



AFRL-AFOSR-JP-TR-2022-0046

Integrated flexible energy system based on two-dimensional (2D) Materials

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06/02/2022
Final Technical Report

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REPORT DOCUMENTATION PAGE

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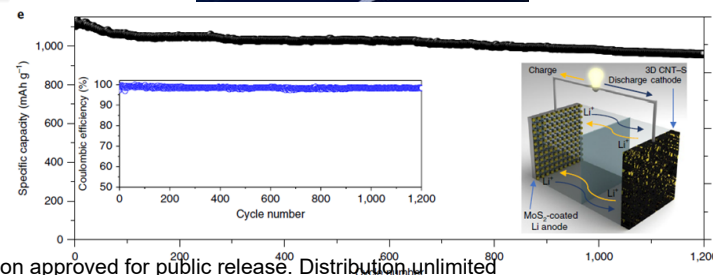
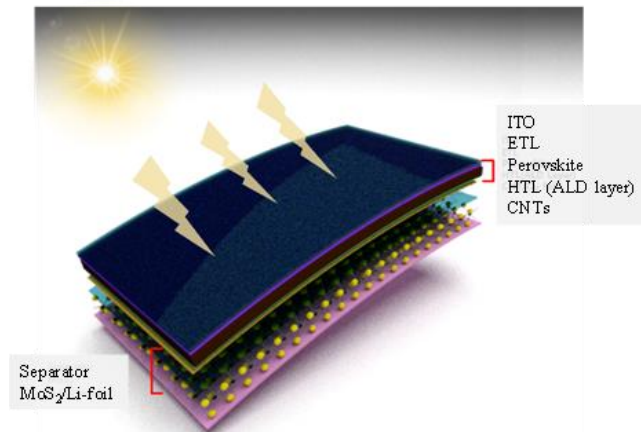
1. REPORT DATE 20220602	2. REPORT TYPE Final	3. DATES COVERED	
		START DATE 20180702	END DATE 20220101
4. TITLE AND SUBTITLE Integrated flexible energy system based on two-dimensional (2D) Materials			
5a. CONTRACT NUMBER	5b. GRANT NUMBER FA2386-18-1-4075	5c. PROGRAM ELEMENT NUMBER	
5d. PROJECT NUMBER	5e. TASK NUMBER	5f. WORK UNIT NUMBER	
6. AUTHOR(S) Wonbong Choi			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF NORTH TEXAS 1155 UNION CIR #305250 DENTON, TX 76203 USA			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AOARD UNIT 45002 APO AP 96338-5002		10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR IOA	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-JP-TR-2022-0046
12. DISTRIBUTION/AVAILABILITY STATEMENT A Distribution Unlimited: PB Public Release			
13. SUPPLEMENTARY NOTES			
14. ABSTRACT Development of integrated, flexible, self-powered energy system with two major functionalities - high efficiency planar perovskite solar cell for energy conversion (> 20% efficiency) and 2D Li-S rechargeable battery for energy storage (> 500 Wh/kg and 1,000 cycles)			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U	SAR 23
19a. NAME OF RESPONSIBLE PERSON TONY KIM			19b. PHONE NUMBER (Include area code) 315-227-7008



NRF/AFOSR Joint Research Program Final Report (US Team)



- **Title:** Integrated Flexible Energy System based on Two-Dimensional (2D) Materials
- **Award Number:** FA2386-18-1-4075
- **Project Period:** July 2, 2018 – July 1, 2021 (* No cost extension till January 1, 2022)
- **Principle Investigators:**
(US-PI) Prof. Wonbong Choi (*University of North Texas*),
(KR-PI) Prof. Hyunjung Shin (*Sungkyunkwan Univ, Korea*)





NRF/AFOSR Joint Research Program Summary (US Team report)



• Project Vision

Development of integrated, flexible, self-powered energy system with two major functionalities - high-efficiency planar perovskite solar cell for energy conversion (> 20% efficiency) and 2D Li-S rechargeable battery for energy storage (> 500 Wh/kg and 1,000 cycles)

• USAF / DoD / Industry Relationship Highlights

- Produced two (2) patents and seven (7) journal papers in high-impact journals.
- Developed electrocatalysts coated 3D CNF cathode and hybrid electrolyte resulting in high energy density Li-S battery (>500Wh/kg).
- Meeting with AF researchers for presenting the progress of the project @ MRS 2019 Fall meeting.
- Two patents have been licensed to a start-up company to perform development of the technology for practical application (awarded ONR-STTR project)
- An in-situ Raman battery cell tester has been installed and performed ion transport study during the No Cost Extension period.

• (Team) Collaboration Synergy Highlights

- UNT researchers visited SKKU and performed characterization of the integrated energy system, & sent cathode samples to SKKU and performed its device integration & characterization.
- Reported unusually high ionic conductivity on 2D MoS₂ nanofilm exceeding 1 S/cm, which is more than two orders of magnitude higher than the state-of-the-art solid ionic materials. (ACS Nano)

• Follow-on awards enabled by Korea nano/AOARD support

- DURIP grant (FA9550-21-1-0162) has been awarded for studying in-situ ion transport in 2D materials.
- This work has been highlighted in UNT: 1. "Studying High-charge Transport in 2D Materials" (<https://research.unt.edu/news/studying-high-charge-transport-2d-materials>); 2. Research Leadership Award, UNT (<https://vpaa.unt.edu/fs/recognition/SFE-award-winners21>)

• Top Cited Papers

- 6 journal papers and two patents have been produced
- Nanoengineering to achieve high efficiency practical lithium-sulfur batteries, Nanoscale Horizons, 1, 467 (2020)
- Mixed Phase 2D Mo_{0.5}W_{0.5}S₂ Alloy as a Multi-Functional Electrocatalyst for a High-Performance Cathode in Li-S Batteries, Jr. Materials Chemistry A (2020)
- Unusual-High Ion Conductivity in Large-Scale Patternable Two-Dimensional MoS₂ Film, ACS Nano (2021)



Unusual-High Ion Conductivity in Large-Scale Patternable Two-Dimensional MoS₂ Film



- The advancement of ion transport applications will require the development of new materials with a high ionic conductivity that is stable, scalable, and micro-patternable.
- We report unusually high ionic conductivity of Li⁺, Na⁺, and K⁺ in 2D MoS₂ nanofilm exceeding 1 S/cm, which is more than two orders of magnitude when compared to that of conventional solid ionic materials.
- The high ion conductivity of different cations can be explained by the mitigated activation energy *via* percolative ion channels in 2H-MoS₂, including the 1D ion channel at the grain boundary, as confirmed by modeling and analysis.
- We obtain field-effect modulation of ion transport with a high on/off ratio. The ion channel is large-scale patternable by conventional lithography, and the thickness can be tuned down to a single atomic layer.

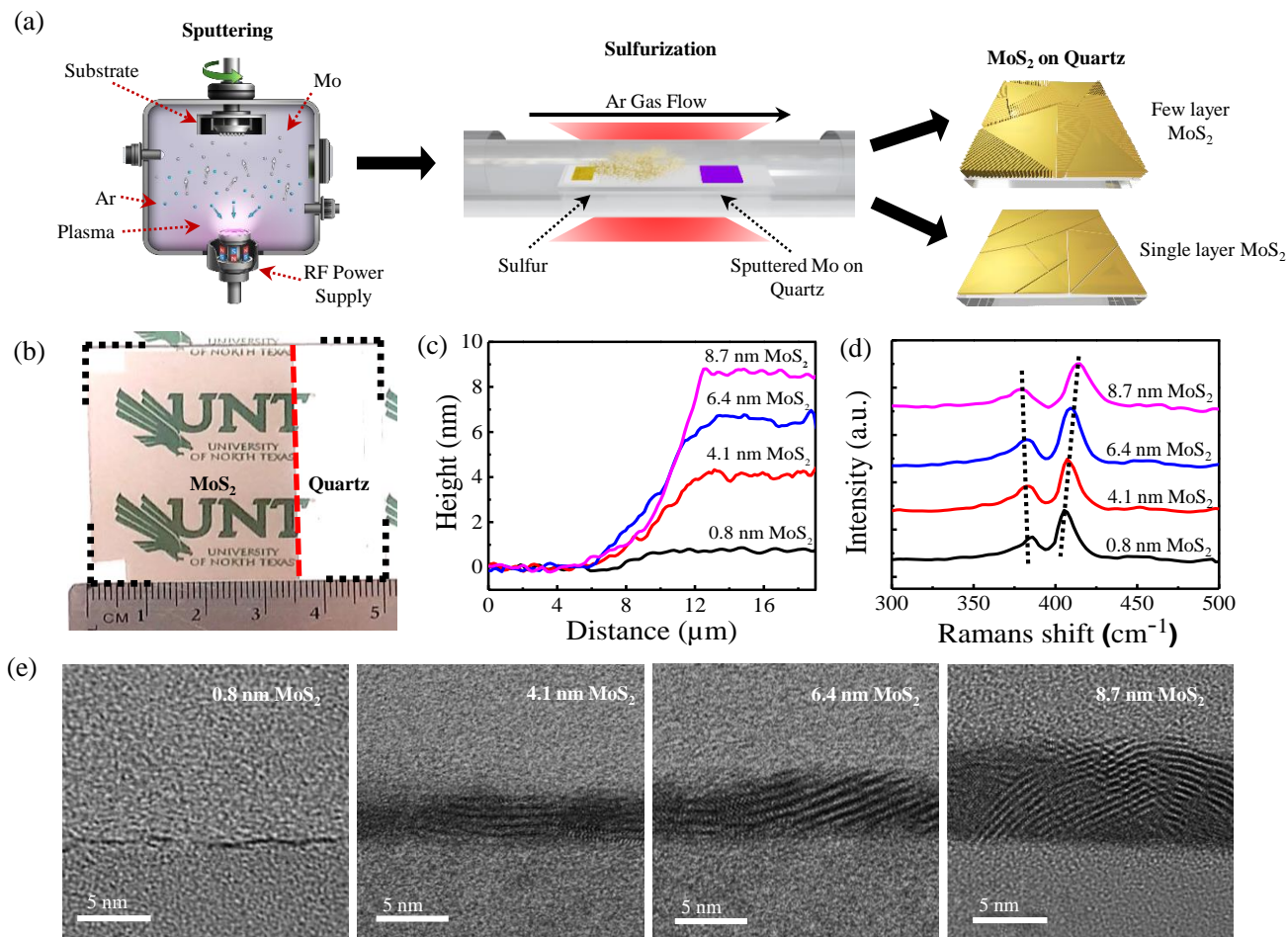
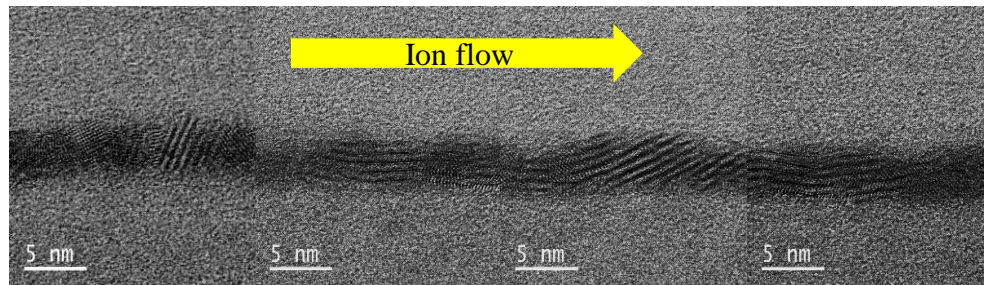
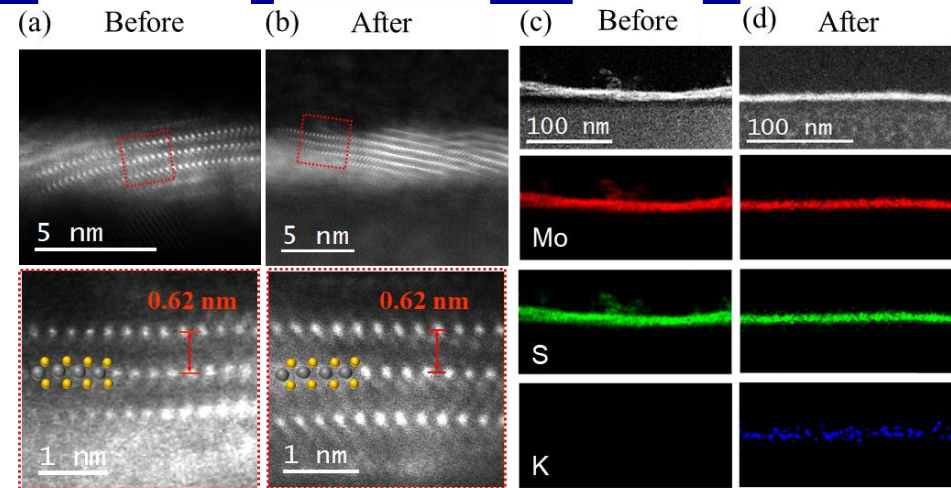
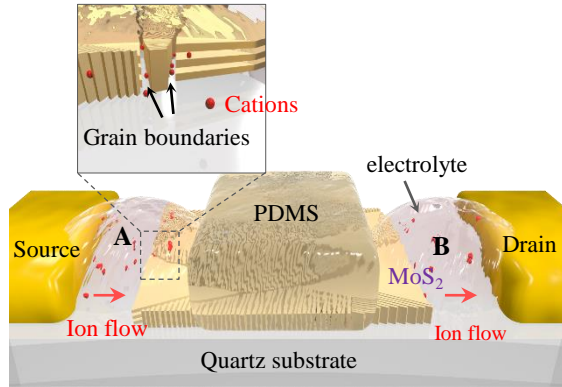


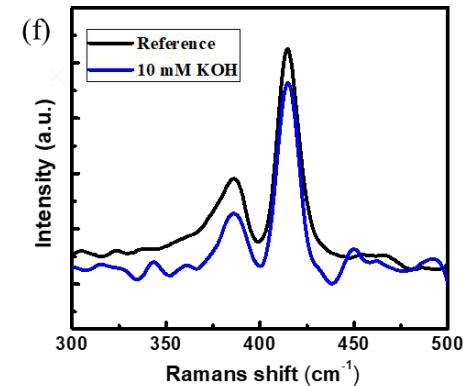
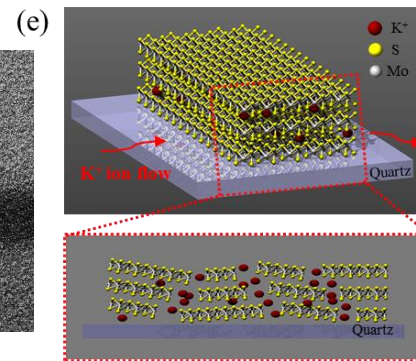
Figure. (a) Schematic diagram of the MoS₂ nanofilm fabrication processes. (b) Optical image for MoS₂ nanofilm on a quartz substrate. (c) AFM height profiles showing the thickness of synthesized MoS₂ nanofilm. (d) The Raman spectrum of MoS₂ nanofilm on a quartz substrate. (e) The cross-sectional HRTEM images of MoS₂ nanofilm with varying thickness.



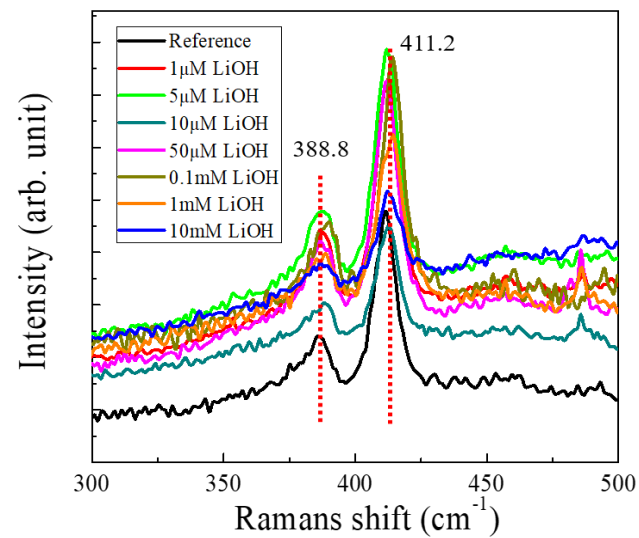
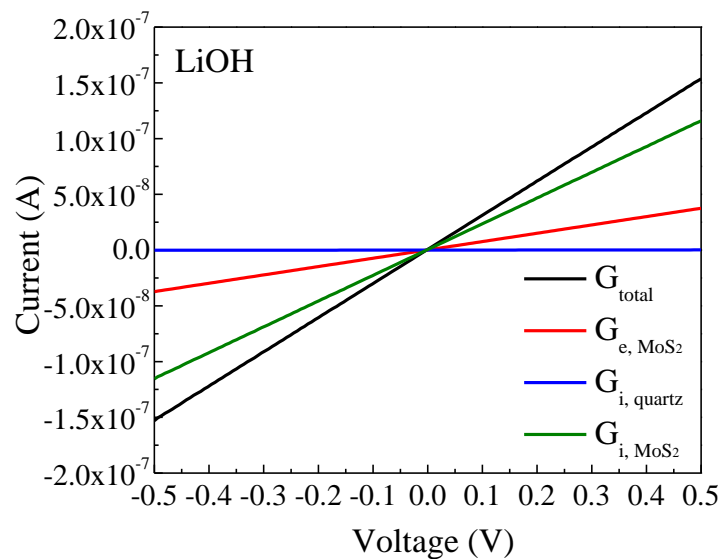
Gate modulated ion conductivity through MoS₂ channel



HRTEM image of MoS₂ film cross section



- Our theoretical findings were confirmed using HRTEM analysis where, we confirm the 1D grain boundary diffusion of K⁺ ions across the MoS₂ nanofilm. It is noted that the ions do not flow across the interface or within the interlayer.
- The ion flow is strictly across the grain boundaries and therefore, we were able to achieve very high ion conductivity.
- Previously, we observed this phenomena while developing passivation layers for Li anodes. Currently, this study has helped us for designing novel catalyst materials for preventing polysulfide shuttling effect in sulfur cathodes used for Li-S battery.



$$G_{\text{total}} = G_{\text{e, quartz}} + G_{\text{i, quartz}} + G_{\text{e, MoS}_2} + G_{\text{i, MoS}_2}$$



Unusually high-ion conductivity through MoS₂ channel

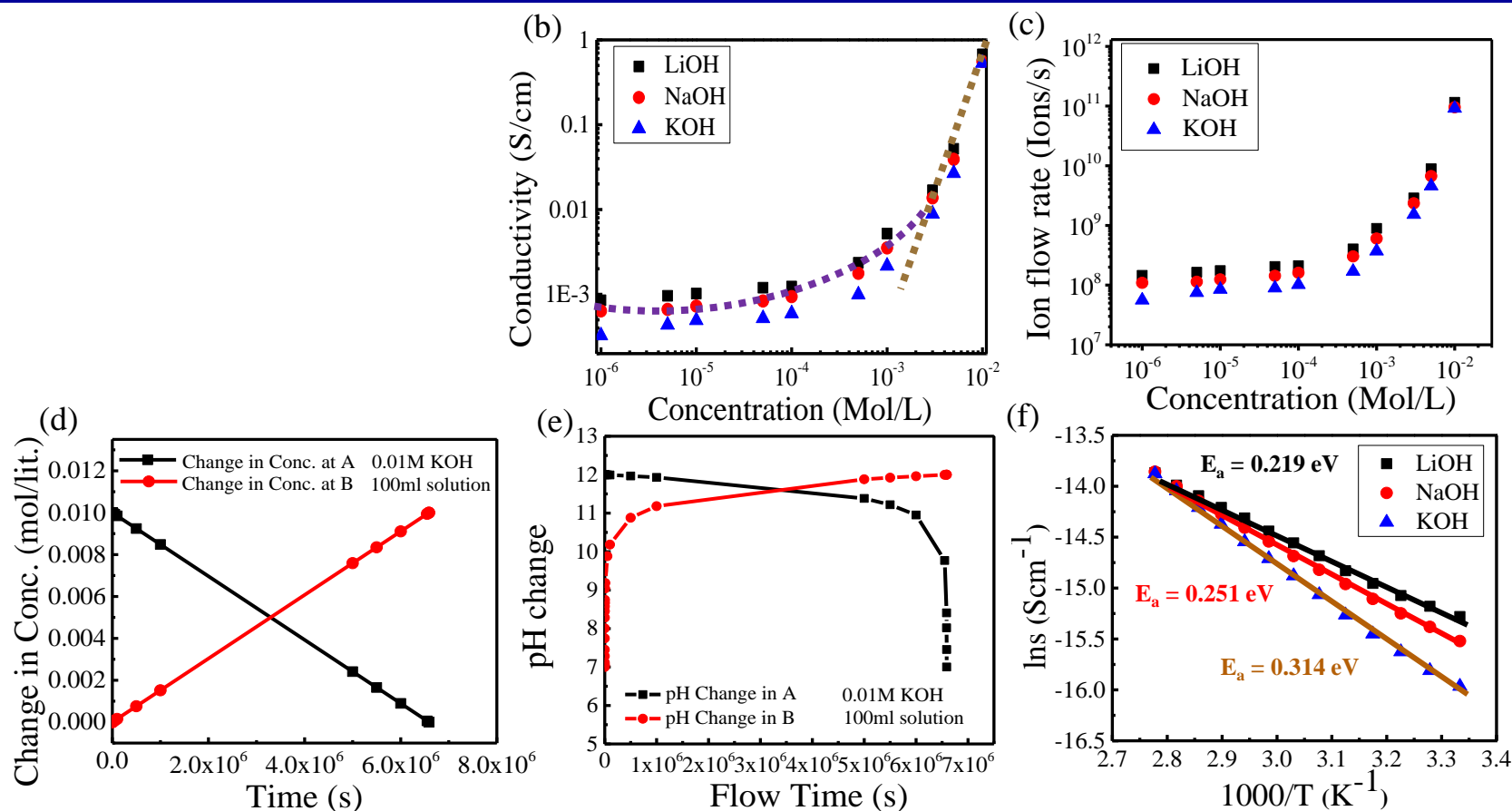
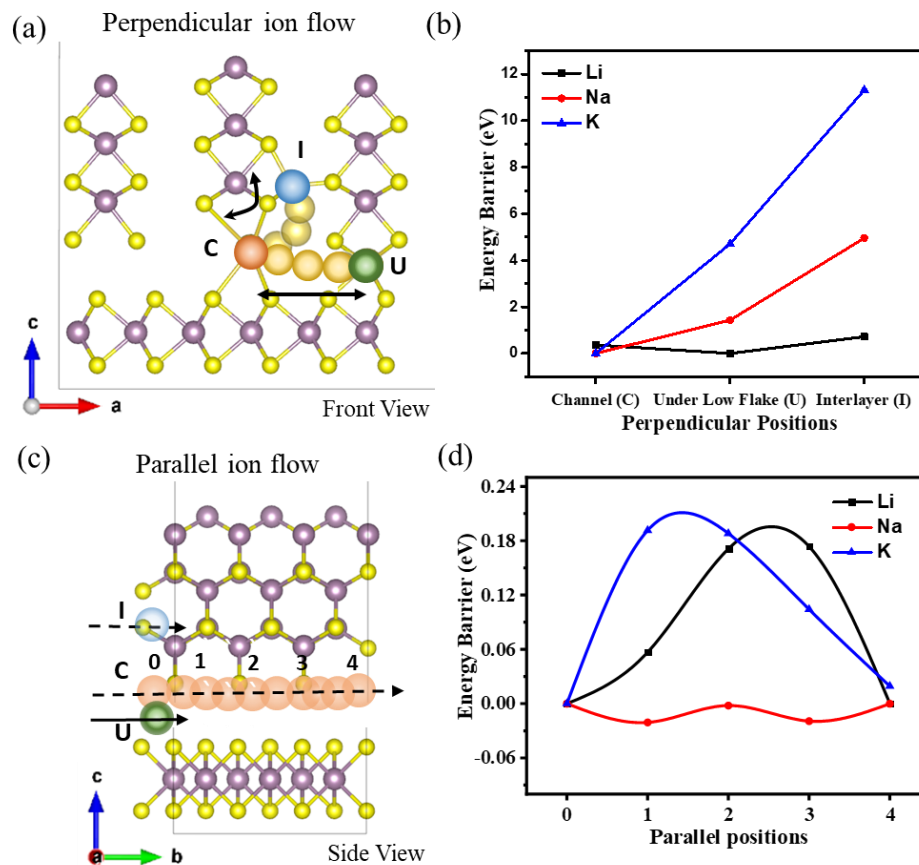


Figure. (b) Ionic conductivity as a function of the LiOH, NaOH, and KOH concentrations from 1 μ M to 10 mM measured through MoS₂ nanofilm. (c) Ion flow rate per second calculated using conductivity data. (e) Change in concentration with time during ion flow study resulting in pH change of ionic solution at side A and B in MoS₂ ion-flow device similar to Figure (a). (f) Arrhenius plot of the conductivity ($\ln(\sigma)$) vs. inverse temperature ($1000/T$) for MoS₂ nanochannel in 10mM LiOH, NaOH, and KOH.



Gate modulated ion conductivity through MoS₂ channel



- The high ion conductivity of different cations can be explained by the mitigated activation energy via percolative ion channels in 2H-MoS₂, including the 1D ion channel at the grain boundary, as confirmed by modeling and analysis.
- We discover a novel ion flow route in 2H-MoS₂ nanofilm that affects the ion-conductivity using DFT simulations. (Data was obtained from our collaborators from Prof. KJ Choi, UTD).
- We found that 1D grain boundary diffusion channel allows perpendicular ion flow especially for Li ions without any energy barrier. This results prove important for designing materials for advanced LSBs.



Gate modulated ion conductivity through MoS₂ channel

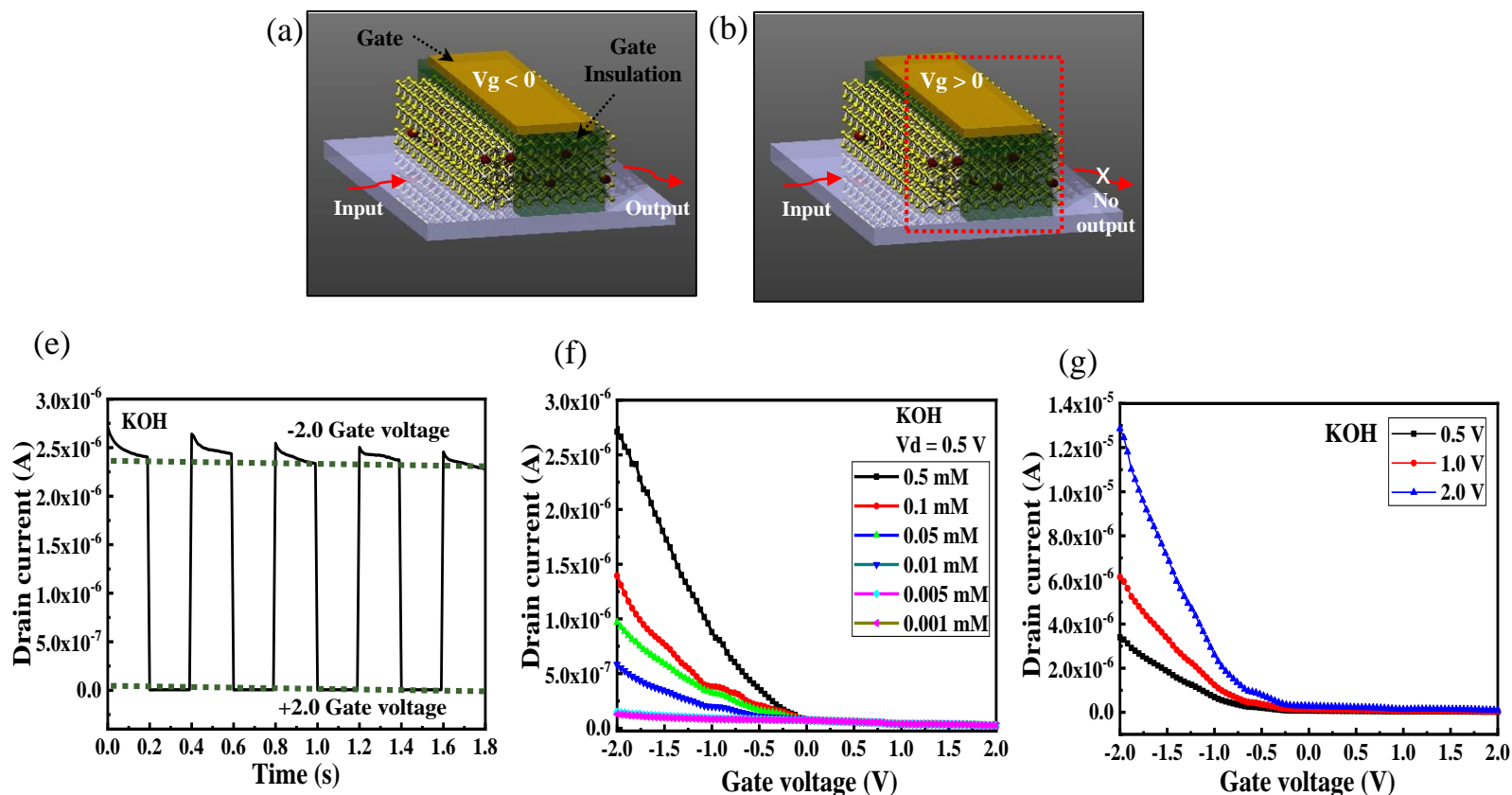


Figure . (a, b) Schematic of ionic gating in MoS₂ nanofilm. (e) Time traces of gate-induced KOH ionic current with the applied different gate voltage (+2 and -2 V). (f) ionic charge transfer characteristics (I_d - V_g curve) of KOH concentrations from 1 μ M to 10 mM measured through MoS₂ nanofilm. (g) The I_g - V_g curve of KOH with different drain current from 0.5 to 2.0V.

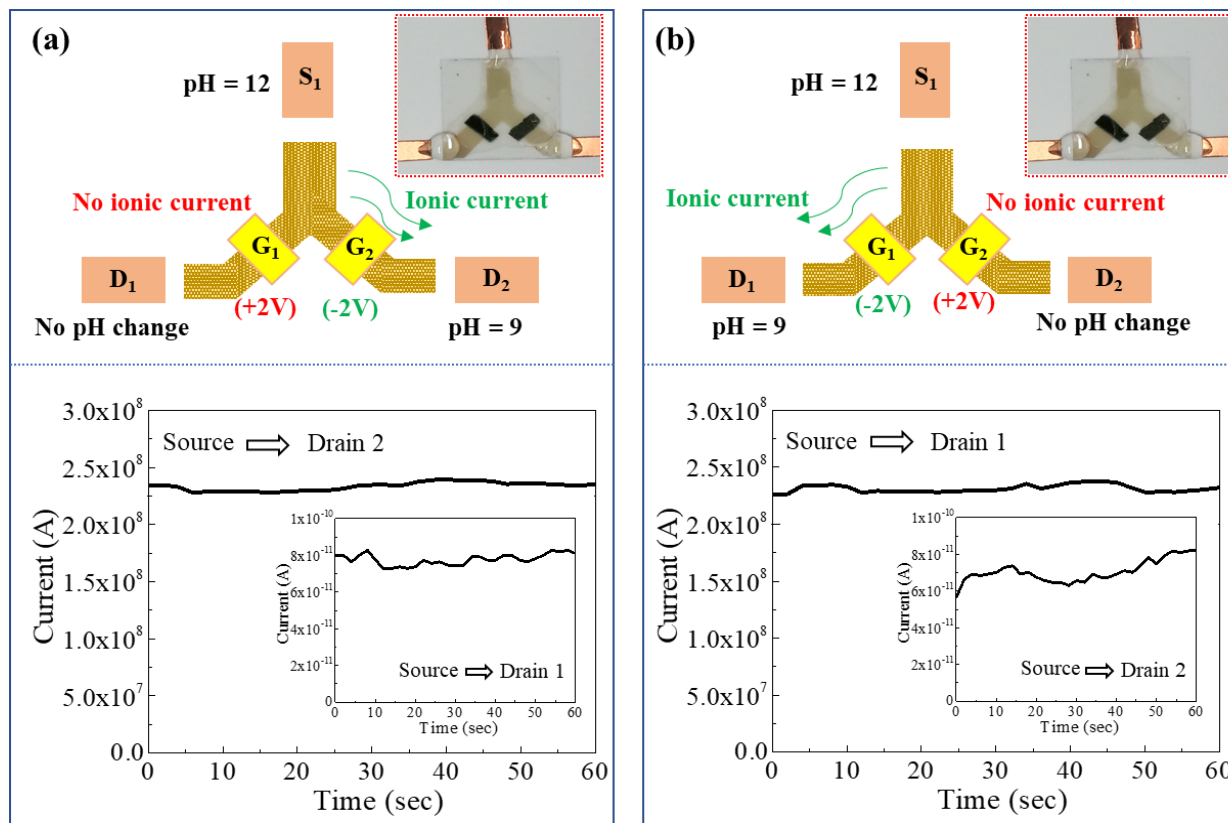


Figure. The schematics show ion flow characteristics in a Y-shaped MoS₂ nanochannel with applying gate voltage of (a) $V_g^1 = +2V$ and $V_g^2 = -2V$ and (b) $V_g^1 = -2V$ and $V_g^2 = +2V$, at constant $V_{sd} = 0.5V$. At $V_g = +2V$, no ion flow occurs through the MoS₂ film, while there is the ion flow with $V_g = -2V$ resulting in pH change of the electrolyte solution. Our results confirm that ion flow can be modulated *via* electrical gating.



High energy density Li-S battery enabled by defect engineered molybdenum tungsten disulfide alloy catalyst



- The practical application of Li-S battery (LSB) is limited by its intrinsic hurdles such as lithium polysulfides (LiPSs) shuttling effect and limited sulfur loading and its utilization in cathode.
- We develop a defect engineered $\text{Mo}_x\text{W}_{1-x}\text{S}_{2-y}$ alloy catalyst (D-MoWS) deposited on carbon nanofiber (CNF) via a facile hydrothermal synthesis followed by a thermal-solvent vapor etching method to expedite the LiPSs redox kinetics and resolve the limit of sulfur utilization in LSB.
- The LSB cells assembled using the D-MoWS catalyst coated CNF-S cathode show the highest specific capacity of $1,586 \text{ mAh g}^{-1}$ and excellent areal capacity upto 13.5 mAh cm^{-2} at high areal sulfur loading of 10 mg cm^{-2} , resulting in the highest energy density of 1090 Wh kg^{-1} (w.r.t total weight of anode and cathode).
- Our mechanistic study and ex-situ SEM analysis prove that D-MoWS catalyst accelerates the LiPSs conversion, prevents the shuttling effect and Li-metal corrosion, therefore, effectively reduces the negative/positive electrode capacity (N/P) ratio to the lowest reported value of 1.7.

S. Bhojate, B. Park, S. Oh, W. Choi, Jr. Power Sources (under review) (2021)

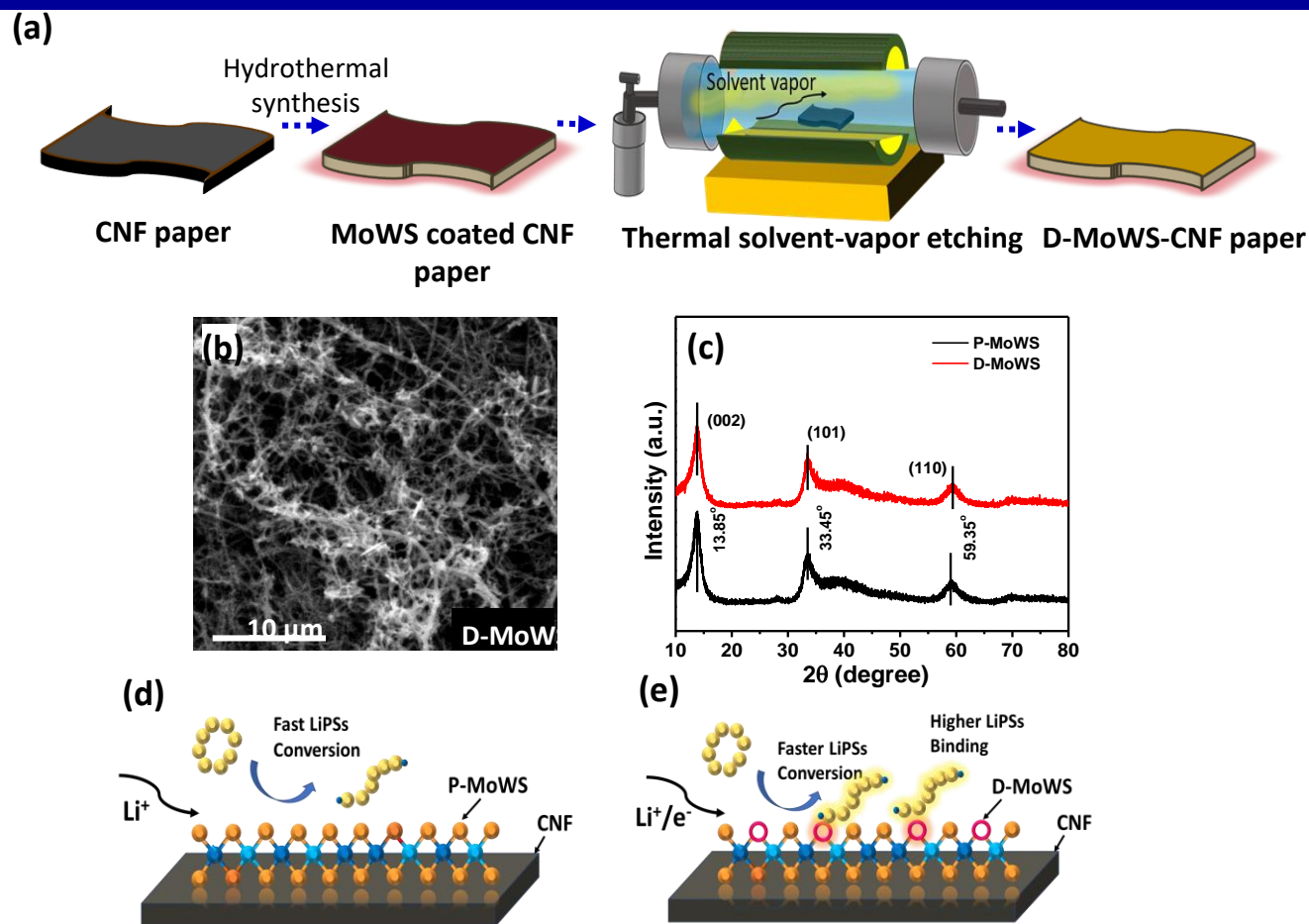


Figure. (a) Schematics illustrating the synthesis process of hydrothermally grown MoWS catalyst on CNF paper and its defect engineering process. Low magnification FESEM image of (b) defect engineered (D-MoWS) catalysts on CNF paper. (c) XRD analysis of P- and D-MoWS catalyst on CNF. (d,e) A schematic of P- and D-MoWS-CNF structure representing the effect of defect engineering on polysulfide binding and conversion.

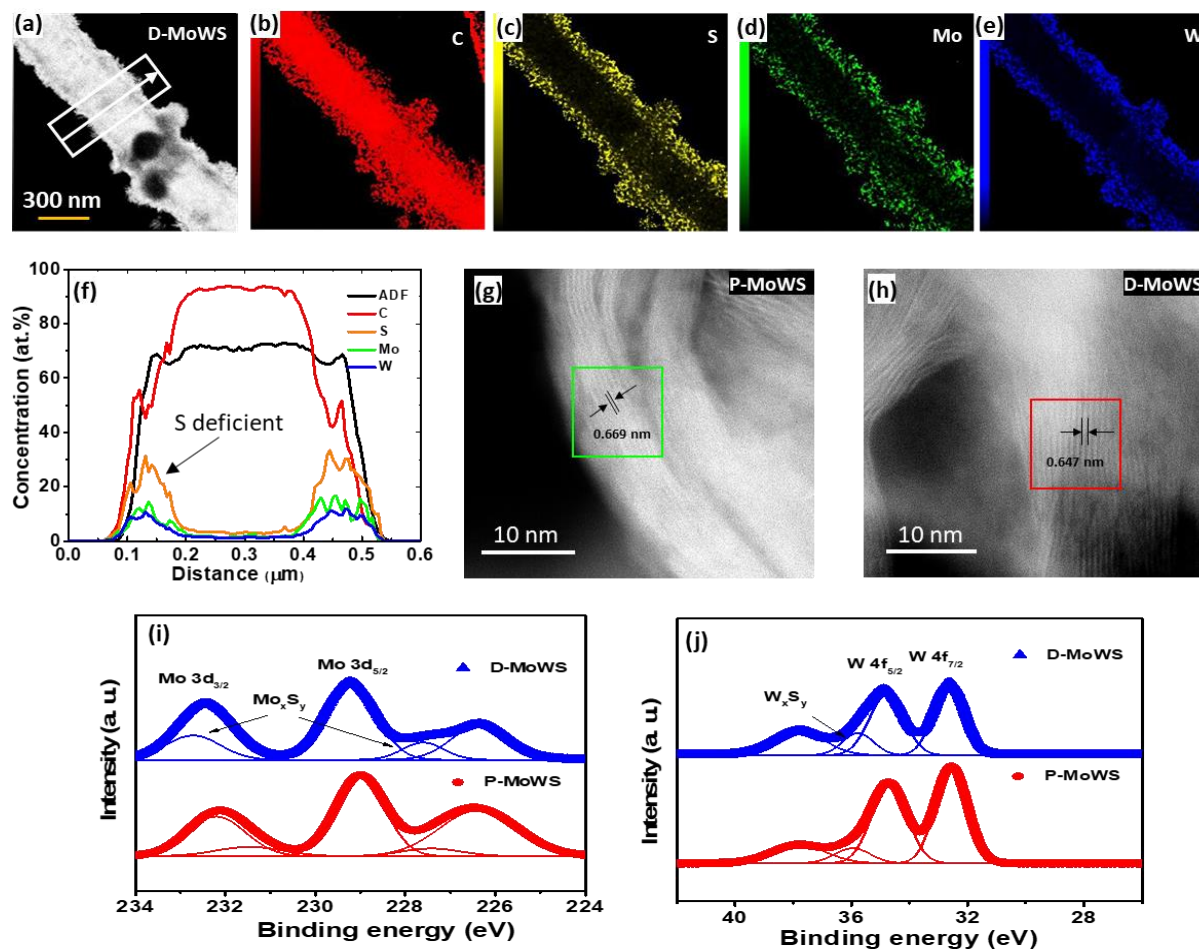
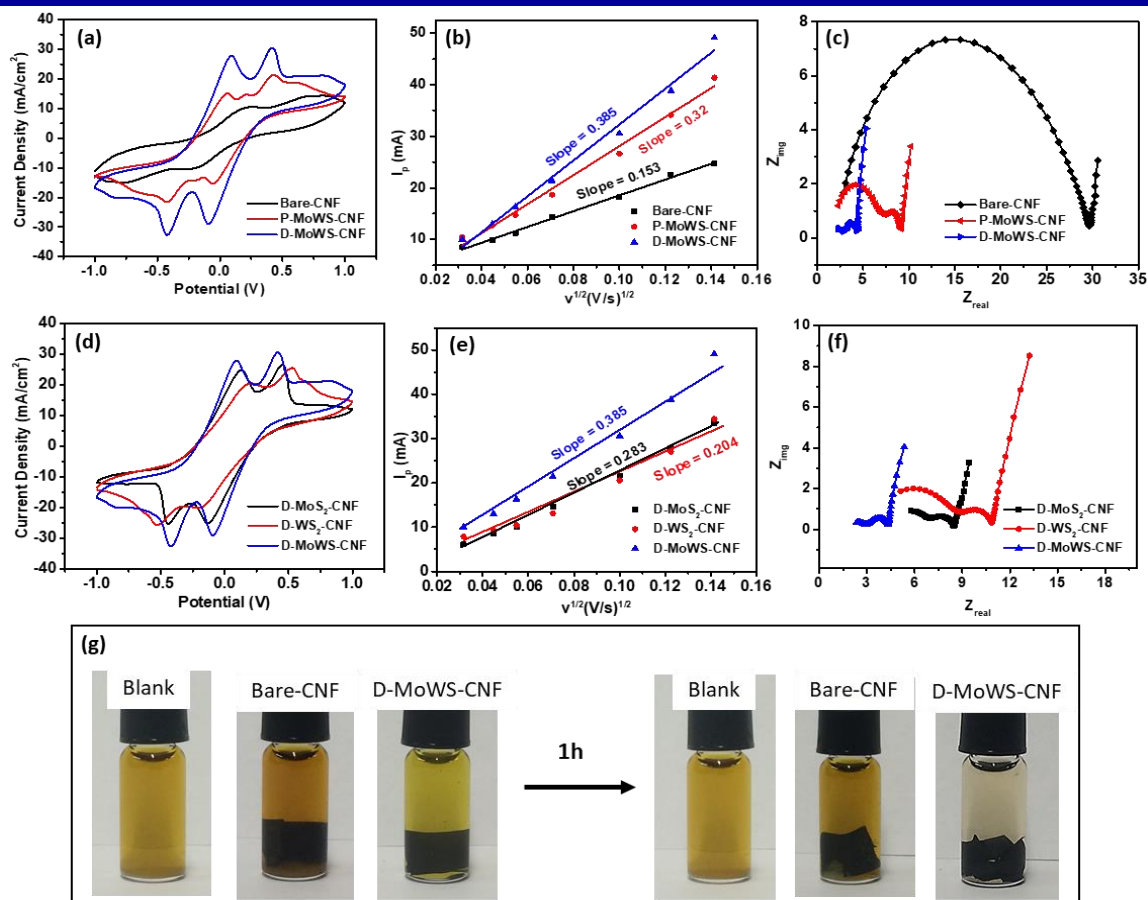


Figure. (a-e) HRTEM images and their EDS mapping for MoWS coated CNF after sulfur etching. The EDS mapping of MoWS coated CNF showing the uniform distribution of Mo, W, S, and C elements. (f) The intensity profile shows the concentration distribution for Mo, W, C, and S elements corresponding to the profile shown in Fig. (a). After etching, there was a ~32% decrease in the S-peak intensity. High magnification HR-STEM analysis for (g) P-MoWS and (h) D-MoWS catalyst. XPS analysis for P-MoWS and D-MoWS catalyst (i) Mo 3d spectra and (j) W 4f spectra.



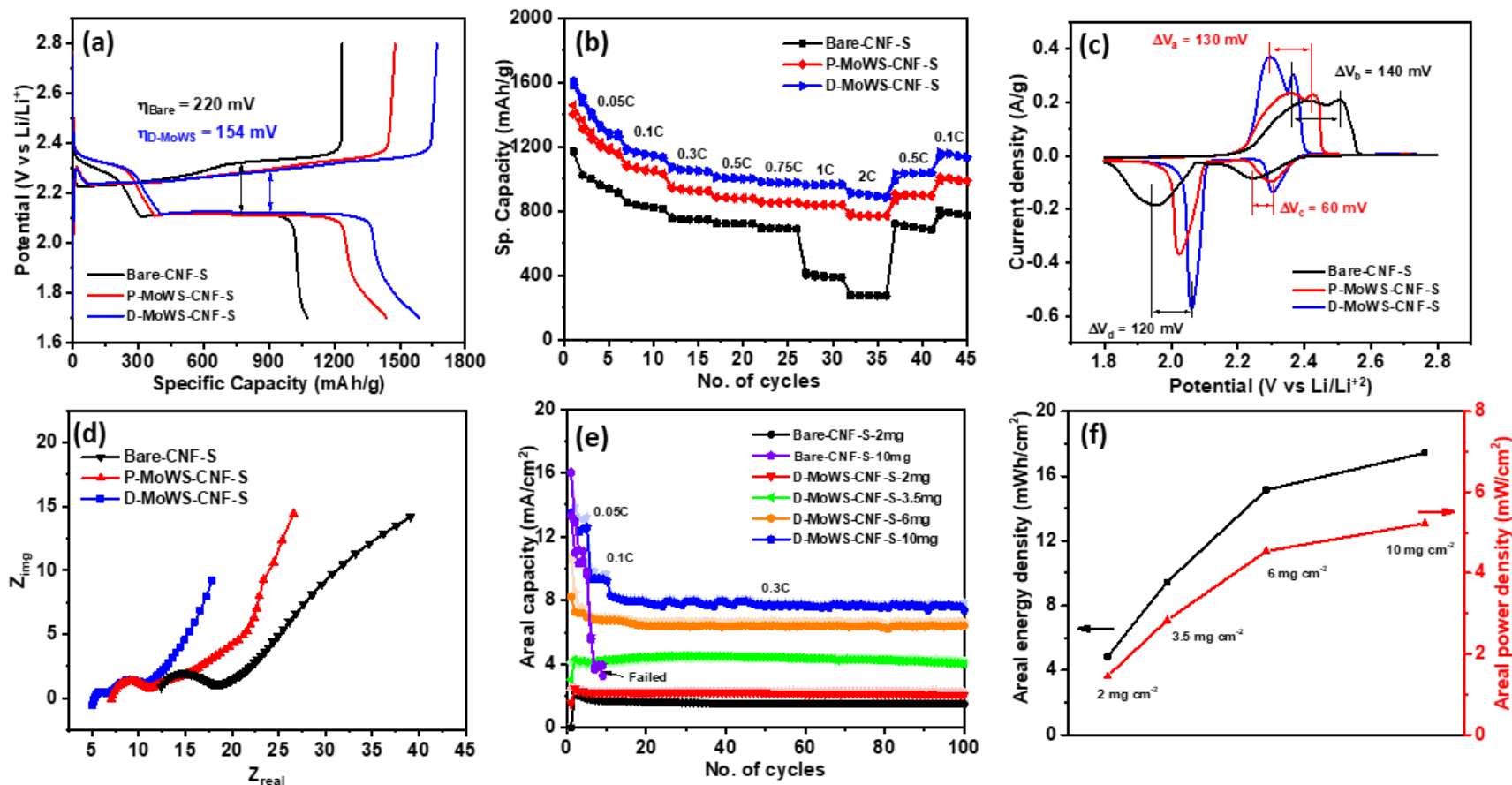
Defect-Engineered 2D MoWS alloy electrocatalyst for high efficiency Li-S battery (1)



- The symmetrical cell test performed using D-MoWS-CNF paper showed high redox peaks representing oxidation and reduction of lithium polysulfide ($0.5M Li_2S_6$) used as polysulfide solution in electrolyte.
- Our study confirms that D-MoWS alloy catalyst has superior performance as compared to pristine or defected MoS₂ and WS₂ catalysts with low overall series resistance and high Li ion diffusion kinetics.
- The Li_2S_6 dipping test shows that polysulfides get adsorbed on the D-MoWS surface and clears the solution within short time of 1h



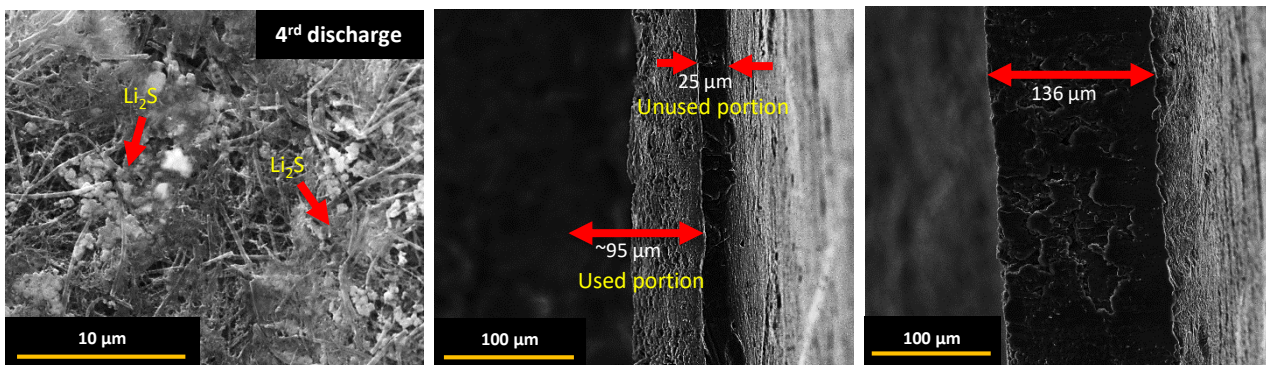
Li-S battery cell performance assembled with defect-engineered 2D MoWS-CNF cathode



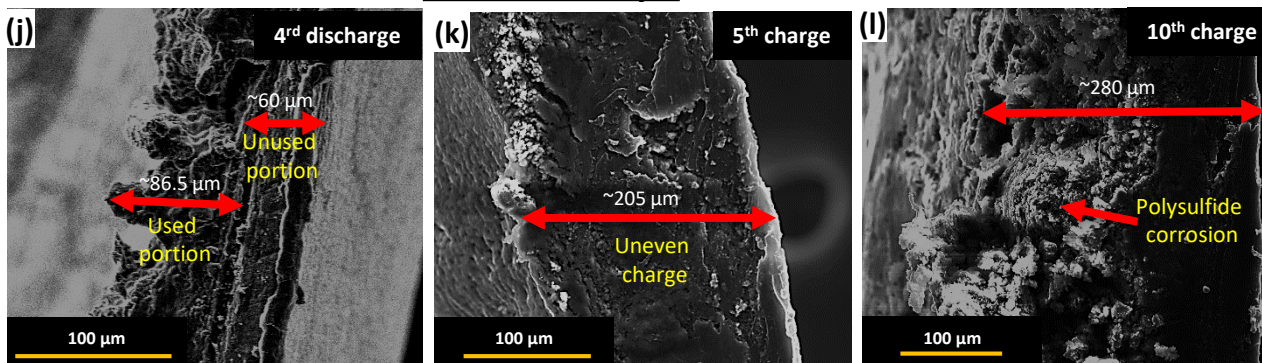
- Full cell analysis assembled with D-MoWS catalyst deposited carbon nanofiber (CNF)-S cathode showed highest specific capacity of 1580 mAh/g, and higher rate capability during galvanostatic charge discharge test and c-rate analysis.
- The cyclic voltammetry test showed high oxidation-reduction of D-MoWS-CNF-S cathode.
- The catalyst exhibit very high LiPS conversion even at high sulfur loading of 10 mg cm⁻²



With catalyst



Without catalyst



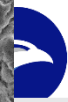
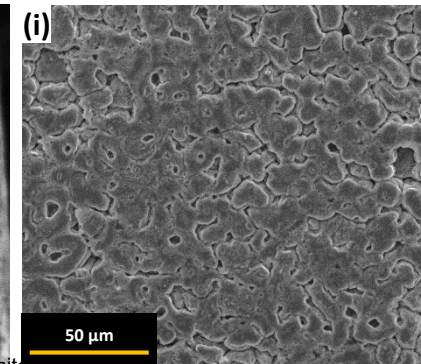
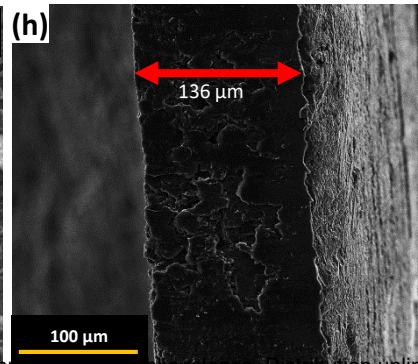
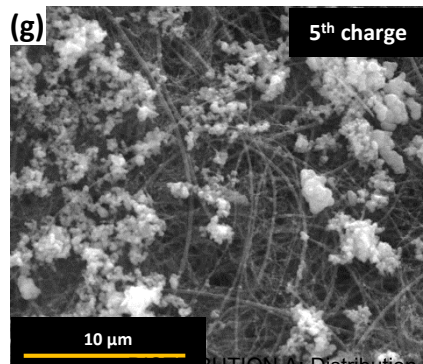
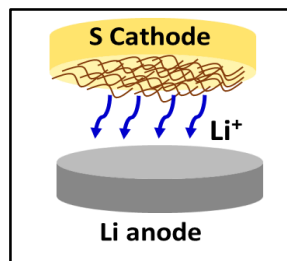
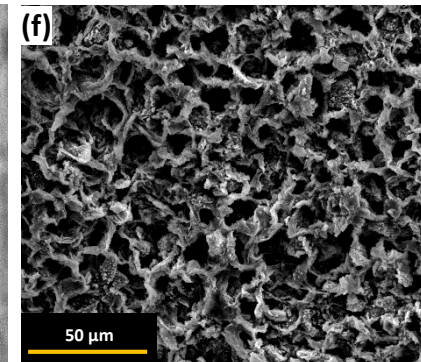
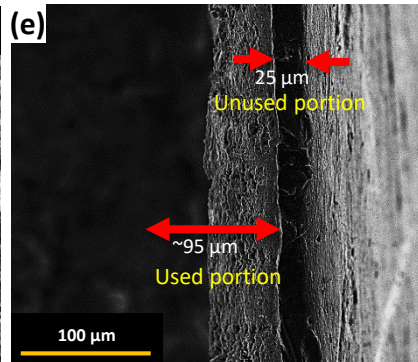
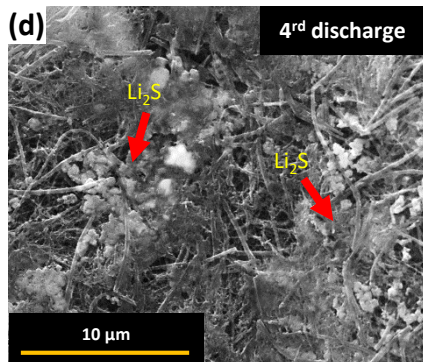
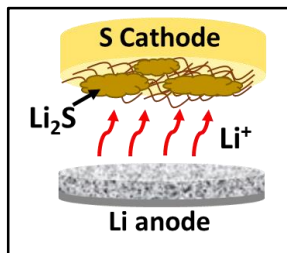
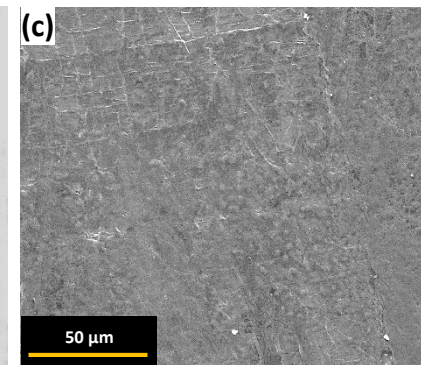
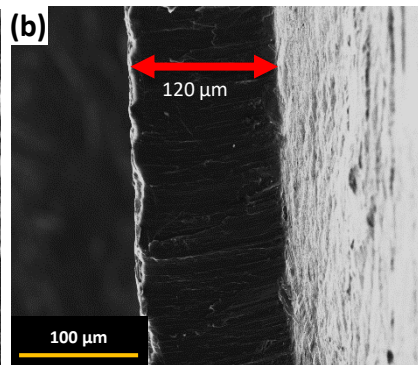
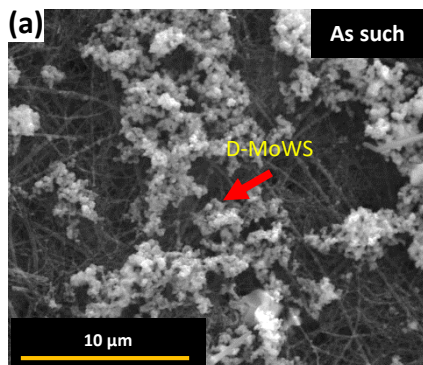
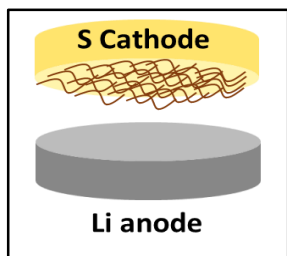


With D-MoWS catalyst

Top view of S cathode

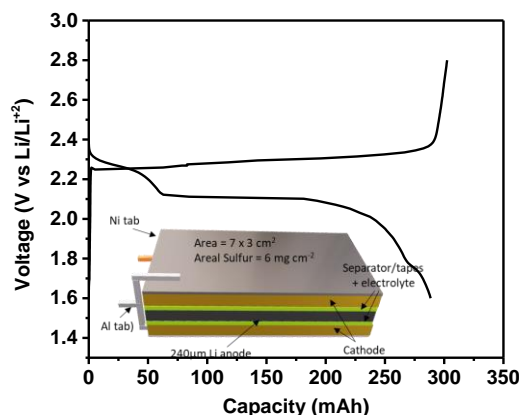
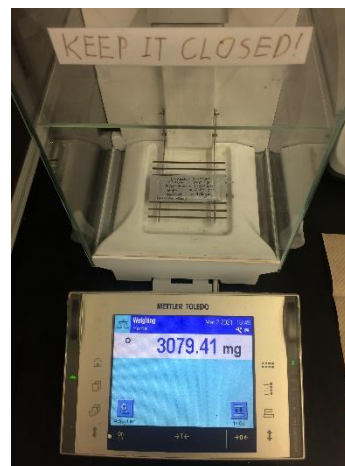
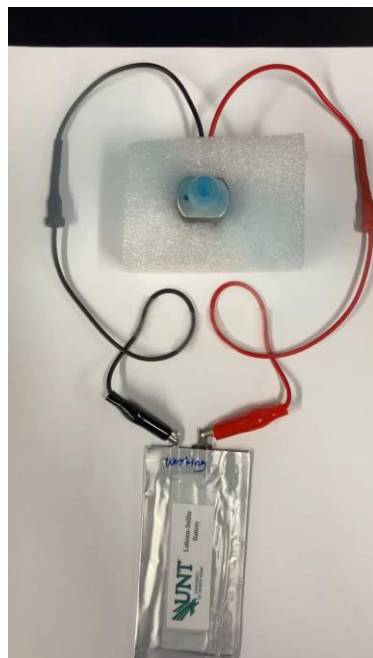
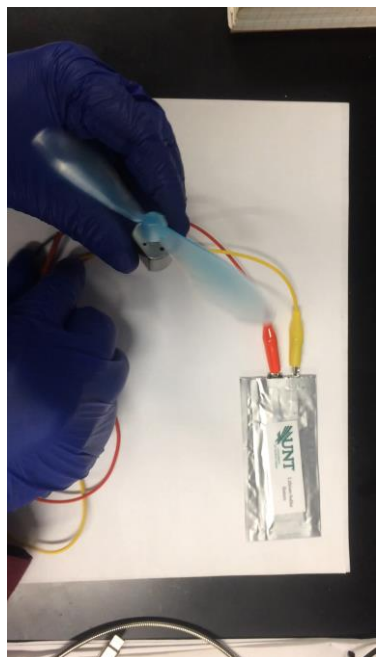
Cross-sec. view of Li anode

Top view of Li anode





Pouch-type Li-S battery performance



Pouch-type Li-S battery using our newly invented hybrid electrolytes and D-MoWS catalyst-CNF-S cathode, and its performance. We obtained a very high specific capacity of ~300 mAh/single cell and demonstrated electric fan running. The battery is lighter than Li-ion battery and energy density is about two times higher.

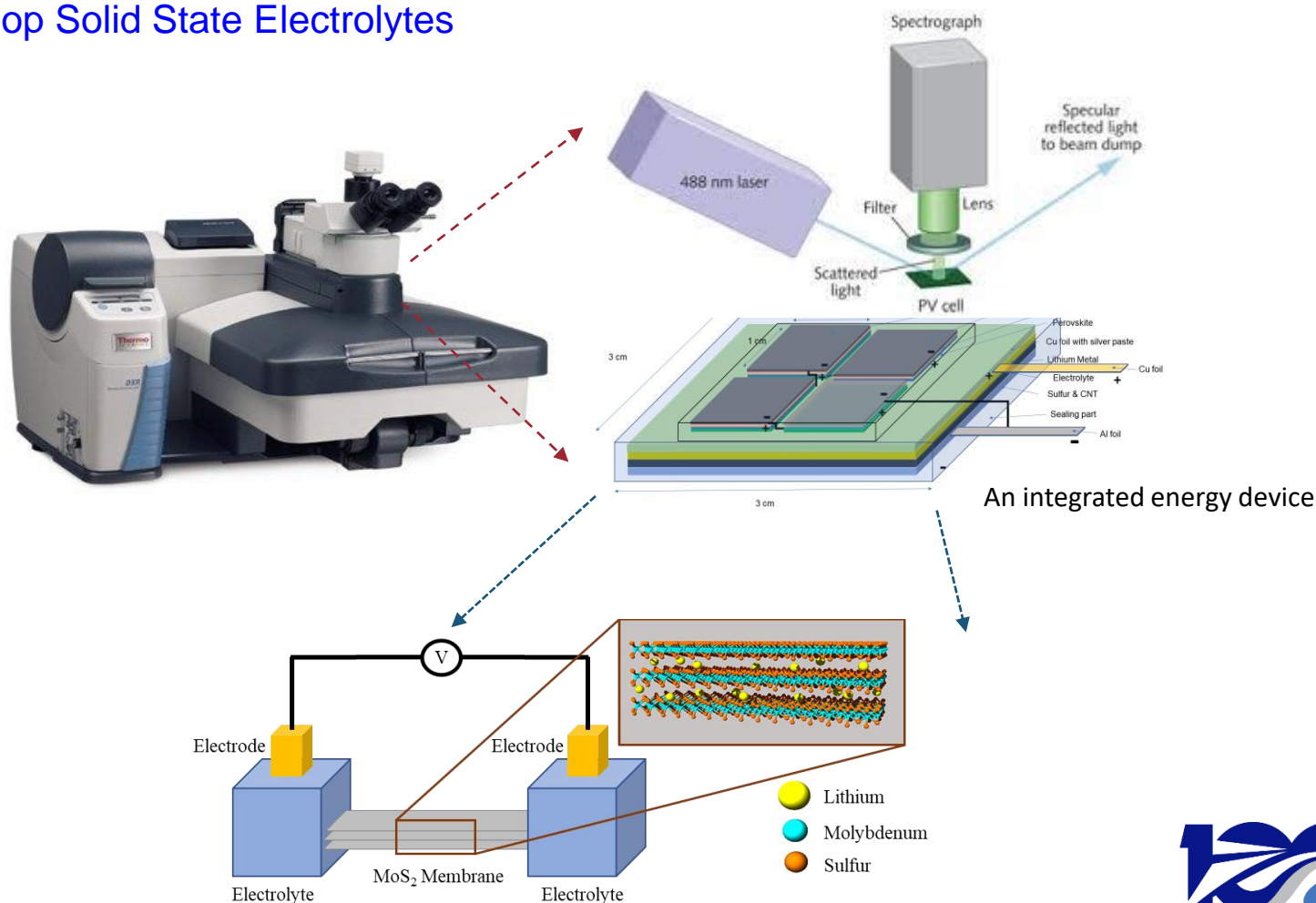


In-situ characterization of microstructure under ion-transport & illumination



Raman analysis + ion transport under solar illumination

- Characterization of coated 2D materials/Li-metal
- Develop Solid State Electrolytes





Summary (1)

- We report unusually high ionic conductivity of Li^+ , Na^+ , and K^+ in 2D MoS_2 nanofilm exceeding 1 S/cm, which is more than two orders of magnitude when compared to that of conventional solid ionic materials. The mechanism of the high ion conductivity was studied - the mitigated activation energy *via* percolative ion channels in 2H- MoS_2 , including the 1D ion channel at the grain boundary.
- We obtain field-effect modulation of ion transport with a high on/off ratio. The ion channel is large-scale patternable by conventional lithography, and the thickness can be tuned down to a single atomic layer.
- We develop a defect engineered $\text{Mo}_x\text{W}_{1-x}\text{S}_{2-y}$ alloy catalyst (D-MoWS) deposited on carbon nanofiber (CNF) via a facile hydrothermal synthesis followed by a thermal-solvent vapor etching method to expedite the LiPSs redox kinetics and resolve the limit of sulfur utilization in LSB. The cells assembled using the catalyst coated CNF-S cathode show the highest specific capacity of 1,586 mAh g^{-1} and excellent areal capacity of 13.5 mAh cm^{-2} at high areal sulfur loading of 10mg cm^{-2} , resulting in the highest energy density of 1090 Wh kg^{-1} (w.r.t total weight of anode and cathode), and the lowest negative/positive electrode capacity (N/P) ratio of 1.7.
- We developed a novel hybrid cathode structured with a hybrid electrolyte and MoWS alloy catalyst directly coated on CNF paper, and melt-infused with sulfur. The tri-junction interface of CNF-sulfur-SSE/MoWS within the cathode provides high sulfur utilization at high-sulfur loading and low E/S ratio of 2 $\mu\text{L}/\text{mg}$ for high energy density of over 500Wh/kg.



Summary (2)

- Novel catalysts of 2D MoWS₂ alloy with 2H (semiconducting)-1T (metallic) mixed-phase were synthesized on carbon nanotubes (CNTs) by a two-step process of co-sputtering and sulfurization. The cathode comprising 2D MWS₂-CNTs exhibits the synergistic effect of an accelerated electron transfer, higher LiPSs binding effect, and catalytic performance, as confirmed by our electrochemical analysis. As a result, Li-S battery cell assembled with the 2D MoWS₂/CNT/S cathode shows a high specific capacity of 1,228 mAh/g at 0.1 C and much higher cyclic stability as compared to the pristine cathodes. Our results confirm that the 2D MoWS₂ alloy catalyst deposited on the CNTs can effectively
- We assembled Li-S battery with the perovskite solar cell and characterized its performance. The charging/discharging by powering the solar cell is working. The integrated device was fabricated and optimized for a higher efficiency.
- In-situ Raman analyzer has been purchased and assembled for studying in-situ battery cell performance test investigating phase stability of 2D MoS₂ and solid-state Li-S battery mechanism with varying E/S ratio and sulfur loading amount.



Publications (1)

Paper #1: Nanoengineering to achieve high efficiency practical lithium-sulfur batteries, E Cha, M Patel, S Bhoyate, V Prasad, W Choi, *Nanoscale Horizons*, 1, 467 (2020) (Impact Factor = 9.94) This paper presents one of the rare and most important synopsis for Li-S battery research with respect to high sulfur loading, low electrolyte content and critical energy densities necessary for designing of commercial Li-S batteries. We have reviewed each aspect of Li-S battery components in detail including enhancement of electrochemical properties of sulfur cathodes, lithium anodes, and electrolyte to address practical limitations and ways to overcome them.

Paper #2: Improving Lithium–Metal Battery Performance under Lean Electrolyte through MoS₂ Coating, Eunho Cha, Hongkyung Lee, Wonbong Choi, *ChemElectroChem* 10.1002/celec.201901735, CHEMELCTROCHEM, 2019 (IF=3.975) This paper presents a new perspective into addressing the practical parameters that has large impact on the overall energy density of Li-S batteries, electrolytes-sulfur ratio and sulfur loading amount, while demonstrating improved cycle life by the protective molybdenum disulfide (MoS₂) coating on lithium metal anode.

Paper #3: Mixed Phase 2D Mo_{0.5}W_{0.5}S₂ Alloy as a Multi-Functional Electrocatalyst for a High-Performance Cathode in Li–S Batteries, S Bhoyate, J Kim, E Lee, E Lee, J Park, J Kim, W Choi, Jr. *Materials Chemistry A* (2020) (IF=11.301) In this article, for the first time we introduce a new 2D Mo_{0.5}W_{0.5}S₂ alloy as the catalyst for enhanced lithium polysulfide transformation to mitigate the polysulfide shuttling effect and improve the life cycle of Li-S battery. As compared to the traditional catalyst systems, our idea of 2D alloy creates inherently mixed 2H-1T structural phases which were not previously observed in the literature. In addition to this, we prove that extremely low catalyst concentration (<0.2mg/cm²) in sulfur cathodes is sufficient for improving the performance of Li-S battery.

Paper #4: Stable and High-Energy-Density Zn-Ion Rechargeable Batteries Based on a MoS₂-Coated Zn Anode, S Bhoyate, S Mhin, J Jeon, K Park, J Kim, W Choi, *ACS Appl. Mater. & Interfaces*, doi.org/10.1021/acsami.0c06009 (2020) (IF=8.758) While this research is outside of the scope for flexible Li-S cell, it does provide the stepping-stones to the validity of using the MoS₂ protected Li anodes for the commercially available Li-ion batteries.



Publication (2)



Paper

Paper #5. Unusual-High Ion Conductivity in Large-Scale Patternable Two-Dimensional MoS₂ Film, Juhong Park, Sanket Bhoyate, Young-Hoon Kim, Young-Min Kim, Young Hee Lee, Patrick Conlin, Kyeongjae Cho, Wonbong Choi, **10.1021/acsnano.1c04054, ACS Nano (2021) (IF: 14.588)**

Paper #6. High energy density Li-S battery enabled by defect engineered molybdenum tungsten disulfide alloy catalyst, Sanket Bhoyate, Bumsu Park, Sang Ho Oh, Wonbong Choi, **Jr. Power Sources (under submission) (2021) (IF: 8.87)**

Patent

- 1. 2D TMD alloys as catalysts for cathode in Li- S batteries (17/219,523; UNTP.P0027US/1001149548), W. Choi (2020)**
- 2. Cathode with hybrid electrolytes for high-energy density Li-S batteries (63/170,862; UNTP.P0033USP1/1001159087). W. Choi and S. Bhoyate (2021)**

* The patents have been licensed to a Start-up company (ARK Power Tech) to perform development of proprietary Li-S battery technologies

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