully synthesize tellurene using liquid solution method and demonstrate promising transistor performance. We are not aware of any other experimental research in tellurium, tellurene and 1D van der Waals materials in general. To explore the isolation of a single Te atomic chain, we will have collaborative and interdisciplinary approach: 1) Liquid solution based synthesis of ultrathin "nanowire" type of Te and eventually to realize a single Te atomic chain or sub-nm Te nanowire, 2) Exploration of laser thinning or laser exfoliation of Te nanowires or nanosheets to realize a single Te atomic chain or sub-nm Te nanowire, 3) Use of chemical etching, interaction, ultrasound, shock-wave to realize a single Te atomic chain or sub-nm Te nanowire.

Accomplishments: This is the final report for ARO Grant No. W911NF-17-1-0573 entitled "Isolation of a Single Tellurium Atomic Chain" as a STIP award for the period 09/1/2017 through 5/31/2018. The ARO program director responsible for the grant is Dr. Joe Qiu. The PI and co-PI is Prof. Peide Ye and Prof. Wenzhuo Wu of Purdue University. The objective of this project is to explore one-dimensional (1D) van der Waals nanomaterial - tellurium (Te) - and to isolate and realize a single atomic chain of Te. Although thousands of publications in van der Waals 2D materials including graphene, MoS₂ and phosphorene in the past decade, we are not aware of any single experimental work on 1D van der Waals nano-materials such as Te or selenium (Se) in the recent wave of 2D research. Using liquid solution synthesis, we are able to form a 2D form of tellurium which we call it tellurene, which is published in Nature Electronics in 2018 eventually. Tellurene, which, unlike graphene, can have an inherent and direct bandgap (0.35-2.0 eV layer dependent) and, unlike MoS₂ or other transition-metal dichalcogenides (TMDs) with strong d-orbital coupling, can have carrier mobility on the order of 10⁴ cm²/Vs, unlike phosphorene, is very stable in ambient. The PI and co-PI are uniquely qualified to explore the isolation of a single Te atomic chain structure as the limit of all nano-materials because they are the first in the world to successfully synthesize tellurene using liquid solution method and demonstrate promising transistor performance. In this particular seeding project, they explored and successfully realize the controllable synthesis a single atomic Te chains or few Te chains in carbon nanotubes or boron nitride nanotubes. They eventually carried out details of optical and electrical

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characterization to confirm the realization of single to few atomic chains of Te synthesis.

Training Opportunities: Within this project period, we supported two Ph.D. students working on this project with one on materials synthesis and one on device fabrication and characterization as proposed in our project.

Results Dissemination: A major research paper is under preparation for this successful project. We also plan to present this result at 2018 APS March Meeting.

Honors and Awards: The PI received Arden Bement Jr. Award in 2018.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)

Participant: Gang Qiu

Person Months Worked: 9.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Yixiu Wang

Person Months Worked: 9.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Co PD/PI

Participant: Wenzhuo Wu

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

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as of 26-Nov-2018

Isolation of a Single Tellurium Atomic Chain

Professor Peide D. Ye and Wenzhuo Wu, Purdue University, STIP Award

This is the final report for ARO Grant No. W911NF-17-1-0573 entitled “Isolation of a Single Tellurium Atomic Chain” as a STIP award for the period 09/1/2017 through 5/31/2018. The ARO program director responsible for the grant is Dr. Joe Qiu. The PI and co-PI is Prof. Peide Ye and Prof. Wenzhuo Wu of Purdue University. The objective of this project is to explore one-dimensional (1D) van der Waals nanomaterial - tellurium (Te) - and to isolate and realize a single atomic chain of Te. Although thousands of publications in van der Waals 2D materials including graphene, MoS₂ and phosphorene in the past decade, we are not aware of any single experimental work on 1D van der Waals nano-materials such as Te or selenium (Se) in the recent wave of 2D research. Using liquid solution synthesis, we are able to form a 2D form of tellurium which we call it tellurene, which is published in Nature Electronics in 2018 eventually. Tellurene, which, unlike graphene, can have an inherent and direct bandgap (0.35-2.0 eV layer dependent) and, unlike MoS₂ or other transition-metal dichalcogenides (TMDs) with strong d-orbital coupling, can have carrier mobility on the order of 10⁴ cm²/Vs, unlike phosphorene, is very stable in ambient. The PI and co-PI are uniquely qualified to explore the isolation of a single Te atomic chain structure as the limit of all nano-materials because they are the first in the world to successfully synthesize tellurene using liquid solution method and demonstrate promising transistor performance. In this particular seeding project, they explored and successfully realize the controllable synthesis a single atomic Te chains or few Te chains in carbon nanotubes or boron nitride nanotubes. They eventually carried out details of optical and electrical characterization to confirm the realization of single to few atomic chains of Te synthesis.

As a typical elemental 1D van der Waals material, ultra-narrow tellurium nanowire (Te NW) with few-chain limit is expected to exhibit intriguing physical properties which are markedly different from that in bulk form. In this work, we successfully isolated 1D vdW Te NW into few-chain even single-chain limit by carbon nanotube (CNT) or boron nitride nanotube (BNNT) encapsulation. The number controlling of Te atomic chains was realized by selectively choosing the inner diameter (ID) of CNTs. The change in Raman spectra suggests weak interaction between single-atomic Te chain with CNTs and intense inter-chain interaction as the number of chains increasing. By encapsulating with BNNT, we successfully obtained the current carrying capacity of ultra-narrow Te NW with 2 nm limit. What is more, compared with the SiO₂-supported counterparts, the ampacity of Te NW can be dramatically enhanced by 6 times up to 39×10⁶ A cm⁻², exceeding most metal and alloys materials. The CNTs with varying ID were taken as templates for filling with ultra-narrow Te NWs, as the schematic illustrated in Fig. 1a. From the high-angle annular dark field STEM (HAADF-STEM) image (Fig. 1b), we can see that majority of the single-wall CNTs (SWCNTs) were successfully filled with single-atomic Te chain with the average diameter of 0.8 nm. It is hard to get individual SWCNT for TEM characterization since it tends to be attached with neighbors in form of bundle (Inset image in Fig. 1b). As the ID of SWCNTs increased to 1.2 nm, three parallel Te chains could be isolated as demonstrated by high-resolution transition electron microscopy (HRTEM), while the encapsulation of larger-diameter multi-wall CNTs (MWCNTs) of 2 nm would result into border NWs with ~ 19 Te atomic chains as shown in Fig. 1, c to d. These results suggest that few-chains Te NW could be successfully isolated by the geometrical constraint of CNTs. In addition, the controlling of chains number can also be realized by tuning the ID of CNTs. The chain-dependent lattice vibration of Te NW was investigated by Raman spectroscopy. Fig. 1e shows the Raman spectra of single Te atomic chain encapsulated by SWCNT excited by 633 nm line in air ambient environment. At least four active Raman peaks could be observed. Among of these, peaks located 156 cm⁻¹ and 173 cm⁻¹ could be appointed to the vibration mode of SWCNT. After eliminating the influence of SWCNT, the intrinsic Raman spectrum of the single-atomic Te chain could be obtained as shown in Fig. 1f (the bottom line marked with red rectangular). Remarkably, the breathing mode A1 is almost substantially quenched compared with bulk crystal. It is reasonable since geometrical confinement of CNTs would block lateral expansion of Te atoms, resulting into the weakening of A1 mode. Besides, since the energies of A1 and E2 modes are very close, the significant change of the A1 mode will also impact the energy and vibration of E2 mode, which would lead to the hybridization of them. Thus, the E2 mode exhibits such a small intensity that we cannot detect it clearly. The peaks belonged to E1 mode exhibits a clear shift towards low frequency at 81 cm⁻¹, which is in well accordance with our theoretical calculation for free-standing single Te chain. It suggests that the vdW interaction between single Te atomic chain and SWCNT is very weak, and the Te chain could be fully relaxed in SWCNT and exist stably in the configuration of 3-fold-symmetry helical coils. As the number of Te chains increasing from 3 to bulk (ID of CNT increasing from 1.2 nm to >10 nm), clear redshift

of all the three modes could be observed as shown in Fig. 1e and 1g. For example, the E1 peak significantly shifted from 108 cm^{-1} for 3 chains to 92 cm^{-1} for bulks. Similar with previously reported tellurene⁴, the unique chiral-chain vdW structure of Te would cause the weakening intra-chain covalent atomic bonding and enhancement of vdW interaction between individual chains as the number increasing. Therefore, Te atoms could more easily restore back in bulk sample, resulting into the Raman frequency reduction of A1 vibration mode. On the contrary, long-range Coulombic interactions would dominate the vibration mode of individual Te atomic chain in few-chain samples and lead to the hardening of intra-chain E vibration mode.

For Te-BNNT devices with a typical MIS structure, the channel current is mainly decided by two factors: Schottky barrier height and tunneling resistance of insulator. Although Ni has a relatively high work function which is close to the Fermi level of Te, the direct contact at metal/semiconductor would result in the high Schottky barrier height introduced by the metal induced gap state. The BNNT could provide a perfect insulating layer for inner Te NW, which would significantly reduce the influence of MIGS. However, the introducing of BN would in turn result in the large contact resistance and lowering of the channel current. Therefore, we need to optimize the thickness of BN layer to realize the maximization of current carrying capacity in devices. Fig. 2a illustrates the fabrication process of devices. After source/drain pattern, low power SF_6/Ar plasma etching was used to realize the controlled thinning of BN insulator layer. Then, the samples were immediately loaded into metallization chamber followed by Ni/Au (30/100nm) deposition. Fig. 2b shows the I-V curves of typical devices as a function of etching time. Notably, the breakdown current is greatly enhanced up to $22\text{ }\mu\text{A}$ after 20 s etching, at least 50 times larger than that in original devices. The I-V curves of all devices exhibit linear relationship at small V_d s, while they would change exponentially as applied V_d s exceeding puncture voltage (V_p). As shown in Fig. 2c, the smallest V_p of 0.15 V was obtained as the etching time extended to 20 s. Tunneling resistance could be calculated to be $2.4\text{ K}\Omega\cdot\mu\text{m}$, which is almost one order of magnitude smaller than that of devices without etching (about $21\text{ K}\Omega\cdot\mu\text{m}$). It is worthy noted that the over etching of BN would deteriorate the performance of Te-BNNT devices. This could be explained by the poor dispersing efficiency of Joule heating and high Schottky barrier at Ni/Te contact. The encapsulation of BNNT would provide an ideal shielding for inner Te NW from external environment. In-situ temperature-dependent Raman spectroscopy was conducted to explore the limit of this passivation, as shown in Fig. 2d-e. Te NWs shielded by BNNT could sustain a high temperature up to $400\text{ }^\circ\text{C}$, while the unencapsulated NWs could be easily destroyed at $250\text{ }^\circ\text{C}$. Besides, Raman peaks of Te tend to shift towards low frequency as the increasing of temperature, which is related to the non-crystallizing phase change induced by high temperature. We measured the ampacity of Te NW supported on SiO_2 substrate for comparison (Fig. 2f). Obviously, the maximum value ($38.8\times 10^6\text{ A cm}^{-2}$) is obtained for Te-BNNT devices with channel length of 100 nm, which is almost 6 times larger than that in bare Te NW devices ($7.4\times 10^6\text{ A cm}^{-2}$). This high value even exceeds most metal or alloy materials such as Au, Al and Cu etc as listed in Fig. 2g. Such dramatic enhancement of ampacity could be attributed to extremely high thermal conductivity of BN (about $360\text{ W/m}\cdot\text{K}$) and low thermal resistance at BN/Te interface.

Using CNTs as growth template, we successfully isolated 1D vdW Te NWs into few-chain even single-chain limit. The lattice vibration exhibits a clear dependence on the number of Te atomic chains, which could be demonstrated by the shift of Raman frequency. By encapsulation with BNNT, the measurement of electrical transport properties for ultra-narrow Te NW (about 19 atomic chains) was realized. Besides, the ampacity of Te NW could also be improved by BNNT shielding. Their study suggest a clear evolution of the coupling effect between 1D vdW Te atomic chains and provides a deep understanding of nanoconfined 1D materials. After the successful demonstration of synthesis capability at single atomic chain scale, they are looking for the full funded project to continue the work with electrical/optical fundamental studies and high level device performance demonstrations. A major research paper is under preparation for this successful project.

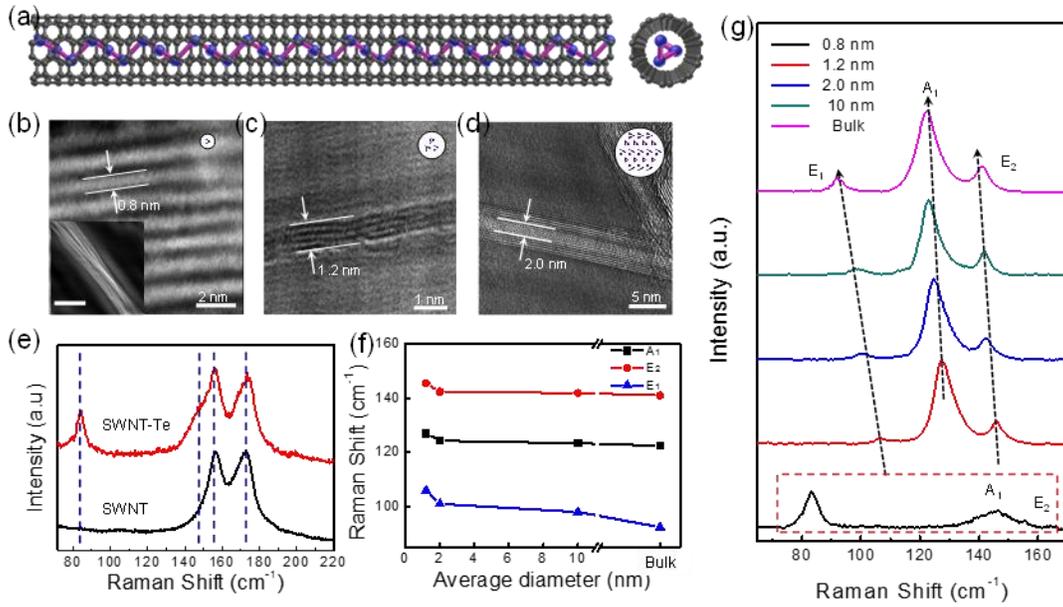


Fig. 1 | Characterization of ultra-narrow Te NW isolated down to few-chain limit by CNT encapsulation. (a) Schematic illustration of single Te atomic chain in SWCNT. (b) HAADF-STEM image of single Te atom chain confined in SWCNT with ID of 0.8 nm. Inset image shows the low-magnification image, and scale bar is 20 nm. (c-d) HRTEM images of triple chain and 19 chain of Te shielded by CNT. The average ID of CNTs is 1.2 nm and 2 nm, respectively. (e) Raman spectra of single-chain Te shielded by SWCNT. (f) The shift of Raman peak frequency as dependent of average ID of CNT. (g) Raman spectrum evolution of Te with ID of CNT.

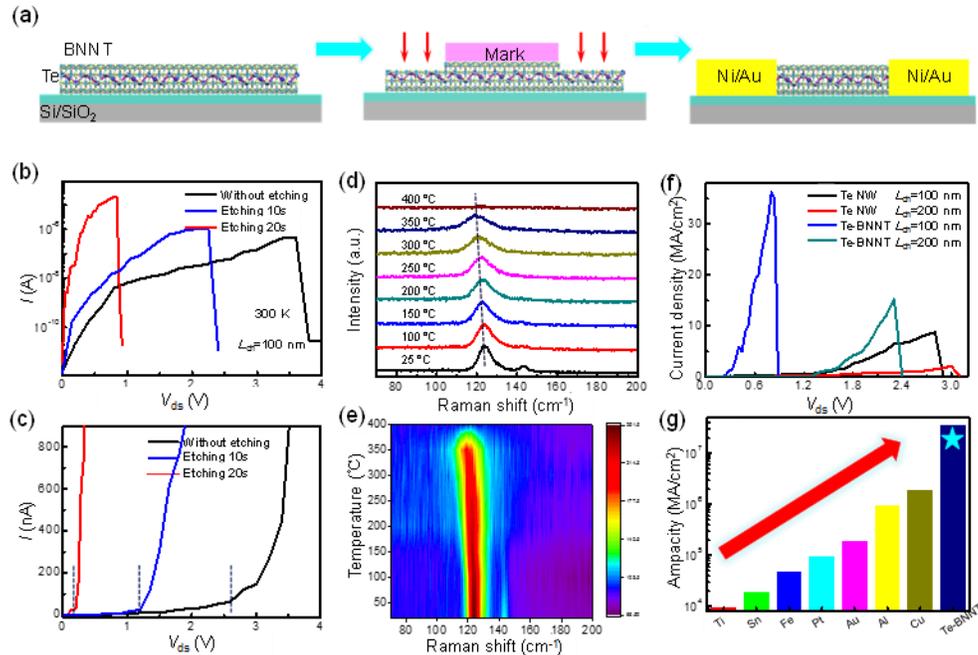


Fig. 2 | Thermal stability and ampacity of the Te encapsulated by BNNT. (a) Schematic representation of steps for device fabrication. (b) Logarithmic scale and (c) Linear scale plot of I-V characteristics in Te-BNNT devices with different etching time. (d) In-suit temperature-dependent Raman spectra of Te-BNNT. (e) Mapping plot of Raman shift according to (d). (f) Curves of current density versus applied voltage of Te-BNNT devices and corresponding control devices on SiO₂. (g) Comparison of ampacity of Te-BNNT with different metal materials.