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RPPR Final Report
as of 16-Dec-2019

Agency Code:

Proposal Number: 66522MS **Agreement Number: W911NF-15-1-0414**
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Begin Performance Period: 01-Aug-2015 **End Performance Period:** 30-Apr-2019
Report Term: 0-Other

Submitted By: Chenggang Tao Email: cgtao@vt.edu
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STEM Degrees: **STEM Participants:**

Major Goals: The major goals of this research are to investigate novel thermodynamic phenomena of atomically thin layered materials, and to elucidate the interplay between local structures and dynamic behaviors as well as external field effects, by developing time-dependent in situ scanning probe techniques, combined scanning tunneling microscopy (STM) and atomic force microscopy (AFM). The proposed research aims to provide fundamental understanding of the mechanisms governing dynamic processes in two-dimensional (2D) materials. Results obtained from this project will be applied to mass transport, growth, shaping, site-specific heterogeneous catalysis, and gas sensing, and will have significant and broad impact on national security by providing predictive information regarding stability, reliability, and lifetime of devices based on 2D materials, and also for optimizing preparation of 2D materials.

Accomplishments: We have successfully reached these goals. During the whole report period, we have published 12 peer reviewed papers in high impact journals, such as JACS, Nano Letters, Angew. Chem, ACS Nano., etc. (1-12), presented 15 conference presentations in national and international conferences, and received 4 awards. Below are the research activities were performed during the whole period and the highlight of our remarkable accomplishments.
In the first year of ARO support, we have investigated the interfaces in mono- and few-layered MoS2, TiSe2 and graphene. We have made several remarkable observations about these systems, including unique edge states of MoS2 and charge density waves in TiSe2. We have performed experiments on monolayer vacancy island growth induced by a vertical electrical field on TiSe2, which is the beginning of studying dynamic properties of atomically thin TMDs.

These layered materials were prepared on various substrates, including insulating substrates such as SiO2 and sapphire. We have successfully fabricated electrodes on the samples and obtained structural and electronic properties of interfaces in these layered materials, which is essential for the next step to study surface dynamics and electromigration that require multiple electrodes to induce an in-plane electrical field.

In the second year of ARO support, we have investigated interfaces and atomic point defects in 2D materials and heterostructures. Our successful results include the first-time observation of continuous edges in WS2/MoS2 heterobilayers, and characterization of atomic point defects in few layer PtSe2, etc. In addition, our studies on charge density waves and oxidation behaviors in 2D TiSe2 were published in JACS and Angew Chem., respectively.

In the third year of ARO support, our main focus lays on atomic scale investigations of dynamic properties of

interfaces and defects in 2D materials under external stimuli. In our experiments, we have successfully prepared 2D materials on various insulating substrates (such as SiO_2, mica and sapphire) with multiple electrodes and examined the dynamic properties under applied fields, including vertical and lateral electrical fields. We also performed experimental studies of dynamic processes driven by in-plane fields in 2D materials.

During the whole period, our remarkable accomplishments include study of the dynamics of monolayer vacancy island growth on 1T-$TiSe_2$ surfaces driven by vertical electrical fields, investigations of atomic point defects in few-layer $PtSe_2$, the first-time observation of continuous edges in WS_2/MoS_2 heterobilayers with atomic resolution, the kinetic and thermal dynamic properties of the phase transformation in ultrathin In_2Se_3, and etc. The results have been published in 12 peer-reviewed papers in high impact journals.

Training Opportunities: During this project, we have trained 3 phd students and more than 10 undergraduate students.

RPPR Final Report
as of 16-Dec-2019

Results Dissemination: Publications (total 12)

1. H. S. Zheng, Y. Choi, F. Baniasadi, D. K. Hu, L. Y. Jiao, K. Park, C. G. Tao, Visualization of point defects in ultrathin layered 1T-PtSe2. 2D Mater 6, 041005 (2019).
2. F. Zhang, Z. Wang, J. Y. Dong, A. M. Nie, J. Y. Xiang, W. G. Zhu, Z. Y. Liu, C. G. Tao, Atomic-Scale Observation of Reversible Thermally Driven Phase Transformation in 2D In2Se3. ACS Nano 13, 8004-8011 (2019).
3. Y. L. Li, X. Y. Liu, C. H. Chen, J. Duchamp, R. Huang, T. F. Chung, M. Young, T. Chalal, Y. P. Chen, J. R. Heflin, H. C. Dorn, C. G. Tao, Differences in self-assembly of spherical C60 and planar PTCDA on rippled graphene surfaces. Carbon 145, 549-555 (2019).
4. D. K. Hu, T. Q. Zhao, X. F. Ping, H. S. Zheng, L. Xing, X. Z. Liu, J. Y. Zheng, L. F. Sun, L. Gu, C. G. Tao, D. Wang, L. Y. Jiao, Unveiling the Layer-Dependent Catalytic Activity of PtSe2 Atomic Crystals for the Hydrogen Evolution Reaction. Angew Chem Int Edit 58, 6977-6981 (2019).
5. Z. H. Cheng, H. Abuzaid, Y. F. Yu, F. Zhang, Y. L. Li, S. G. Noyce, N. X. Williams, Y. C. Lin, J. L. Doherty, C. G. Tao, L. Y. Cao, A. D. Franklin, Convergent ion beam alteration of 2D materials and metal-2D interfaces. 2D Mater 6, 034005 (2019).
6. H. S. Zheng, S. Valtierra, N. Ofori-Opoku, C. H. Chen, L. F. Sun, S. S. Yuan, L. Y. Jiao, K. H. Bevan, C. G. Tao, Electrical Stressing Induced Monolayer Vacancy Island Growth on TiSe2. Nano Lett 18, 2179-2185 (2018).
7. F. Zhang, Z. Lu, Y. Choi, H. Liu, H. Zheng, L. Xie, K. Park, L. Jiao, C. Tao, Atomically Resolved Observation of Continuous Interfaces between an As-Grown MoS2 Monolayer and a WS2/MoS2 Heterobilayer on SiO2. ACS Applied Nano Materials 1, 2041 (2018).
8. Y. Li, C. Chen, J. Burton, K. Park, J. R. Heflin, C. Tao, Self-Assembled PCBM Bilayers on Graphene and HOPG Examined by AFM and STM. Nanotechnology 29, 185703 (2018).
9. L. F. Sun, C. H. Chen, Q. H. Zhang, C. Sohrt, T. Q. Zhao, G. C. Xu, J. H. Wang, D. Wang, K. Rossnagel, L. Gu, C. G. Tao, L. Y. Jiao, Suppression of the Charge Density Wave State in Two-Dimensional 1T-TiSe2 by Atmospheric Oxidation. Angew Chem Int Edit 56, 8981-8985 (2017).
10. J. Y. Wang, H. S. Zheng, G. C. Xu, L. F. Sun, D. K. Hu, Z. X. Lu, L. N. Liu, J. Y. Zheng, C. G. Tao, L. Y. Jiao, Controlled Synthesis of Two-Dimensional 1T-TiSe2 with Charge Density Wave Transition by Chemical Vapor Transport. J Am Chem Soc 138, 16216-16219 (2016).
11. A. Mills, Y. F. Yu, C. H. Chen, B. V. Huang, L. Y. Cao, C. G. Tao, Ripples near edge terminals in MoS2 few layers and pyramid nanostructures. Appl Phys Lett 108, 081601 (2016). (cover article)
12. Chuanhui Chen, Husong Zheng, Adam Mills, James R. Heflin, C. Tao, Temperature Evolution of Quasi-one-dimensional C60 Nanostructures on Rippled Graphene. Sci Rep 5, 14336 (2015).

Conference presentations (total 15)

1. The 71st Southeastern Regional Meeting of the American Chemical Society (SERMACS), “Molecular Self-assembly on 2D Materials Studied by STM”, Savannah, GA (Oct. 2019) (Invited)
2. 2019 American Physical Society (APS) March Meeting, “Reversible Thermally Driven Phase Transformation in Ultrathin Ferroelectric In2Se3 Layers”, by Fan Zhang, Zhe Wang, Anmin Nie, Jianyong Xiang, Wenguang Zhu, Zhongyuan Liu, Chenggang Tao, Boston, MA (Mar. 2019)
3. 2019 American Physical Society (APS) March Meeting, “Differences in Self-Assembly of Spherical C60 and Planar PTCDA on Rippled Graphene”, by Yanlong Li, Xiaoyang Liu, Chuanhui Chen, James Duchamp, Rong Huang, Ting-Fung Chung, Maxwell Young, Tarek Chalal, Yong Chen, Randy Heflin, Harry Dorn, Chenggang Tao, Boston, MA (Mar. 2019)
4. The 78th Annual Physical Electronics Conference, “Intrinsic Point Defects in Ultrathin 1T-PtSe2”, by H. Zheng, Y. Choi, F. Baniasadi, D. Hu, L. Jiao, K. Park, C. Tao, Durham, NH (Jun. 2018)
5. The 233rd ECS Meeting, “Stable Azaheterometallofullerene M2@C79N (M = Y, Gd, Tb) in Novel Electronic and Magnetic Applications”, by K. M. Kirkpatrick, X., Y. Li, J. Duchamp, C. Tao, A. A. Popov, H. C. Dorn, Seattle, WA (May 2018)
6. 2018 American Physical Society (APS) March Meeting, “STM characterization of point defects in few-layer PtSe2”, by H Zheng, F Baniasadi, Y Choi, K Park, C Tao, Los Angeles, CA (Mar. 2018)
7. 2018 American Physical Society (APS) March Meeting, “Effects of Intrinsic Surface Defects on Morphology and Electronic Structure of a Thin PtSe2 Film from First-principles”, by Y Choi, H Zheng, F Baniasadi, C Tao, K Park, Los Angeles, CA (Mar. 2018)
8. The 64th Annual American Vacuum Society (AVS) Meeting, “STM and STS study of MoS2/WS2 heterostructures grown by chemical vapor deposition”, by F. Zhang, Z. Lu, H. Zheng, K. Park, L. Jiao, C. Tao, Tampa, FL (Oct. 2017)
9. American Physical Society (APS) March Meeting, “STM study of quasi-1D C60 nanostructures on rippled graphene”, New Orleans, LA (Mar. 2017) (talk by graduate student, Chuanhui Chen)
10. The 83rd Annual Meeting of the Southeastern Section of the American Physical Society, “Local Probe Investigation of Interfaces in 2D?Materials”, Charlottesville, VA (Nov. 2016) (invited)

11. The 63rd Annual American Vacuum Society (AVS) Meeting, “Local Probe Investigation of 1D Structures and Interfaces in 2D Materials”, Nashville, TN (Nov. 2016) (invited)
12. The 83rd Annual Meeting of the Southeastern Section of the American Physical Society, “Temperature evolution of quasi-1D C60 nanostructures on rippled graphene”, Charlottesville, VA (Nov. 2016) (talk by graduate student, Chuanhui Chen)
13. 76th Physical Electronics Conference, “Vertical electrical field induced monolayer island growth on TiSe2”, Fayetteville, Arkansas (June 2016)
14. APS March Meeting, “Vertical electrical field induced island growth in layered TiSe2”, Baltimore, Maryland (March 2016)
15. 62nd Annual American Vacuum Society (AVS) Meeting, “Local Probe Investigation of 1D Structures and Interfaces in 2D Materials”, San Jose, California (Nov 2015)

Honors and Awards: Honors and Awards (total 4)
1. Student Travel Award at the 64th Annual American Vacuum Society (AVS) Meeting, received by graduate student, Fan Zhang (Oct. 2017)
2. The Physics Department Graduate Teaching Assistant Excellence Award, Virginia Tech, received by graduate student, Chuanhui Chen (2017)
3. The Center Collaboration Incentive Award from the Center for Soft Matter and Biological Physics, Virginia Tech, received by graduate student, Chuanhui Chen (2017)
4. Student Travel Award at the 83rd Annual Meeting of the Southeastern Section of the American Physical Society, received by graduate student, Chuanhui Chen (2016)

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Chenggang Tao
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Chuanhui Chen
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Husong Zheng
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

RPPR Final Report
as of 16-Dec-2019

Participant Type: Graduate Student (research assistant)
Participant: Fan Zhang
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Title: Investigation of Dynamic Phenomena in Atomically Thin Layered Materials

Grant #: W911NF-15-1-0414

PI: Chenggang Tao

Virginia Tech

Blacksburg, VA 24061

Accomplishments

The major goals of this research are to investigate novel thermodynamic phenomena of atomically thin layered materials, and to elucidate the interplay between local structures and dynamic behaviors as well as external field effects, by developing time-dependent *in situ* scanning probe techniques, combined scanning tunneling microscopy (STM) and atomic force microscopy (AFM). The proposed research aims to provide fundamental understanding of the mechanisms governing dynamic processes in two-dimensional (2D) materials. Results obtained from this project will be applied to mass transport, growth, shaping, site-specific heterogeneous catalysis, and gas sensing, and will have significant and broad impact on national security by providing predictive information regarding stability, reliability, and lifetime of devices based on 2D materials, and also for optimizing preparation of 2D materials.

We have successfully reached these goals. During the whole report period, we have published **12 peer reviewed papers in high impact journals, such as JACS, Nano Letters, Angew. Chem, ACS Nano., etc.** (*1-12*), presented **15 conference presentations in national and international conferences**, and received **4 awards**. Below are the research activities were performed during the whole period and the highlight of our remarkable accomplishments.

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In the third year of ARO support, our main focus lays on atomic scale investigations of dynamic properties of interfaces and defects in 2D materials under external stimuli. In our experiments, we

have successfully prepared 2D materials on various insulating substrates (such as SiO_2, mica and sapphire) with multiple electrodes and examined the dynamic properties under applied fields, including vertical and lateral electrical fields. We also performed experimental studies of dynamic processes driven by in-plane fields in 2D materials.

During the whole period, our remarkable accomplishments include study of the dynamics of monolayer vacancy island growth on 1T-$TiSe_2$ surfaces driven by vertical electrical fields, investigations of atomic point defects in few-layer $PtSe_2$, the first-time observation of continuous edges in WS_2/MoS_2 heterobilayers with atomic resolution, the kinetic and thermal dynamic properties of the phase transformation in ultrathin In_2Se_3, and etc. The results have been published in 12 peer-reviewed papers in high impact journals. Some highlights of our work are listed below.

1. Intrinsic Point Defects in Ultrathin Layered $PtSe_2$ (2D Materials 6, 041005 (2019))

Among 2D transition metal dichalcogenides (TMDs), platinum diselenide ($PtSe_2$) stands at a unique place in the sense that it undergoes a phase transition from type-II Dirac semimetal to indirect-gap semiconductor as thickness decreases. Defects in 2D TMDs are ubiquitous and they play crucial roles in understanding electronic, optical, and magnetic properties and tailoring them for desirable applications. Here we investigate intrinsic point defects in ultrathin *1T*-$PtSe_2$ layers grown on mica through the chemical vapor transport method, using STM and first-principles calculations. We found five distinct defects from STM topography images and obtained the local density of states of the defects. By combining the STM results with the first-principles calculations, we identified the types and characteristics of these defects, which are Pt vacancies at the topmost and next monolayers, Se vacancies in the topmost monolayer, and Se antisites at Pt sites within the topmost monolayer. Interestingly, our study shows that the Se antisite defects are the most abundant with the lowest formation energy in a Se-rich growth condition, in contrast to cases of 2D TMD MoS_2 family. Our findings will directly influence tuning of carrier mobility, charge carrier relaxation, and electron-hole recombination rates by defect engineering or growth condition in thin semiconductor $PtSe_2$ layers.

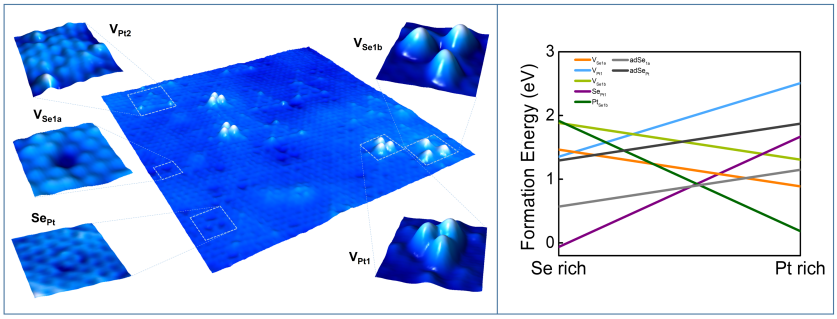


Figure 1. Left: Atomically resolved STM image of various intrinsic point defects in few-layer *1T*-$PtSe_2$. Inset: zoom-in images of each type of defects. Right: Formation energies for the different types of point defects (2D Materials 6, 041005 (2019))

2. Reversible Thermally Driven Phase Transformation in 2D Ferroelectric In_2Se_3 (ACS Nano 13, 8004 (2019))

Phase transformation in emerging 2D materials is crucial for understanding and controlling the interplay between structure and electronic properties. In this work, we investigate 2D In_2Se_3 synthesized via chemical vapor deposition, a recently discovered 2D ferroelectric material. We observed that In2Se3 layers with thickness ranging from a single layer to ~20 layers stabilized at the β phase with a superstructure at room temperature. At around 180 K, the β phase converted to a more stable β′ phase that was distinct from previously reported phases in 2D In2Se3. The kinetics of the reversible thermally driven β-to-β′ phase transformation was investigated by temperature- dependent transmission electron microscopy and Raman spectroscopy, corroborated with the expected minimum-energy pathways obtained from our first-principles calculations. Furthermore, density functional theory calculations reveal in- plane ferroelectricity in the β′ phase. Scanning tunneling spectroscopy measurements show that the indirect bandgap of monolayer β′ In_2Se_3 is 2.50 eV, which is larger than that of the multilayer form with a measured value of 2.05 eV. Our results on the reversible thermally driven phase transformation in 2D In_2Se_3 with thickness down to the monolayer limit and the associated electronic properties will provide insights to tune the functionalities of 2D In_2Se_3 and other emerging 2D ferroelectric materials and shed light on their numerous potential applications (e.g., nonvolatile memory devices).

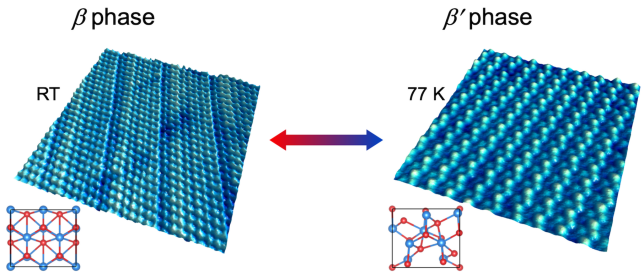


Figure 2. Atomic-Scale Observation of Reversible Thermally Driven Phase Transformation in 2D In_2Se_3 (ACS Nano 13, 8004 (2019)).

3. Electrical Stressing Induced Monolayer Vacancy Island Growth on $TiSe_2$ (Nano Letters 18, 2179 (2018))

Using vacancy monolayer islands on $TiSe_2$ surfaces as a model system, we have observed nonlinear area evolution and growth from triangular to hexagonal driven by electrical stressing. The observed growth dynamics represent a 2D departure from the linear area growth law expected for bulk vacancy clustering. Our simulations of monolayer island evolution using phase-field modeling and first-principles calculations are in good agreement with our experimental observations, and point toward preferential edge atom dissociation under STM scanning driving the observed nonlinear area growth. We further quantified a parabolic growth rate dependence with respect to the tunneling current

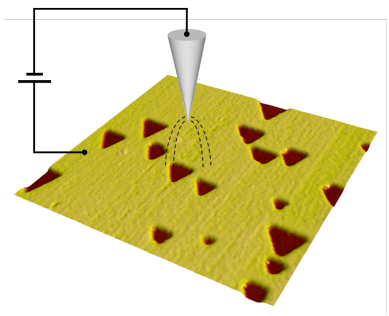


Figure 3. Left: Schematic illustration of the experiment setup for exploring the dynamics of monolayer vacancy island growth on 1T-$TiSe_2$. Right: Square root of the area of an island vs time and the calculated result of a phase-field simulation (Nano Letters 18, 2179 (2018)).

magnitude. The results could be potentially important for device reliability in systems containing ultrathin transition metal dichalcogenides and related 2D materials subject to electrical stressing.

4. Atomically Resolved Observation of Interfaces in 2D Heterostructures on SiO_2 (ACS Appl. Nano Mat. 1, 2041 (2018))

2D heterostructures synthesized through the chemical vapor deposition (CVD) method allow the creation and tuning of intriguing electronic and optical properties of 2D materials. Especially, local structures in the heterostructures, such as interfaces, edges, and point defects, are critical for their wide range of potential applications. However, up to now atomic-scale measurements of local structures in as-grown 2D heterostructures on insulating substrates are still rare. Here we report our scanning tunneling microscopy and spectroscopy study of as-grown MoS_2 monolayer and WS_2/MoS_2 heterobilayer on SiO_2. The heterobilayer appears smoother than the MoS_2 monolayer, with a root-mean-square roughness of 0.230 nm in the former and 0.329 nm in the latter. For the first time, to our knowledge, we directly observed a novel type of continuous interface between the MoS_2 monolayer and the top layer of the heterobilayer with atomic resolution. Our STS results and density functional theory calculations revealed the band gaps of the heterobilayer and the MoS_2 monolayer. The finding of the continuous interfaces and the systematic characterizations could have significant impacts on the optimization and design of new 2D heterostructures.

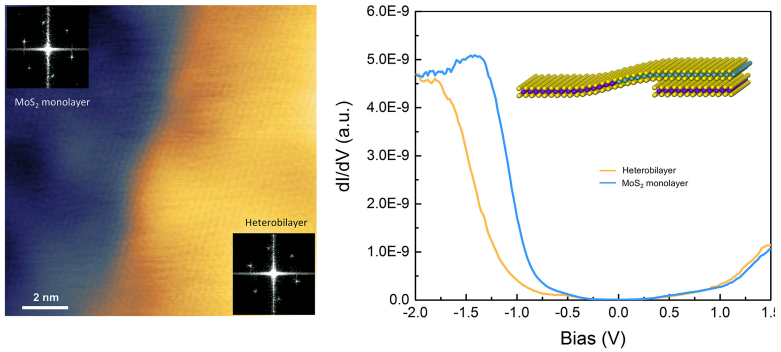


Figure 4. Left: Atomically resolved STM image of a continuous interface between as grown MoS_2 monolayer and WS_2/MoS_2 heterobilayer on SiO_2. Inset: FFT images of the monolayer and heterobilayer regions. Right: dI/dV spectra for the MoS_2 monolayer (blue) and the heterobilayer (yellow). Inset, the schematic drawing of the continuous interfaces (ACS Appl. Nano Mat. 1, 2041 (2018)).

5. Self-Assembly of C_{60} and PTCDA on Rippled graphene (Carbon 145, 549 (2019))

It was recently recognized that graphene and other 2D materials exhibit nonplanar aberrations such as a rippled surface. Understanding the self-assembly of organic semiconductor molecules on monolayer 2D curved graphene surfaces is a paramount issue for ultimate application in semiconductor and optoelectronic devices. Herein, we report on the preparation of C_{60} and perylenetetracarboxylic dianhydride (PTCDA) molecules absorbed on a rippled graphene surface. We find that the spherical C_{60} molecules form a quasi-hexagonal close packed (hcp) structure, while the planar PTCDA molecules form a disordered herringbone structure. These 2D layered systems have been characterized by experimental STM imaging and computational density functional theory (DFT) approaches. The DFT computational results exhibit interaction

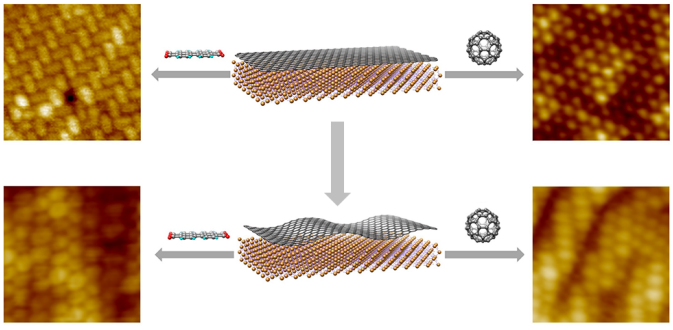


Figure 5. Schematic drawings and STM images revealing the differences in self-assembly of spherical C_{60} and planar PTCDA on rippled graphene surfaces (Carbon 145, 549 (2019)).

energies for absorbed molecule/rippled graphene complexes located in the 2D graphene valley sites that are significantly larger in comparison with absorbed idealized planar/molecule graphene 2D complexes. In addition, we report that the absorbed PTCDA molecules prefer different orientations when the rippled graphene peak regions are compared to the valley regions. This difference in orientations causes the PTCDA molecules to form a disordered herringbone structure on the rippled graphene surface.

6. Edges and domain boundaries in MoS_2 nanostructures (App. Phys. Lett. 108, 081601 (2016), cover article)

We have examined CVD-grown MoS_2 mono- and few-layer nanoplatelets and pyramid nanostructures on gallium nitride (GaN) and highly oriented pyrolytic graphite (HOPG) respectively. From STM images, we observed that there are ripple structures near characteristic curved regions close to the MoS_2 edge terminals (Figures 6a and 6b). These ripple structures have typical heights of 11.0 ± 3.5 Å and widths of 80.3 ± 20.4 Å.

We further examined a MoS_2 nanostructure with much higher density of edges, MoS_2 nanopyramids. The curving features observed in both MoS_2 few-layer nanoplatelets and nanopyramids occur along the edges as well as flattened corners (which is similar to the hexagonal shaped monolayer islands), indicating that both types of edges are curving down to the lower MoS_2 layer. The scanning tunneling spectroscopy (STS) measurements on the basal planes of the MoS_2 terraces show a band gap of 1.44 ± 0.12 eV that agrees well with the band gap of bulk MoS_2 from previous studies. Spectroscopies on the curving part near the corners of the pyramids, however, show a band gap of 1.96 ± 0.10 eV, consistent with past photoluminescence spectroscopy and STS measurements of the monolayer MoS_2 band gap. Yet, compared to previous STS measurements of the monolayer MoS_2 band gap on graphite, our reported value is lower by up to 0.5 eV. This discrepancy in band gap width could be due to a result of different interactions between the underlying terrace, the mismatch at the MoS_2-substrate interface, and the curving parts near the edge terminals or terrace basal planes with the layer above. On the basal terrace plane, the layer interaction with lower layers is the same as bulk MoS_2. It appears that there is decoupling around the edges and corners from both the bulk and substrate below that causes a shift in electronic properties from MoS_2 in its bulk state to MoS_2 as an isolated monolayer.

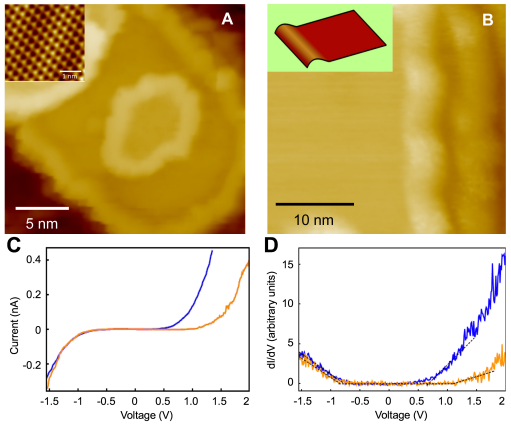


Figure 6. Constant current STM images of few-layered MoS_2. (A) A small MoS_2 island showing curved edges. The upper left inset shows an atomic resolution image of the MoS_2 top layer. (B) A zoom-in image of the curved MoS_2 edges. (C) I-V and (D) dI/dV spectra taken on the basal planes of the MoS_2 pyramid terrace (blue) and on the curved regions of the MoS_2 pyramid terraces (yellow) (APL, 108, 081601 (2016)).

7. CDW in few-layer $TiSe_2$ (J. Am. Chem. Soc. 138, 16216 (2016))

We have characterized the atomic crystal structure of the as-grown $TiSe_2$ flakes (~ 5 nm thick) with STM at both room temperature and low temperature. To obtain the intrinsic surface structure of the $TiSe_2$ flakes, we deposited metal contacts to the flakes grown on sapphire using shadow mask for direct STM imaging without transferring them to conducting substrates. The large-scale STM image in Fig. 7b of the as-grown $TiSe_2$ flakes obtained at room temperature shows very smooth surface compared with the films grown by MBE, and in some regions small vacancy islands were resolved with a depth of ~ 0.6 nm, in accordance with the c-axis unit-cell length of bulk $TiSe_2$ as sketched in Fig. 7a, which may be originated from the defects formed during the growth or by post-growth surface oxidation. The atomically resolved STM image shows well-ordered hexagonal packing of Se atoms with an interatomic spacing of 3.5 ± 0.1 Å (Fig. 7c), in consistence with the atomic structure of 1T-$TiSe_2$ as illustrated in Figure 7a. At T = 77 K, the atomic scale STM images and corresponding 2D fast Fourier transform (FFT) image reveal a 2 × 2 superlattice suggesting the occurrence of CDW order at low temperature (Figures 7d and 7e).

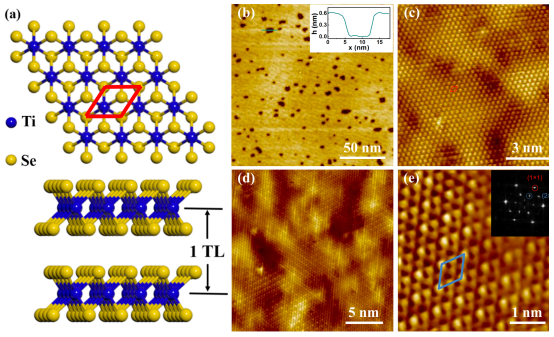


Figure 7. (a) Schematic crystal structure of 1-T $TiSe_2$. (b) Large-scale STM topographic image of the as-grown $TiSe_2$ flakes at room temperature (V_s = 1.0 V, I = 0.2 nA). The inset is the line profile crossing a vacancy island marked by the green line. (c) Atomically resolved STM topographic image at room temperature (V_s = 1.0 V, I = 0.2 nA). (d) and (e) At T = 77 K, atomically resolved STM topographic images ((d) V_s = 0.2 V, I = 0.3 nA and (e) V_s = 0.1 V, I = 0.4 nA). Inset, the corresponding FFT image of (e) (JACS 138, 16216 (2016)).

8. Fullerene self-assembly nanostructures on graphene (Sci. Rep. 5, 14336 (2015))

We experimentally realize quasi-1D fullerene nanostructures on rippled graphene by utilizing the linear periodic potential in graphene as a template (Fig. 8). C_{60} molecules were deposited onto graphene grown by the CVD method on Cu foil. Through carefully controlling the subtle balance between the weak periodic potential and the surface mobility of C_{60}, C_{60} molecules on rippled graphene are arranged into a novel 1D C_{60} chain structure with widths ranging from two to three molecules wide. To the best of our knowledge, this is the first experimental realization of 1D C_{60} structures on graphene. Highly ordered 1D molecular configurations are excellent model systems and prototypes of 1D quantum confinement of electronic states, and thus the results may have potential importance in electronic nanodevices, spintronics and solid-state quantum computation.

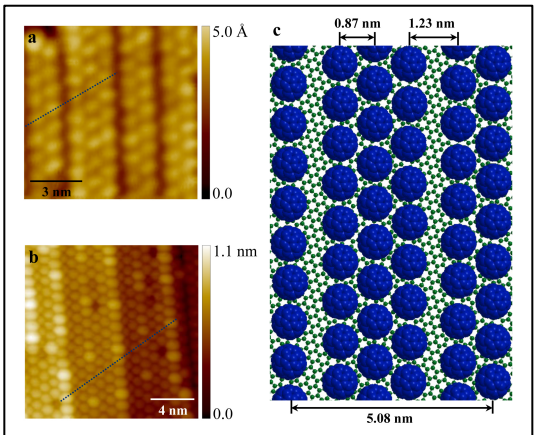


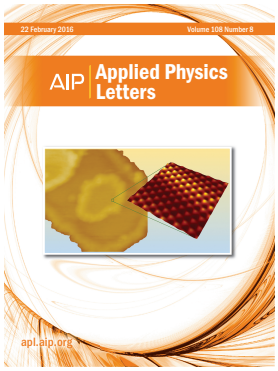
Figure 8. Quasi-1D C_{60} nanostructures on rippled graphene (a) STM image of bimolecular and trimolecular C_{60} chains. (b) STM image of the hexagonal close packed quasi-1D stripes. (c) Schematic model of C_{60} chains in (a).

These quasi-1D structures can be further tuned by varying the temperature, from a chain structure with widths of two or three C_{60} molecules, transferring to a quasi-hexagonal close packed 1D stripe structure (Fig. 8). In our experiments, temperature is the main tunable parameter. Based on the subtle balance between the C_{60}-C_{60} intermolecular and the

C_{60}-graphene interactions, as well as the size of the graphene ripples due to the moiré patterns, we expect that the quasi-1D C_{60} structures on rippled graphene can be further tuned and controlled by varying the size of the ripples, the coverage of adsorbed C_{60} molecules, and the temperature.

Publications (total 12)

1. H. S. Zheng, Y. Choi, F. Baniasadi, D. K. Hu, L. Y. Jiao, K. Park, C. G. Tao, Visualization of point defects in ultrathin layered 1T-$PtSe_2$. ***2D Mater*** **6**, 041005 (2019).
2. F. Zhang, Z. Wang, J. Y. Dong, A. M. Nie, J. Y. Xiang, W. G. Zhu, Z. Y. Liu, C. G. Tao, Atomic-Scale Observation of Reversible Thermally Driven Phase Transformation in 2D In_2Se_3. ***ACS Nano*** **13**, 8004-8011 (2019).
3. Y. L. Li, X. Y. Liu, C. H. Chen, J. Duchamp, R. Huang, T. F. Chung, M. Young, T. Chalal, Y. P. Chen, J. R. Heflin, H. C. Dorn, C. G. Tao, Differences in self-assembly of spherical C_{60} and planar PTCDA on rippled graphene surfaces. ***Carbon*** **145**, 549-555 (2019).
4. D. K. Hu, T. Q. Zhao, X. F. Ping, H. S. Zheng, L. Xing, X. Z. Liu, J. Y. Zheng, L. F. Sun, L. Gu, C. G. Tao, D. Wang, L. Y. Jiao, Unveiling the Layer-Dependent Catalytic Activity of $PtSe_2$ Atomic Crystals for the Hydrogen Evolution Reaction. ***Angew Chem Int Edit*** **58**, 6977-6981 (2019).
5. Z. H. Cheng, H. Abuzaid, Y. F. Yu, F. Zhang, Y. L. Li, S. G. Noyce, N. X. Williams, Y. C. Lin, J. L. Doherty, C. G. Tao, L. Y. Cao, A. D. Franklin, Convergent ion beam alteration of 2D materials and metal-2D interfaces. ***2D Mater*** **6**, 034005 (2019).
6. H. S. Zheng, S. Valtierra, N. Ofori-Opoku, C. H. Chen, L. F. Sun, S. S. Yuan, L. Y. Jiao, K. H. Bevan, C. G. Tao, Electrical Stressing Induced Monolayer Vacancy Island Growth on $TiSe_2$. ***Nano Lett*** **18**, 2179-2185 (2018).
7. F. Zhang, Z. Lu, Y. Choi, H. Liu, H. Zheng, L. Xie, K. Park, L. Jiao, C. Tao, Atomically Resolved Observation of Continuous Interfaces between an As-Grown MoS_2 Monolayer and a WS_2/MoS_2 Heterobilayer on SiO_2. ***ACS Applied Nano Materials*** **1**, 2041 (2018).
8. Y. Li, C. Chen, J. Burton, K. Park, J. R. Heflin, C. Tao, Self-Assembled PCBM Bilayers on Graphene and HOPG Examined by AFM and STM. ***Nanotechnology*** **29**, 185703 (2018).
9. L. F. Sun, C. H. Chen, Q. H. Zhang, C. Sohrt, T. Q. Zhao, G. C. Xu, J. H. Wang, D. Wang, K. Rossnagel, L. Gu, C. G. Tao, L. Y. Jiao, Suppression of the Charge Density Wave State in Two-Dimensional 1T-$TiSe_2$ by Atmospheric Oxidation. ***Angew Chem Int Edit*** **56**, 8981-8985 (2017).



10. J. Y. Wang, H. S. Zheng, G. C. Xu, L. F. Sun, D. K. Hu, Z. X. Lu, L. N. Liu, J. Y. Zheng, C. G. Tao, L. Y. Jiao, Controlled Synthesis of Two-Dimensional 1T-$TiSe_2$ with Charge Density Wave Transition by Chemical Vapor Transport. ***J Am Chem Soc*** **138**, 16216-16219 (2016).
11. A. Mills, Y. F. Yu, C. H. Chen, B. V. Huang, L. Y. Cao, C. G. Tao, Ripples near edge terminals in MoS_2 few layers and pyramid nanostructures. ***Appl Phys Lett*** **108**, 081601 (2016). (cover article)
12. Chuanhui Chen, Husong Zheng, Adam Mills, James R. Heflin, C. Tao, Temperature Evolution of Quasi-one-dimensional $C6_0$ Nanostructures on Rippled Graphene. ***Sci Rep*** **5**, 14336 (2015).

Conference presentations (total 15)

1. The 71st Southeastern Regional Meeting of the American Chemical Society (SERMACS), "Molecular Self-assembly on 2D Materials Studied by STM", Savannah, GA (Oct. 2019) (Invited)
2. 2019 American Physical Society (APS) March Meeting, "Reversible Thermally Driven Phase Transformation in Ultrathin Ferroelectric In_2Se_3 Layers", by Fan Zhang, Zhe Wang, Anmin Nie, Jianyong Xiang, Wenguang Zhu, Zhongyuan Liu, Chenggang Tao, Boston, MA (Mar. 2019)
3. 2019 American Physical Society (APS) March Meeting, "Differences in Self-Assembly of Spherical C_{60} and Planar PTCDA on Rippled Graphene", by Yanlong Li, Xiaoyang Liu, Chuanhui Chen, James Duchamp, Rong Huang, Ting-Fung Chung, Maxwell Young, Tarek Chalal, Yong Chen, Randy Heflin, Harry Dorn, Chenggang Tao, Boston, MA (Mar. 2019)
4. The 78th Annual Physical Electronics Conference, "Intrinsic Point Defects in Ultrathin 1T-$PtSe_2$", by H. Zheng, Y. Choi, F. Baniasadi, D. Hu, L. Jiao, K. Park, C. Tao, Durham, NH (Jun. 2018)
5. The 233rd ECS Meeting, "Stable Azaheterometallofullerene $M_2@C_{79}N$ (M = Y, Gd, Tb) in Novel Electronic and Magnetic Applications", by K. M. Kirkpatrick, X., Y. Li, J. Duchamp, C. Tao, A. A. Popov, H. C. Dorn, Seattle, WA (May 2018)
6. 2018 American Physical Society (APS) March Meeting, "STM characterization of point defects in few-layer $PtSe_2$", by H Zheng, F Baniasadi, Y Choi, K Park, C Tao, Los Angeles, CA (Mar. 2018)
7. 2018 American Physical Society (APS) March Meeting, "Effects of Intrinsic Surface Defects on Morphology and Electronic Structure of a Thin PtSe2 Film from First-principles", by Y Choi, H Zheng, F Baniasadi, C Tao, K Park, Los Angeles, CA (Mar. 2018)
8. The 64th Annual American Vacuum Society (AVS) Meeting, "STM and STS study of MoS_2/WS_2 heterostructures grown by chemical vapor deposition", by F. Zhang, Z. Lu, H. Zheng, K. Park, L. Jiao, C. Tao, Tampa, FL (Oct. 2017)
9. American Physical Society (APS) March Meeting, "STM study of quasi-1D C_{60} nanostructures on rippled graphene", New Orleans, LA (Mar. 2017) (talk by graduate student, Chuanhui Chen)
10. The 83rd Annual Meeting of the Southeastern Section of the American Physical Society, "Local Probe Investigation of Interfaces in 2D Materials", Charlottesville, VA (Nov. 2016) (invited)
11. The 63rd Annual American Vacuum Society (AVS) Meeting, "Local Probe Investigation of 1D Structures and Interfaces in 2D Materials", Nashville, TN (Nov. 2016) (invited)
12. The 83rd Annual Meeting of the Southeastern Section of the American Physical Society, "Temperature evolution of quasi-1D C_{60} nanostructures on rippled graphene", Charlottesville, VA (Nov. 2016) (talk by graduate student, Chuanhui Chen)
13. 76th Physical Electronics Conference, "Vertical electrical field induced monolayer island growth on TiSe2", Fayetteville, Arkansas (June 2016)

14. APS March Meeting, “Vertical electrical field induced island growth in layered TiSe2”, Baltimore, Maryland (March 2016)
15. 62nd Annual American Vacuum Society (AVS) Meeting, “Local Probe Investigation of 1D Structures and Interfaces in 2D Materials”, San Jose, California (Nov 2015)

Honors and Awards (total 4)

1. Student Travel Award at the 64th Annual American Vacuum Society (AVS) Meeting, received by graduate student, Fan Zhang (Oct. 2017)
2. The Physics Department Graduate Teaching Assistant Excellence Award, Virginia Tech, received by graduate student, Chuanhui Chen (2017)
3. The Center Collaboration Incentive Award from the Center for Soft Matter and Biological Physics, Virginia Tech, received by graduate student, Chuanhui Chen (2017)
4. Student Travel Award at the 83rd Annual Meeting of the Southeastern Section of the American Physical Society, received by graduate student, Chuanhui Chen (2016)

Major goals

The major goals of this research are to investigate novel thermodynamic phenomena of atomically thin layered materials, and to elucidate the interplay between local structures and dynamic behaviors as well as external field effects, by developing time-dependent in situ scanning probe techniques, combined scanning tunneling microscopy (STM) and atomic force microscopy (AFM). The proposed research aims to provide fundamental understanding of the mechanisms governing dynamic processes in two-dimensional (2D) materials. Results obtained from this project will be applied to mass transport, growth, shaping, site-specific heterogeneous catalysis, and gas sensing, and will have significant and broad impact on national security by providing predictive information regarding stability, reliability, and lifetime of devices based on 2D materials, and also for optimizing preparation of 2D materials.

In Year 1, the goals are to use STM and AFM to characterize atomically thin transition metal dichalcogenides (TMDs). The focus is on local structural and electronic behaviors of various interfaces in these materials. These goals have been achieved by comparative studies of different TMDs (mono- and few-layer MoS_2, $TiSe_2$ and WS2) and graphene on various substrates.

In Year 2, the goal was to use STM and AFM to characterize interfaces and atomic point defects in 2D materials, perform dynamic investigation and start the electromigration measurements. These goals have been achieved by systematic studies of atomic point defects in 2D $PtSe_2$ and interfaces in a 2D heterostructure, MoS2/WS2 heterobilayer. We also investigated how vertical electrical field induced monolayer island growth in 1T-$TiSe_2$. With the capability to fabricate multiple electrodes to 2D materials on insulating substrates, we are now excited to start our research on electromigration and related dynamic behaviors in 2D materials in the third year of the project.

In Year 3, our focus was to perform dynamic investigation and dynamics under external stimuli in 2D materials that have been investigated on structural and electrical properties in Year 1 and Year 2. These goals have been achieved by systematic studies of dynamic behaviors of defects (point defects and step edges) and interfaces in 2D materials (including MoS_2, WS_2, $PtSe_2$, and $TiSe_2$) and 2D heterostructures (e.g., MoS_2/WS_2 heterostructure). We have investigated step edge dynamics in $TiSe_2$ driven by electrical stressing, dynamic behaviors of adsorbates on curved 2D materials by using a model system of C_{60} and PTCDA on ripple graphene, and thermodynamics-driven phase transformation in ultrathin In_2Se_3.

Future Plans

The goals of this research to investigate dynamic behaviors in 2D materials have been successfully achieved by systematic studies of dynamic behaviors of defects (point defects and step edges) and interfaces in 2D materials (including MoS_2, WS_2, $PtSe_2$, and $TiSe_2$) and 2D heterostructures (e.g., MoS_2/WS_2 heterobilayer). We have investigated step edge dynamics in $TiSe_2$ driven by electrical stressing, dynamic behaviors of adsorbates on curved 2D materials by using a model system of C_{60} and PTCDA on ripple graphene, and thermodynamics-driven phase transformation in ultrathin In_2Se_3.

We are now looking forward to perform a new project that will focus on nonequilibrium dynamic behaviors of atomic defects and interfaces in emerging quantum materials, aiming for their applications in quantum information and science. We have demonstrated that atomic defects and interfaces, which are promising candidates for quantum computing, are sensitive to thermal effects and external stimuli. In the new project, we will focus on how a "noisy" thermal environment and external stimuli drive atomic defects and interfaces out of equilibrium and how to affect their quantum conference and structural stability, which are key parameters for their applications in quantum information and science.