Characterization of 2D Materials using XPS, SIMS, & Raman

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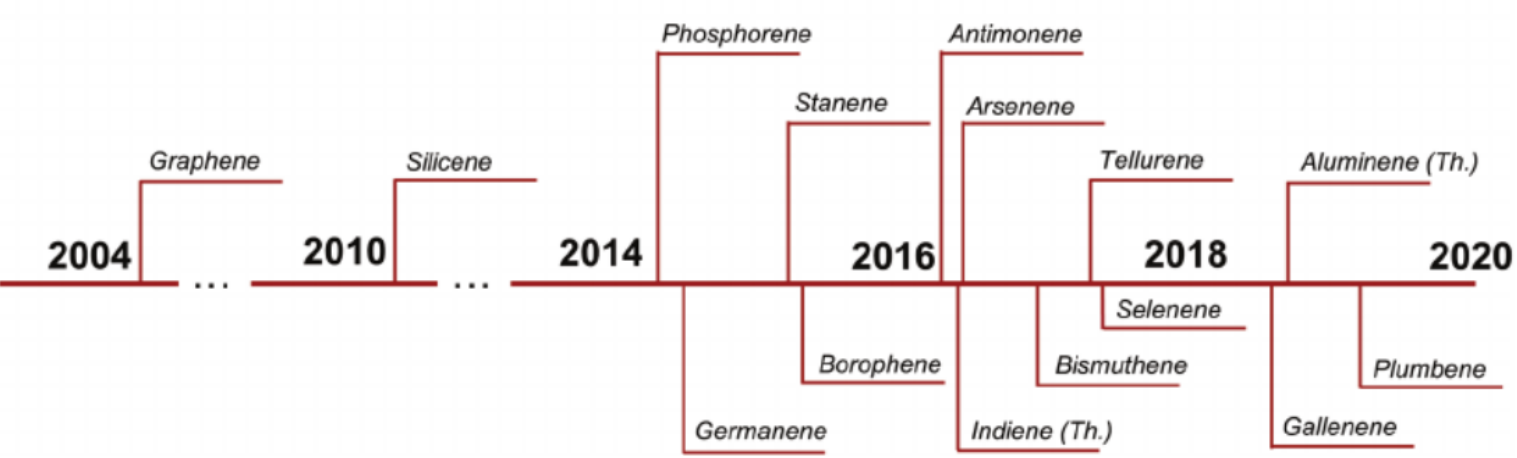
Outline

- Intro to 2D materials and their synthesis
- Introduction to TOF SIMS and utility in 2D materials
- XPS & UPS basic principles and instrumentation
- Characterization of advanced materials with XPS and UPS
- Raman on 2D materials including Polarized Raman and TERS

2D materials: Literature Overview



88 TMDs have been explored since 1960s

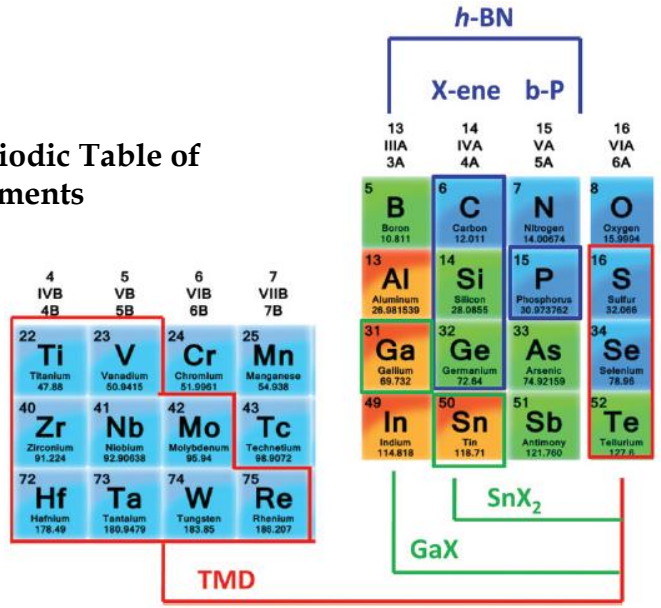
Metals: $ScTe_2$,TaS_2 , etc.

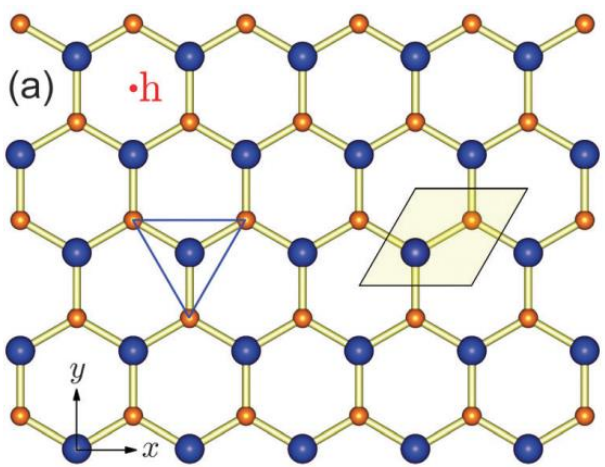
Semiconductors: WSe_2 , MoS_2, WS_2, $MoSe_2$etc.

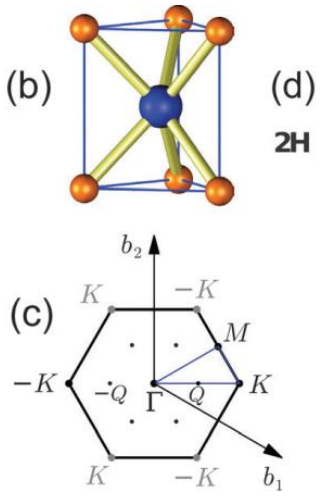
Insulators: $PtSe_2$,PdS_2 , etc.

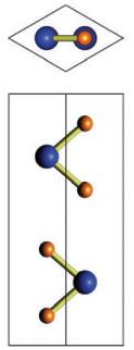
Superconductors: VS_2 , $NbSe_2$, etc.

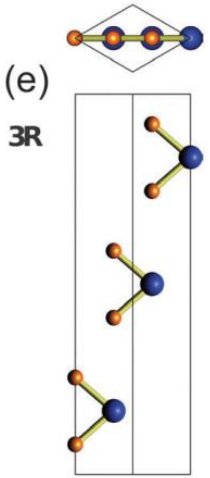
Periodic Table of Elements





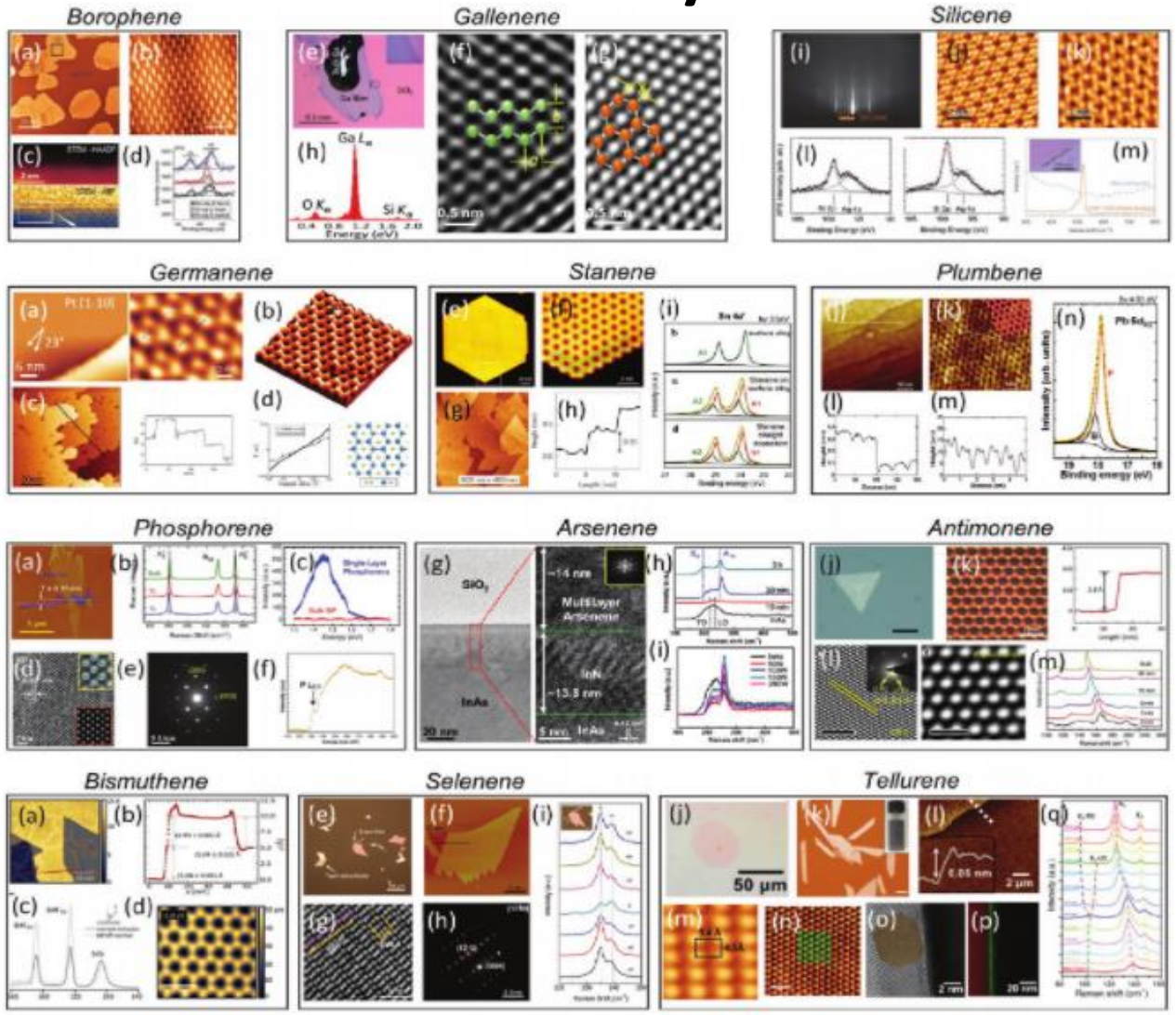




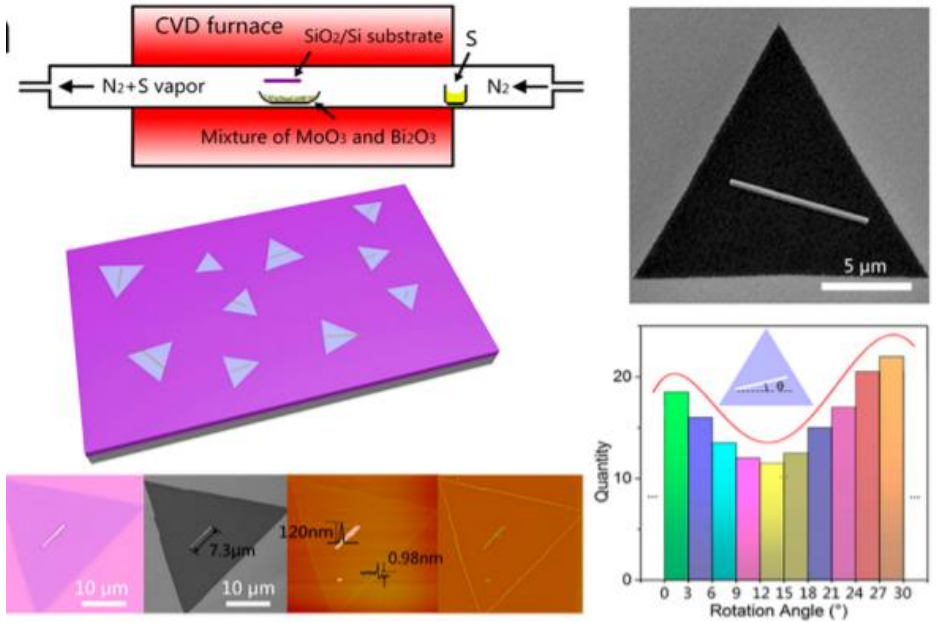


Chem. Soc. Rev.,2015,44,2587
Chem. Rev. 2018, 118, 6091−6133

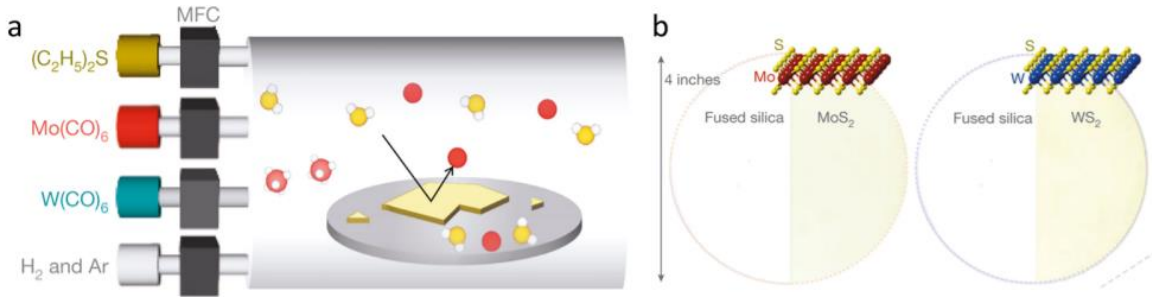
Synthesis of 2D materials



CVD

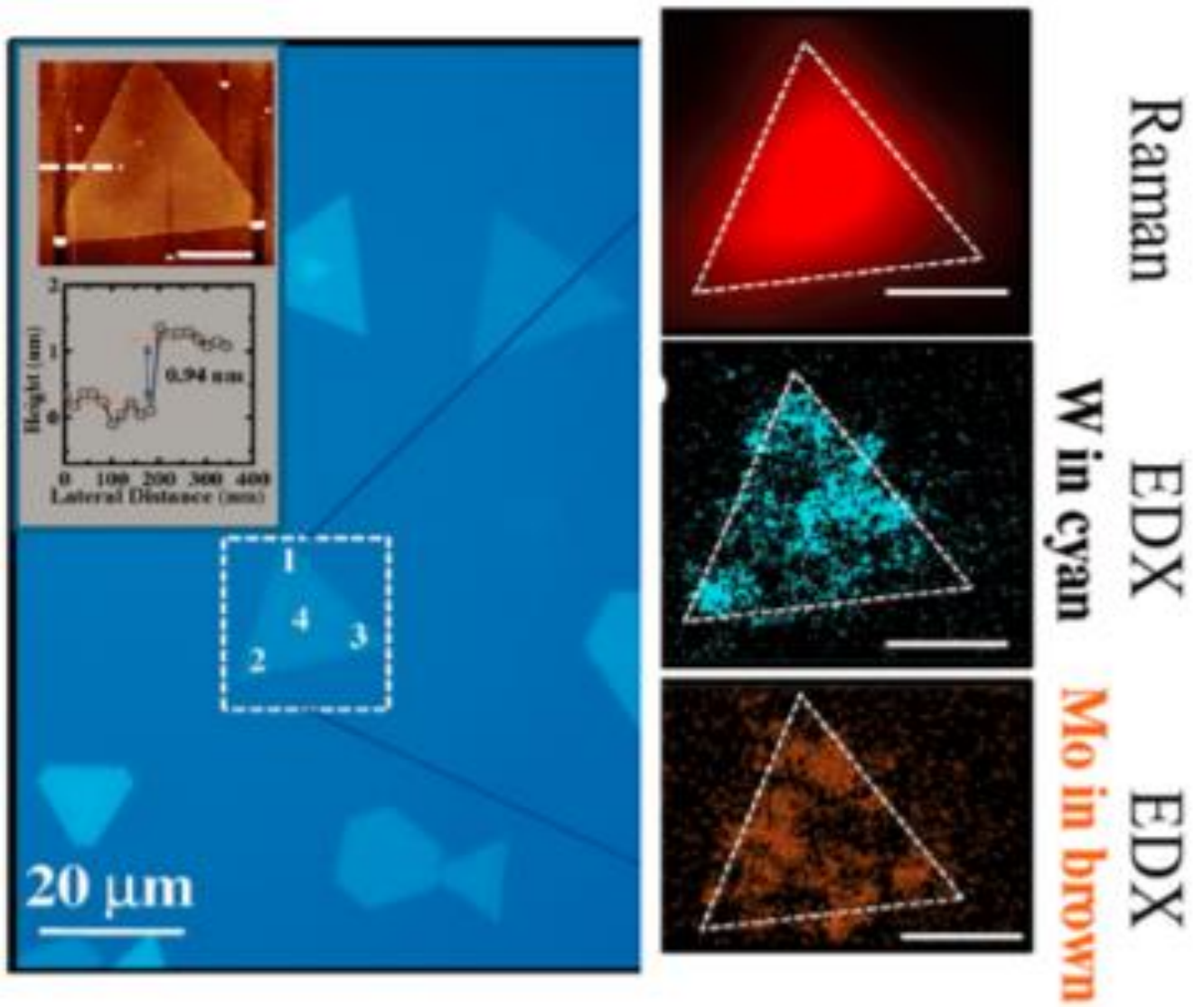


MOCVD



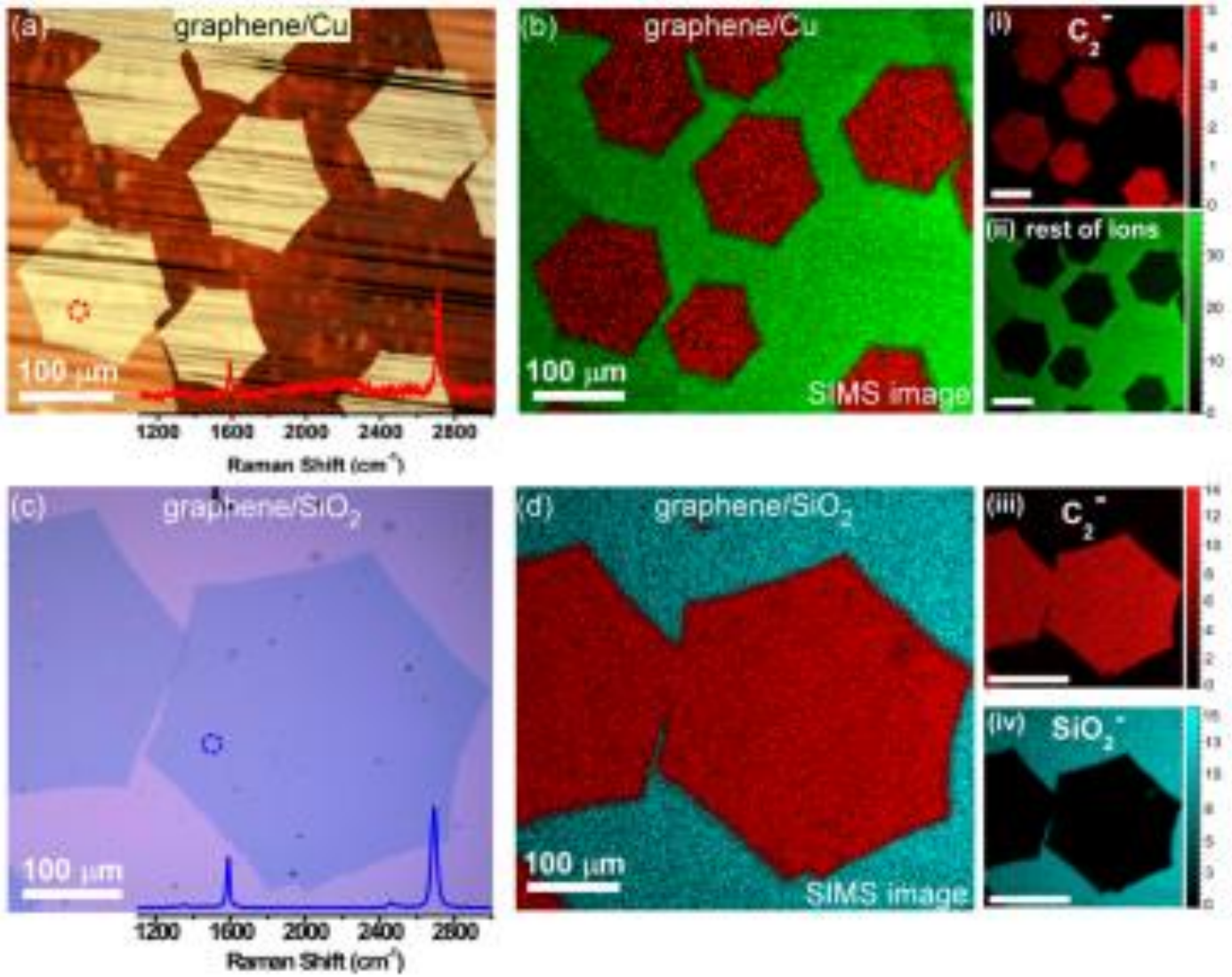
Nano Lett. 2012, 12, 1538−1544
ACS Nano, 2014, 8 6902–6910
Adv. Mater. 2020, 32, 1904302

Characterization in 2D limit: Challenging!

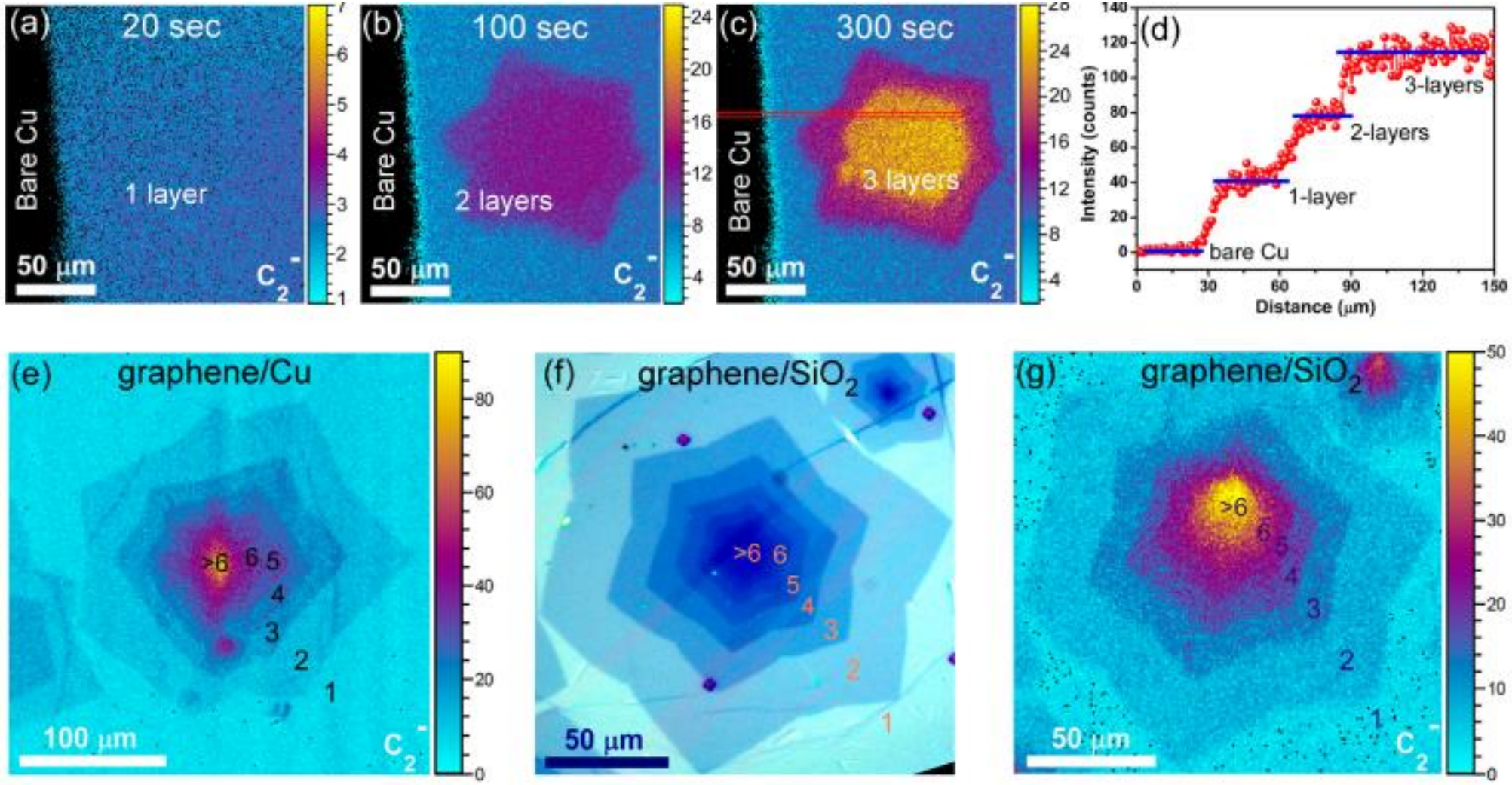


Adv. Mater. 2020, 32, 1904302

SIMS for Elemental analysis of 2D materials



Thickness mapping via SIMS

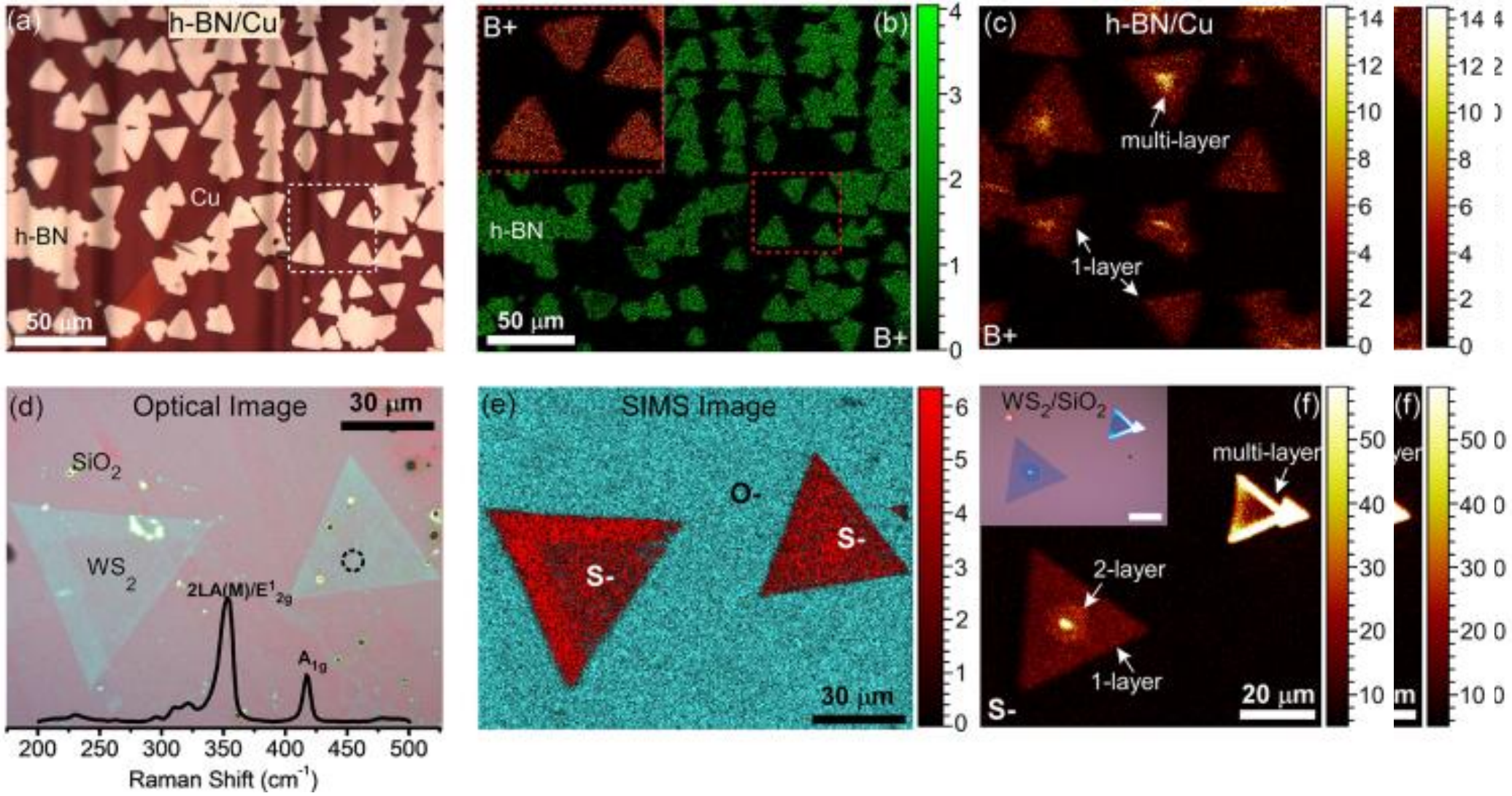


NATURE COMMUNICATIONS 6,7482
Chem. Mater. 2018, 30, 1718−1728

Versatility of Elemental Mapping

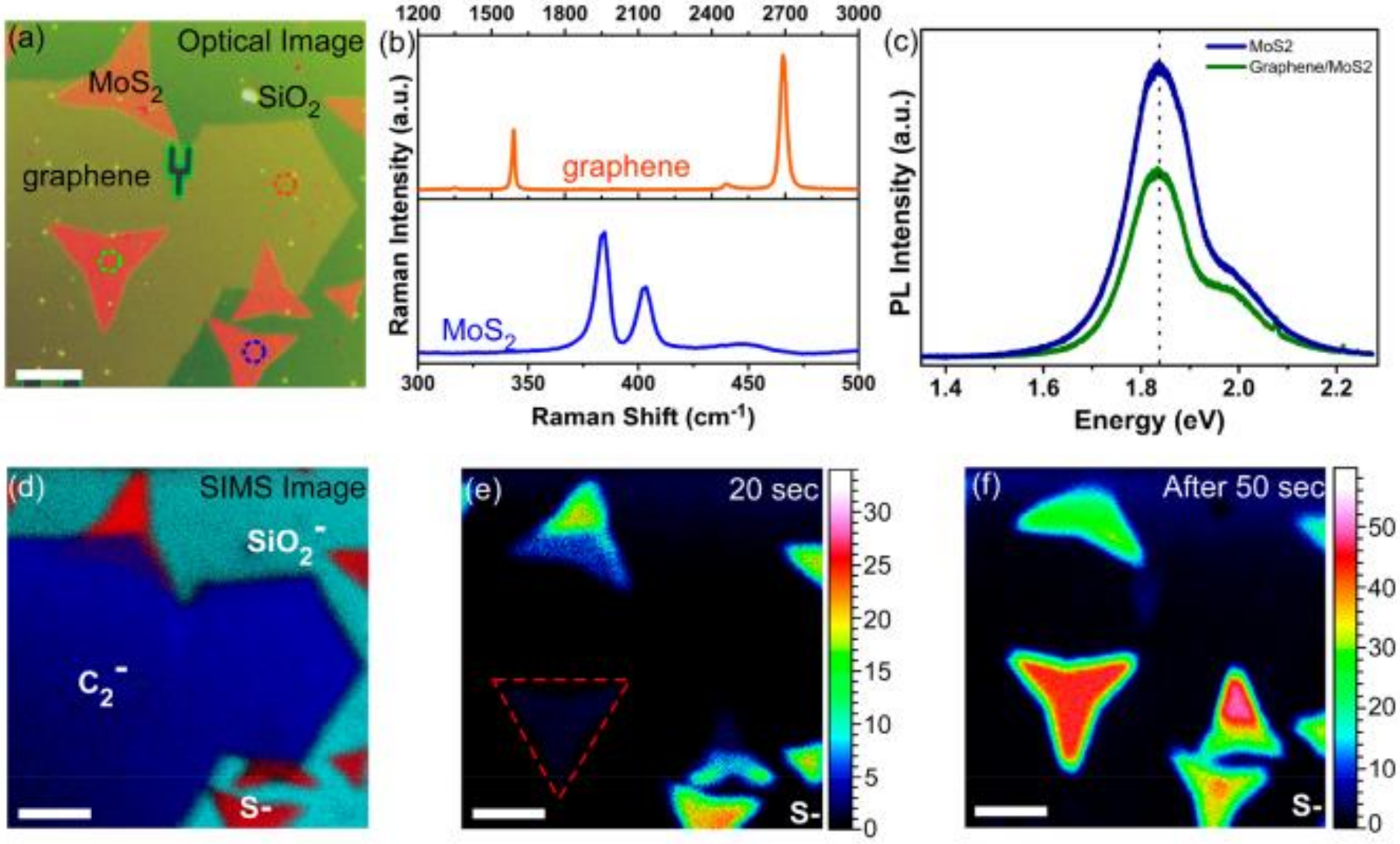
h-BN

WS_2



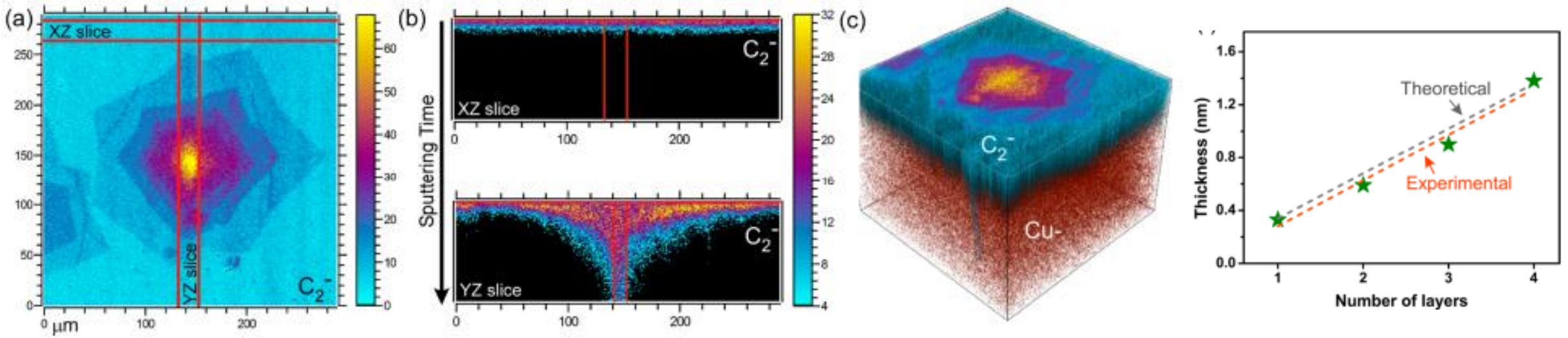
Chem. Mater. 2018, 30, 1718−1728

Mapping on heterostructures



Chem. Mater. 2018, 30, 1718−1728

Thickness mapping via Depth Profiles



Chem. Mater. 2018, 30, 1718−1728

TOF SIMS: THE M6

ToF-SIMS uses a pulsed primary ion beam (Bin+, Cs+, Ar+, etc.) to impact on a sample surface and induce a fragmentation cascade. The result is the desorption of neutrals, secondary ions (+/-) and electrons from the first few monolayers of the sample. The secondary ions can then be accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector

1. High lateral resolution (< 50 nm) with the new Nanoprobe 50

2. Mass resolution > 30,000

3. Unique delayed extraction mode for high transmission with high lateral and high mass resolution simultaneously

4. Unmatched dynamic range and detection limits

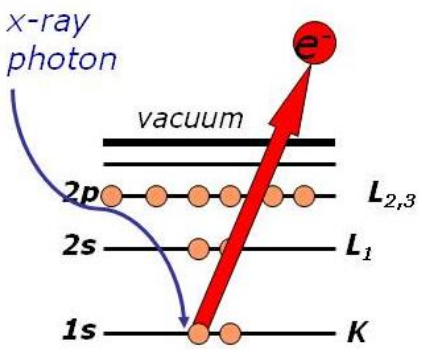
5. TOF MS/MS with CID fragmentation for molecular structure elucidation

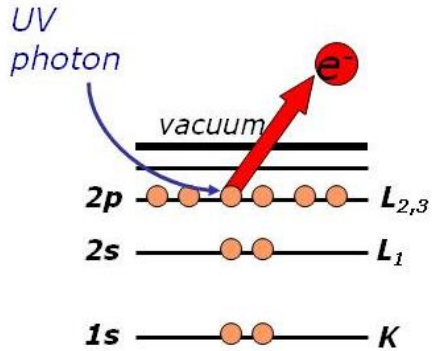
6. New flexible, push-button, closed-loop sample heating and cooling system for long-term operation without user interaction

7. Sophisticated SurfaceLab 7 software including fully integrated Multivariate Statistical Analysis (MVSA) software package

XPS & UPS: An overview

Surface electron spectroscopies





e^- = electron detected in experiment

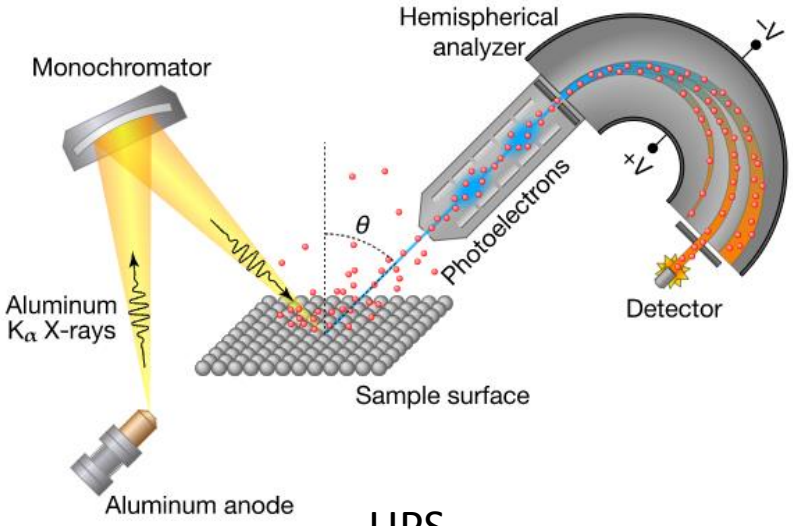
XPS

- core electrons ejected
- gives elemental composition
- provides some info about "environment" of atoms

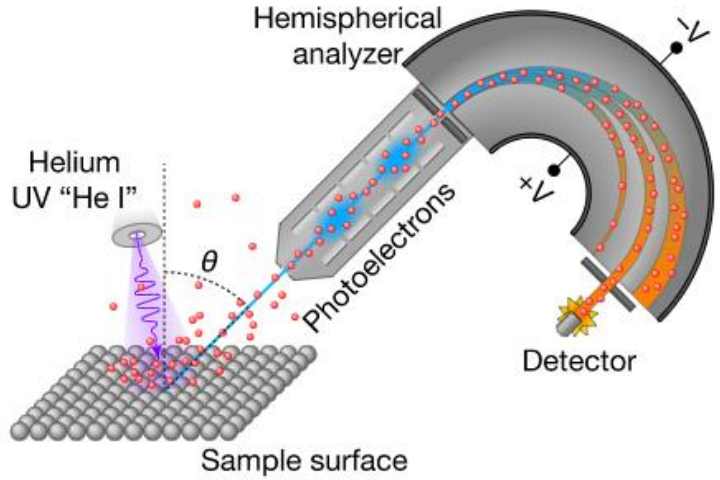
UPS

- valence electrons ejected
- provides estimates for "density of states", frontier orbital energies (HOMO), work function

XPS

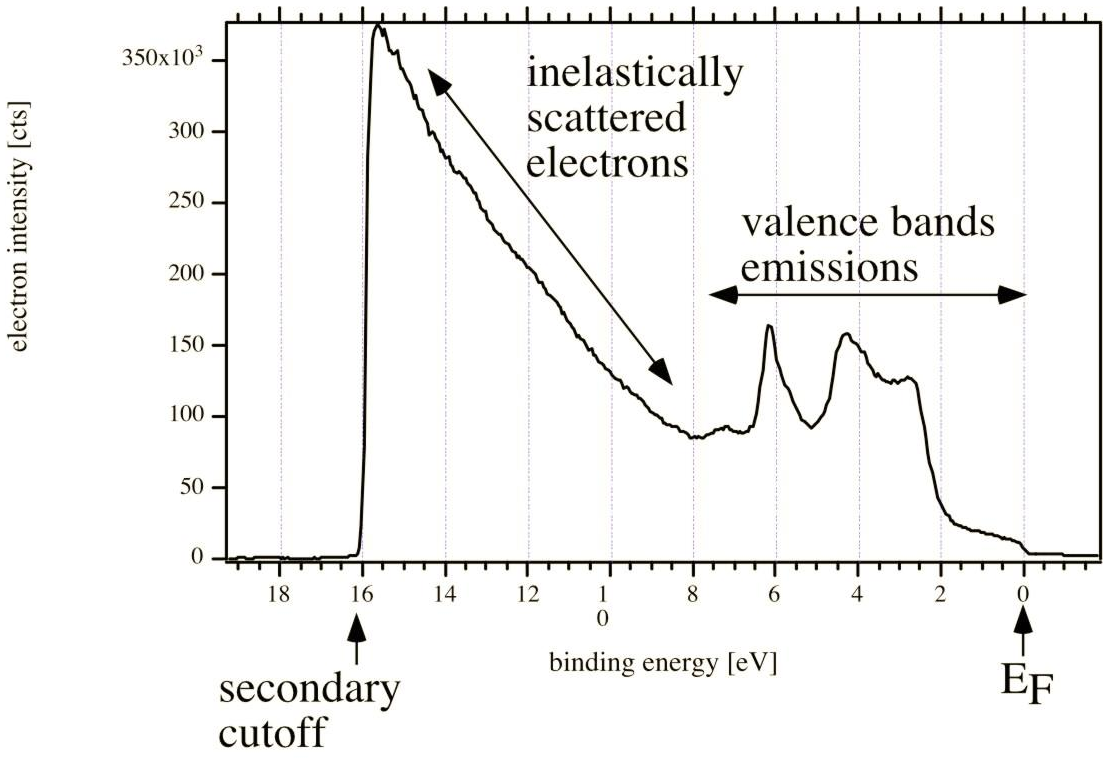


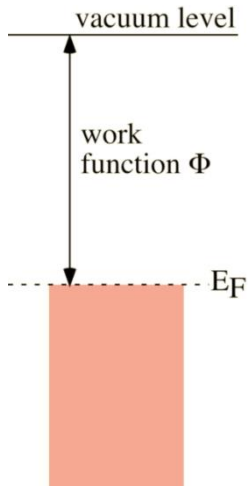
UPS



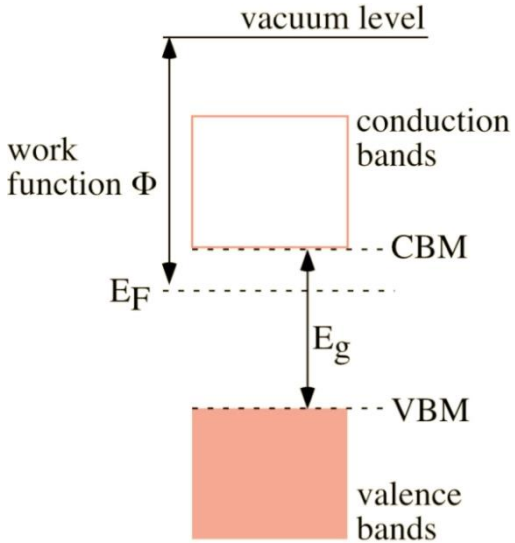
UPS: An overview

UPS spectrum of Au surface





Schematic energy diagram of a metal.



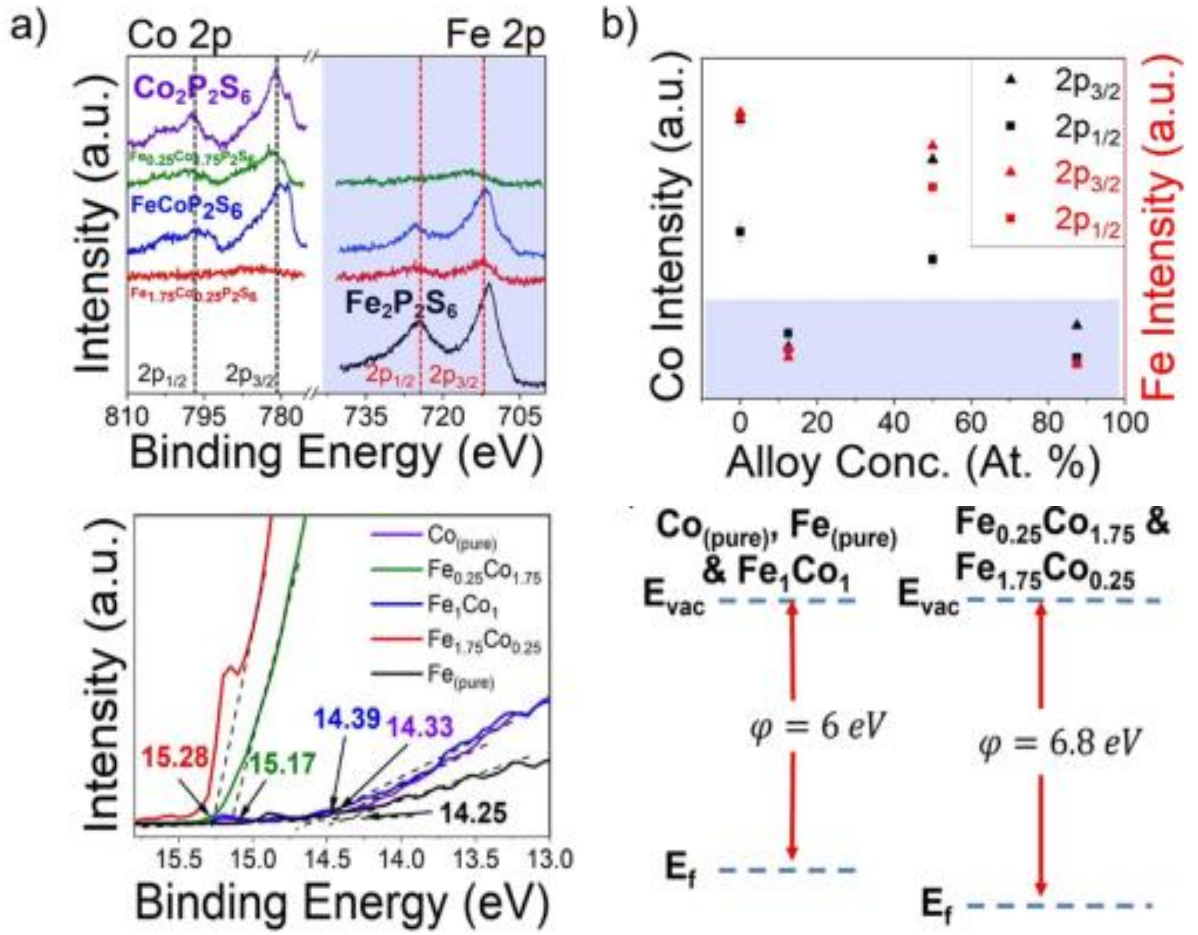
Schematic energy diagram of a semiconductor.

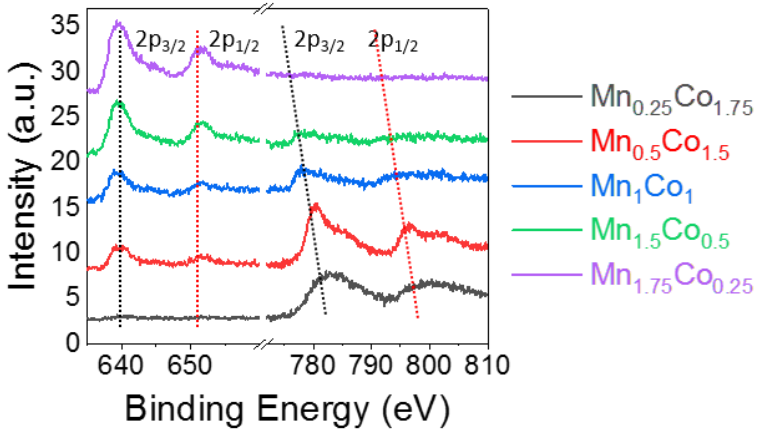
Work function = 21.21 - 15.9 = 5.31 eV

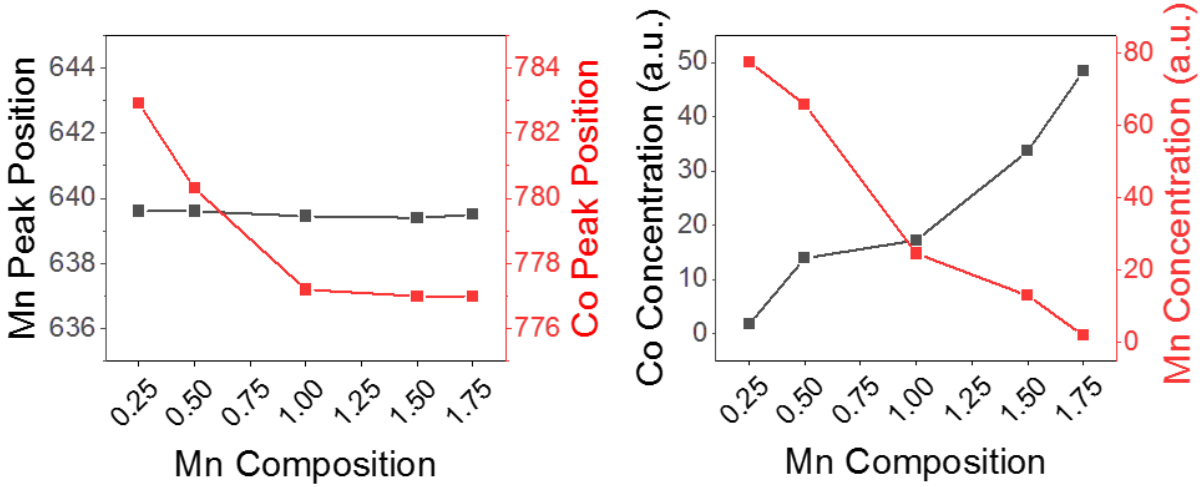
Literature value 5.3 eV

KE=h*v*-BE-Ø
BE=h*v*-KE-Ø

XPS and UPS: $FeCoP_2S_6$ & $MnCoP_2S_6$





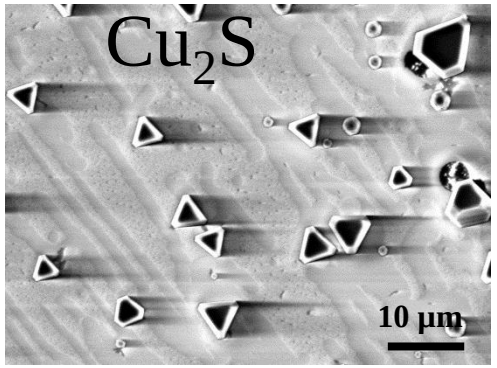


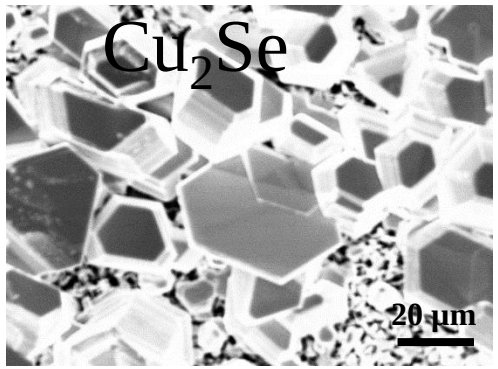
XPS indicates distinct suppression of Fe and Co $2p_{1/2}$ and $2p_{3/2}$ peaks in both Fe and Co-rich samples.
UPS indicates two distinct work functions with both Fe and Co rich systems exhibiting a higher work function shift.

Inorg. Chem. 2021, 60, 17268−17275

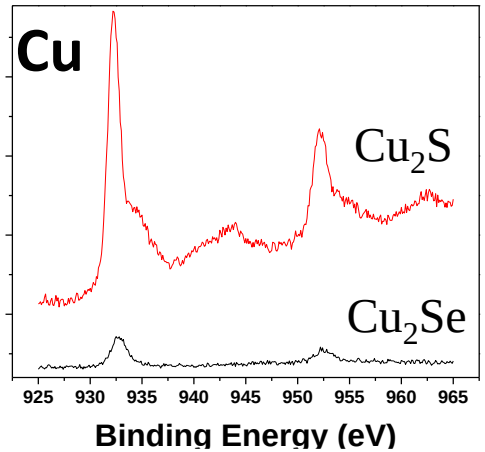
XPS of 2D materials on different substrates

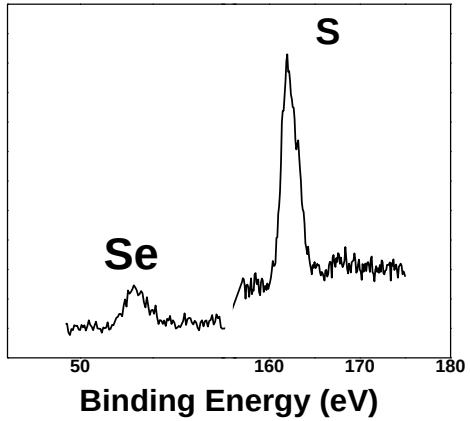
On Sapphire

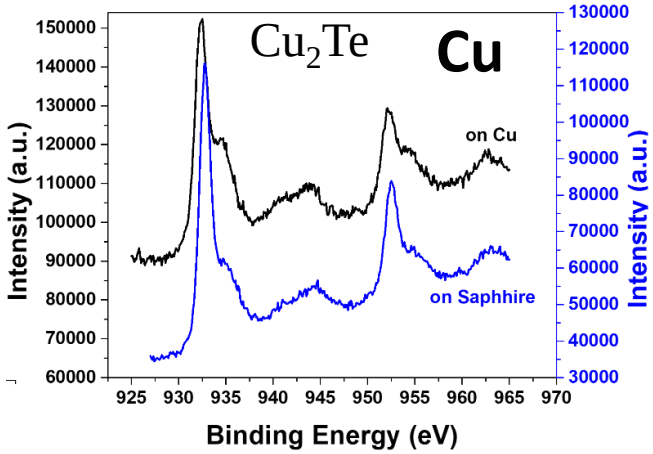


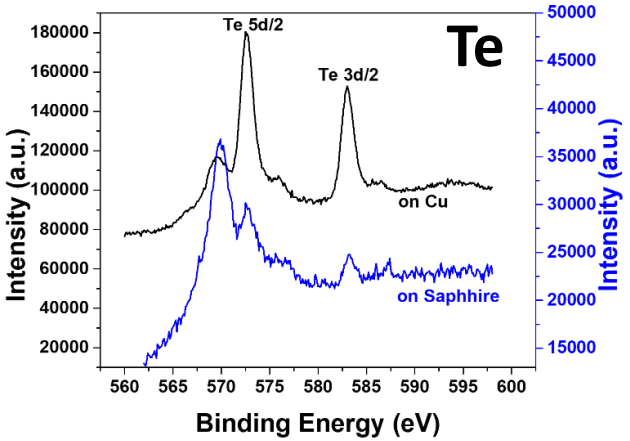


On Tungsten

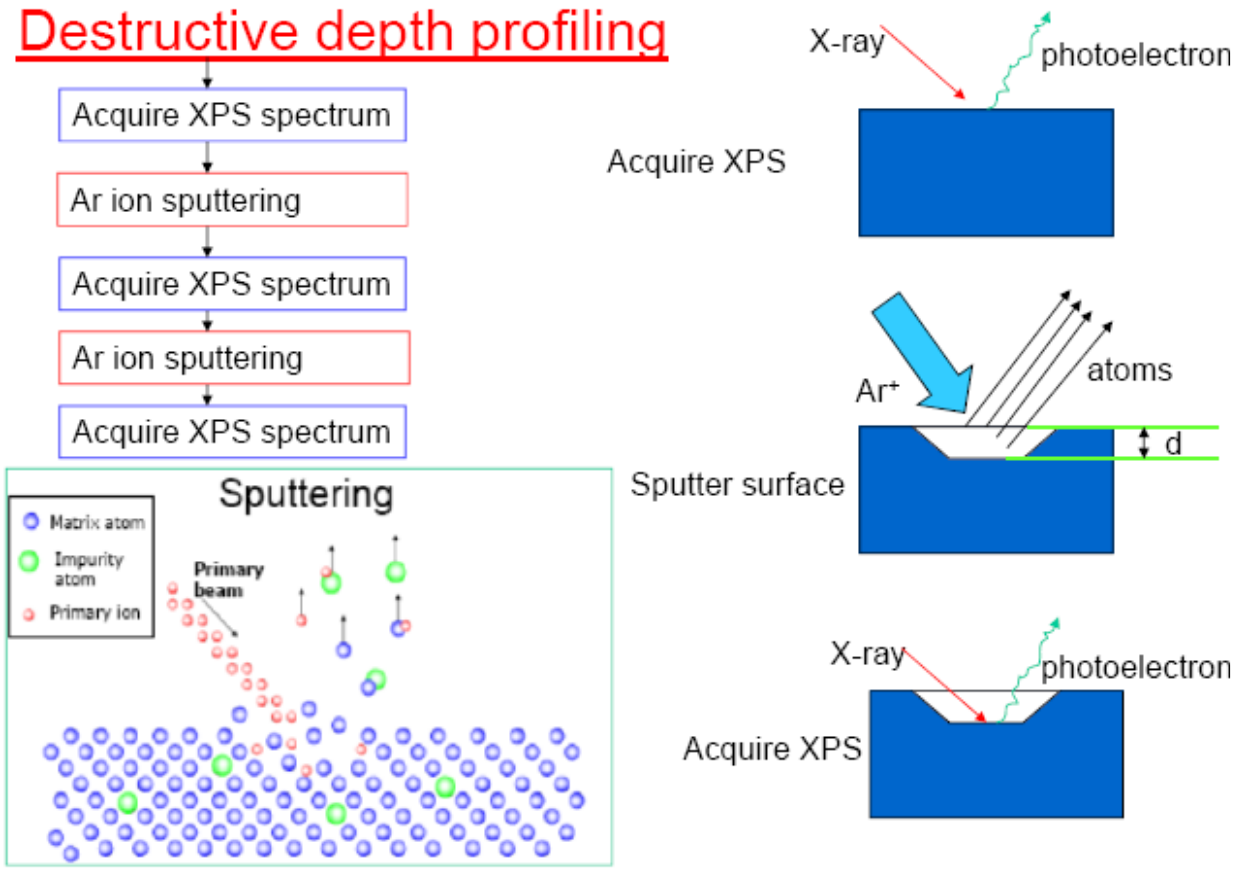


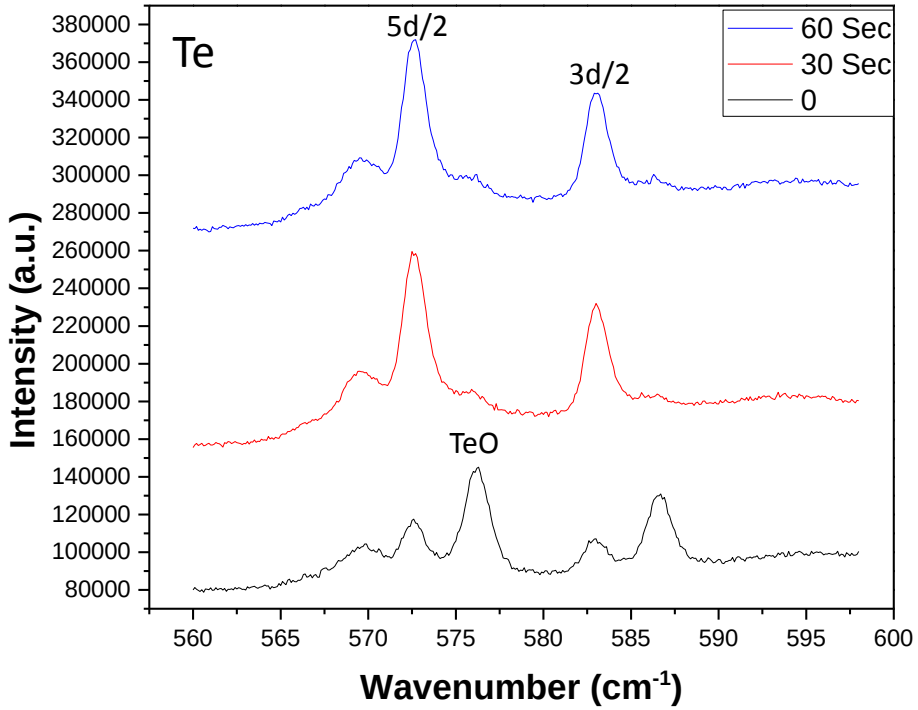




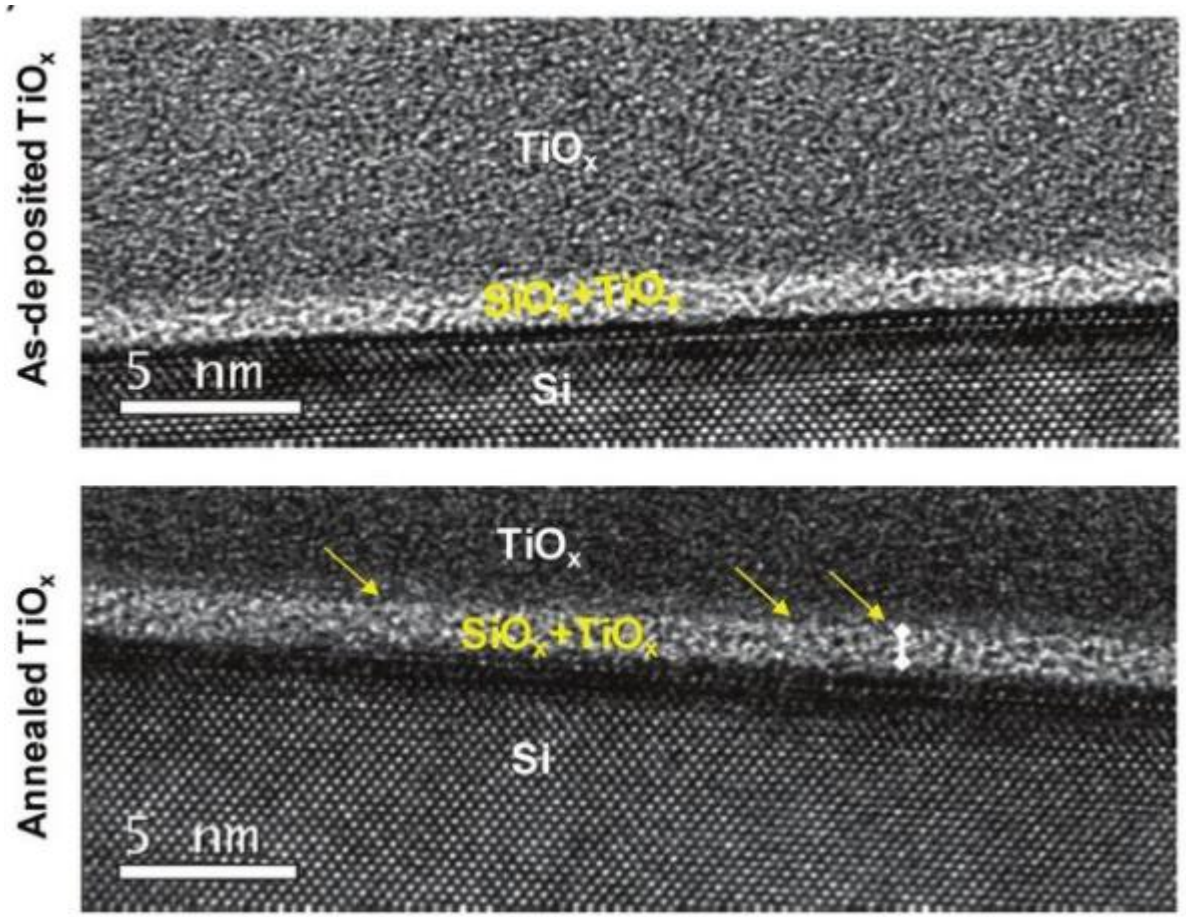


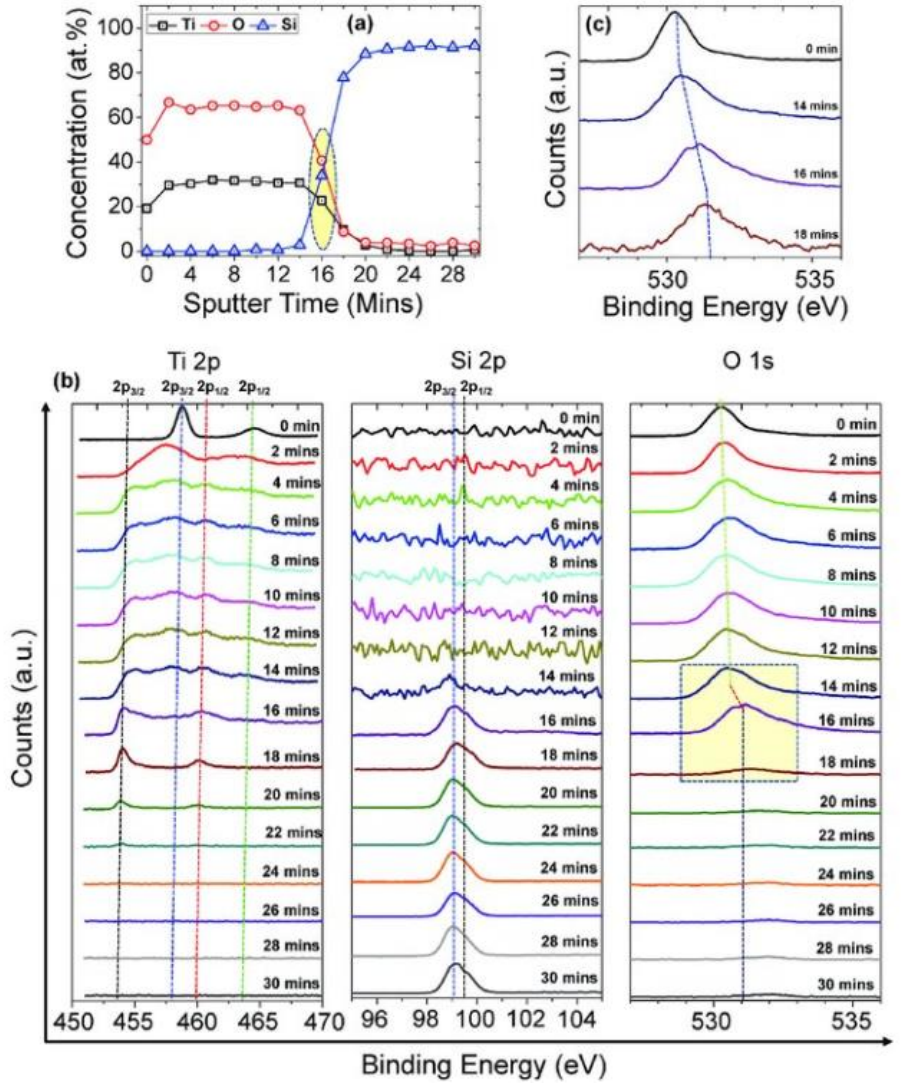
Depth Profiling



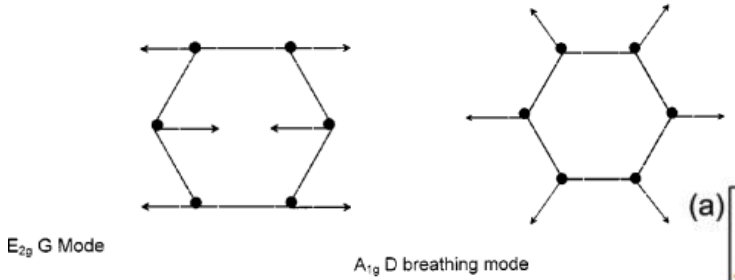


Example: Depth Profile of TiO_x-Si



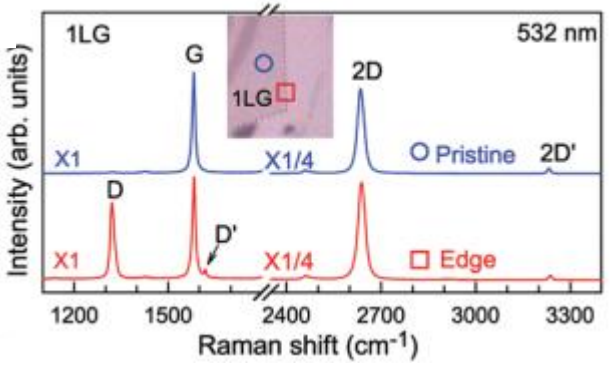


RAMAN for 2D materials

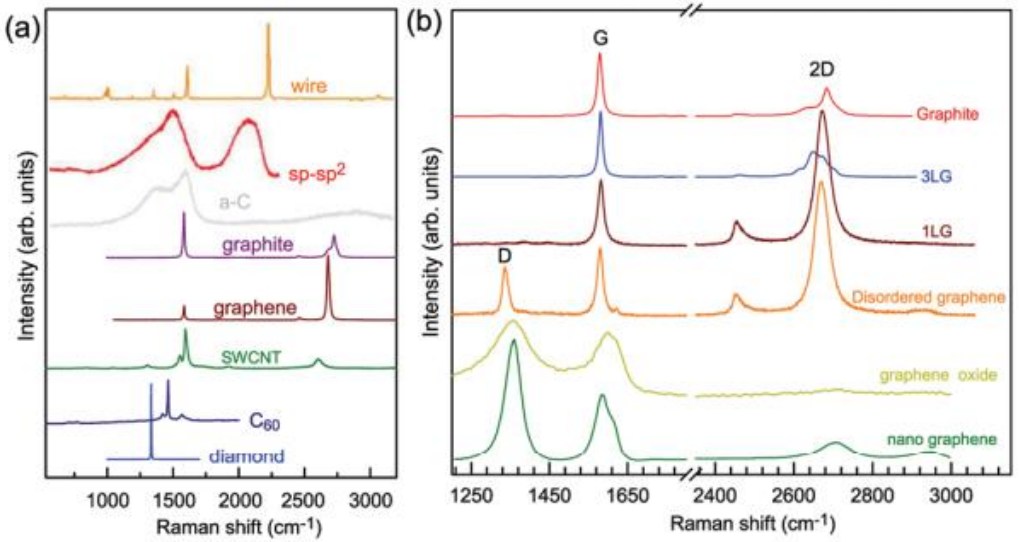


$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a}$$

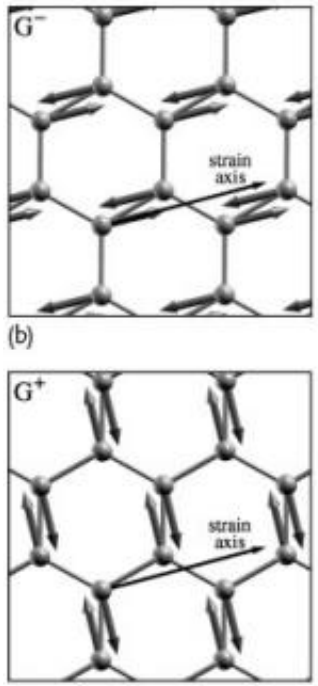
Defects

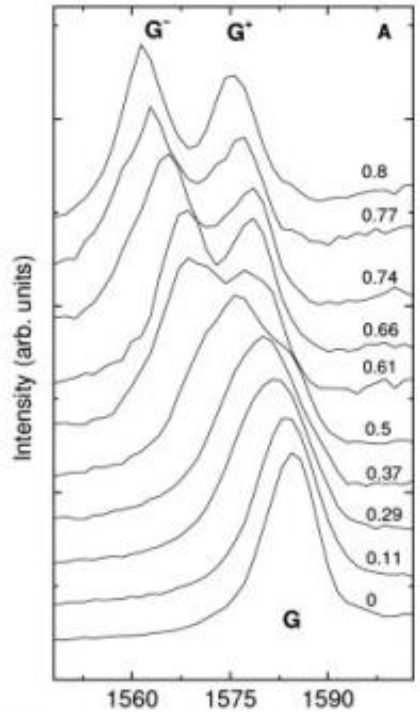


Different types of grown structures



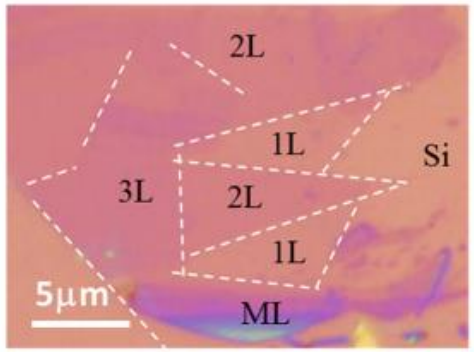
Strain induced Raman

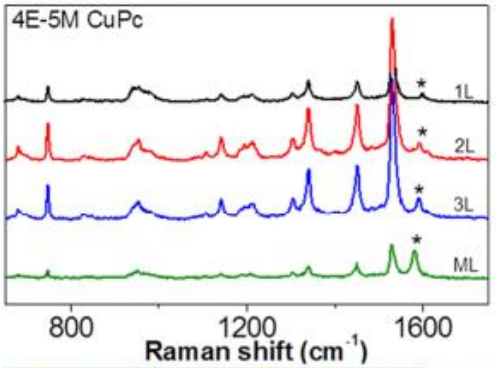


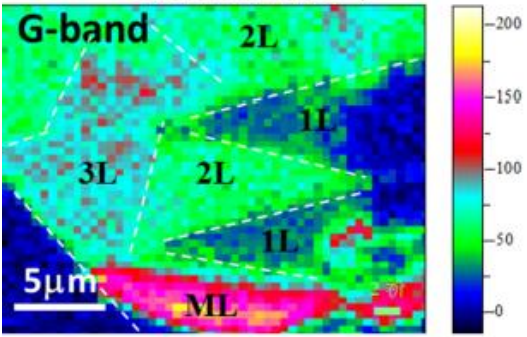


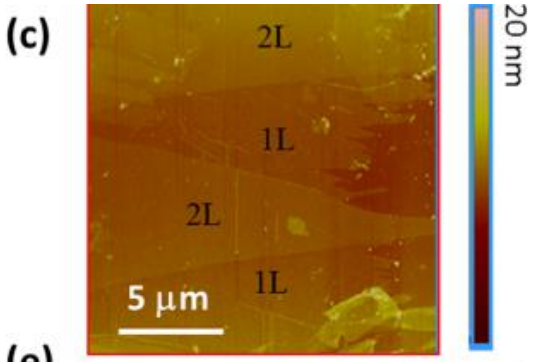
Ferrari et al. PRB (2000) 61, 20
Raman Spectroscopy in Graphene Related Systems, Wiley, 2011

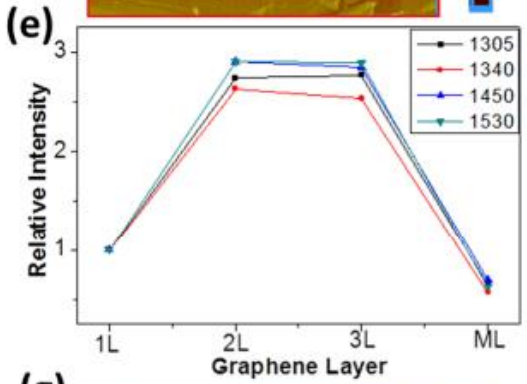
Thickness dependent Raman

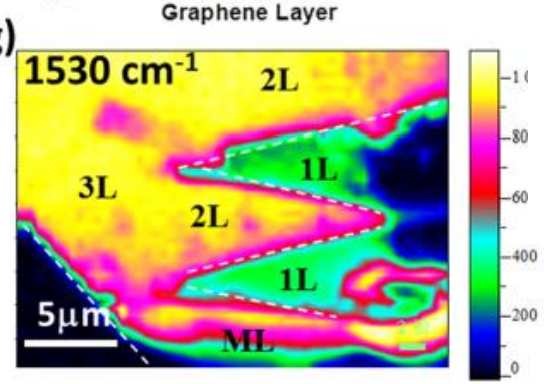


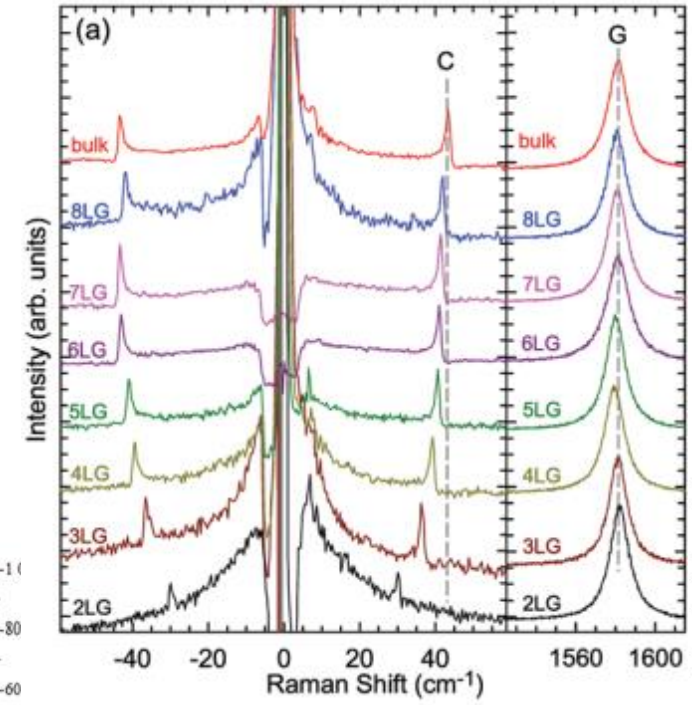


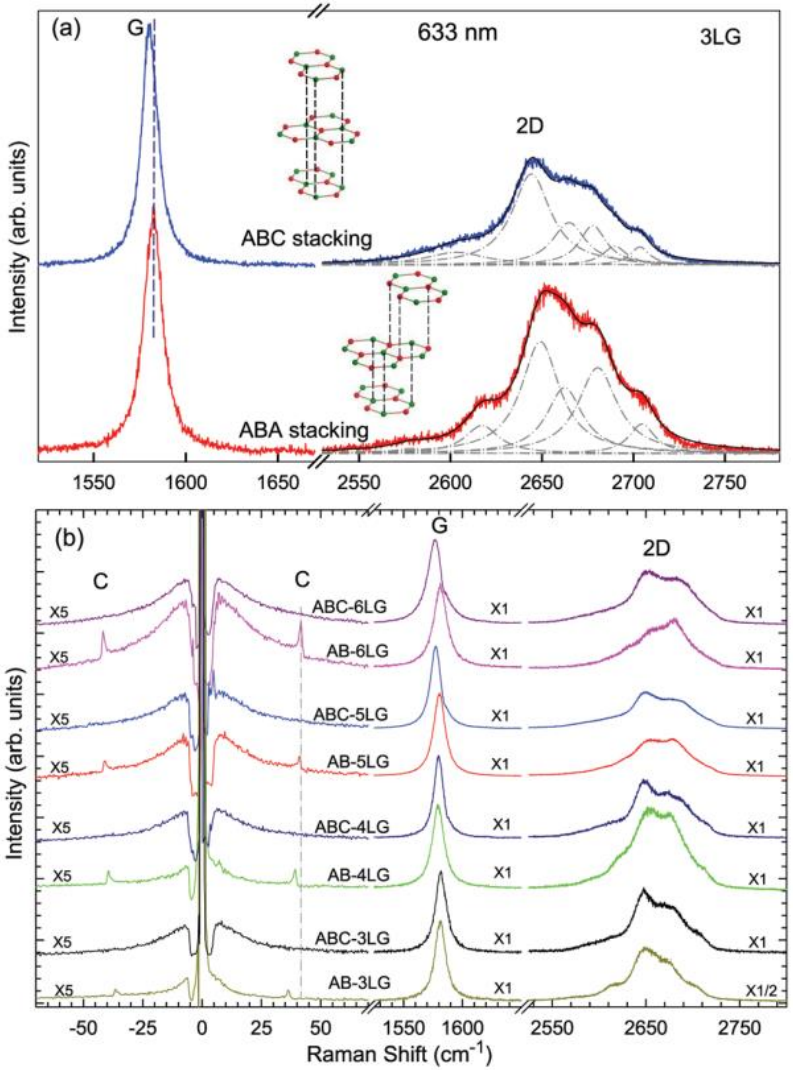








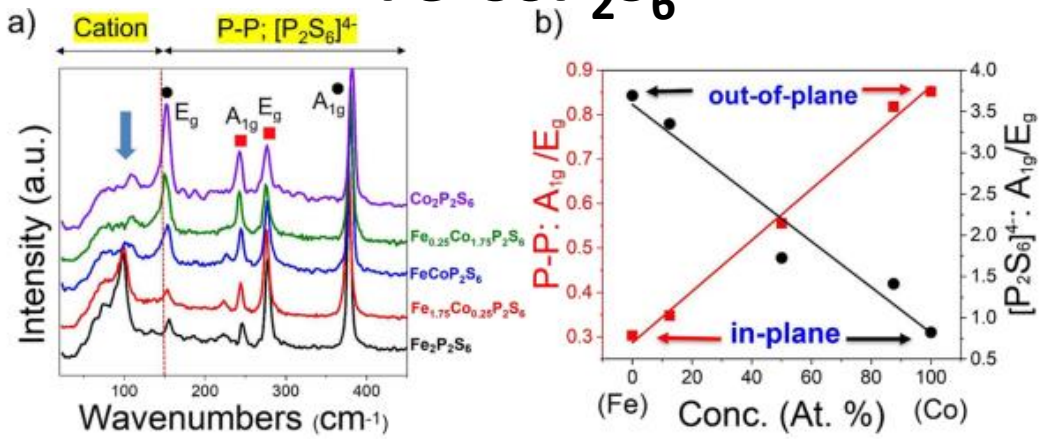




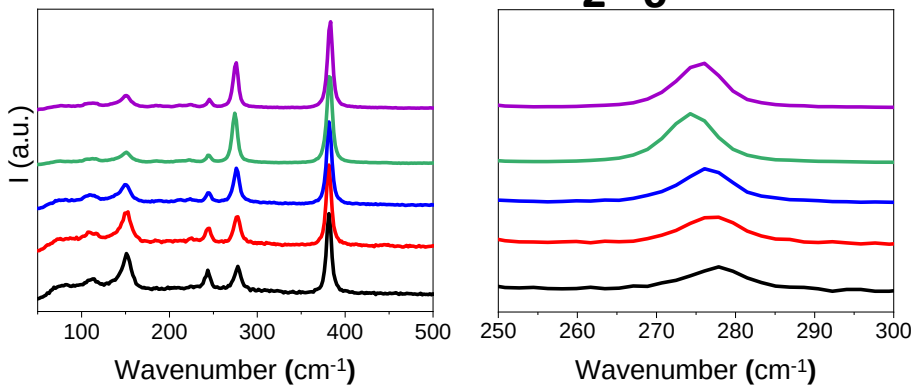
J. Phys. Chem. C 2013, 117, 2369−2376
Carbon, 2016, 99, 118–122

Examples of Raman

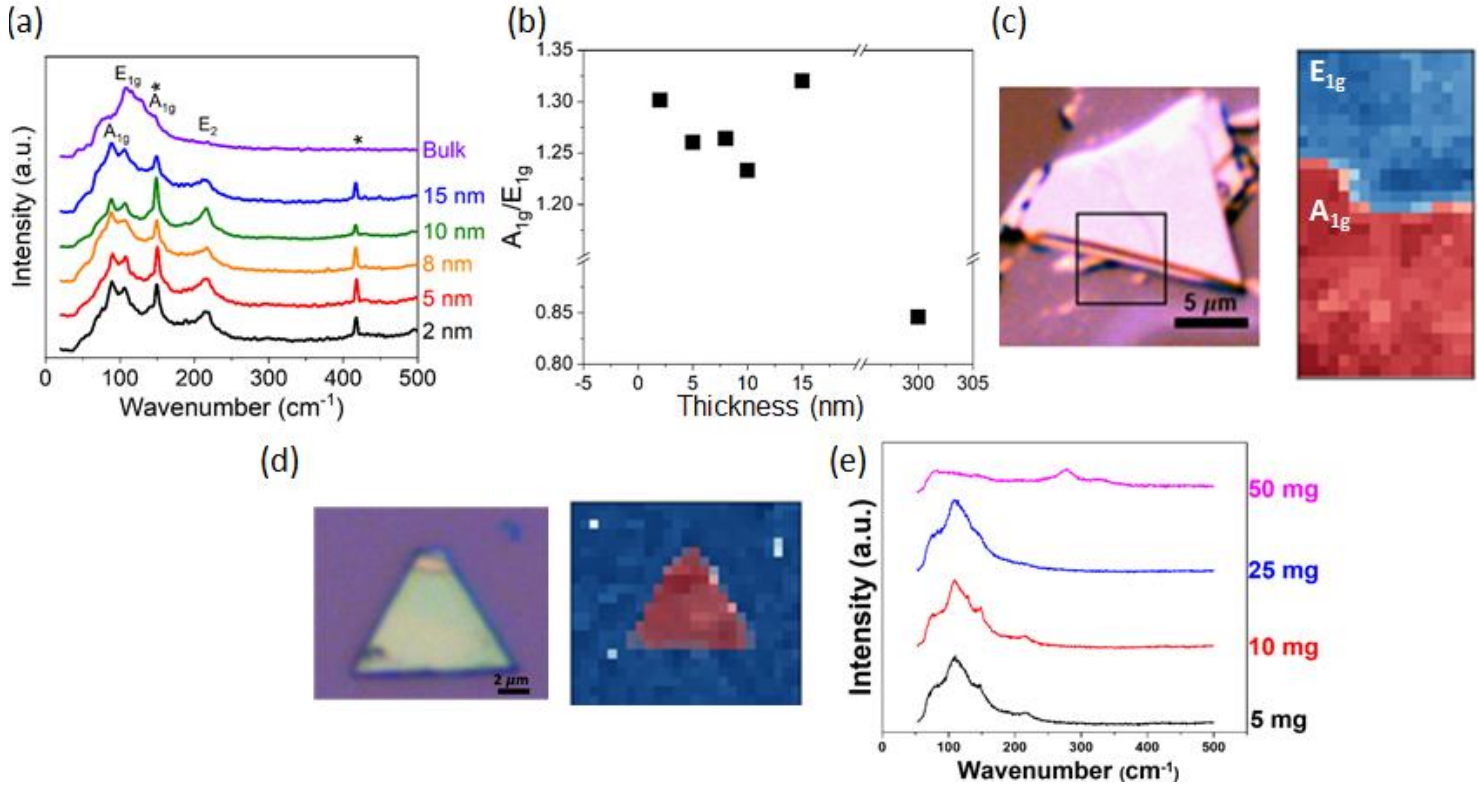
Fe-CoP_2S_6



Mn-CoP_2S_6

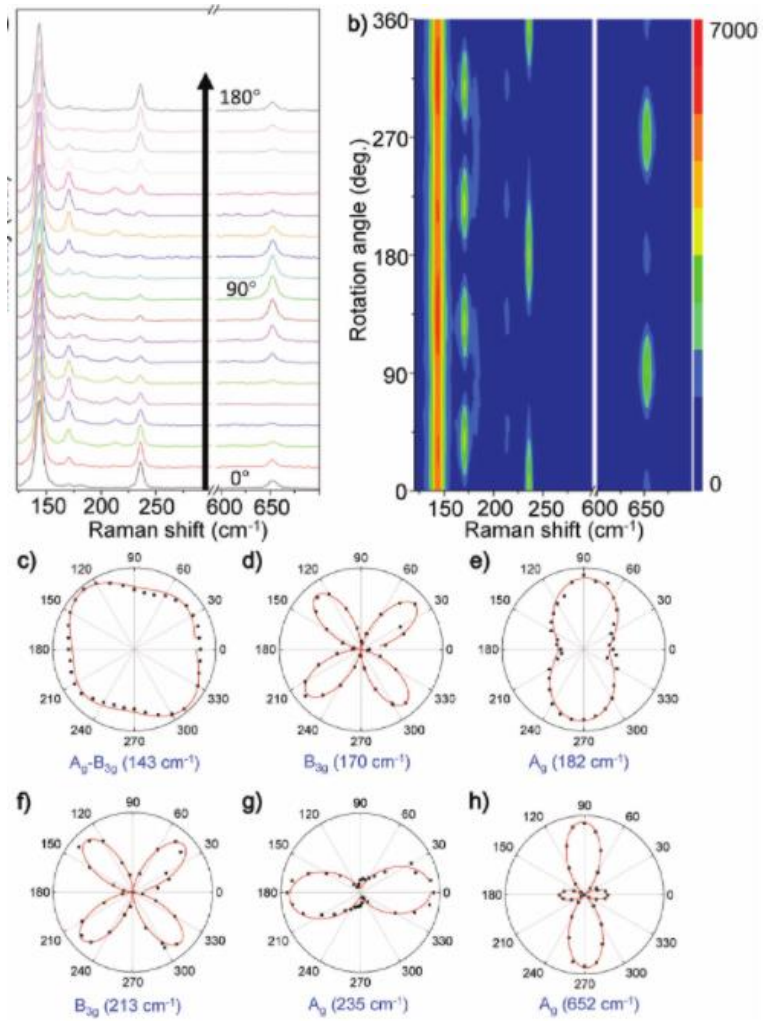


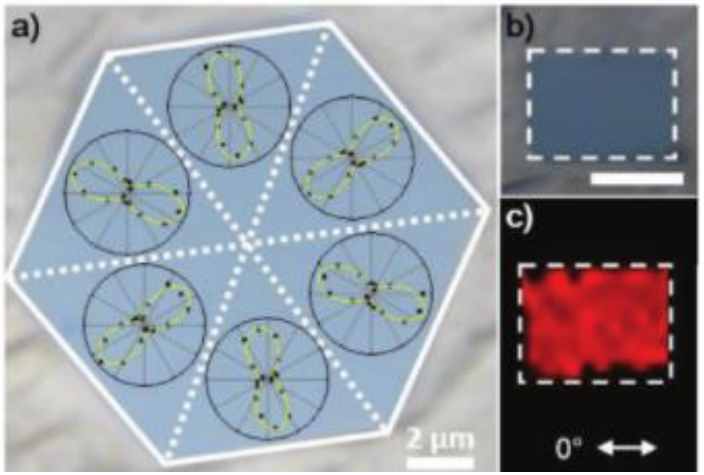
Cu_2Te

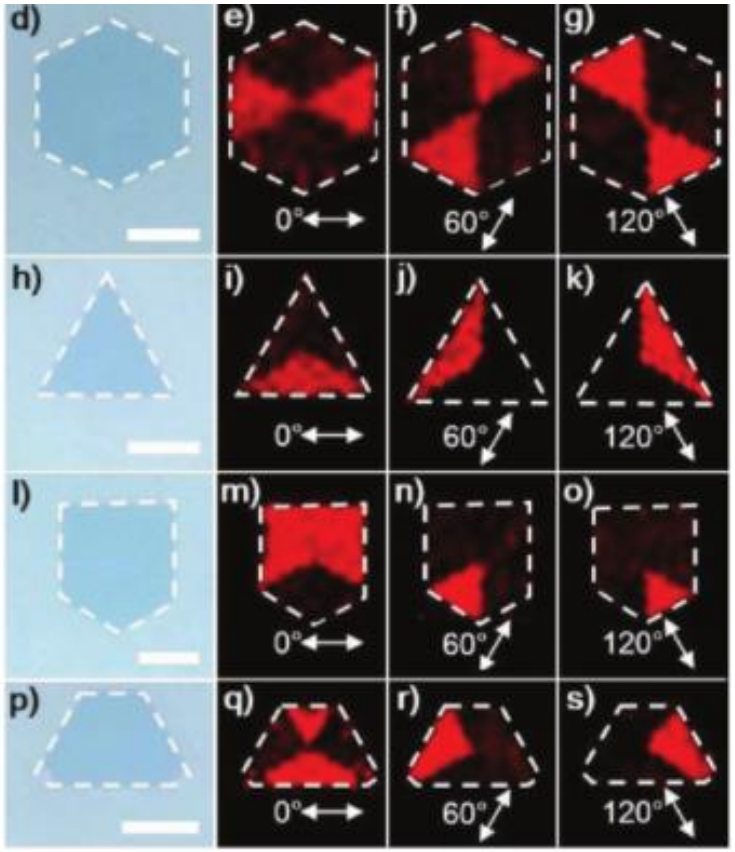


Polarization dependent Raman

Anisotropy in Mo_2C

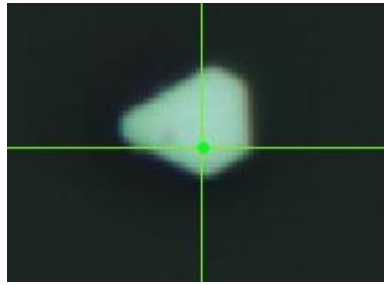


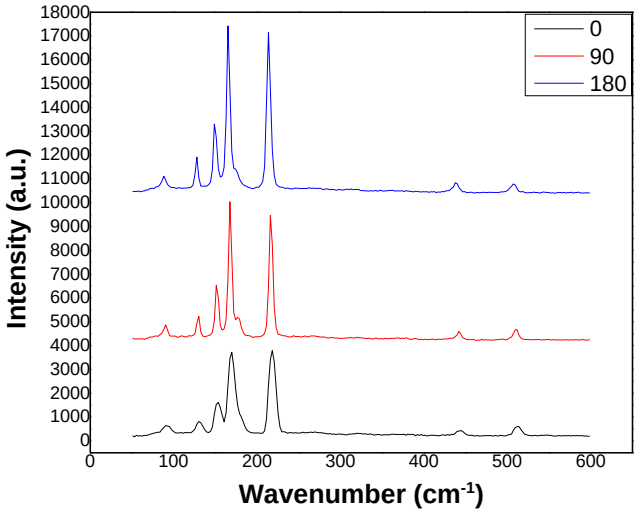


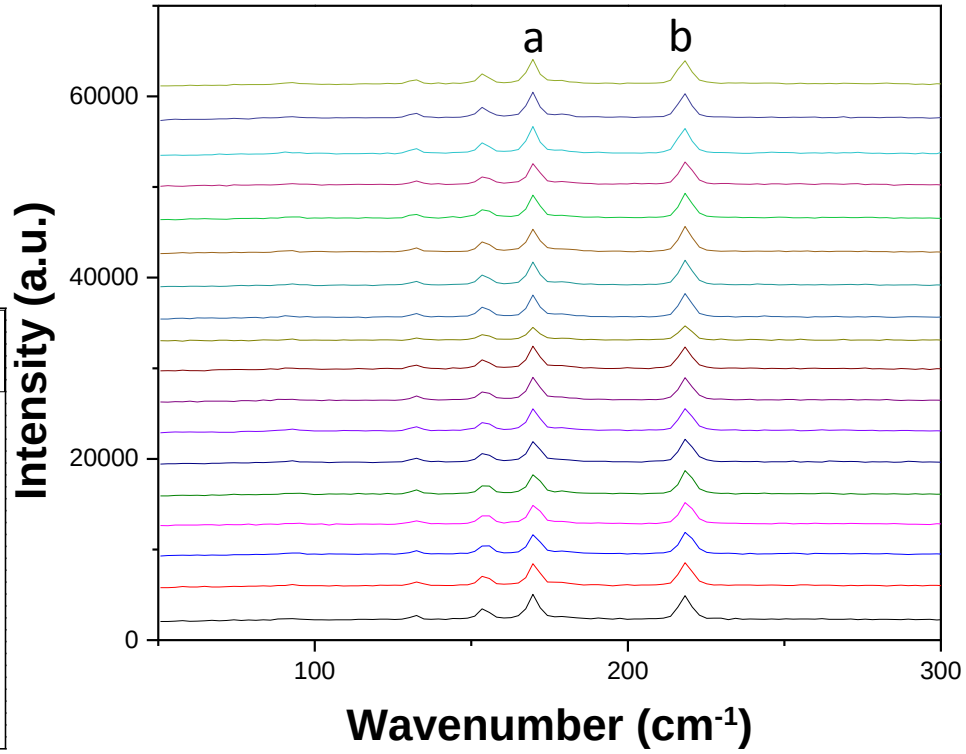


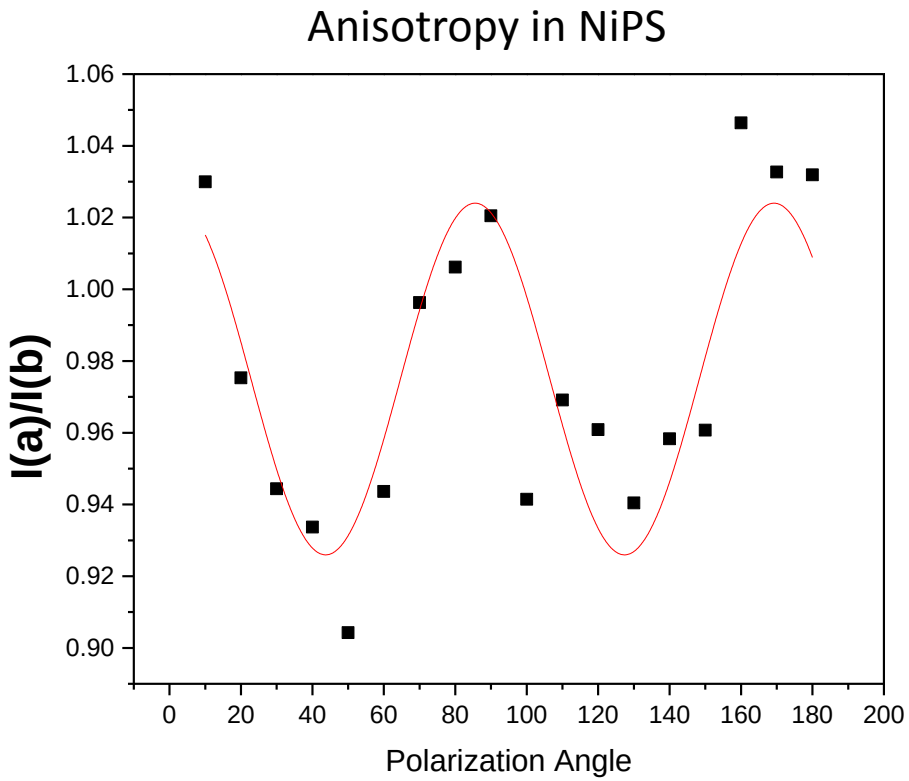
Adv. Mater. 2019, 31, 1807160

Polarization dependent Raman: NiP_2Se_6



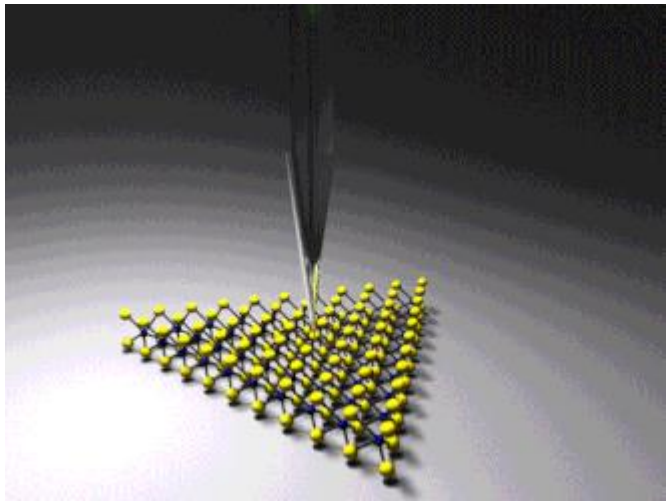


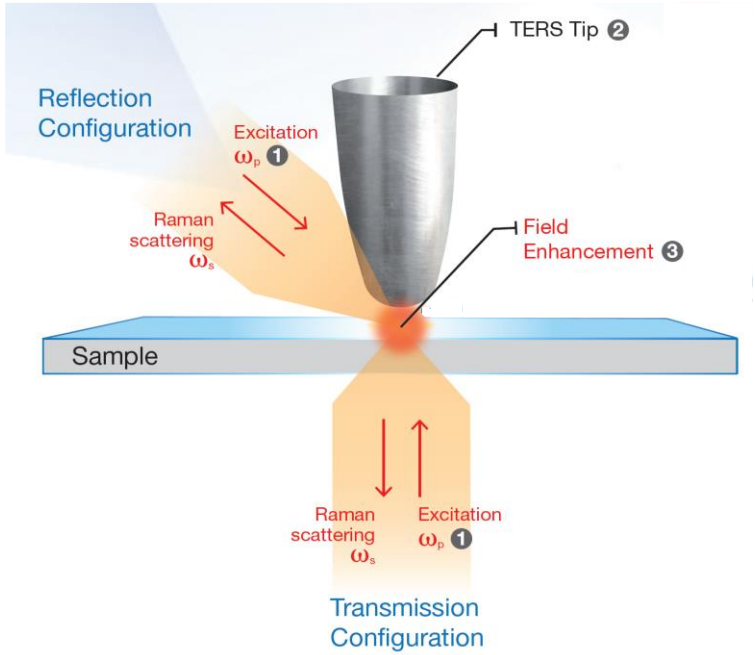




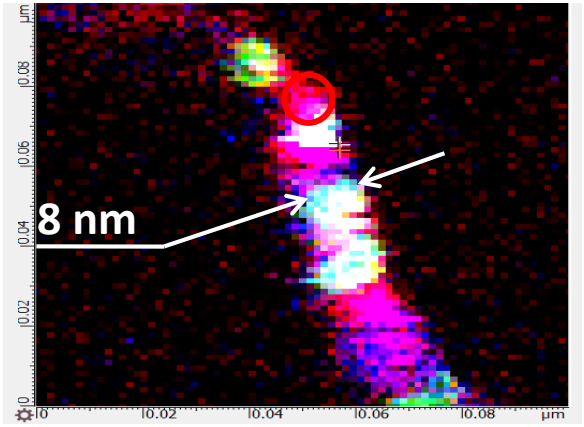
Anisotropy in vibrational modes

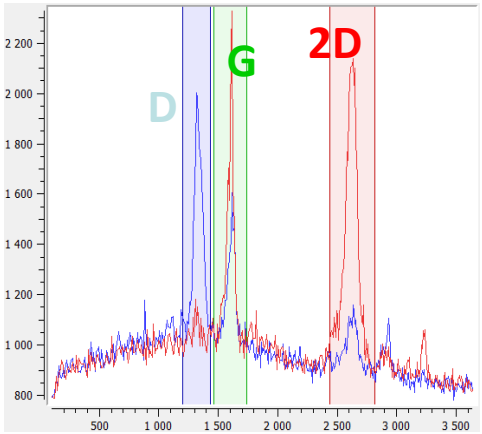
Tip Enhanced RAMAN Spectroscopy (TERS)





CNT





ERS overcomes these limitations as the Raman spectrum obtained originates primarily from the molecules within a few tens of nanometers of the tip.

Nanoscale TER imaging of carbon nanotubes see structural heterogeneity, characterize defect sites, chirality variations, and electronic behavior.

Camden, J. P. *J. Am. Chem. Soc.* 2008, *130* (38), 12616–12617

Conclusions

- XPS can be used to determine elemental composition of layered 2D materials
- UPS can be used to determine work function of layered structures
- TOF SIMS is an important tool to determine thickness dependence mapping and elemental composition map
- Polarized Raman can determine the anisotropy in the layered system.

THANK YOU!

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Questions

Would you please share information on the characterization of 2D materials heterostructures? Particularly, can Raman, XPS, or other surface analysis tools give us information on the twist angle between adjacent 2D layers, for example, the twist angle between graphene layers in bilayer graphene? Thank you!

Application of XPS and Raman in identifying cement hydration mechanism.

Quantitative techniques for Raman and SIMS