2014 UNM REU Nanoscience & Microsystems Program

SAND2014-16389PE

Synthesis of Layered Metal Chalcogenides

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Authors thank the NSF REU Program "UNM Nanoscience & Micro Systems" and DOE for Support

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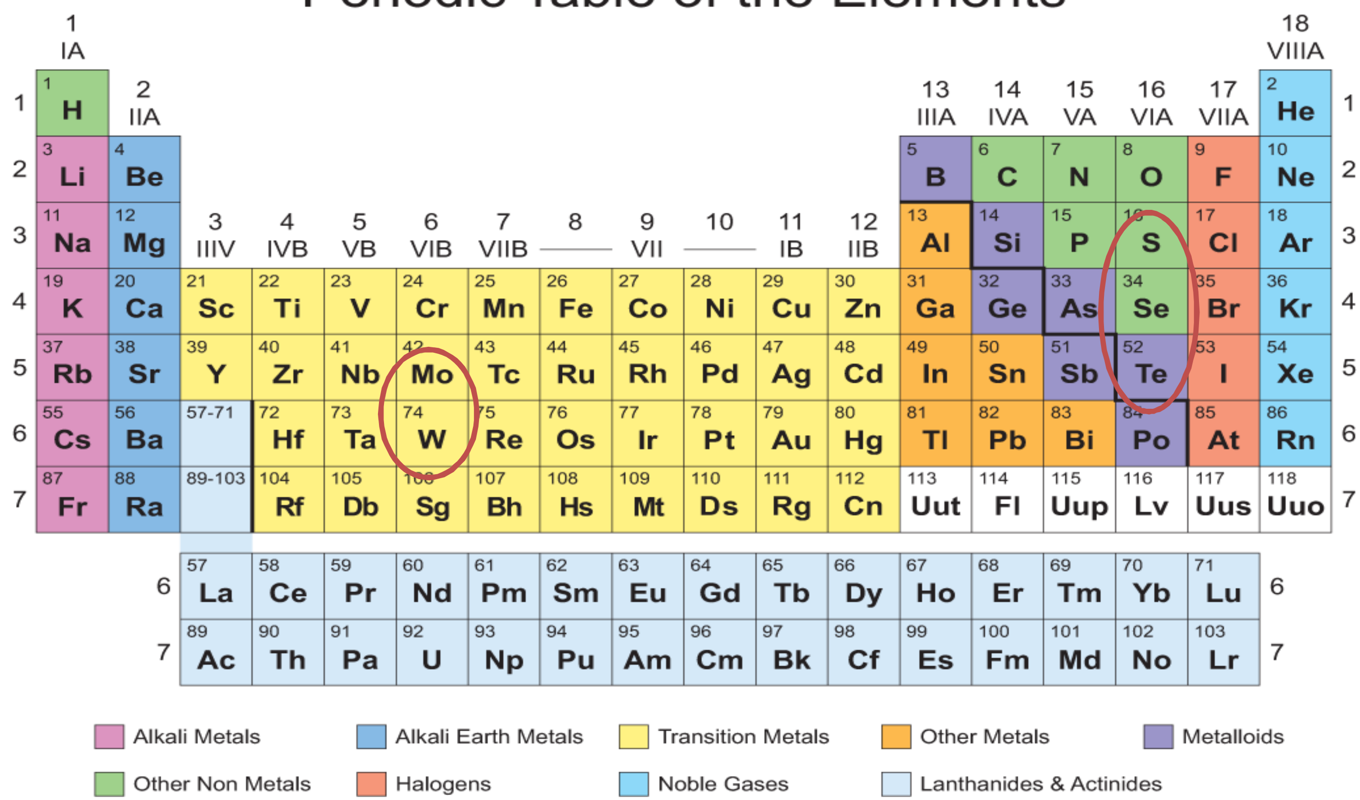
Goals

- Develop synthetic routes for layered metal chalcogenides on nano and bulk scale

- Expand previous research to include: WE_x, MoE_x, $Mo_xW_yE_z$ (E = S, Se, Te)

- Investigate structure-property relationships of custom M-E solid solutions

Periodic Table of the Elements

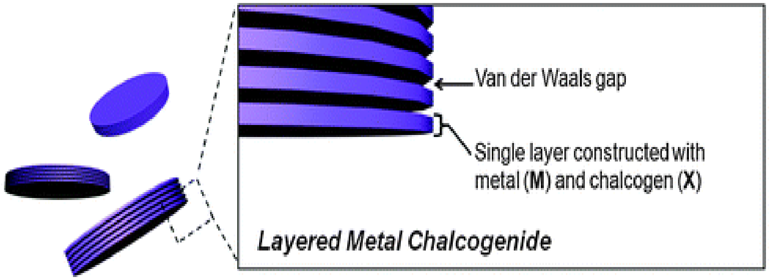


Layered Metal Chalcogenides

- Many are commonly occurring compounds used in: lubricants, batteries, catalysts

- Interested in metal chalcogenide monolayer nanomaterials for varying optical, electronic and catalytic properties

a



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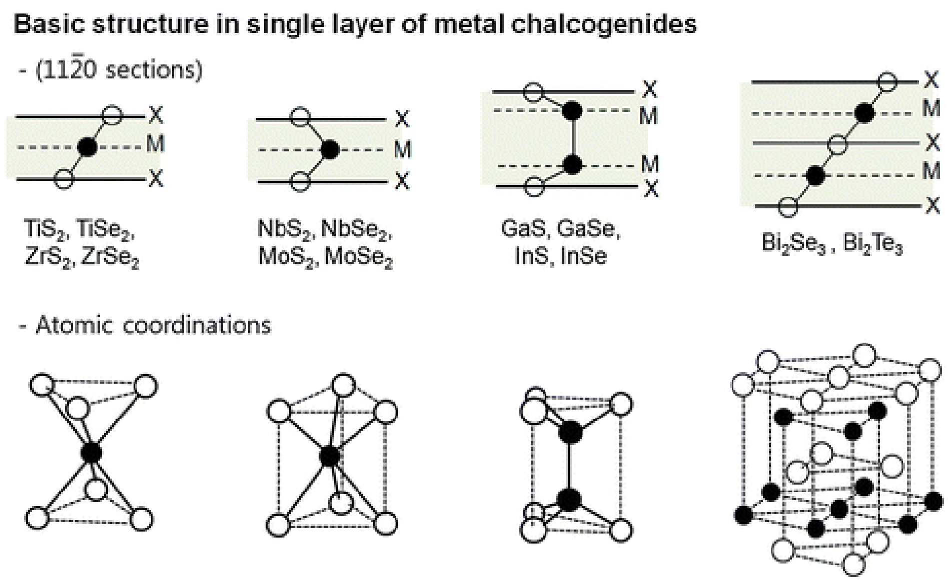


Jae Hyo Han, Sujeong Lee and Jinwoo Cheon, Chem. Soc. Rev.,2013,42, 2581

Project Focuses

Develop synthetic strategies for custom layered compounds

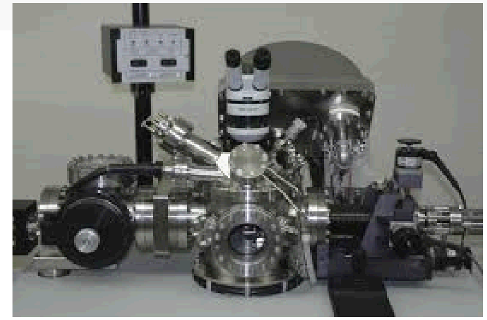
Synthesis of tungsten and molybedium chalcogenide nanomaterials

Develop exfoliation strategies to derive 2D sheets/dispersions

Characterization of crystal structure, bonding state and physical morphology: TEM, XRD, FTIR, Raman

Characterization

Powder X-ray Diffraction (PXRD): phase identification, degree of crystalinity



X-ray Photoelectron Spectroscopy (XPS): Detect oxidation state and chemical composition of product

Raman Spectroscopy: Vibrational modes to detect symmetry

Fourier Transform Infrared Spectroscopy (FTIR): Vibrational modes to detect functional groups

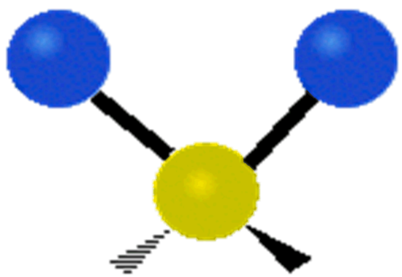
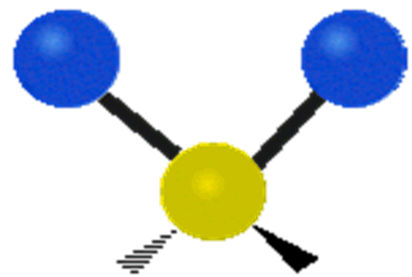
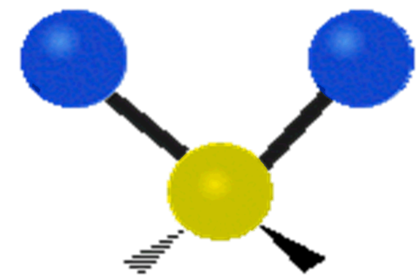
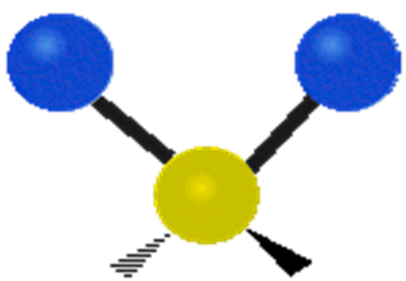
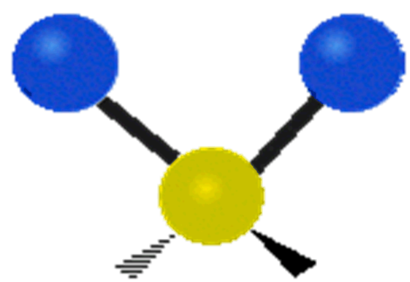
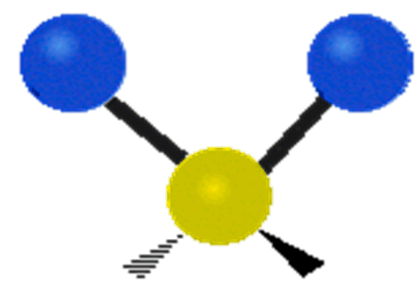
Exploration of the Chalcogens

Elemental sulfur, selenium, tellurium

- RAMAN
- XRD

- There is still a lot unknown about their interactions with other elements

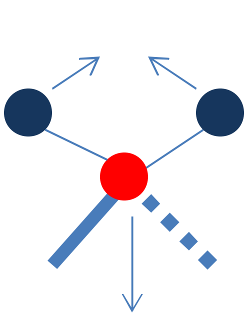
Raman Vibrations

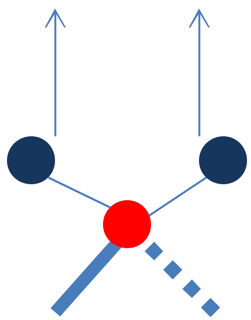
Symmetrical stretching	Asymmetrical stretching	Scissoring (Bending)
		
Rocking	Wagging	Twisting
		

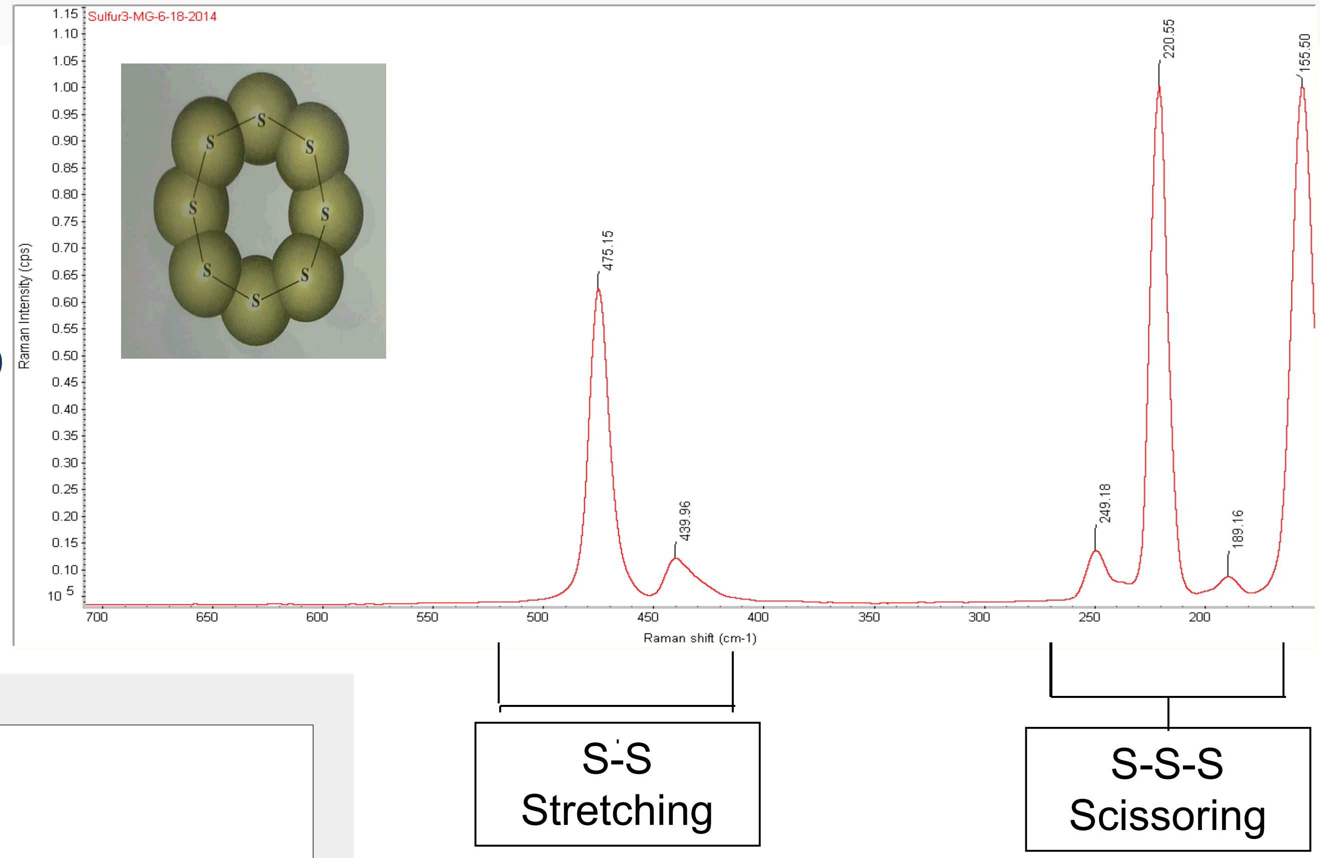
Sulfur

Raman

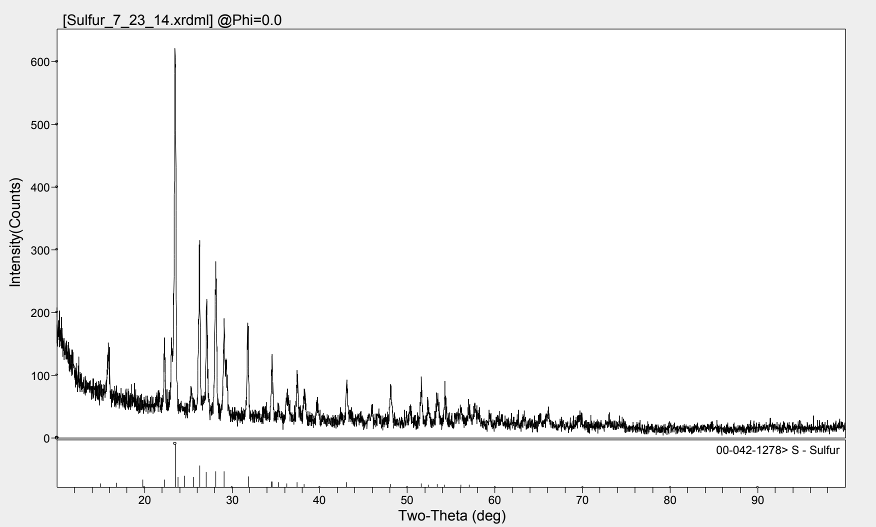
Scissoring Stretching







XRD

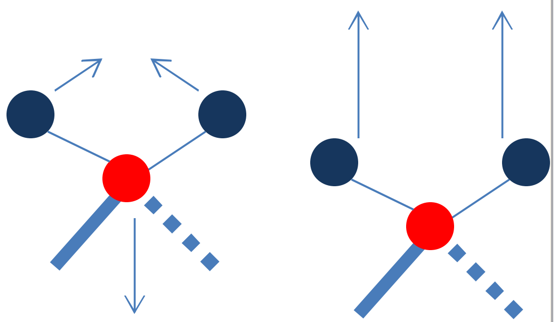


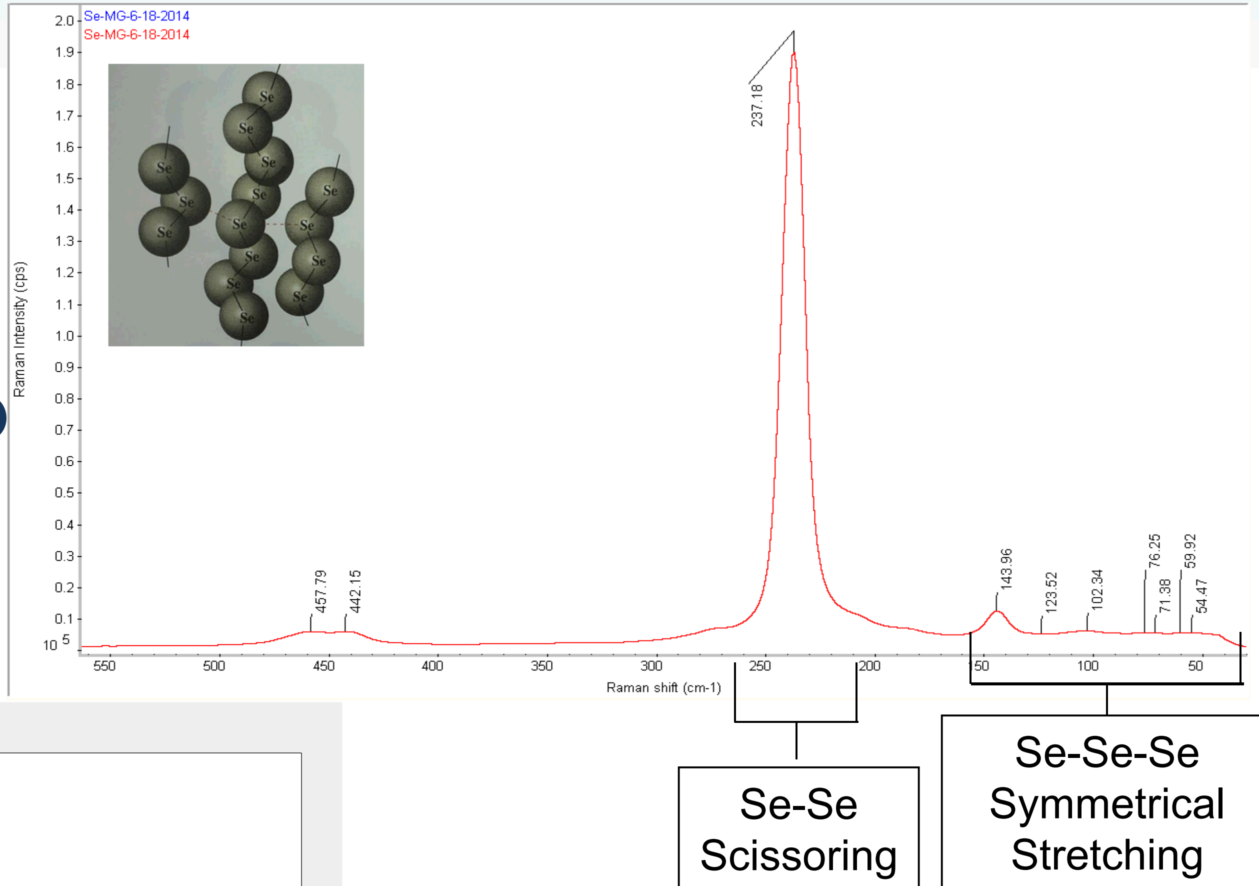
- 20 allotropes
- Exists common S_8 ring
- Rhombic and monoclinic

Selenium

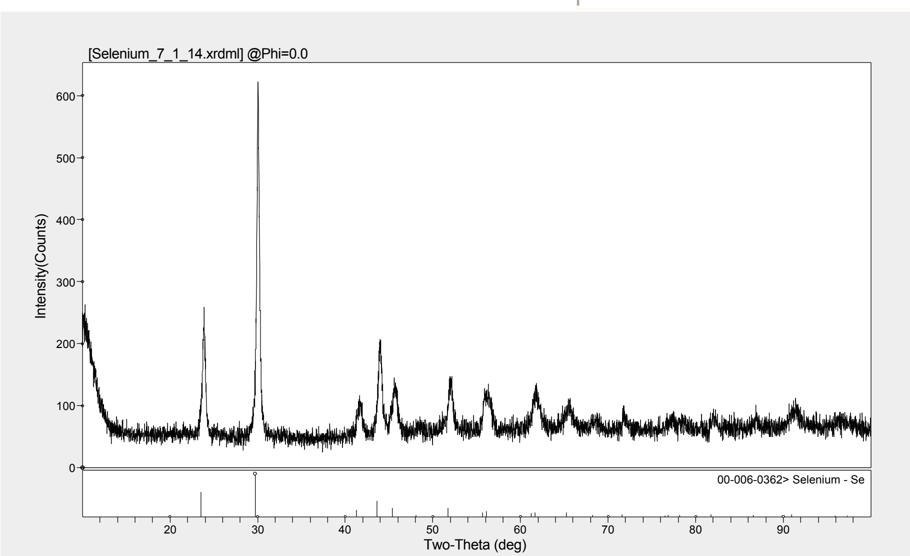
Raman

Scissoring Stretching





XRD

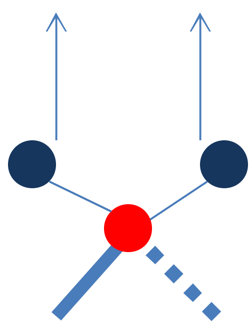


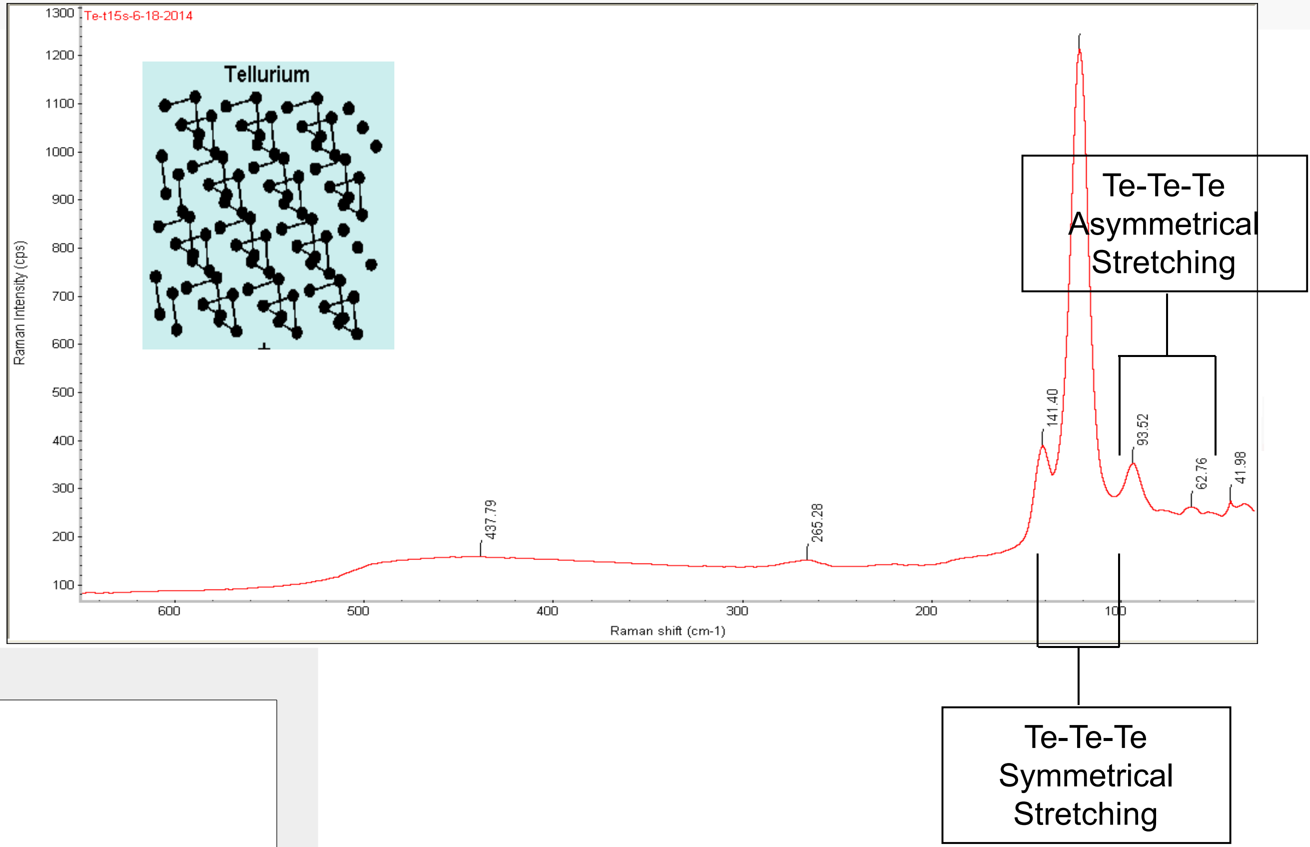
- 5 allotropes
- Exists common Se_2 spiral
- Hexagonal

Tellurium

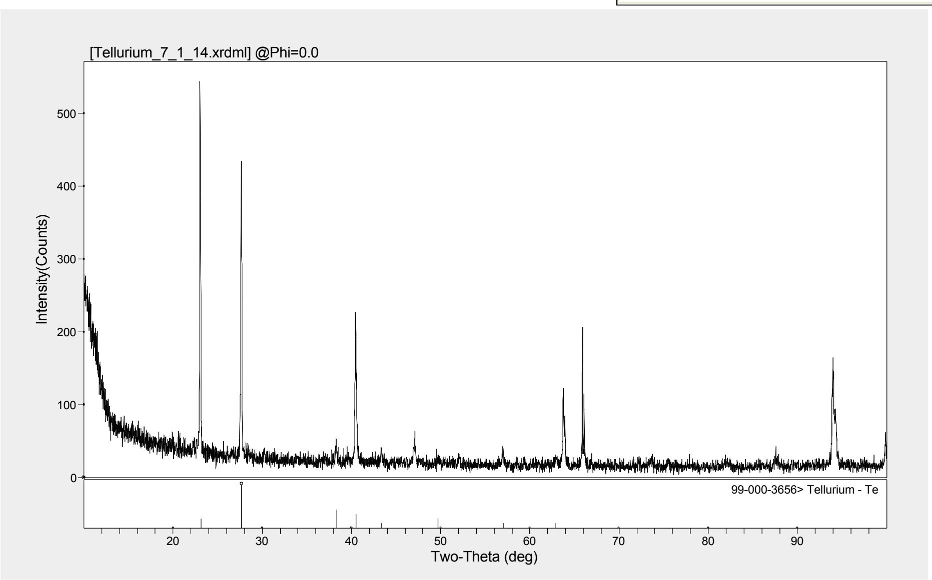
Raman

Stretching





XRD

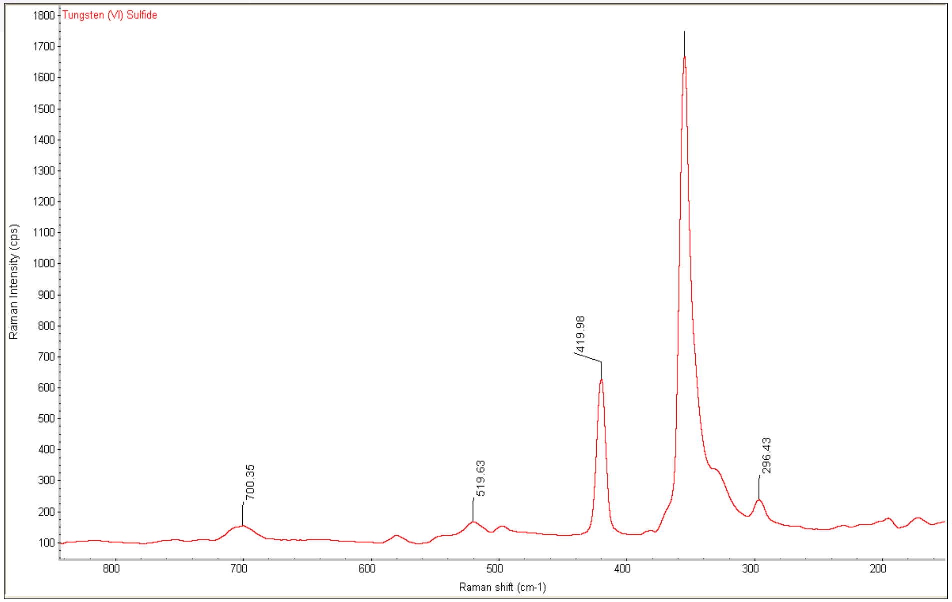


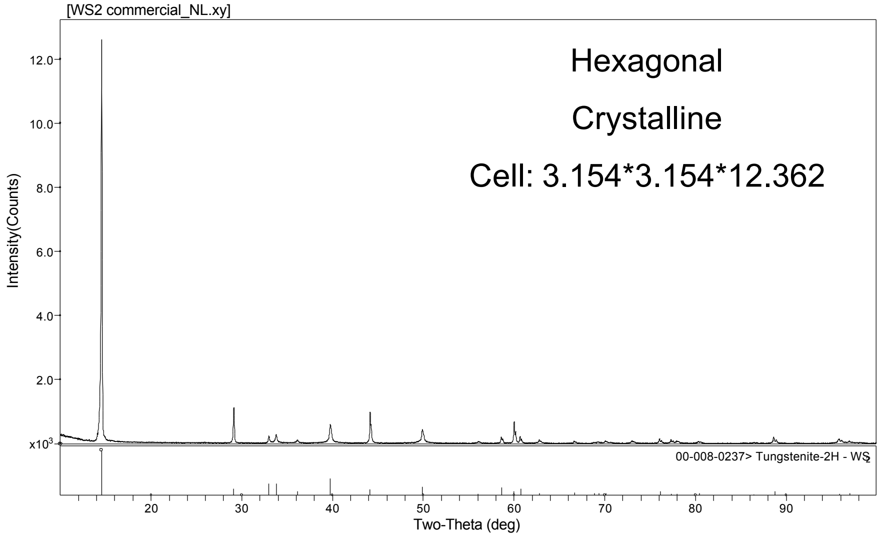
- 1 allotrope
- Exists common Te_2 chain
- Hexagonal

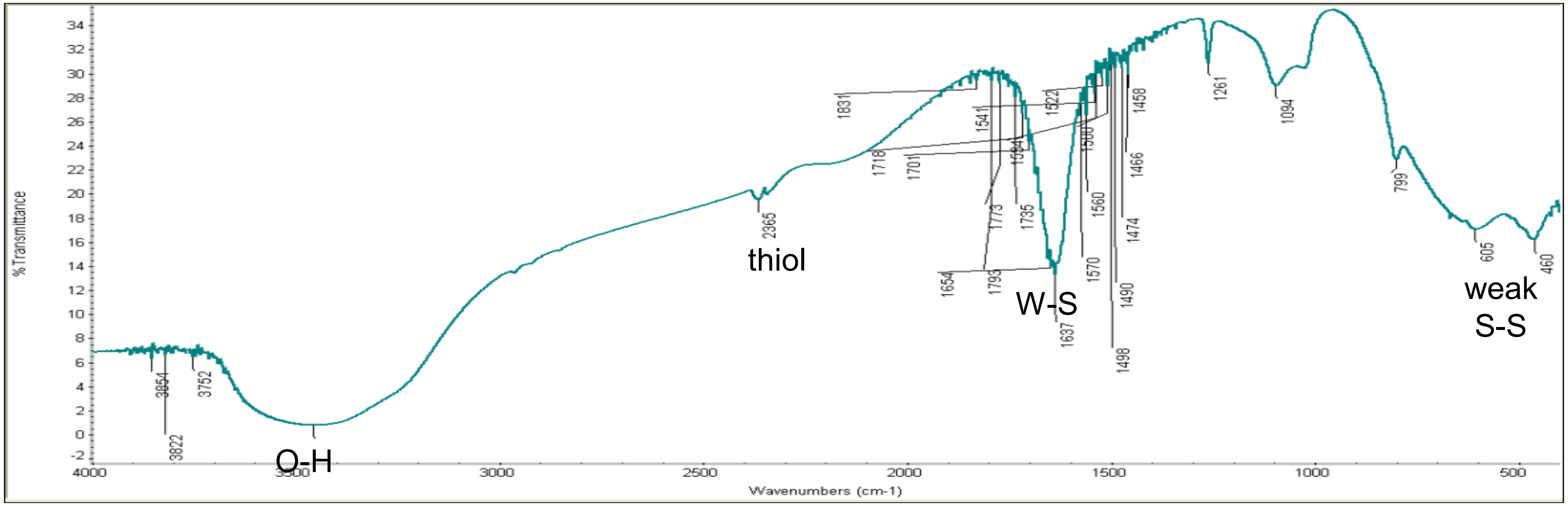
Exploration of Tungsten Sulfide (WS_2)

- RAMAN
- XRD
- FTIR
- XPS

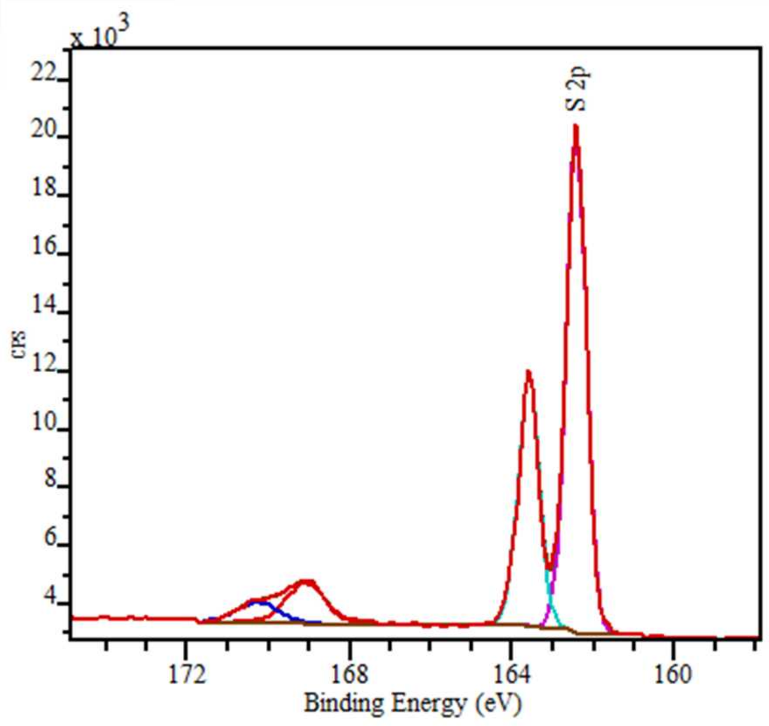
Commercial WS_2

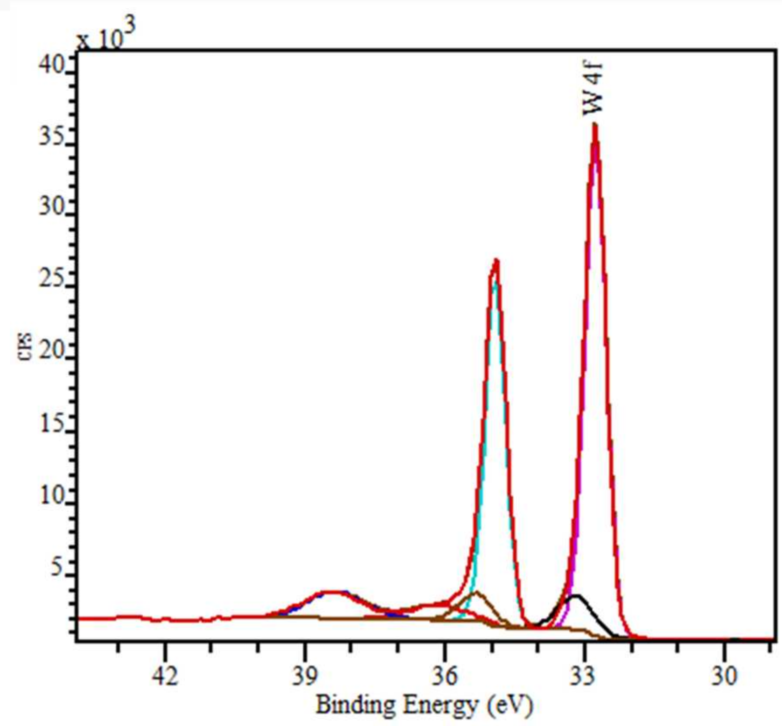


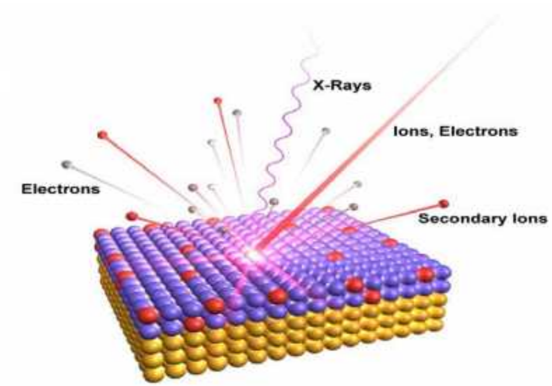




XPS on Commercial WS_2



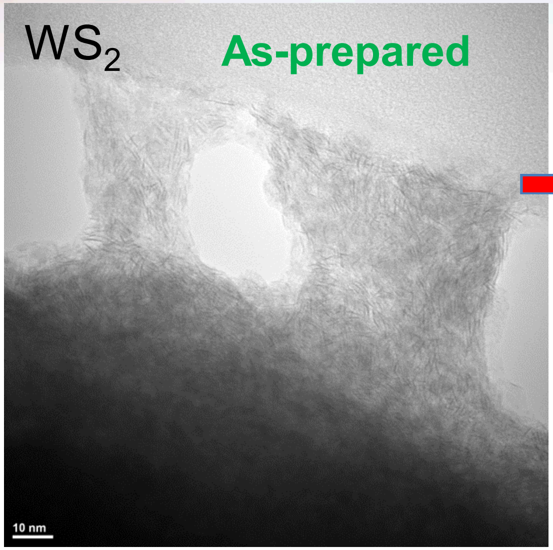


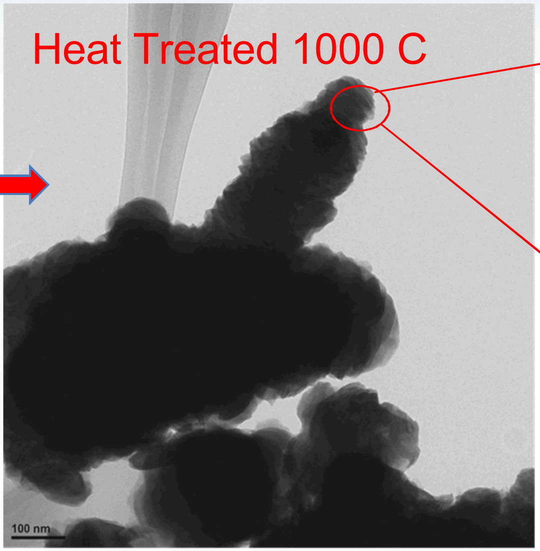


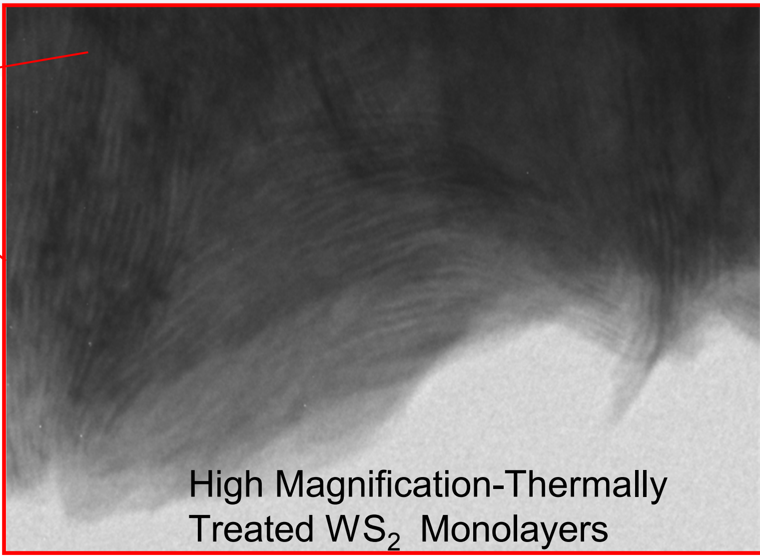
elemental, survey				
C 1s %	**O 1s %**	S 2p %	W 4d %	N 1s %
28.2	**22.3**	31.4	12.9	5.2

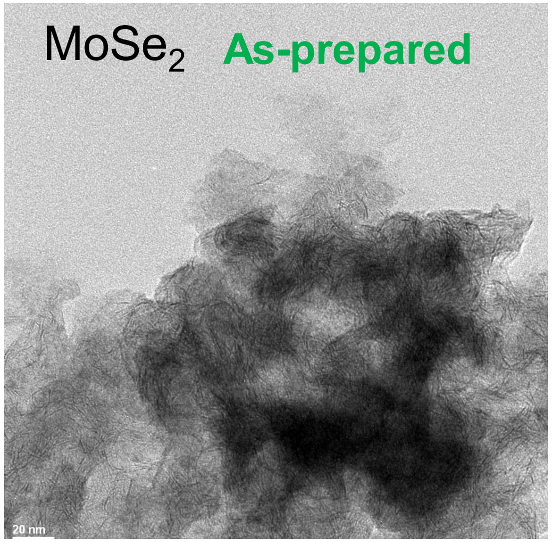
WS2	SO4	WS2	WO2 %	W(V)-W(VI) %
86.8	13.2	82.2	11.2	6.6

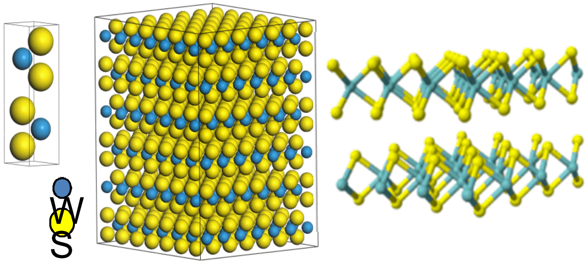
Previous Research



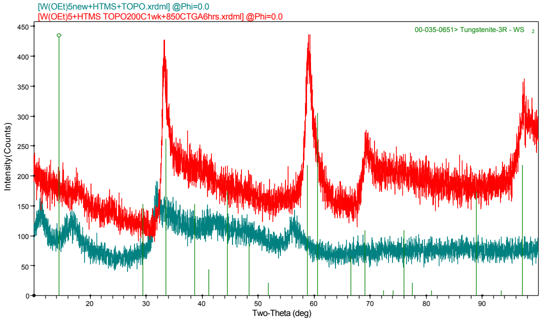








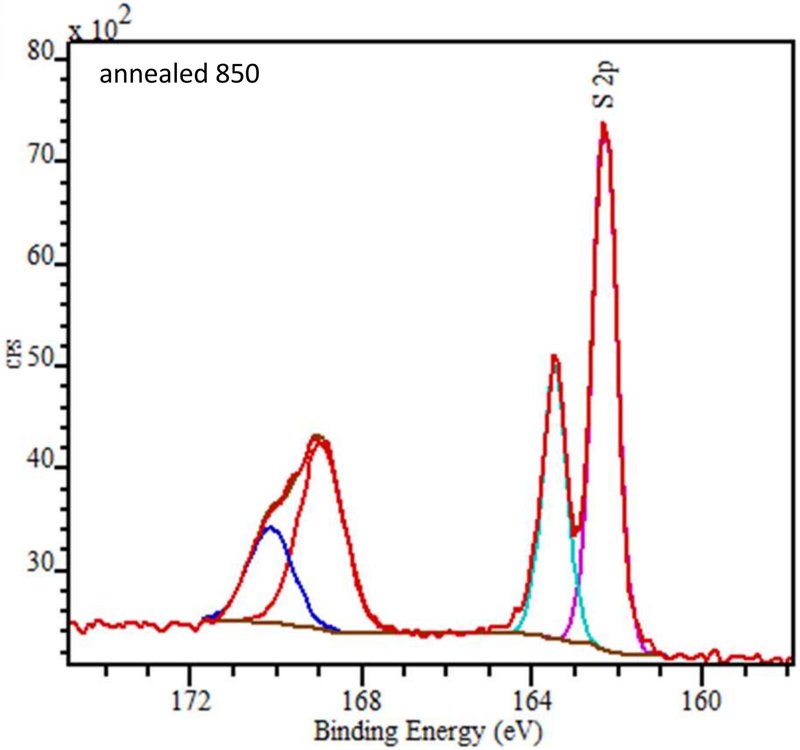
Layered structure of tungsten disulfide nanomaterials

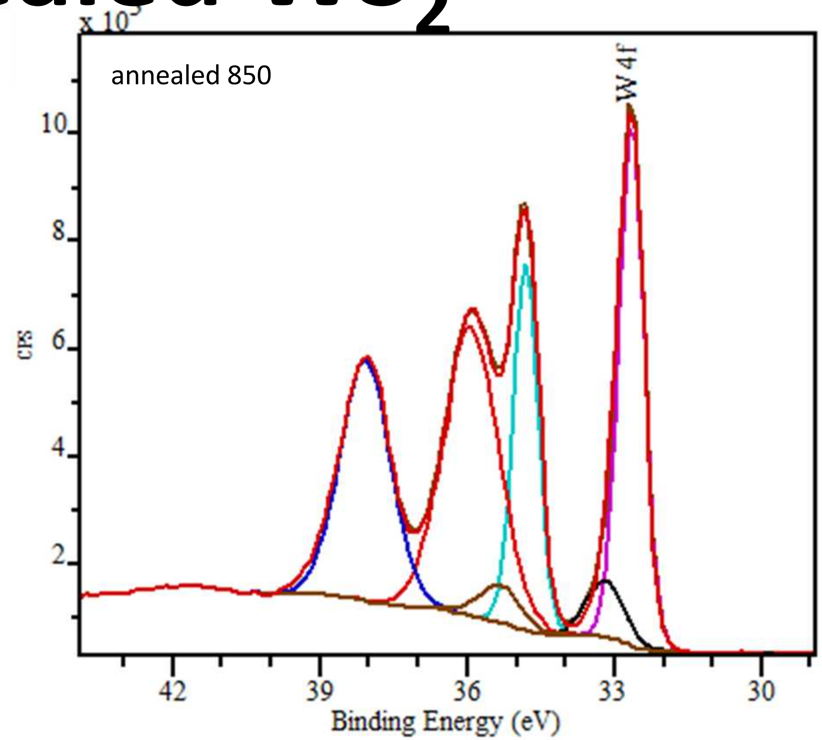


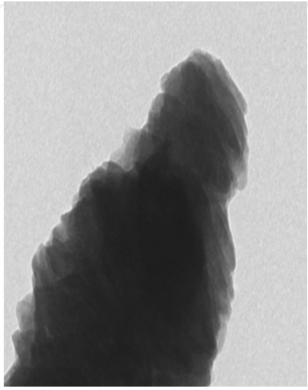
Synthesis of Tungsten & Molybdenum Dichalcogenide Nanoparticles from Metal Alkoxides
B. A. Hernandez-Sanchez, T. J. Boyle, C. D. Hardy, in preparation

1. Altavilla, C.; Sarno, M.; Ciambelli, P., A Novel Wet Chemistry Approach for the Synthesis of Hybrid 2D Free-Floating Single or Multilayer Nanosheets of MS2@oleylamine (M═Mo, W). *Chemistry of Materials* **2011,** *23* (17), 3879-3885.

XPS on Synthesized & Annealed WS_2







elemental, survey				
C 1s %	**O 1s %**	S 2p %	W 4d %	N 1s %
37.1	**38.2**	15.1	8.1	1.5

WS2	SO4	WS2	WO2 %	**W(V)-W(VI) %**
64.3	35.7	43.3	6.8	**49.9**

Synthetic Route

- Nano sized
- Allows for control of size, shape, and crystallinity of nanoparticles

Solvothermal

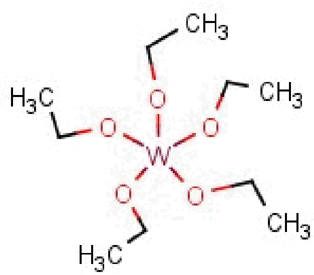
- Heat 200°C for 1-7 days
- Open in glove box
- Check XRD to see if product was obtained

Solution Precipitation

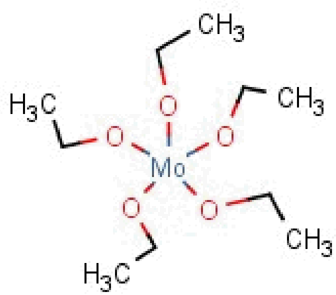
- Mix reaction in three neck round bottom
- Connect to schlenk line
- Remove excess air from tubing
- Backfill with argon
- Heat until desired product formed

Chemical structures

Metal Precursors

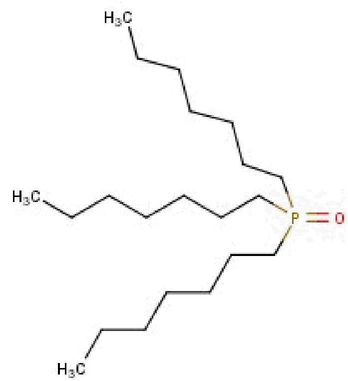


Tungsten (V) ethoxide

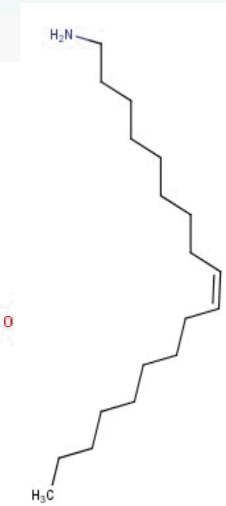


Molybedumn (V) ethoxide

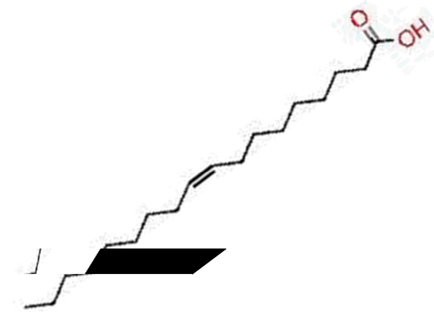
Solvents



Trioctylphosphine oxide

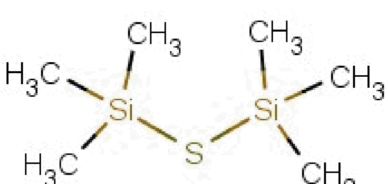


Oleylamine

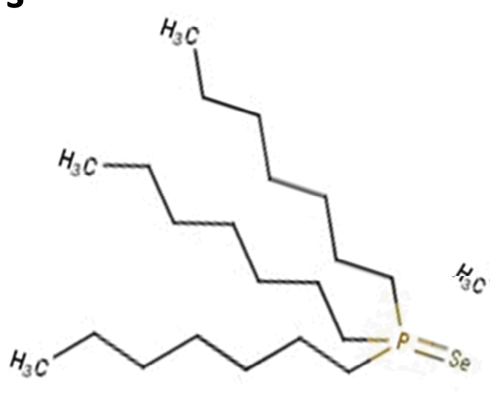


Oleic acid

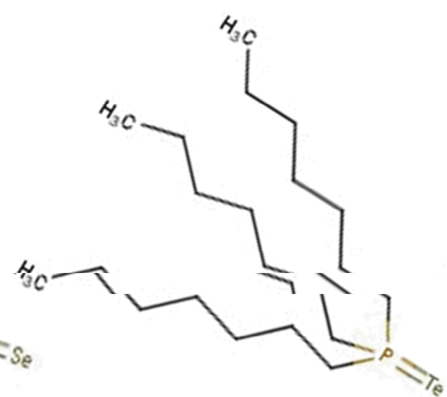
Chalcogen Precursors



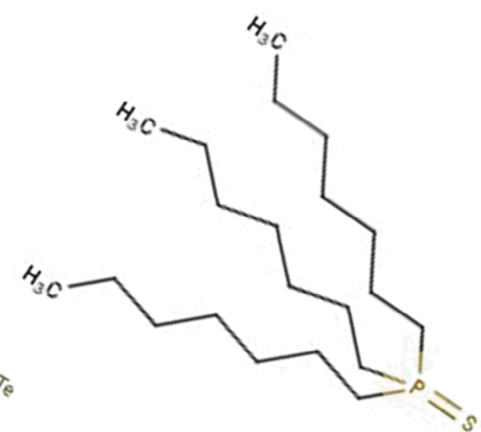
Hexamethyldisilathiane



Se=TOP



Te=TOP



S=TOP

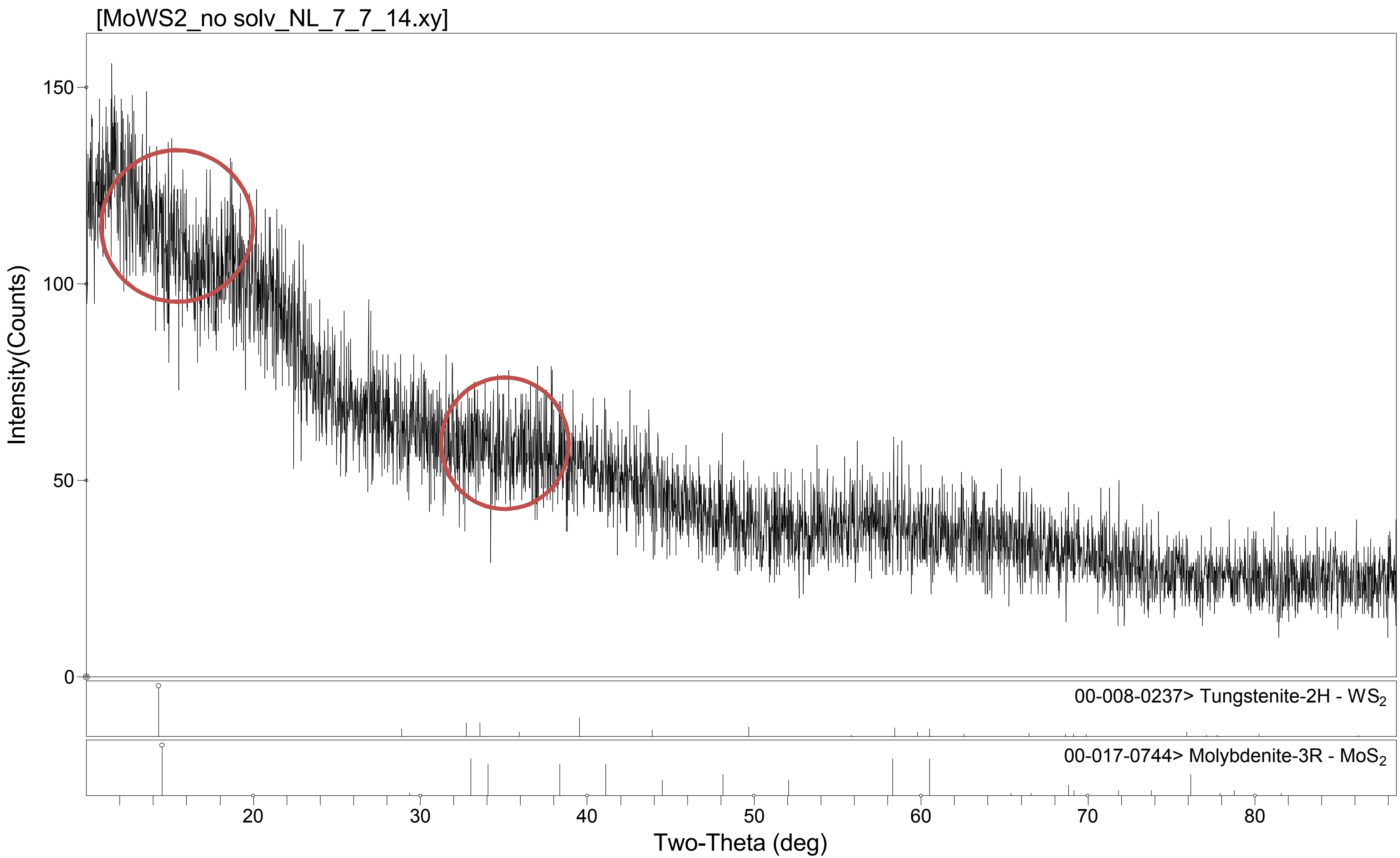
Results Summary

Sulfide Reactions

Precursors	Solvent	Time (days)	Method	Characterization	Appearance of Product	Product expected
$W(OEt)_6$ + 3HTMS	TOPO	7	Solvothermal	Powder XRD, XPS, FTIR	Dark liquid	WS_3
$W(OEt)_5$+3HTMS	TOPO	1	Solvothermal	Powder XRD, XPS , FTIR	Black sticky solid	WS_2
$W(OEt)_5$ + 3HTMS	None	2	Solvothermal	Powder XRD	Black viscous liquid	WS_2
$W(OEt)_5$ + 3HTMS	TOPO	1	Solvothermal	Powder XRD	Black sticky solid	WS_2
.5$W(OEt)_5$ + .5$Mo(OEt)_5$ + 2S=TOP	None	2	Solvothermal	Powder XRD	Black viscous liquid	$(MoW)S_2$
$W(OEt)_5$ + 3S=TOP	TOPO	1	Solvothermal	Powder XRD	Brown sticky solid	WS_2

$.5W(OEt)_5 + .5Mo(OEt)_5 + 2S{=}TOP$

Solvothermal
Neat Reaction



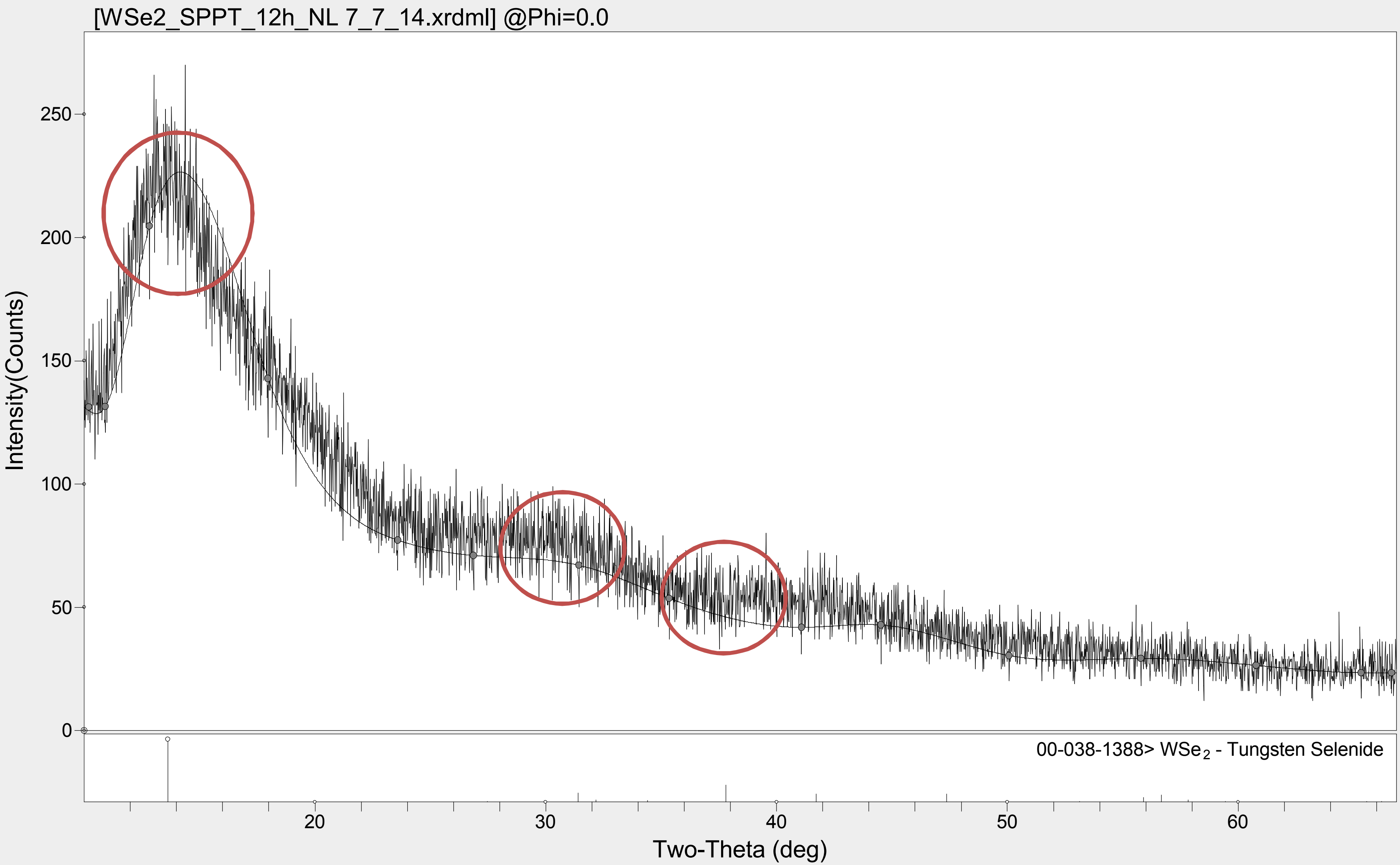
Results Summary

Selenide Reactions

Precursors	Solvent	Time (days)	Method	Characterization	Appearance of Product	Product expected
$W(OEt)_6$ + 2Se=TOP	TOPO	4	Solvothermal	Powder XRD	Dark blue sticky solid	WSe_2
$W(OEt)_5$ + 2Se=TOP	None	2	Solvothermal	Powder XRD	Dark blue liquid	WSe_2
$Mo(OEt)_5$ + 2Se=TOP	TOPO	2	Solvothermal	Powder XRD	Dark liquid	$MoSe_2$
$W(OEt)_5$ + 2Se=TOP	Oleic Acid	17.5 h	Solution Precipitation	Powder XRD	Dark blue liquid	WSe_2
$W(OEt)_5$ + Se=TOP	TOPO	12h	Solution Precipitation	Powder XRD	Black solid stuck to sides of round bottom	WSe_2
$W(OEt)_5$ + 2Se=TOP	Oleyamine	17.5h + 4 days solvothermal +1day	Solution Precipitation/ Solvothermal	Powder XRD	Black viscous liquid	WSe_2

$W(OEt)_5$+ Se=TOP

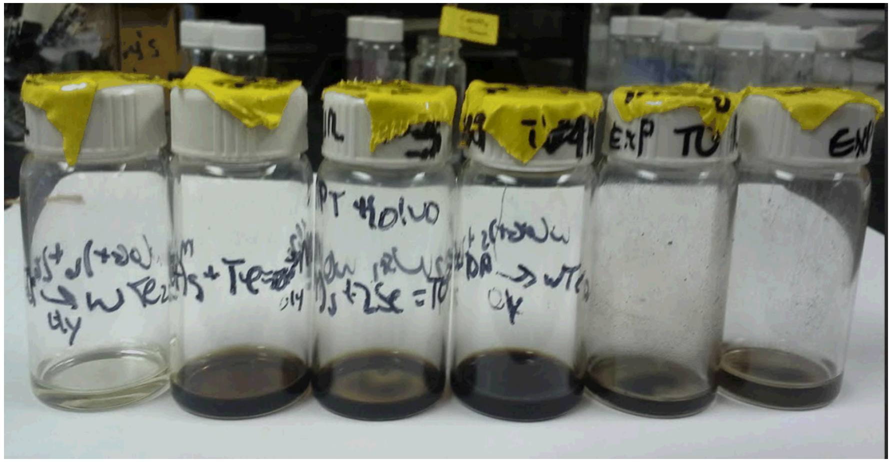
SPPT
Oleylamine



Results Summary

Telluride Reactions

Precursors	Solvent	Time (days)	Method	Characterization	Appearance of Product	Product expected
$W(OEt)_5$ + 2Te=TOP	Oleyamine	15 h	Solution Precipitation	Powder XRD, XPS , FTIR	Black viscous liquid	WTe_2
$Mo(OEt)_5$ + 2Te+TOP	Oleyamine	4+1day	Solvothermal	Powder XRD	Black liquid	$MoTe_2$
$W(OET)_6$ + 2Te=TOP	Oleyamine	4+1day	Solvothermal	Powder XRD, XPS , FTIR	Blue liquid	WTe_2



XRD, FTIR, Raman for Products

XRD

- Showed either nothing or oxide peaks
- No sign of crystalline product

Raman

- Not compatible with my products
- Read only glass of vial

FTIR

- Provided information about surface chemistry
- Indicate presence of thiols and OH stretching

XPS for Products

	Te atoms/ other metal	*Te/ other atoms*	*WTe*	*Te-CxHy*		*WC/ WO2*	*WTe/ WSe/ WS*	*WO3*		*WSe2/ WO2*	*WTe2 / WS2/ WO3*
WTe2 4 days			90.6	9.4			100.0				100.0
WTe2 sppt		10.4	65.9	23.7		52.0	48.0			100.0	
WSe2						61.2	38.8			100.0	
WS3 1 day						15.1	55.1	29.8		19.6	80.4
WS3 7day						39.2	38.4	22.4		44.7	55.3

XPS

- Indicate presence of C, H, O
- Proved that some desired product was formed (<40%)
- Showed that mixture of oxides were formed

Analysis

I did not obtain the expected results…

1. Precursor Purity

    Tech Grade TOPO vs. Reagent Grade (99.9%)

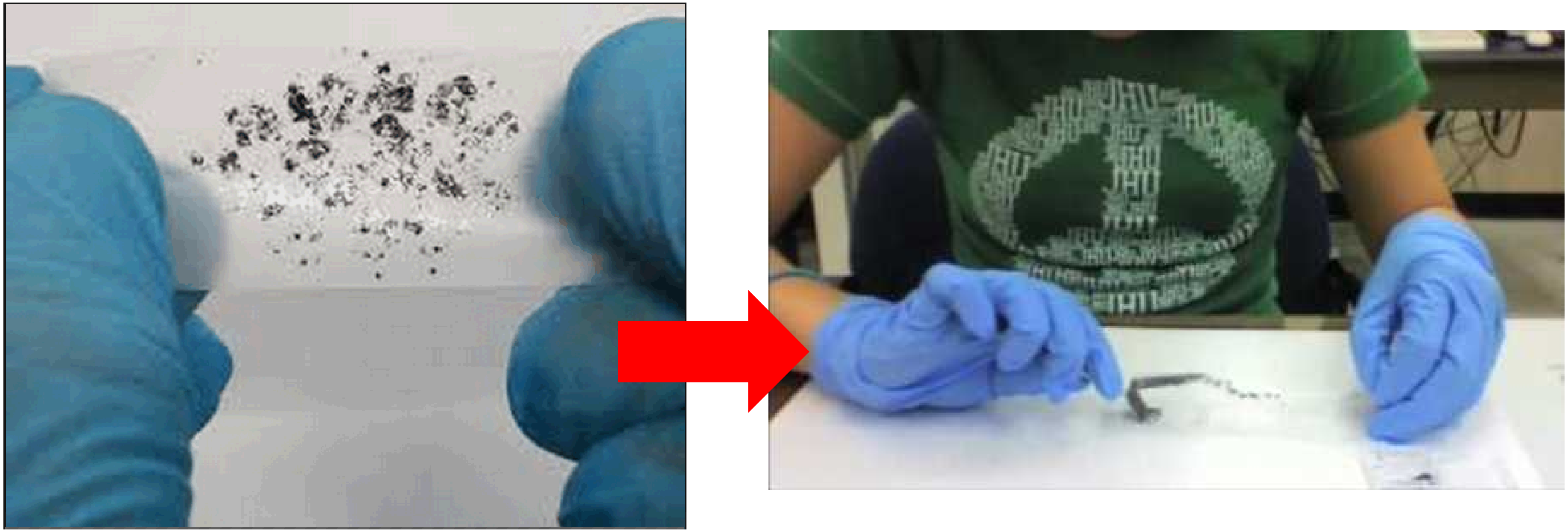
2. Wash process lost product

    Wet “Anhydrous” Solvents

3. Not heated long enough
4. Not reacted at high enough temperature
5. Air sensitivity

Exfoliation

- The process of making single crystals into thin sheets
  - Scotch taping method



Future Work

- Find appropriate reaction time to synthesize correct product

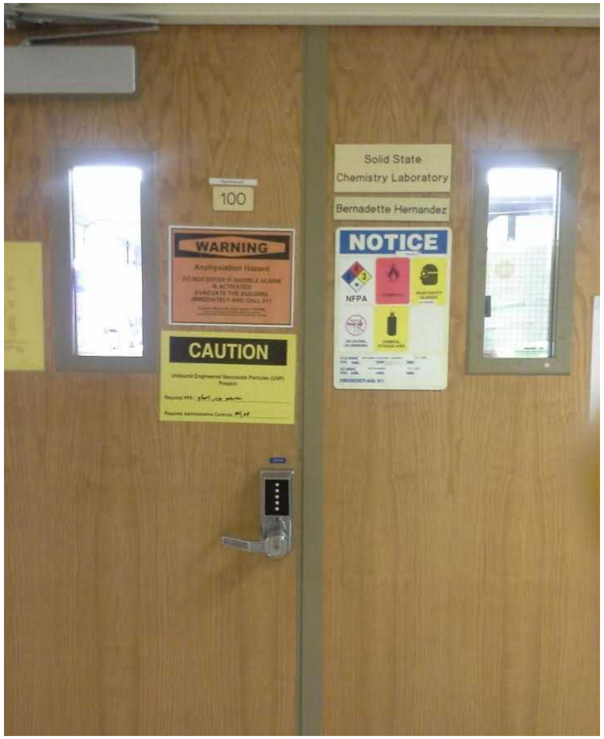
- Synthesize following products using variety of precursors on a small scale

  MoS_2
  WS_2
  $MoSe_2$
  WSe_2
  $MoTe_2$
  WTe_2
  MoWS
  MoWSe
  MoWTe

- Fully characterize products

Additional Outcomes

- Learned multiple characterization techniques: XRD, XPS, FTIR, TEM, Raman,
- Learned Physical Exfoliation of WS_2
- Gained experience in writing proposals
  - CINT Rapid Access Proposal
  - Mike Lilly (Discovery Platform)
- Connected with Sandia scientists
- Lab management
- Lab safety



Acknowledgements

- United States Department of Energy
- Sandia National Laboratories
- University of New Mexico
- Stanley S. Chou and Conner Dykstra
- Dr. Bernadette A. Hernandez-Sanchez