Beyond graphene: The amazing world of layered transition metal dichalcogenides (TMDs)

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Rensselaer
Layered Materials (1959)

What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them... I can hardly doubt that when we have some control of the arrangement of things on a small scale, we will get an enormously greater range of possible properties that substances can have...

R. P. Feynman
There is Plenty of Room at the Bottom
December 29, 1959
Structure of monolayer TMDs

Transition metal dichalcogenides exhibit two main phases:

*Trigonal prismatic (Hexagonal) (P63/mmc)

Semiconductor:
MoS$_2$, WS$_2$
MoSe$_2$, WSe$_2$

Metal:
NbS$_2$, NbSe$_2$

*Octahedral (P2$_1$/m)

Semiconductor:
MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$

Metal:
MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$

Trigonal prismatic is more stable
Multi layer and Single layer behavior

WS₂-crystal

WS₂-Single Layer

Octahedral Phase WS₂

Indirect band gap

Direct band gap


DFT-LDA Plane wave calculations
Single Crystals of MoS$_2$ Several Molecular Layers Thick

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(Received 24 March 1965; in final form 18 June 1965)


Early workers on electron diffraction prepared thin fragments of MoS$_2$\textsuperscript{2,3}; however no direct thickness measurements were made. It is now well known that small MoS$_2$ crystals thin enough to be transparent in the electron microscope can be prepared by the stripping technique using adhesive tape. Crystals of

The called scotch tape method for exfoliating graphite
SINGLE-LAYER MoS₂

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ABSTRACT
MoS₂ has been exfoliated into monolayers by intercalation with lithium followed by reaction with water. X-ray diffraction analysis has shown that the exfoliated MoS₂ in suspension is in the form of one-molecule-thick sheets. X-ray patterns from dried and re-stacked films of exfoliated MoS₂ indicate that the layers are randomly stacked. Exfoliated MoS₂ has been deposited on alumina particles in aqueous suspension, enabling recovery of dry exfoliated MoS₂ supported on alumina.
WS$_2$ Nanotubes: Sulfurization Process

SEM image

TEM images

Open Nanotube Caps

WS₂ Nanotubes: Electronic Properties

Molecular Model

DOS for a (18,18)

Armchair (18,18)

Zigzag (22,0)

Octahedral Inorganic Fullerenes

$WS_2$ nanoparticles
Topological defects and vacancies in TMD


Defects in monolayer TMDs

Point defects: vacancies, divacancies
Komsa et al., PRL, Vol.109, art. 035503 (2012)

Grain boundaries

MoS$_2$ NbSe$_2$ WSe$_2$ WTe$_2$

Semimetal  Semiconductor  Semimetal  Semimetal
Monolayer MoS$_2$ by exfoliation

Atomically Thin MoS$_2$: A New Direct-Gap Semiconductor
Kin Fai Mak, Changgu Lee, James Hone, Jie Shan, and Tony F. Heinz

Emerging Photoluminescence in Monolayer MoS$_2$
Andrea Splendiani, Liang Sun, Yuanbo Zhang, Tianshu Li, Jonghwan Kim, Chi-Yung Chim, Giulia Galli, and Feng Wang

Photoluminescence from Chemically Exfoliated MoS$_2$
Goki Eda, Hisato Yamaguchi, Damien Voiry, Takeshi Fujita, Mingwei Chen, and Manish Chhowalla
WS$_2$ synthesis by CVD

WS$_2$ Monolayer synthesis

Extraordinary Room-Temperature Photoluminescence in Triangular WS$_2$ Monolayers

Edge behavior in WS$_2$ monolayer

Sulfur passivation DFT calculations

Metallic-like behavior at the edges

Mo Valency change at the ribbon’s edge

With HSE hybrid approximation the band gap is 1.4 eV

The band gap with GGA-PBE is 0.71 eV

Role of Oxygen and Sulfur at the edges

With the HSE hybrid approximation
The gaps become more realistic and increase

1.23 eV $\rightarrow$ 1.8 eV (Mo Edge)
0.84 eV $\rightarrow$ 1.6 eV (S Edge)

Planar nanocavities can enhance the light-matter interaction:
- Enhance the exclusive absorption of the 2D materials
- Modification of the spontaneous emission rate

Janish, C. Et al., submitted

Al₂O₃/Al nanocavity
Free standing monolayer
Bare Al film
Monolayer trigonal prismatic TMD exhibit no inversion symmetry and show second harmonic generation:

Kumar, N et al., PRB, Vol. 87, 161403 (2013);

Electrical control of second-harmonic generation in a WSe$_2$ monolayer transistor

Kyle L. Seyler$^1$, John R. Schaibley$^1$, Pu Gong$^2$, Pasqual Rivera$^1$, Aaron M. Jones$^1$, Sanfeng Wu$^1$, Jiaqiang Yan$^{3,4}$, David G. Mandrus$^{3,4,5}$, Wang Yao$^2$ and Xiaodong Xu$^{1,6,*}$
Raman Modes in Bulk TMDs

Trigonal prismatic semiconducting TMDs belong to the same space group P63/mmc (194; Nonsymmorphic; Schoenflies notation point group D6h)

\[ A_{1g} \quad \text{Out of plane} \quad E_{2g} \quad \text{in plane} \]
Raman Monolayer WS$_2$ (CVD)

Layered WSe$_2$ (CVT) by Mechanical Exfoliation

Layered WSe$_2$ (CVT) by Mechanical Exfoliation

Layered WSe$_2$ (CVT) by Mechanical Exfoliation


Density functional perturbation theory Using the code CASTEP
Heterostructures of TMDs

Can we mix layers or have different types of atoms in one layer? Yes

MoS$_2$  WS$_2$

WSe$_2$  WS$_2$

Ultra fast charge transfer 50X10$^{-15}$ sec after optical excitation


Heterostructures of TMDs

p-n junction (atomically thin)

By mechanical exfoliation (scotch tape)
Lee, C-H., et al., Nature nanotechnology, Vol.10 DOI: 10.1038/NNANO.2014.150 (2104)

By CVD

Atomic resolution z-contrast STEM
Heterostructures of TMDs

Photovoltaic effect of the in plane heterojunction (MoS2/WS2) open-loop voltage of 0.12 V and close-loop current of 5.7 pA


Challenges:
• Mass production of single layers
• Control of defects, doping and grain boundaries
• Control of stacking
• Contacts with metals or other TMDs

Photovoltaic effect in MoS2/WSe2 bilayer heterojunction

Lee, C-H., et al., Nature nanotechnology, Vol.10 DOI: 10.1038/NNANO.2014.150 (2104)
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Thank you