Minicurso 3:

Materiais Bidimensionais

Prof. Lídia C. Gomes

Dia 1 (29/01)

General introduction.

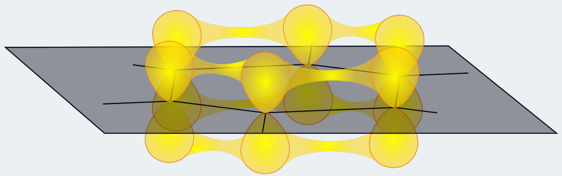
What are 2D materials?

A tiny bit of history.

Some interesting properties.

Dia 2 (30/01)

The origin of dimensionality: an analysis of orbital hybridization in graphene.



Dia 3 (31/01)

Synthesis methods.

Some experimental achievements.

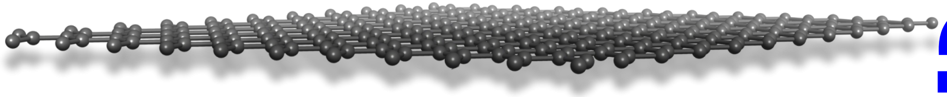
Some help from computers: ML discovery and development of new 2D materials.

Materiais bidimensionais

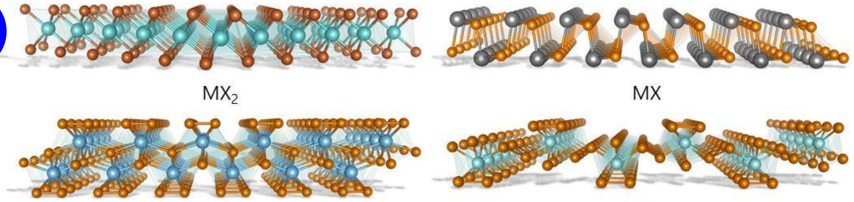
O que são?

Cristais com um ou poucos átomos de espessura

Interações eletrônicas no plano são muito mais fortes do que aquelas na direção perpendicular ao plano.

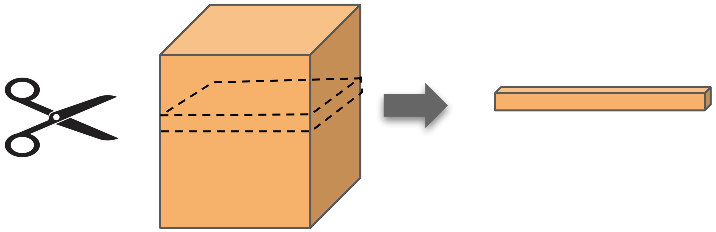


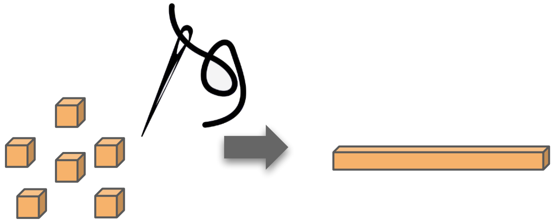
?



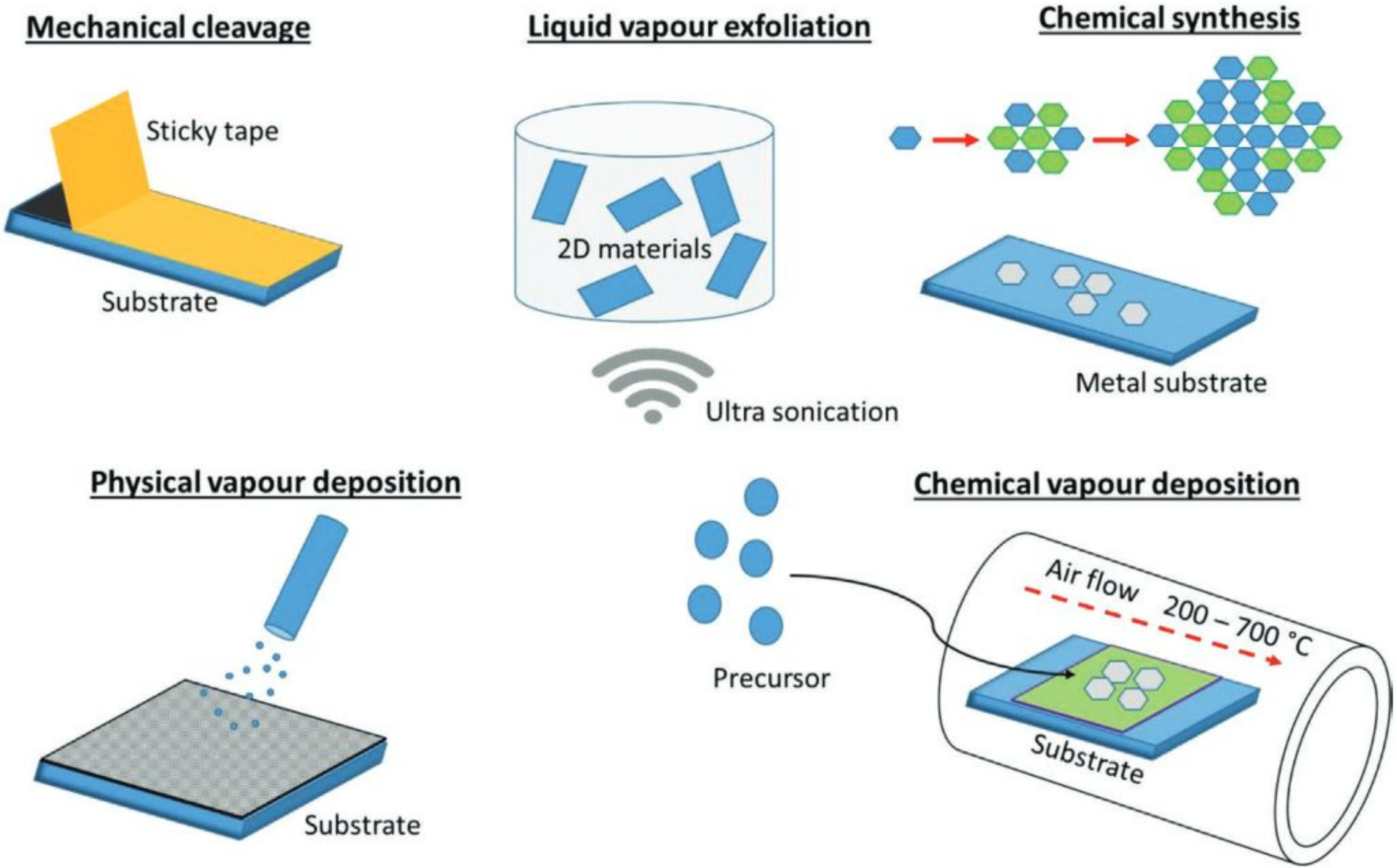
Approaches

Top-down	Bottom-up
mechanical exfoliation	epitaxial growth
liquid exfoliation	chemical vapor deposition (CVD)
ultrasonic exfoliation	pulsed laser deposition
electrochemical exfoliation	wet chemical methods
ionchange exfoliation	microwave assisted method
lithium intercalation exfoliation	topochemical transformation
chemical reduction	





Part. Part. Syst. Charact. 2022, 39, 2200031



Part. Part. Syst. Charact. 2022, 39, 2200031

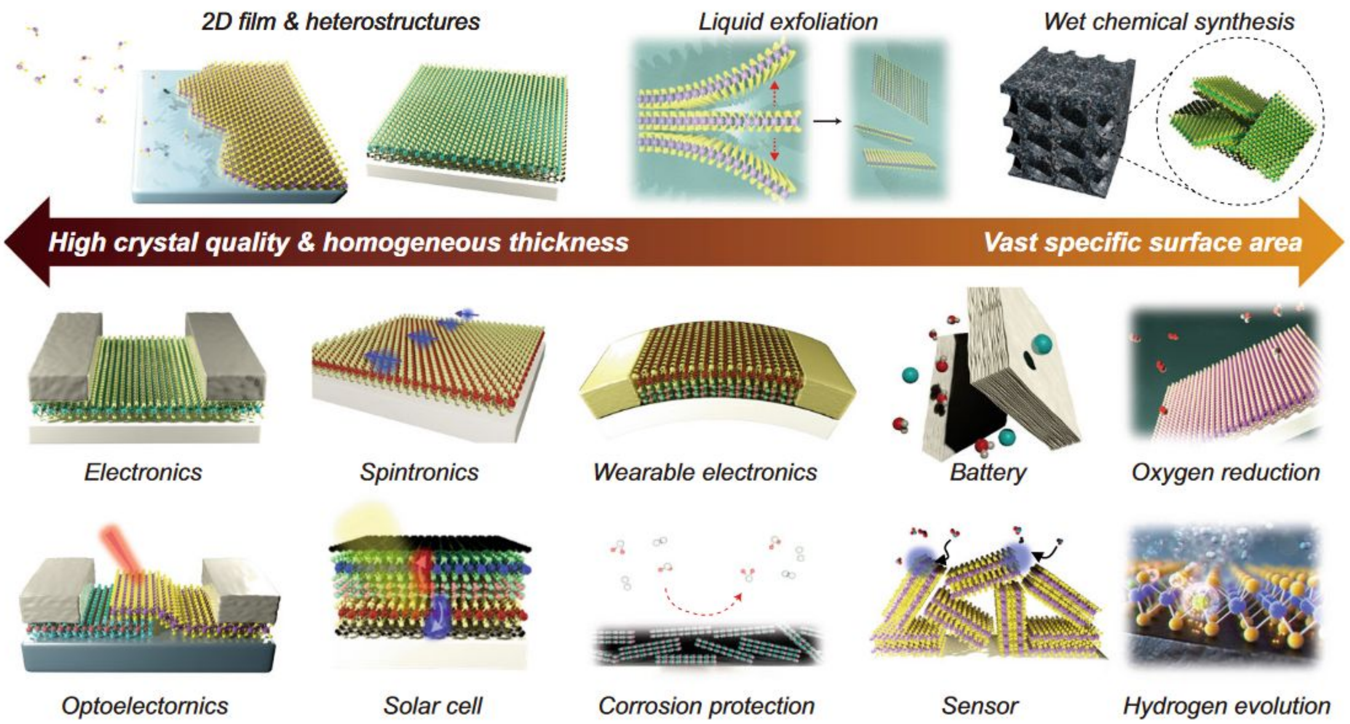
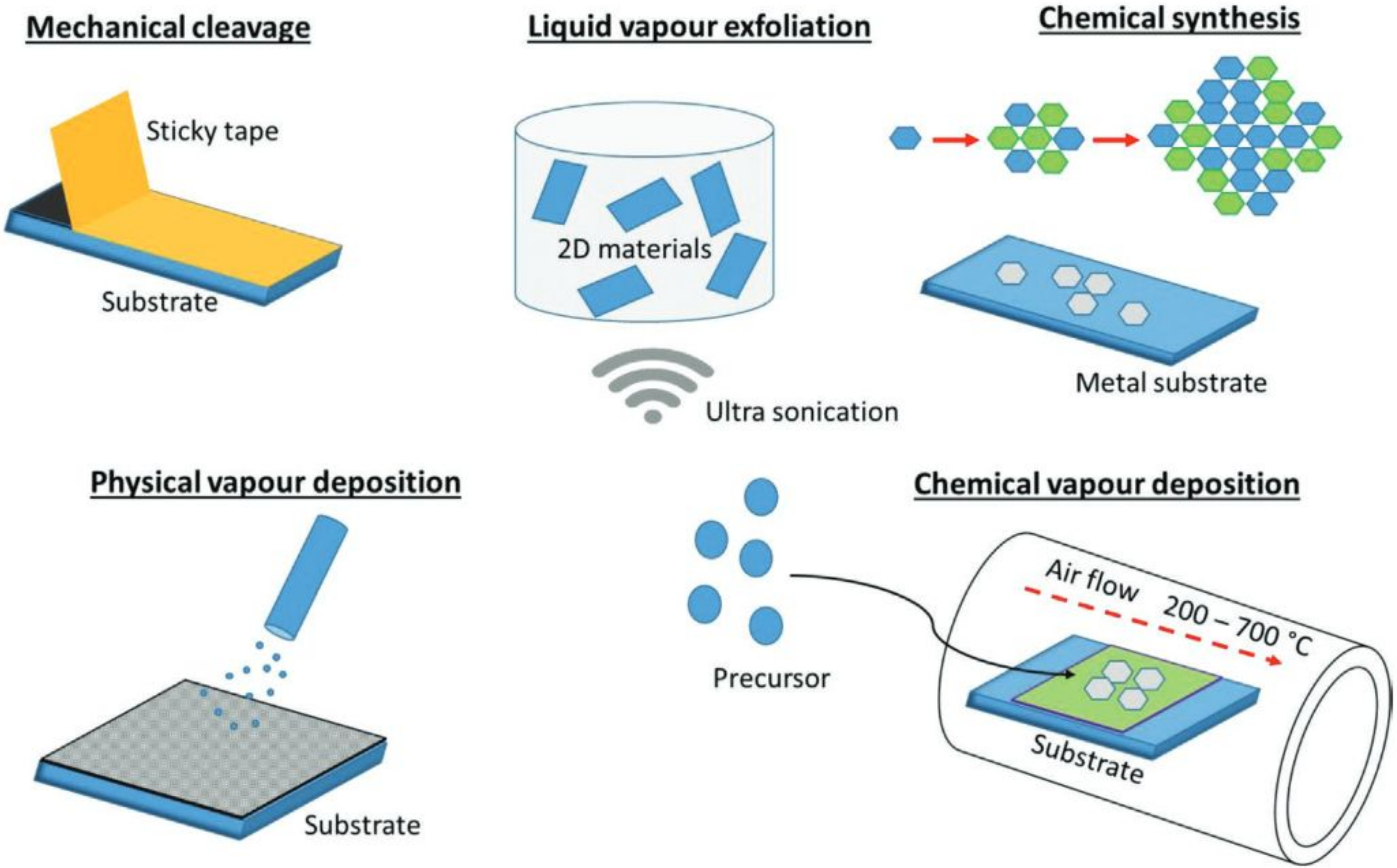
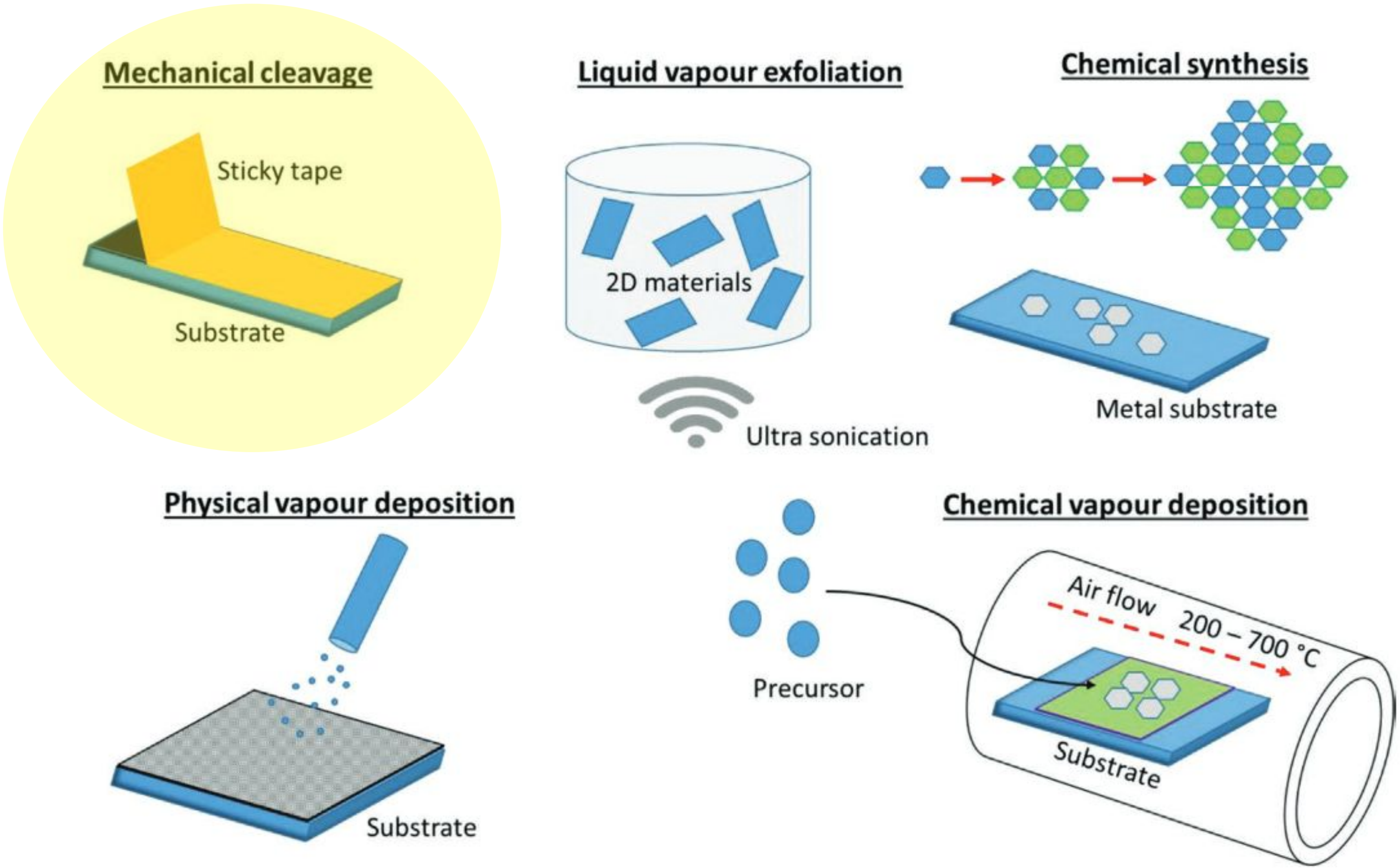


Fig. 1 Specific target-oriented techniques for the mass production of 2D materials. 2D films and heterostructures require high crystal quality and homogeneous thickness for applications such as electronics and spintronics, whereas high-porosity powders with vast specific surface area can be used in contexts such as catalysts and energy storage.

Soo Ho Choi et. al., Nature Comm., 13, 1484, 2022.

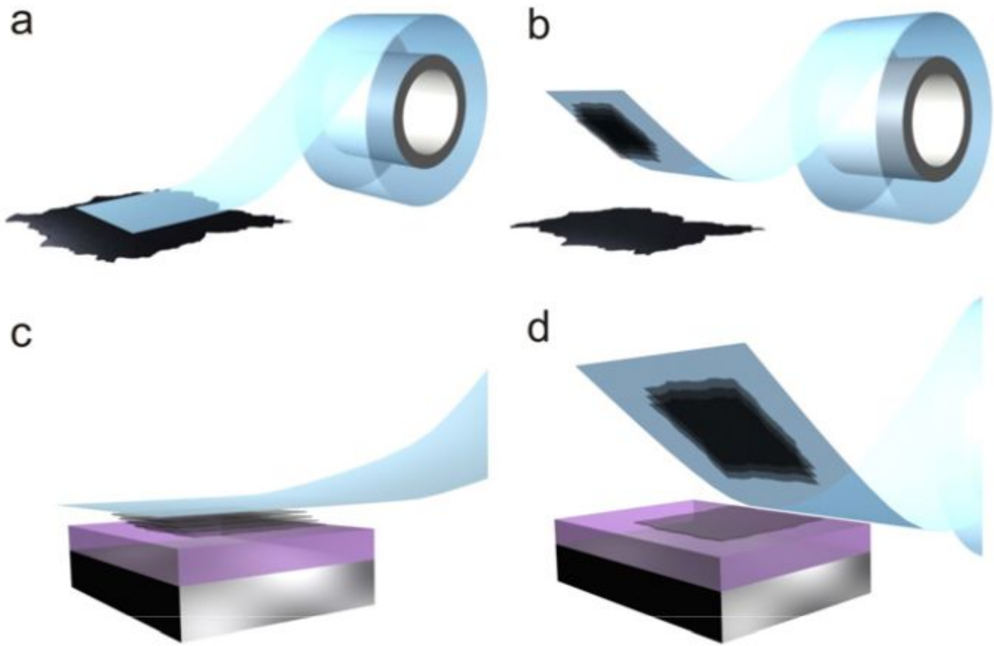


Part. Part. Syst. Charact. 2022, 39, 2200031



Part. Part. Syst. Charact. 2022, 39, 2200031

Micromechanical cleavage



Physics
2010

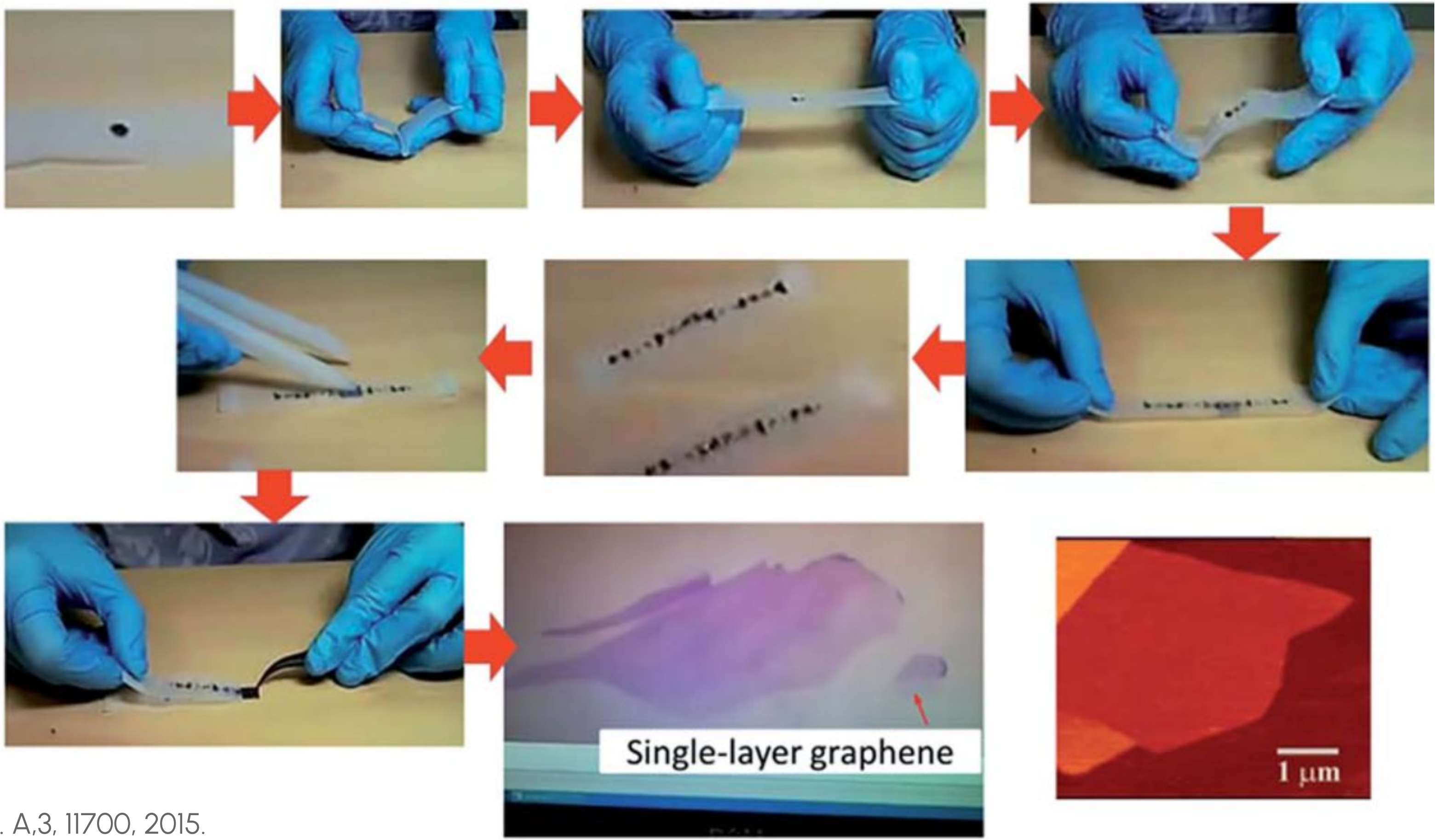
Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap

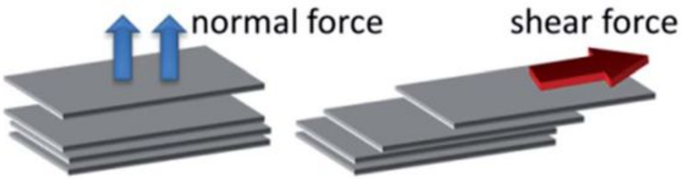
K. Novoselov and A H Castro Neto. Phys. Scr., 014006, 2012

Micromechanical cleavage



J. Mater. Chem. A,3, 11700, 2015.

Micromechanical cleavage



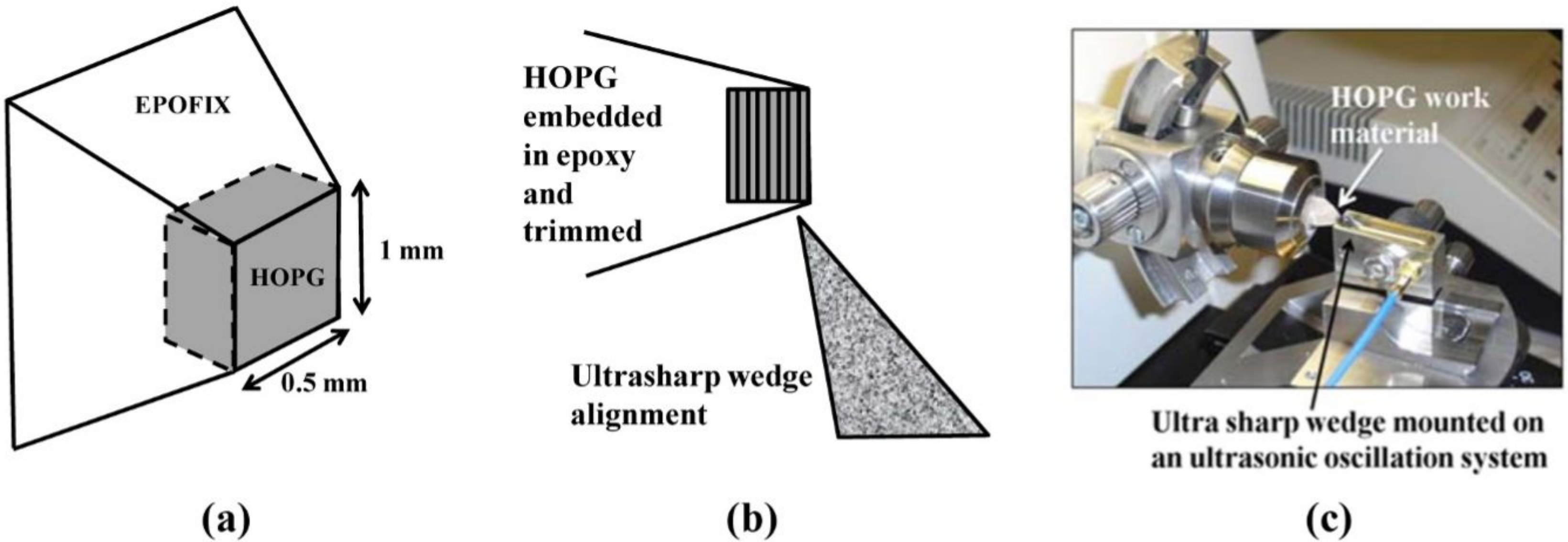
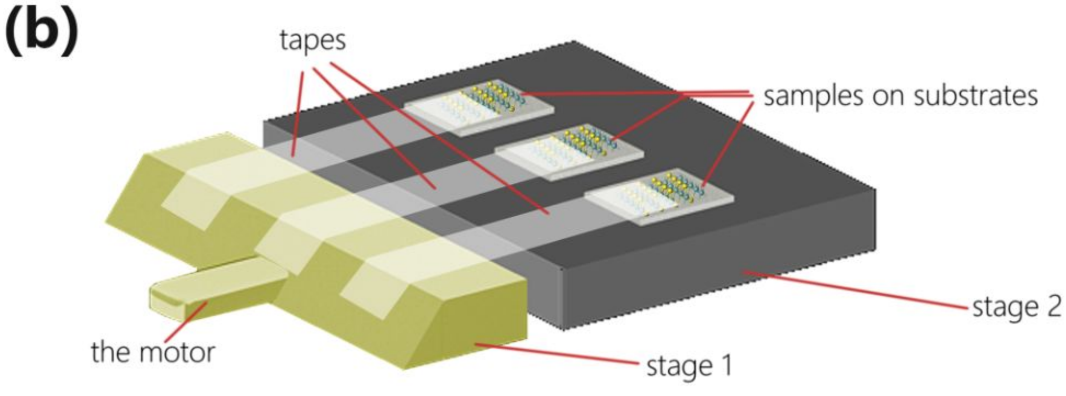
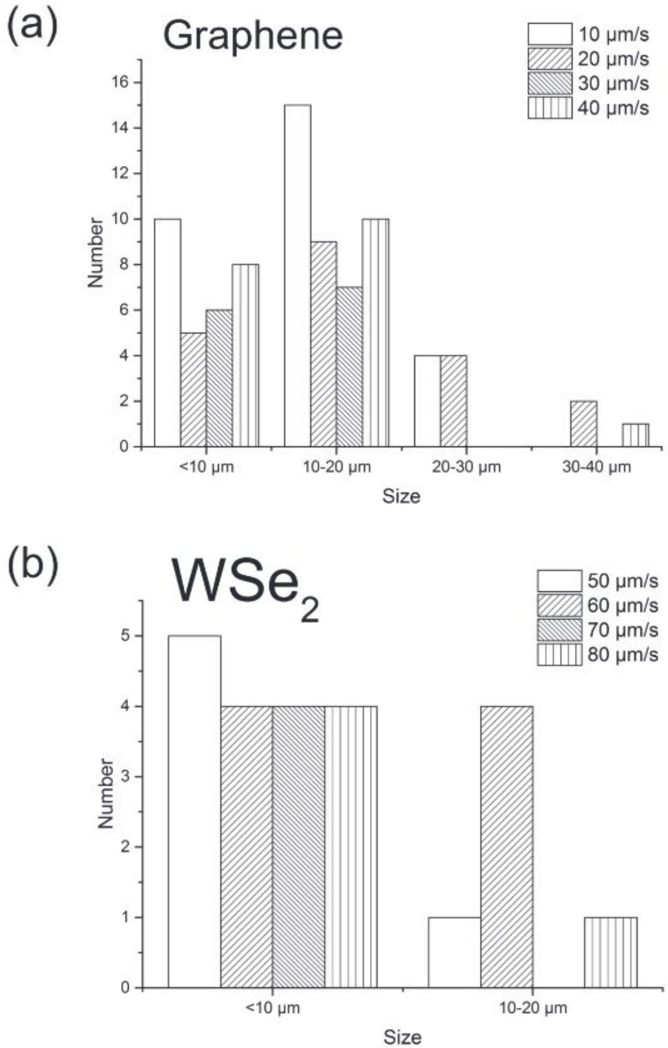


Figure 1 HOPG, SPI grade ZYH. **(a)** HOPG mounted in epofix and trimmed to pyramid shape. **(b)** Setup showing wedge alignment with HOPG layers. **(c)** Actual experimental setup.

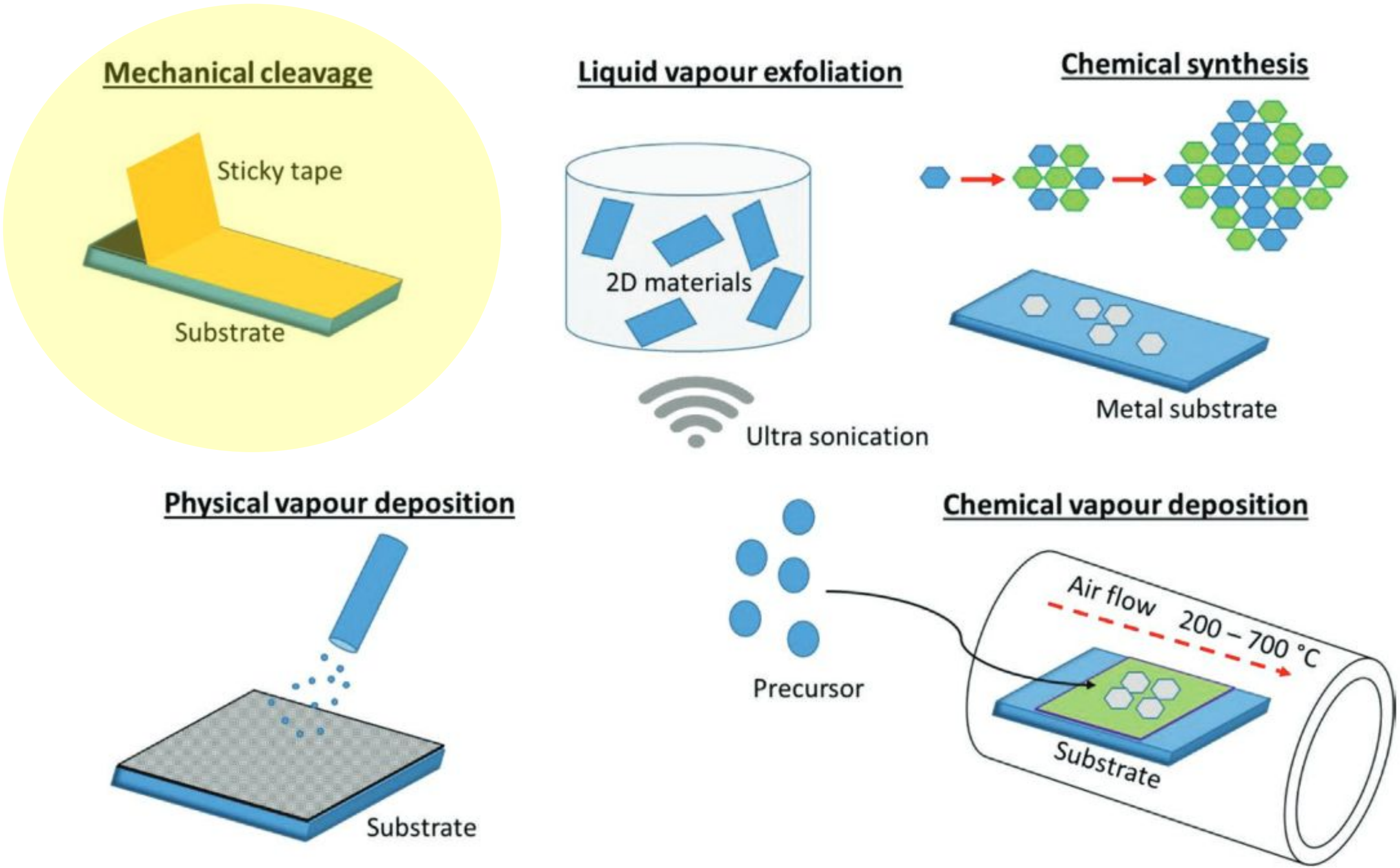
Jayasena and Subbiah Nanoscale Research Letters, 6, 95, 2011

Micromechanical cleavage

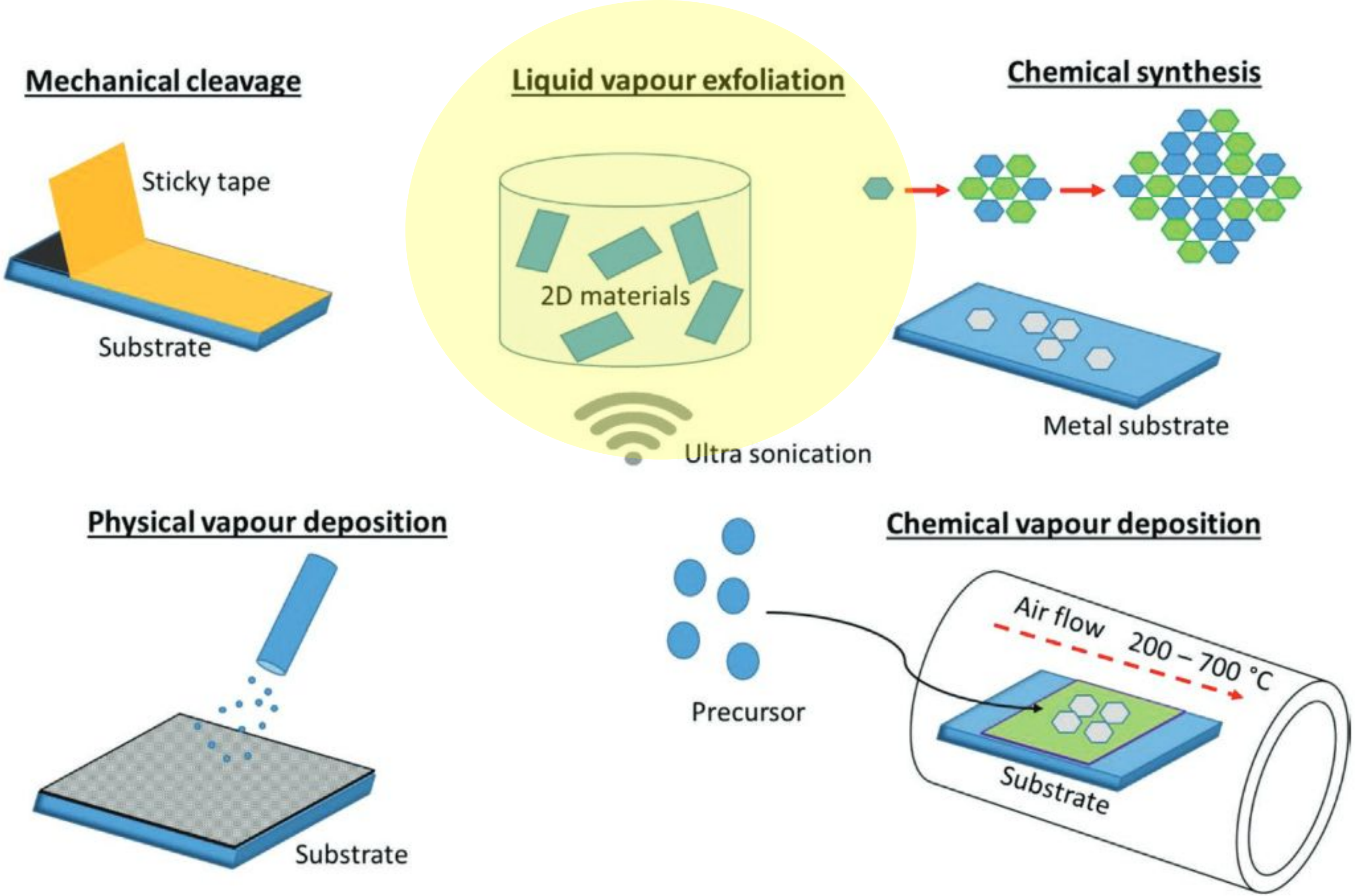




Yuan et. al. AIP Advances 6, 125201, 2016.



Part. Part. Syst. Charact. 2022, 39, 2200031



Part. Part. Syst. Charact. 2022, 39, 2200031

ARTICLES

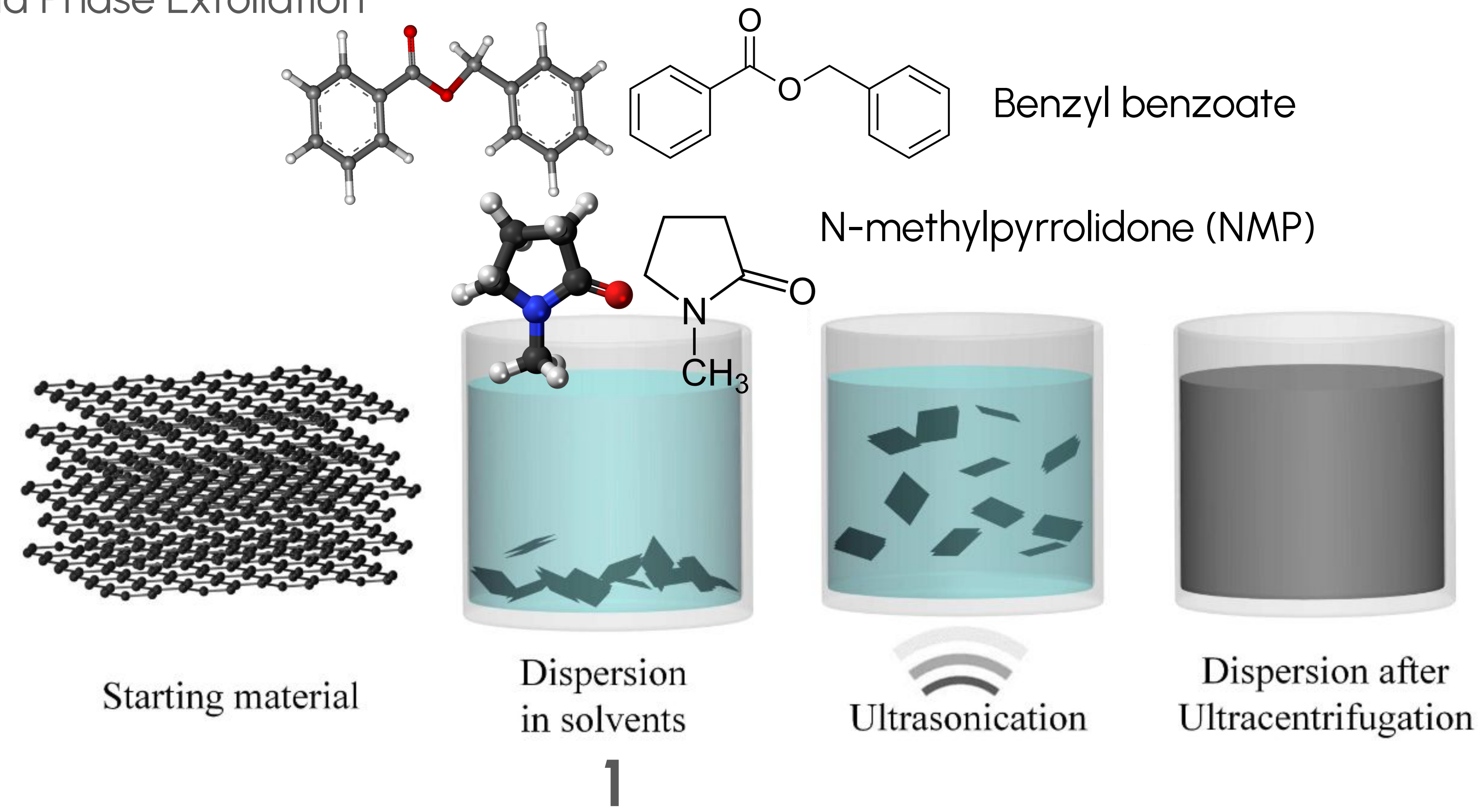
High-yield production of graphene by liquid-phase exfoliation of graphite

YENNY HERNANDEZ[1†], VALERIA NICOLOSI[1†], MUSTAFA LOTYA[1], FIONA M. BLIGHE[1], ZHENYU SUN[1,2], SUKANTA DE[1,2], I. T. McGOVERN[1], BRENDAN HOLLAND[1], MICHELE BYRNE[3], YURII K. GUN'KO[2,3], JOHN J. BOLAND[2,3], PETER NIRAJ[2,3], GEORG DUESBERG[2,3], SATHEESH KRISHNAMURTHY[2,3], ROBBIE GOODHUE[4], JOHN HUTCHISON[5], VITTORIO SCARDACI[6], ANDREA C. FERRARI[6] AND JONATHAN N. COLEMAN[1,2*]

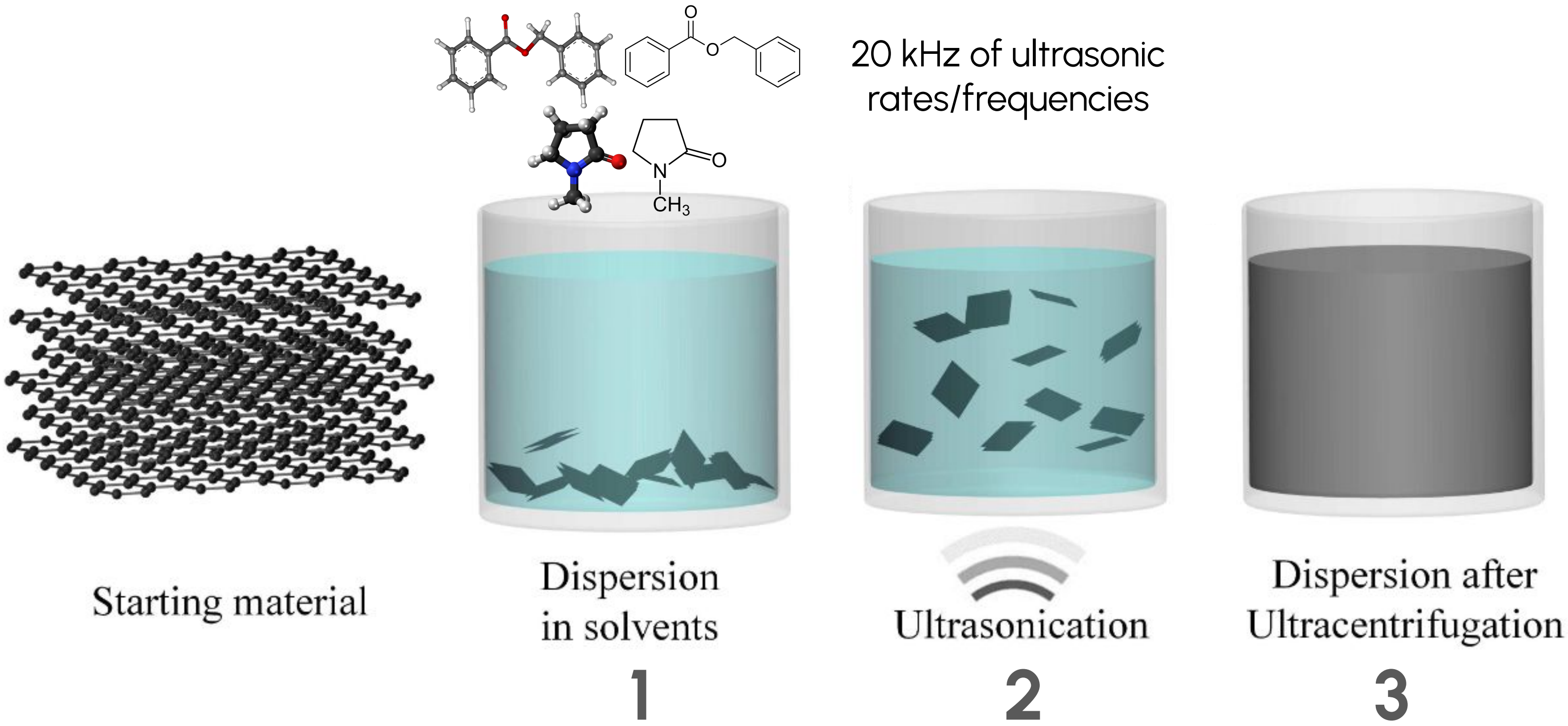
[1]School of Physics, Trinity College Dublin, Dublin 2, Ireland
[2]Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland
[3]School of Chemistry, Trinity College Dublin, Dublin 2, Ireland

Published online: 10 August 2008; doi:10.1038/nnano.2008.215

Liquid Phase Exfoliation



Liquid Phase Exfoliation



Liquid Phase Exfoliation

Esfoliação só ocorre se o custo energético é pequeno

$$\frac{\Delta H_{mix}}{V_{mix}} \approx \frac{2}{T_{flake}}(\delta_G - \delta_{sol})^2 \phi$$

$\delta_i = \sqrt{(E^i_{sur})}$ is the square root of the surface energy of phase i,

$\delta_{Graphite} \sim 70 - 80$ mJ m^{-2}

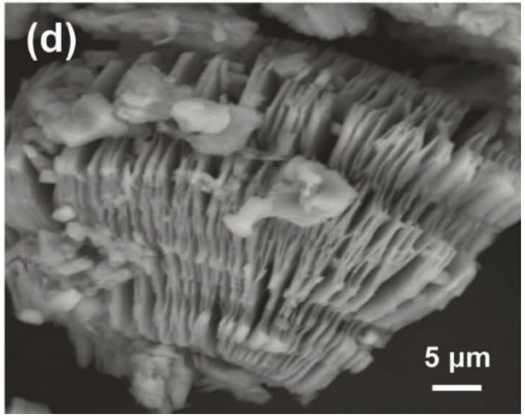
Y. Hernandez et al., Nat. Nanotechnology, 3, 2008.

Liquid Phase Exfoliation of non-vdW materials: MX-enes

ADVANCED MATERIALS
www.advmat.de
Materials Views
www.MaterialsViews.com

Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2

Michael Naguib, Murat Kurtoglu, Volker Presser, Jun Lu, Junjie Niu, Min Heon, Lars Hultman, Yury Gogotsi, and Michel W. Barsoum**



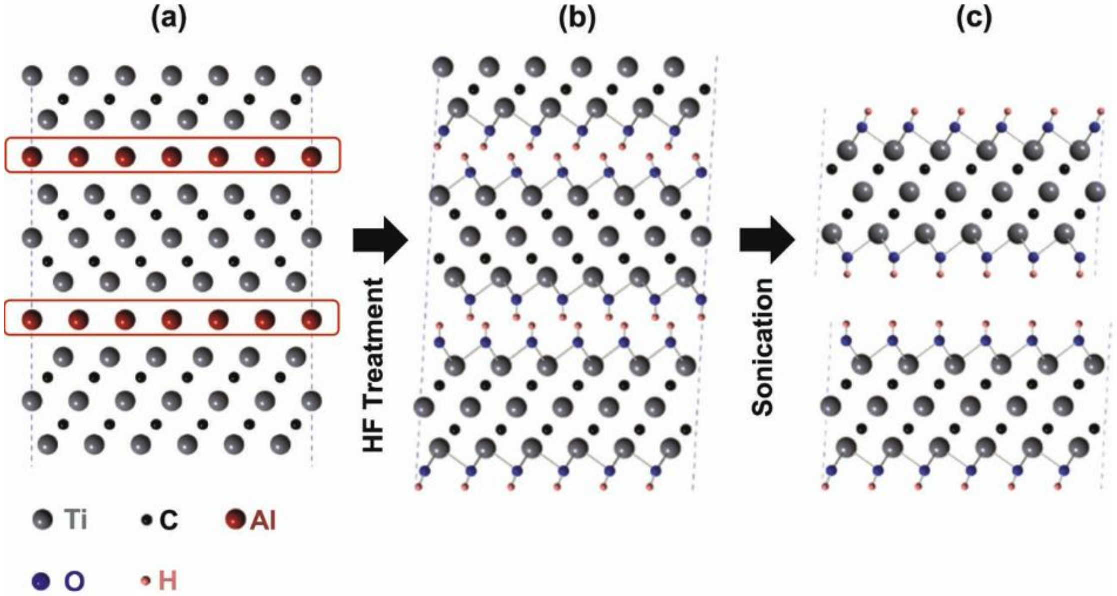
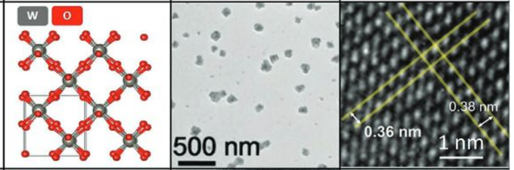
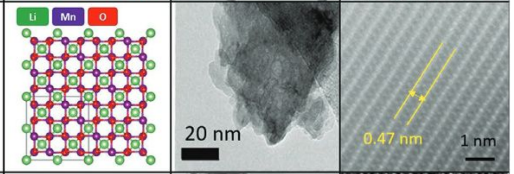
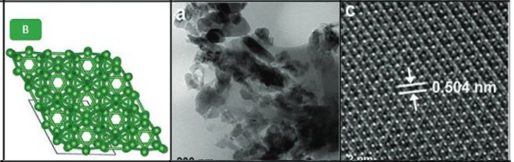
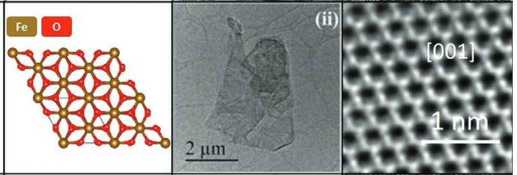
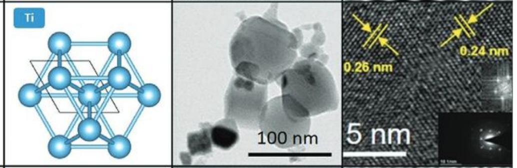
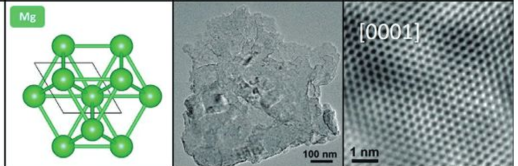
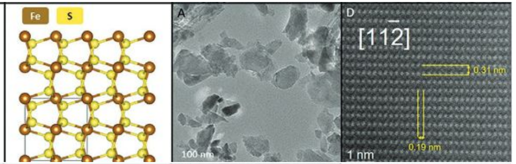
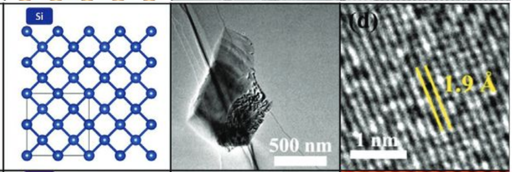
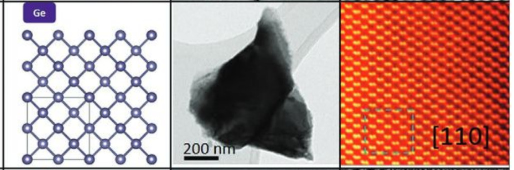
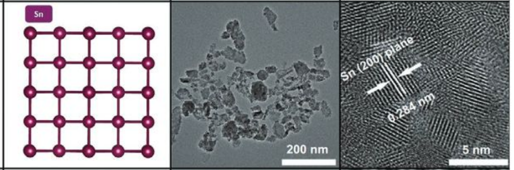
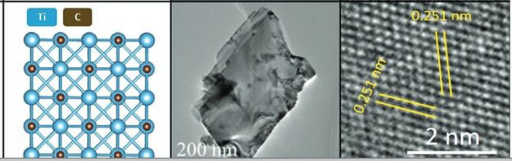


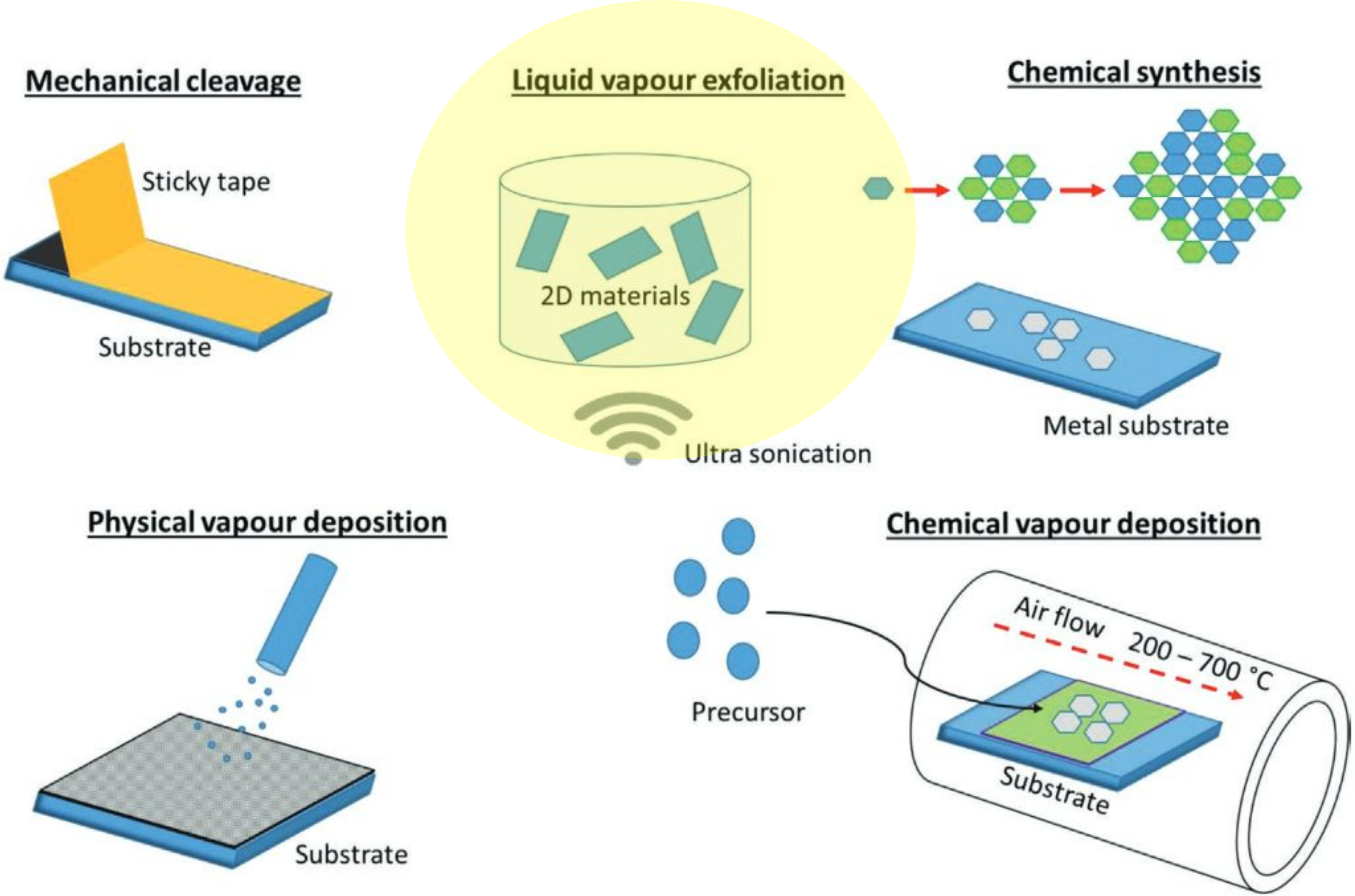
Figure 1. Schematic of the exfoliation process for Ti_3AlC_2. a) Ti_3AlC_2 structure. b) Al atoms replaced by OH after reaction with HF. c) Breakage of the hydrogen bonds and separation of nanosheets after sonication in methanol.

Name Lattice System Year of exfoliation	Crystal Structure / TEM image / HR-TEM/ STEM image
Tungsten oxide (WO_3) Monoclinic 2017	
Lithium Manganese dioxide ($LiMn_2O_4$) Cubic 2017	
Boron (β-B) Rhombohedral 2018	
Hematite (α-Fe_2O_3) Rhombohedral 2018	
Titanium (α-Ti) Hexagonal 2019	
Magnesium (Mg) Hexagonal 2019	

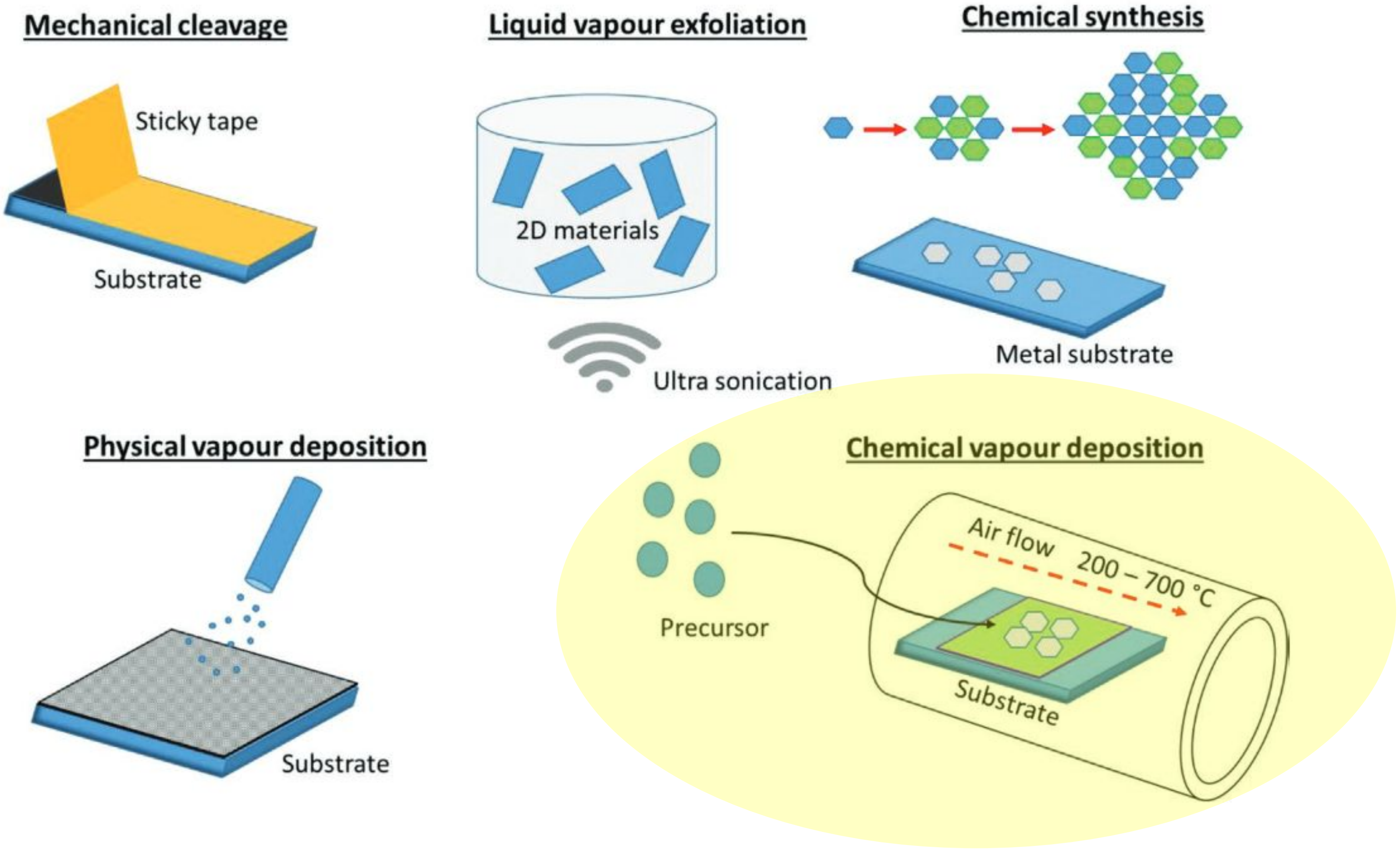
Liquid-Phase Exfoliation of Nonlayered Non-Van-Der-Waals Crystals into Nanoplatelets

*Harneet Kaur and Jonathan N. Coleman**

Pyrite (FeS_2) Cubic 2020	
Silicon (Si) Cubic 2020	
Germanium (Ge) Cubic 2021	
Tin (Sn) Tetragonal 2021	
Titanium carbide (TiC) Cubic 2021	

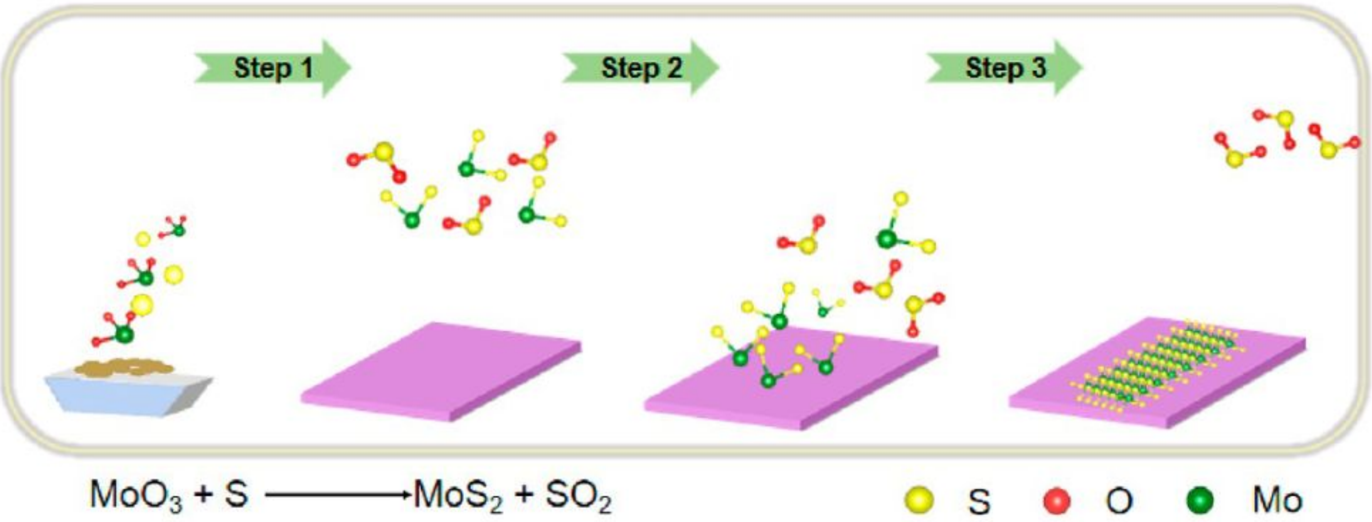


Part. Part. Syst. Charact. 2022, 39, 2200031



Part. Part. Syst. Charact. 2022, 39, 2200031

Chemical Vapor Deposition



Temperatura
Pressão
Precursor
Carrier Gas
Substrato

Biao Qin et al., Chem. Mater., 32, 24, 2020.

Chemical Vapor Deposition

- Classified by **operating conditions**:
  - **Atmospheric pressure CVD (APCVD)** – CVD at atmospheric pressure.
  - **Low-pressure CVD (LPCVD)** – CVD at sub-atmospheric pressures. Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer.
  - **Ultra High vacuum CVD (UHVCVD)** – CVD at very low pressure, typically below 10^{-6} Pa.
  - **Sub-atmospheric CVD** (SACVD) – CVD at sub-atmospheric pressures.

- Classified by **physical characteristics of vapor**:
  - **Aerosol assisted CVD (AACVD)** – the precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically. Suitable for use with non-volatile precursors.
  - **Direct liquid injection CVD (DLICVD)** – the precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors).
  - **Metal organic CVD (MOCVD)** - based on metal organic precursors. Utilizes chemical compounds with low to moderate vapor pressure as precursors.

- Classified by **type of substrate heating**:
  - **Hot wall CVD** – chamber is heated by an external power source and the substrate is heated by radiation from the heated chamber walls.
  - **Cold wall CVD** – only the substrate is directly heated either by induction or by passing current through

Chemical Vapor Deposition: Important parameters

Temperature: one of the main parameters (correlated to the free energy of the reactants). Direct impact on the uniformity and composition. Can promote uniform deposition (higher quality). At high T (> T_{growth}) → single crystal, polycrystalline, amorphous or not even deposition.

Pressure: usually, $P = P_{atm}$. However, low P can help uniformity.

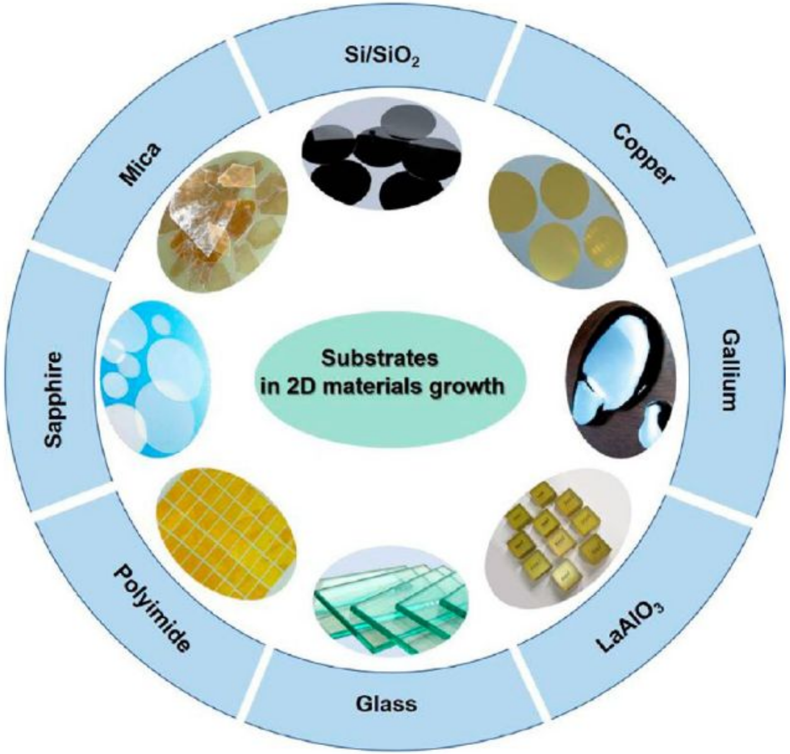
Precursor: gas and solid are common precursors (although gaseous can be better controlled). Relative proportions are important. In recent years, salts (e.g. NaCl) have been added to generate a transition product ($MoO_3 + NaCl \rightarrow MoO_2Cl_2$) and improve growth rate and crystallinity.

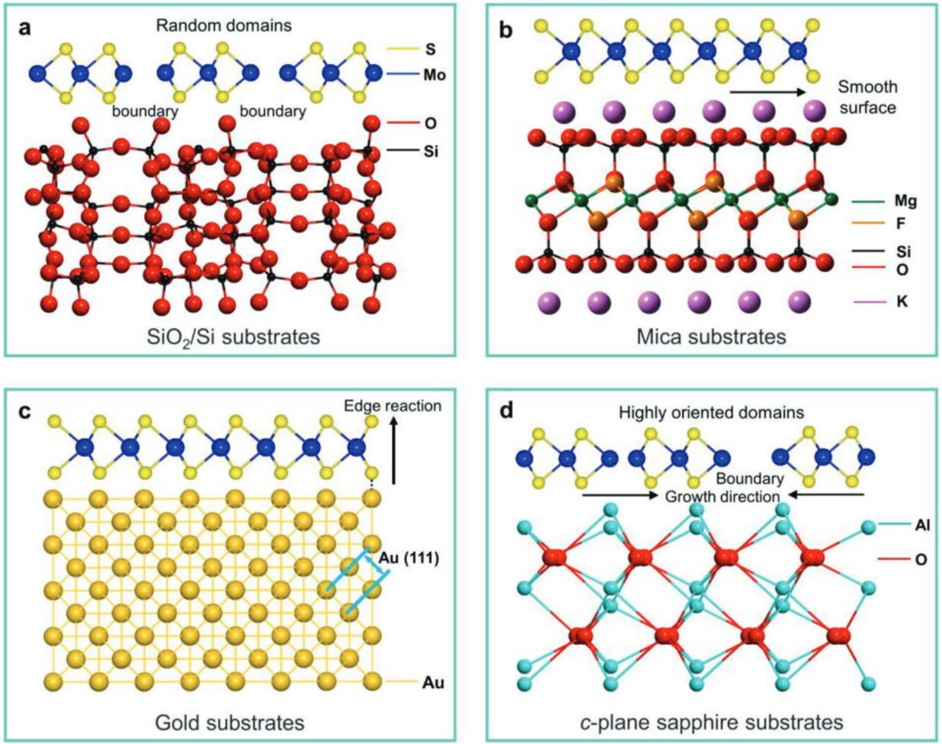
Carrier Gas: rate, ratio, and supply sequence of the carrier gas can affect the size, nucleation density, morphology, and thickness. Reducing the gas flow → reduction of the nucleation density → large-size single crystals with few grain boundaries.

Substrate

Choosing the substrate

Strong impact on the number of nucleation points, size, and quality of the material.





Biao Qin et al., Chem. Mater., 32, 24, 2020.

Shaohua Li et. al., Adv. Mater., 35, 2211855, 2023

Choosing the substrate

pubs.acs.org/cm
Review

Substrates in the Synthesis of Two-Dimensional Materials via Chemical Vapor Deposition

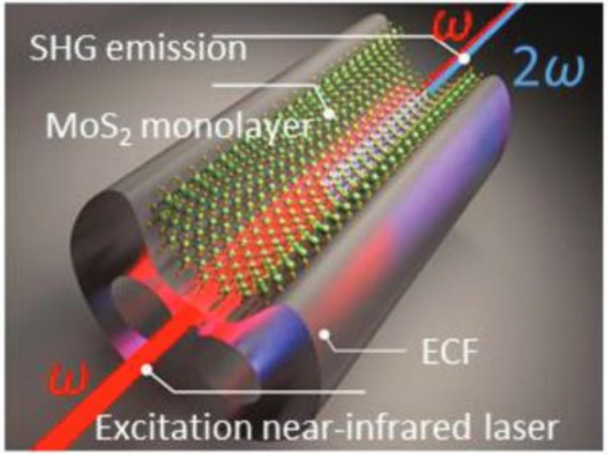
Biao Qin,[‖] Huifang Ma,[‖] Mongur Hossain, Mianzeng Zhong, Qinglin Xia, Bo Li,* and Xidong Duan*

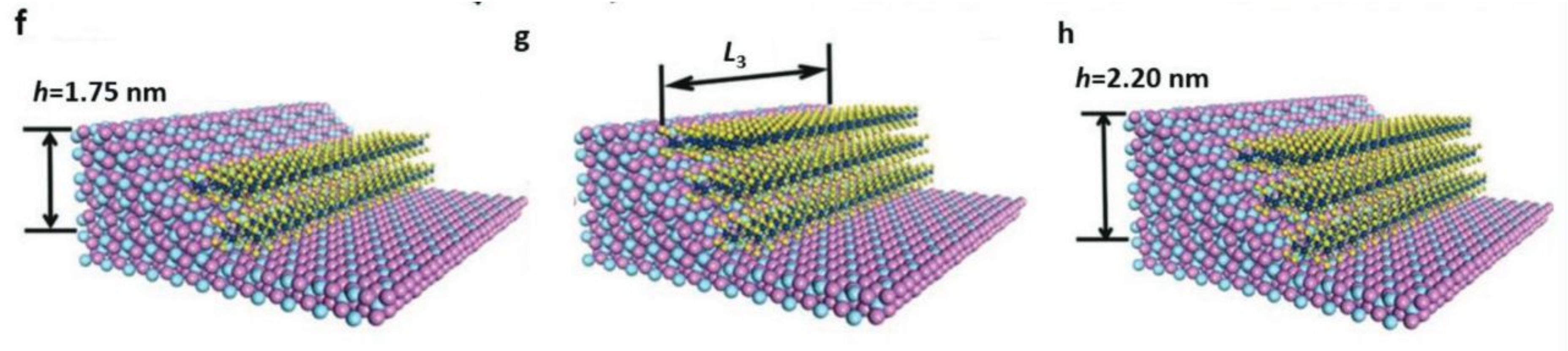
Cite This: https://dx.doi.org/10.1021/acs.chemmater.0c03549
Read Online

"Substrates play three important roles in the synthesis of 2DMs by the CVD method:
adsorbing source materials,
promoting material nucleation,
and stimulating material epitaxial growth."

"...key factors are
the **matching degree of the lattice constant** of the target product and the substrate,
the **thermal expansion coefficient**,
and the **catalytic effect** of the specific substrate on the material."

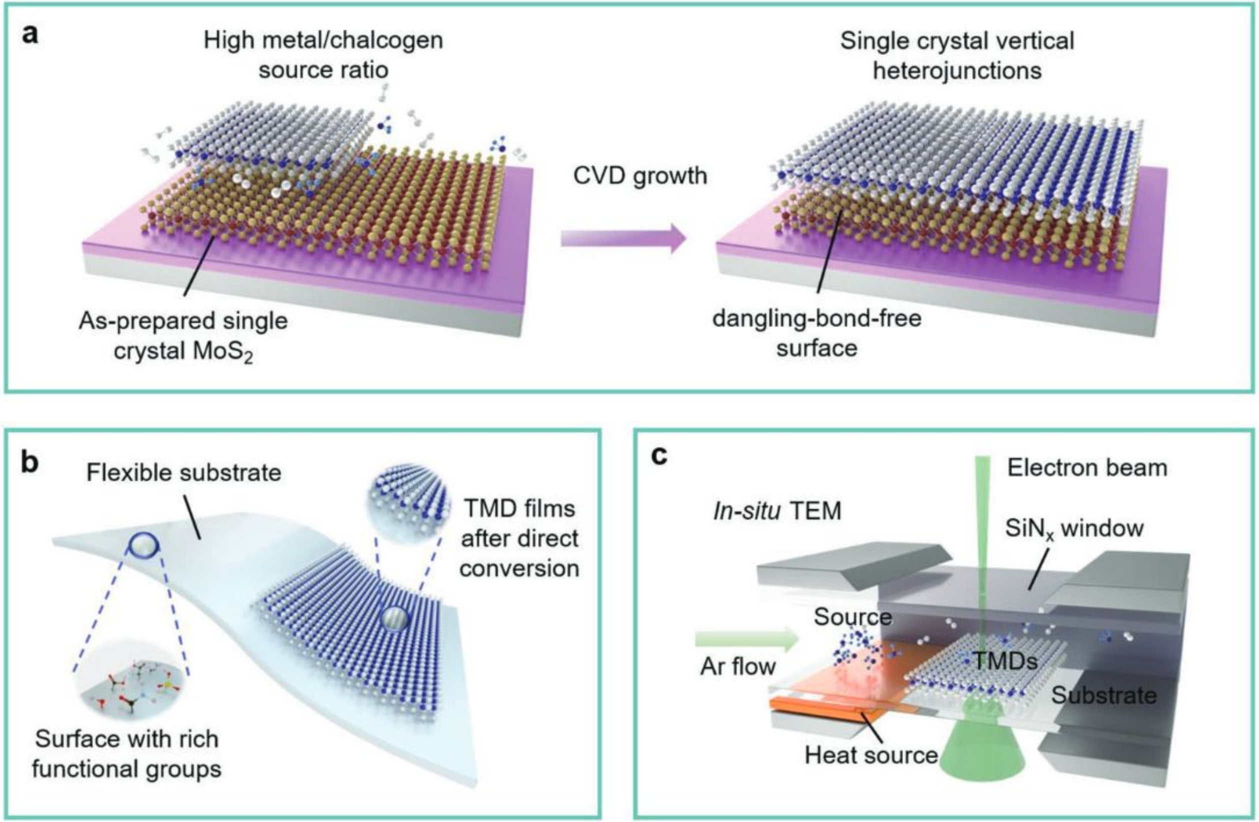
Substrate Engineering





Shaohua Li et. al., Adv. Mater., 35, 2211855, 2023

Substrate Engineering



Shaohua Li et. al., Adv. Mater., 35, 2211855, 2023

LETTERS
PUBLISHED ONLINE: 28 MARCH 2010 | DOI: 10.1038/NNANO.2010.53

nature nanotechnology

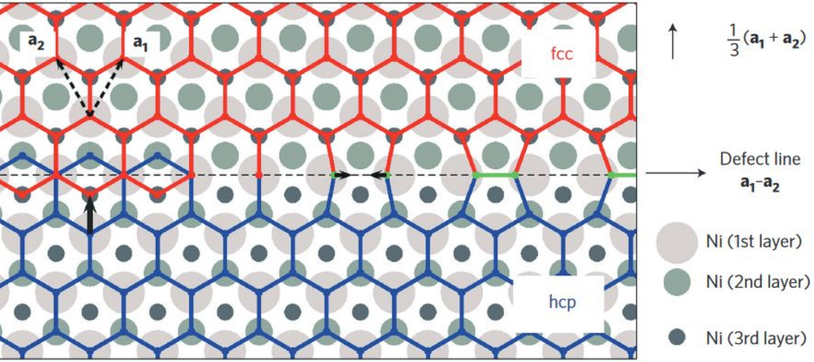
An extended defect in graphene as a metallic wire

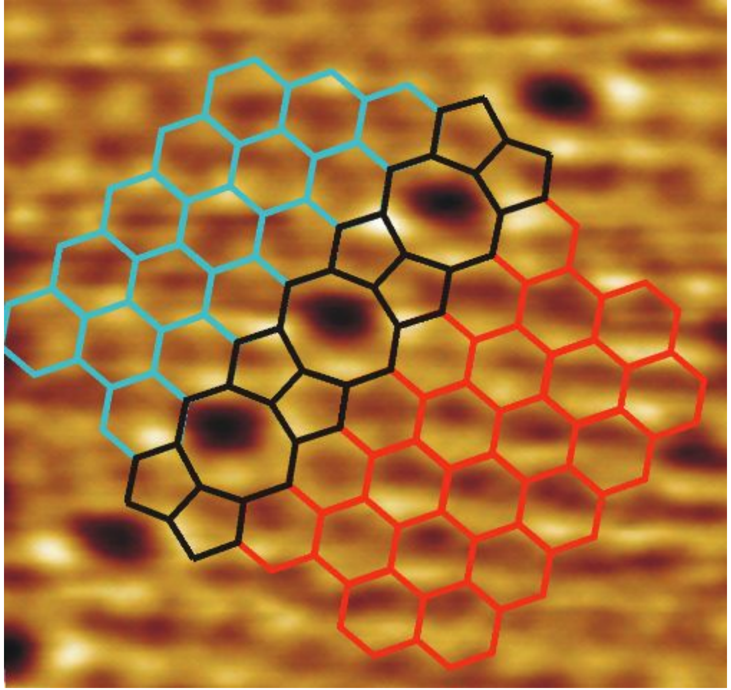
Jayeeta Lahiri, You Lin, Pinar Bozkurt, Ivan I. Oleynik and Matthias Batzill*

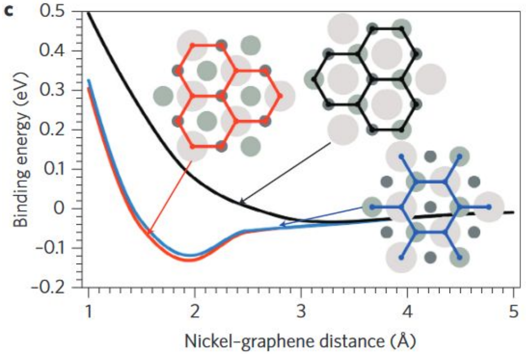
Many proposed applications of graphene require the ability to tune its electronic structure at the nanoscale[1,2]. Although charge transfer[3] and field-effect doping[4] can be applied to manipulate charge carrier concentrations, using them to

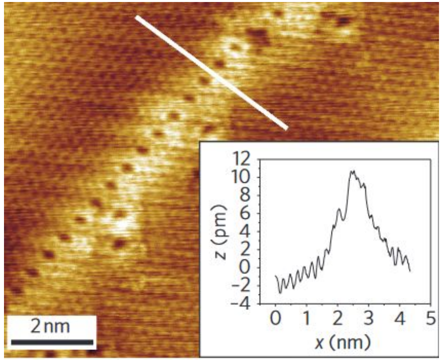
sheets in registry to each other with atomic precision. Such a scaffold can only be a two-dimensional atomic lattice for which graphene has a close epitaxial relationship, such as Ni(111).

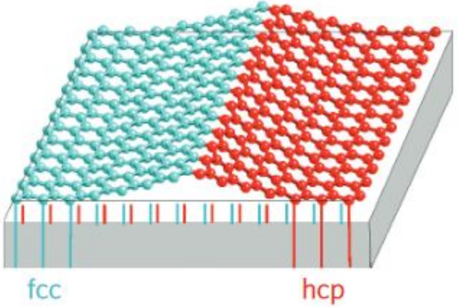
Graphene grows on Ni(111) with half of the carbon atoms situated



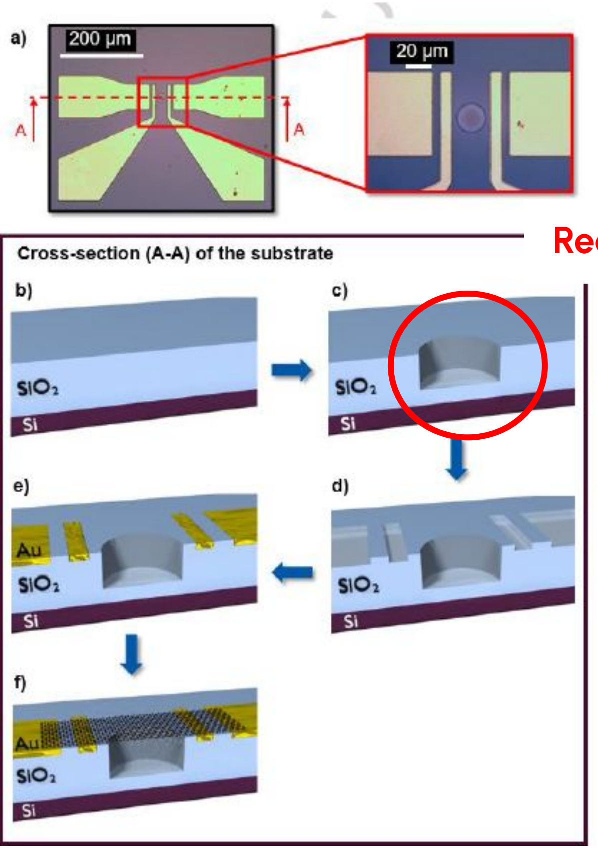


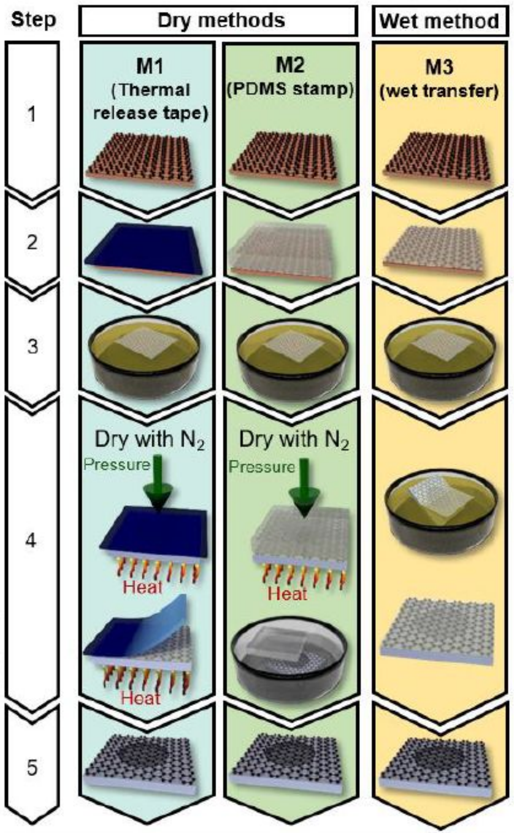


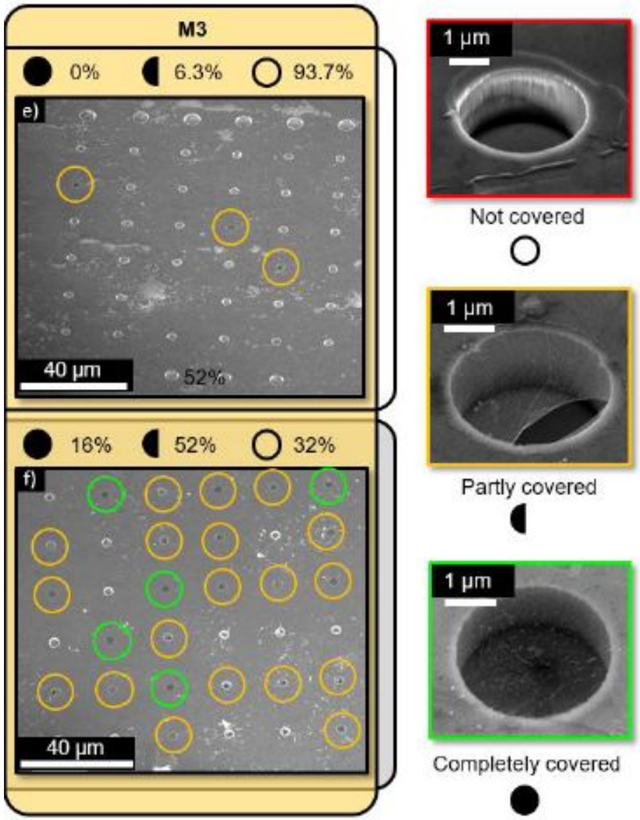




Free-Standing samples

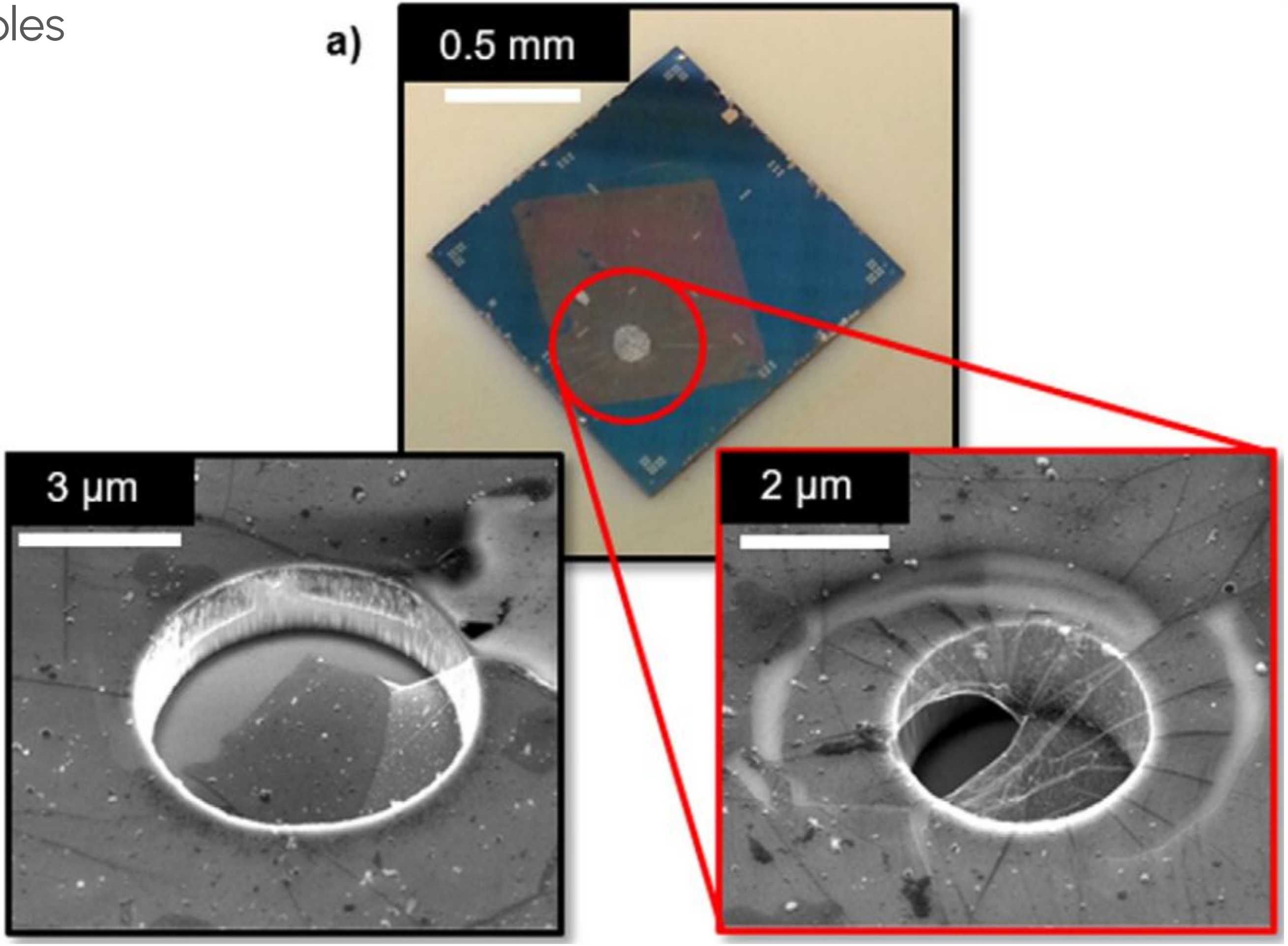






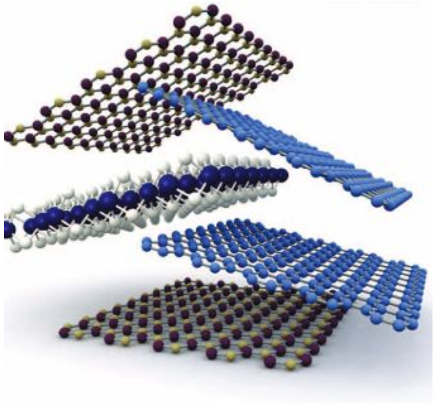
S. Wagner, et. al., Micro. Eng. 159, 108, 2016.

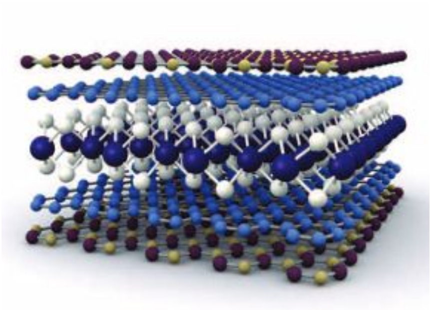
Free-Standing samples

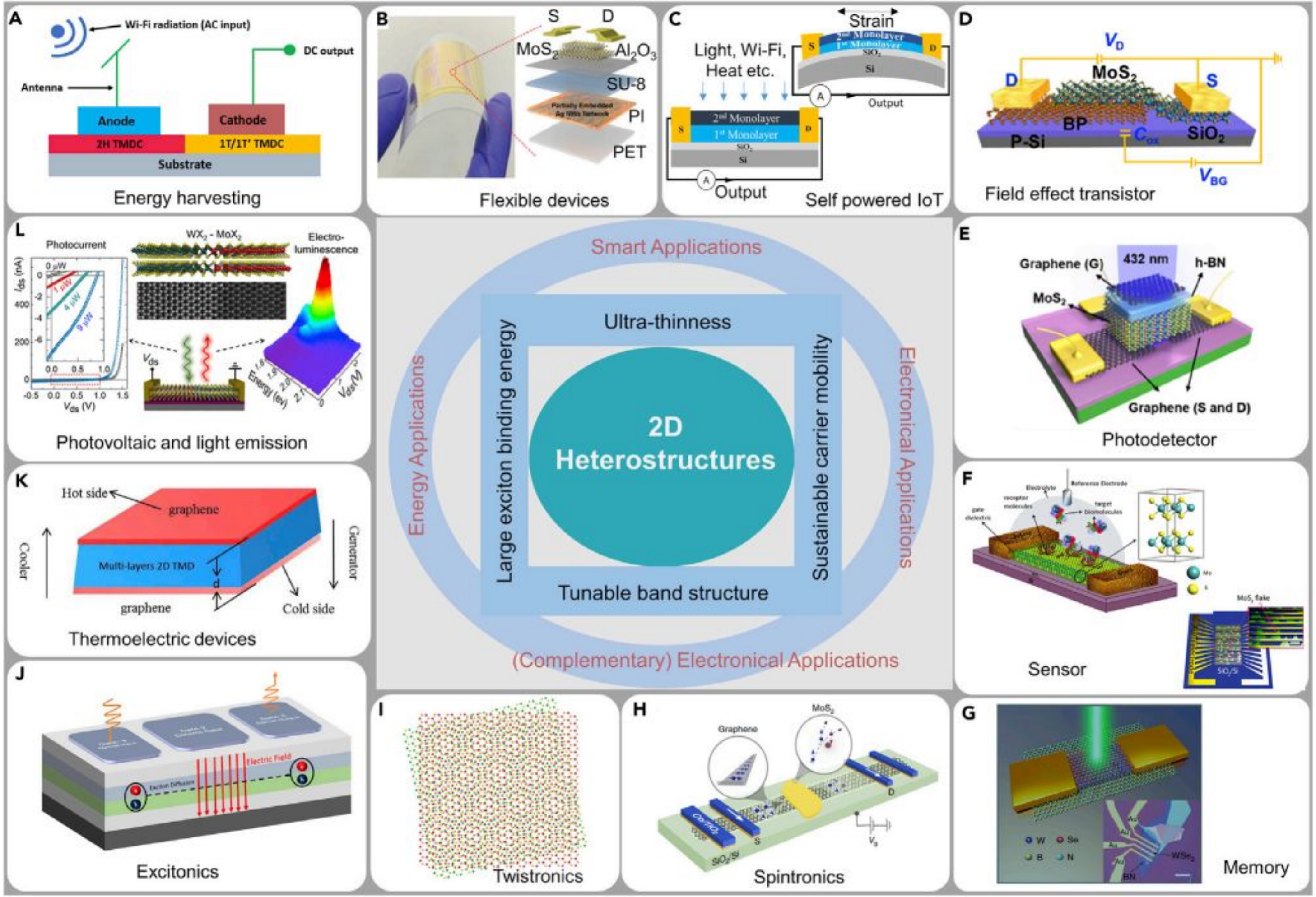


S. Wagner, et. al., Micro. Eng. 159, 108, 2016.

Heteroestruturas







K. S. Novoselov, Science, 353, 2016

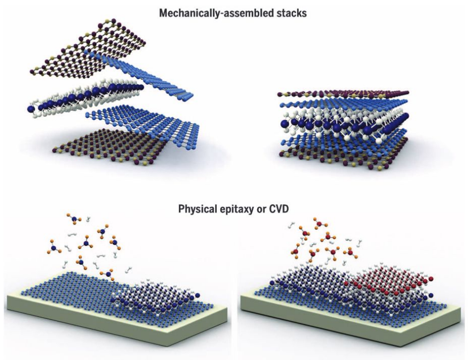
S. K. Chakraborty, iScience 25, 103942, 2022

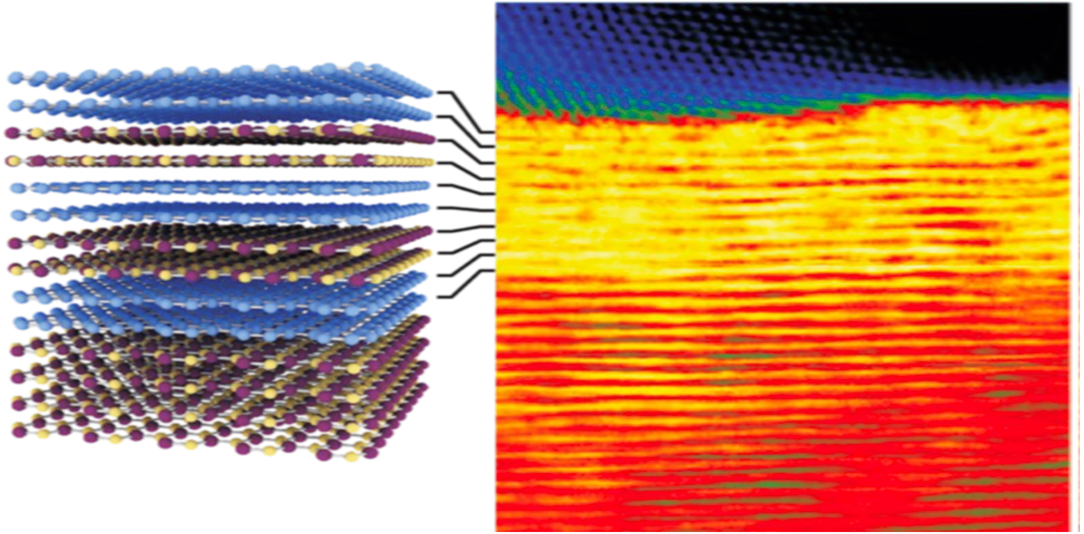
Heteroestruturas

LETTERS
PUBLISHED ONLINE: 29 JULY 2012 | DOI: 10.1038/NMAT3386
nature materials

Cross-sectional imaging of individual layers and buried interfaces of graphene-based heterostructures and superlattices

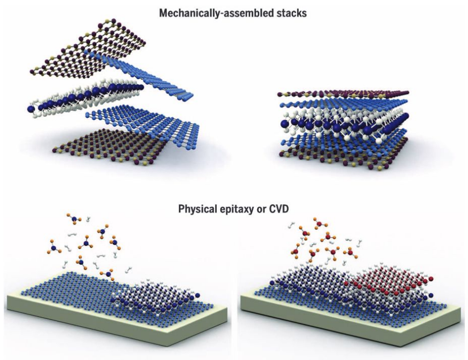
S. J. Haigh[1]*, A. Gholinia[1], R. Jalil[2], S. Romani[3], L. Britnell[2], D. C. Elias[2], K. S. Novoselov[2], L. A. Ponomarenko[2], A. K. Geim[2] and R. Gorbachev[2]*





S. J. Haigh et al. Nature Materials (2012)
Butler et. al. ACS Nano, 7, 2898 (2013)
K. S. Novoselov et. al, Science, 353 (2016)

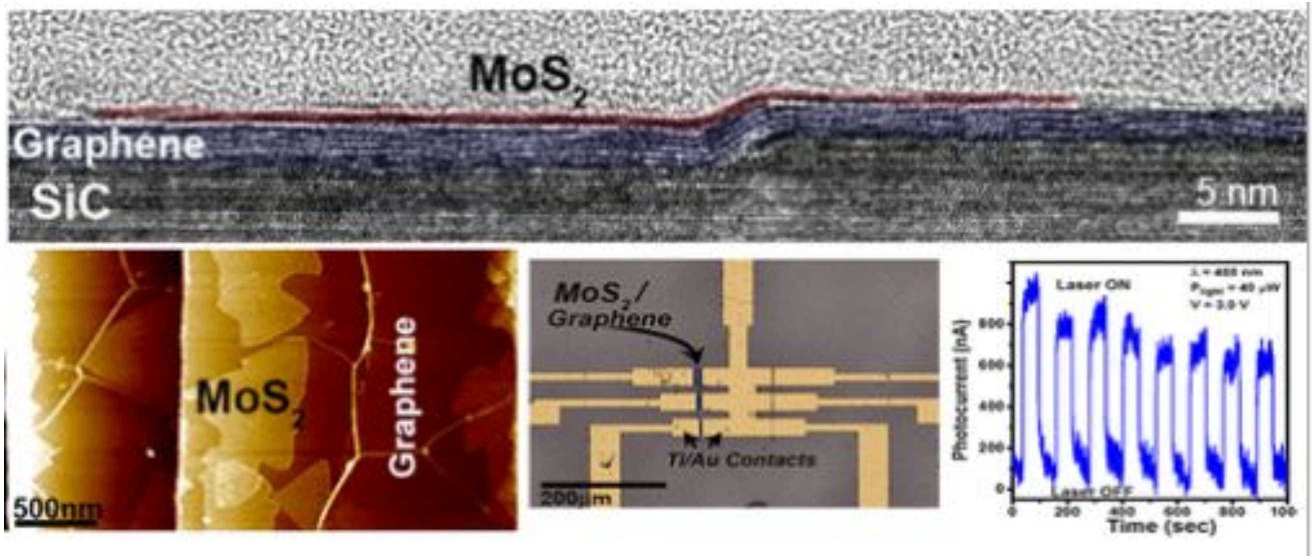
Heteroestruturas



Direct Synthesis of van der Waals Solids

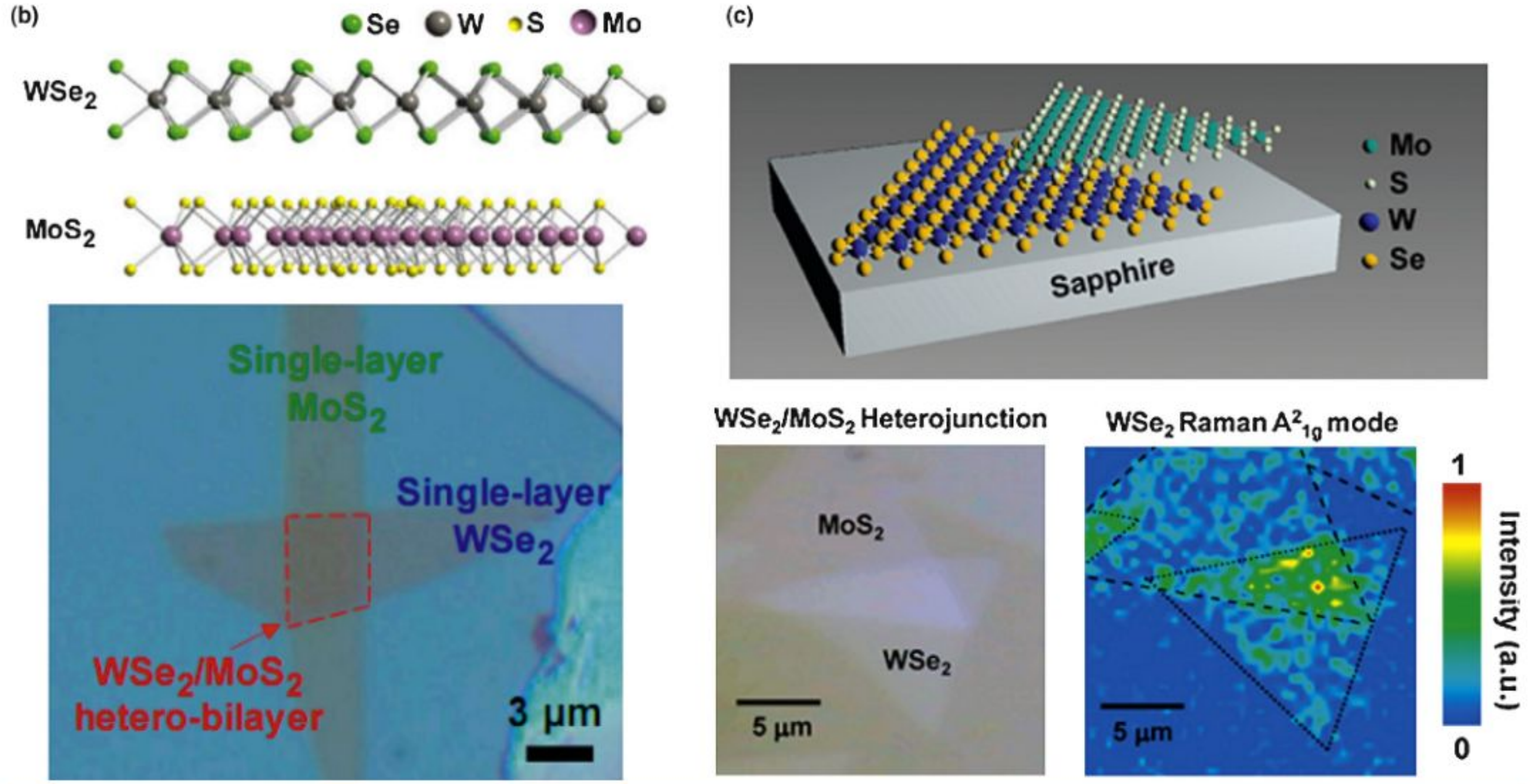
Yu-Chuan Lin,[†] Ning Lu,[‡] Nestor Perea-Lopez,[§] Jie Li,[⊥] Zhong Lin,[§] Xin Peng,[‡] Chia Hui Lee,[†] Ce Sun,[‡] Lazaro Calderin,[†] Paul N. Browning,[†] Michael S. Bresnehan,[†] Moon J. Kim,[‡] Theresa S. Mayer,[⊥] Mauricio Terrones,[§] and Joshua A. Robinson[†,*]

[†]Department of Materials Science and Engineering and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, Pennsylvania 16802, United States, [‡]Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas 75080, United States, [§]Department of Physics and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, Pennsylvania 16802, United States, and [⊥]Department of Electrical Engineering, The Pennsylvania State University, State College, University Park, Pennsylvania 16802, United States



S. J. Haigh et al. Nature Materials (2012)
Butler et. al. ACS Nano, 7, 2898 (2013)
K. S. Novoselov et. al, Science, 353 (2016)

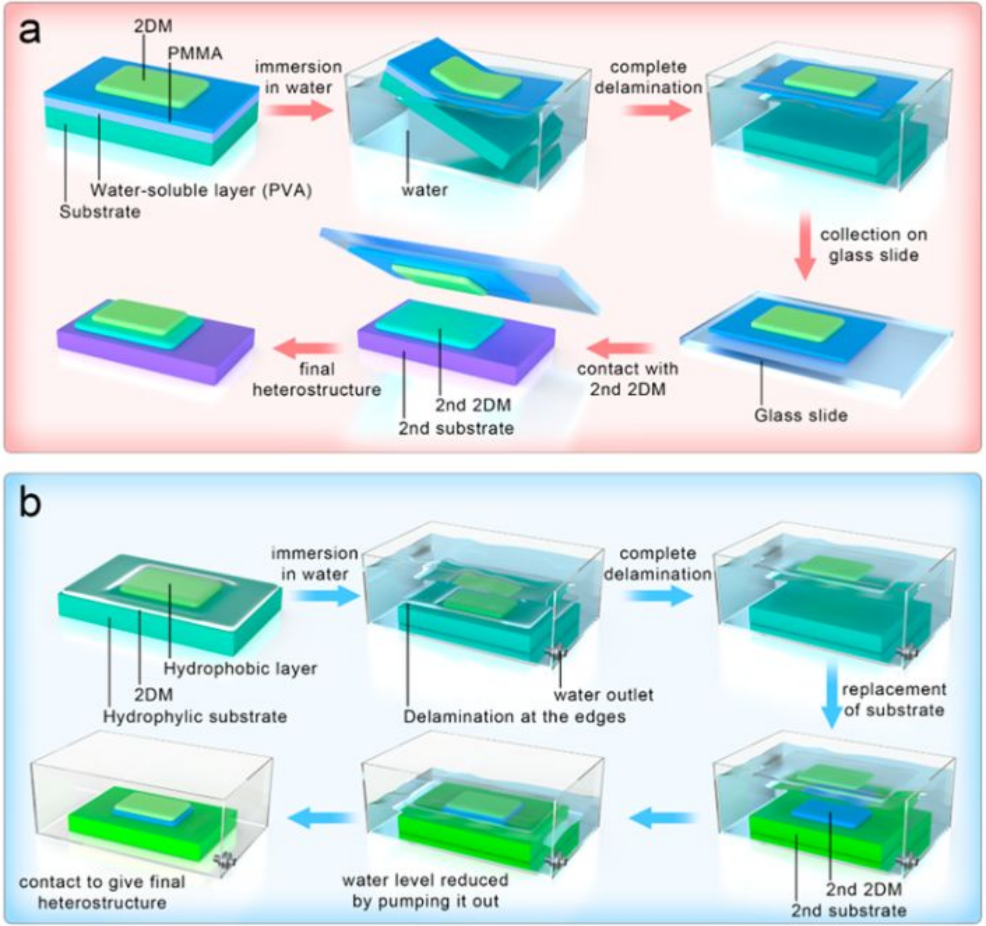
Heteroestruturas



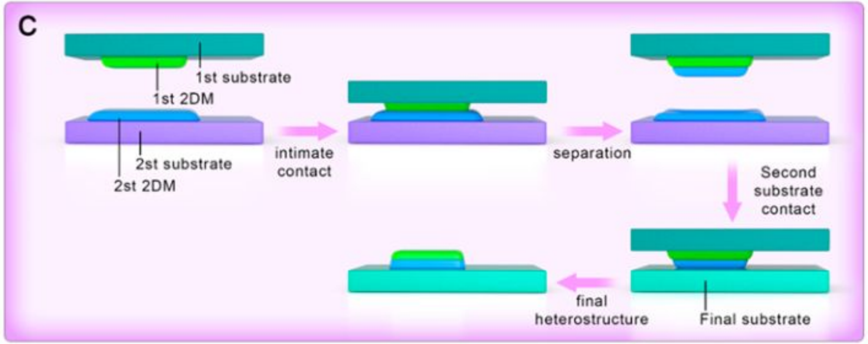
Ming-Yang Li et. al., Materials Today, 19, 2016

PMMA transfer method

Poly (methyl methacrylate) (PMMA): thermoplastic synthetic polymer



vdW lift and transfer method.



Wedging method

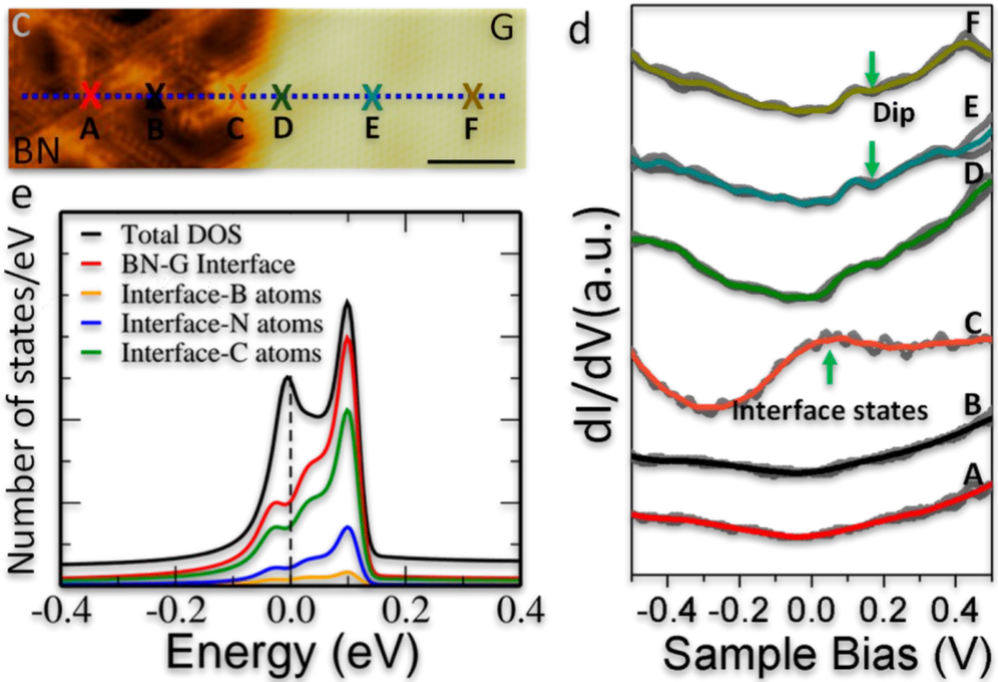
Phuong V. Pham et. al., Chem. Rev., 122, 6514, 2022.

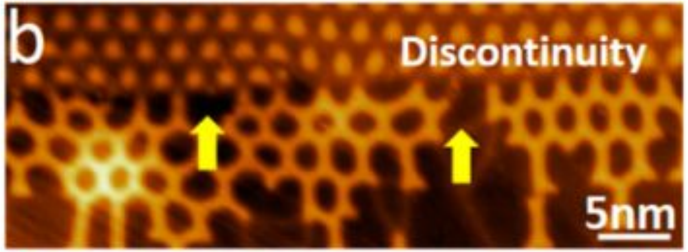
Heteroestruturas

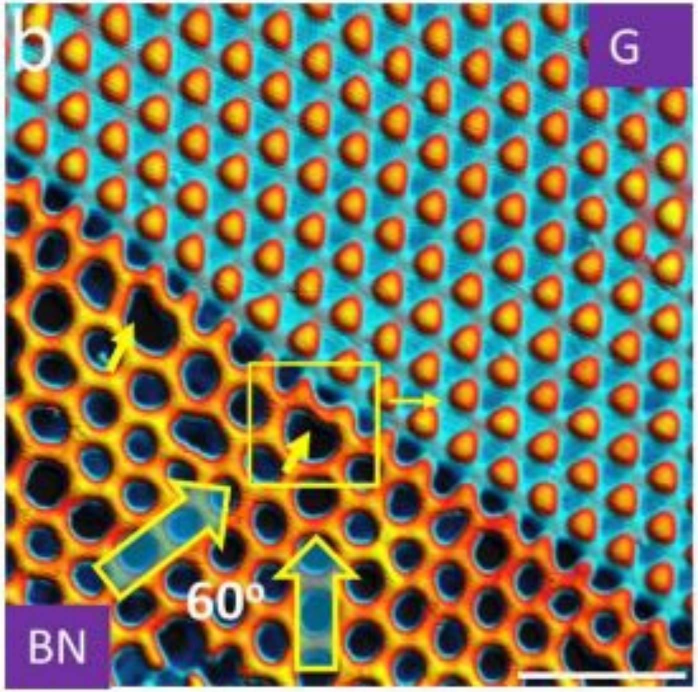
NANO LETTERS
Letter
pubs.acs.org/NanoLett

Lattice Relaxation at the Interface of Two-Dimensional Crystals: Graphene and Hexagonal Boron-Nitride

Jiong Lu,[†,‡,#] Lídia C. Gomes,[‡,§,#] Ricardo W. Nunes,[§] A. H. Castro Neto,[‡,∥] and Kian Ping Loh*[,†,‡]





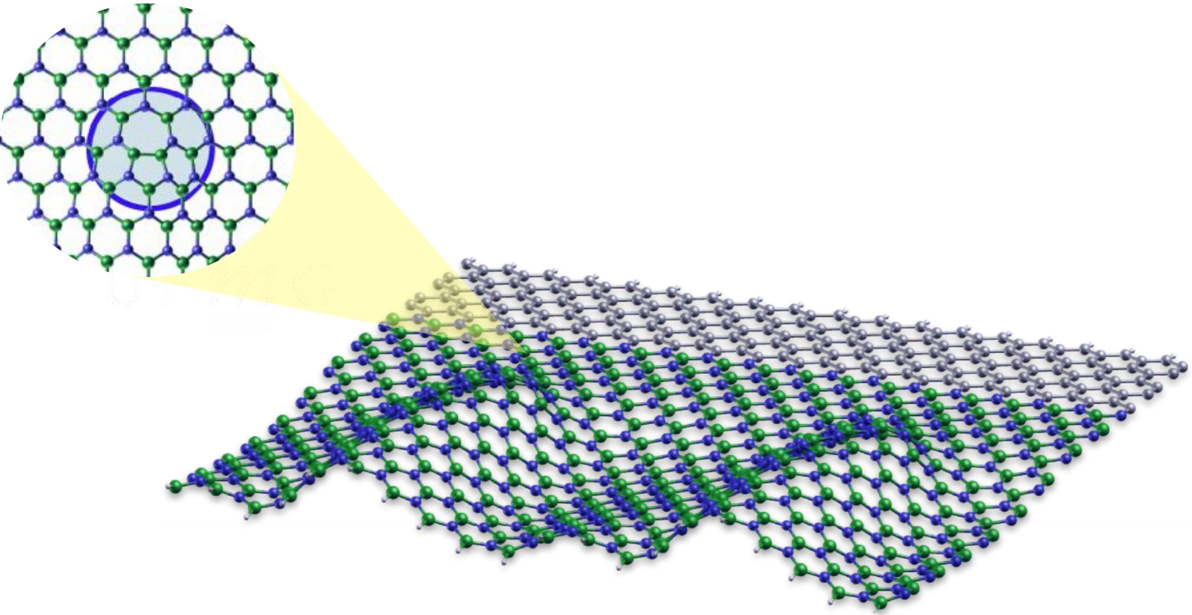


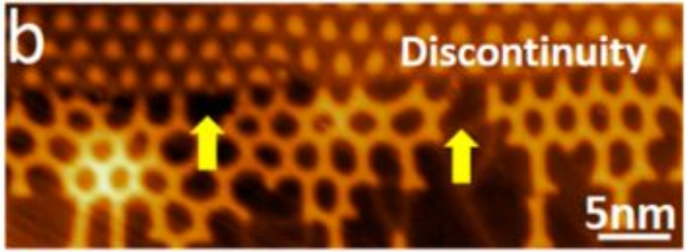
Heteroestruturas

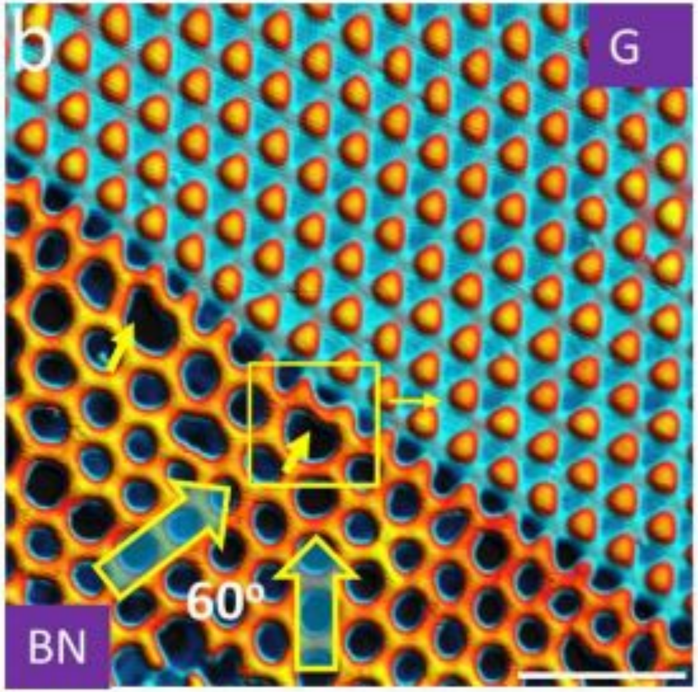
NANO LETTERS
Letter
pubs.acs.org/NanoLett

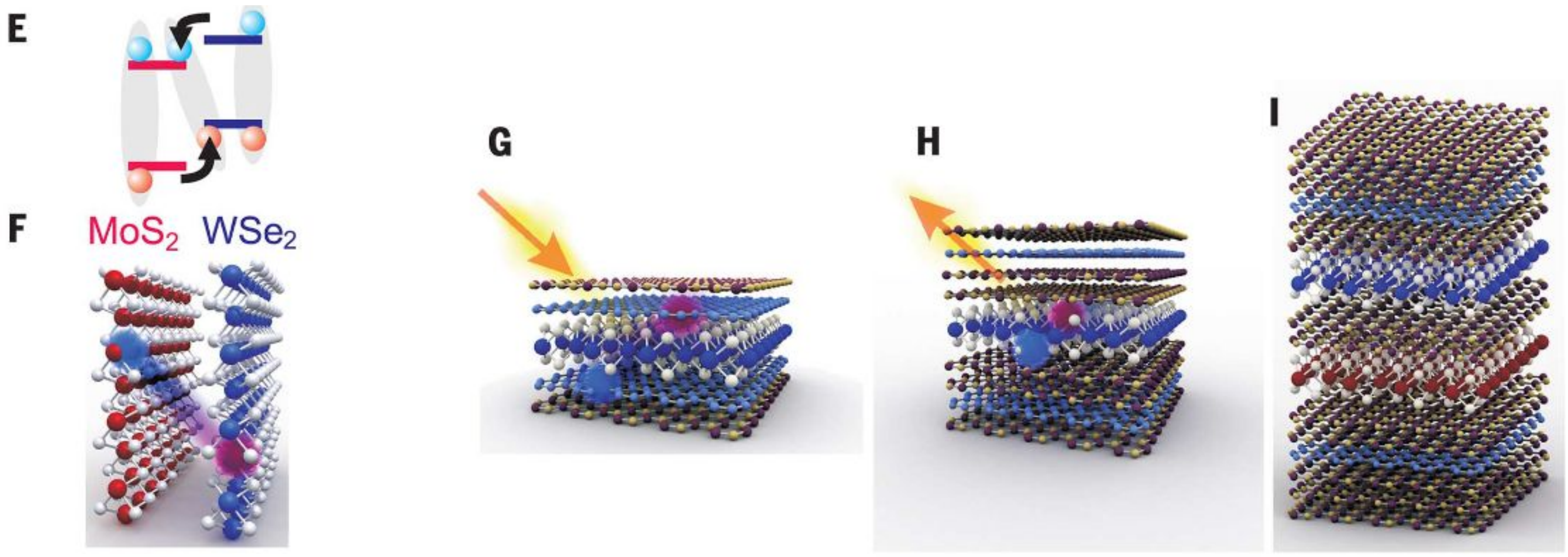
Lattice Relaxation at the Interface of Two-Dimensional Crystals: Graphene and Hexagonal Boron-Nitride

Jiong Lu,[†,‡,#] Lídia C. Gomes,[‡,§,#] Ricardo W. Nunes,[§] A. H. Castro Neto,[‡,∥] and Kian Ping Loh*[,†,‡]





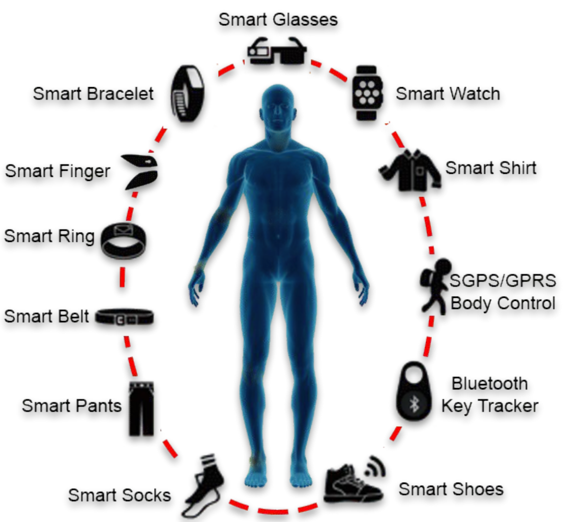




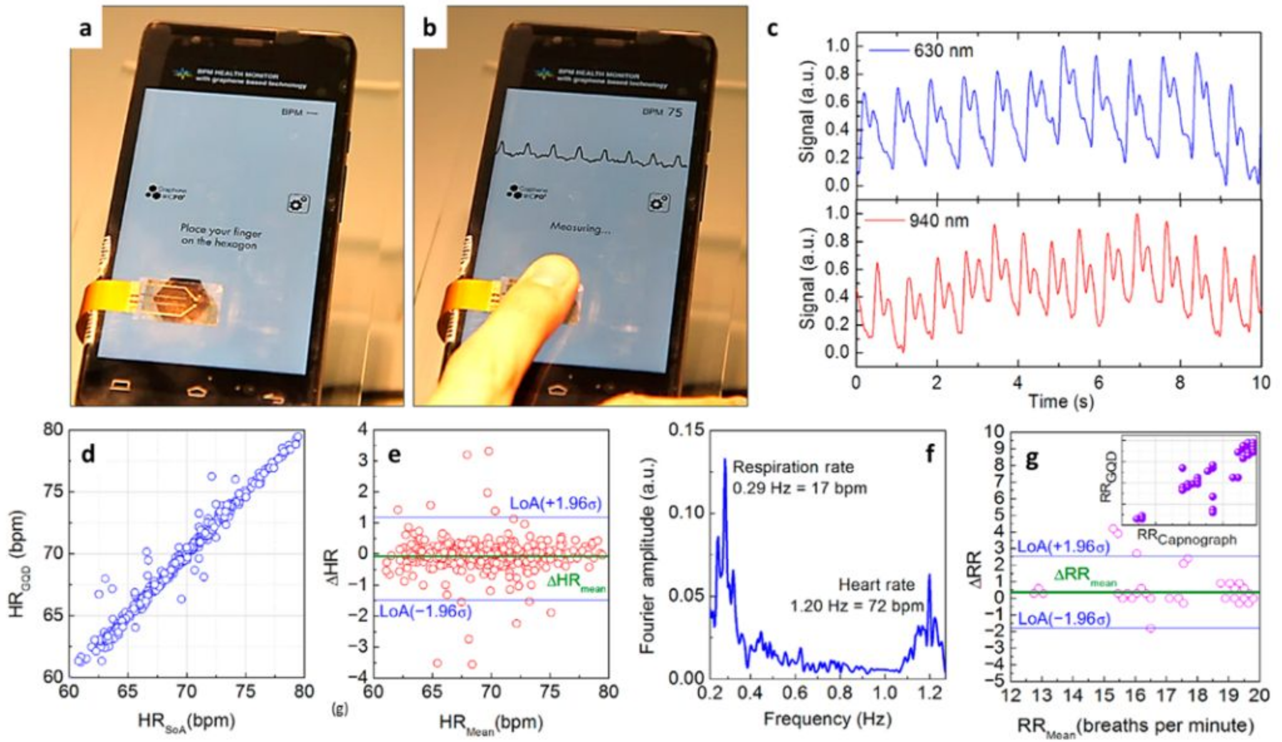
K. S. Novoselov, Science, 353, 2016

Photodetectors for Biomedical Applications

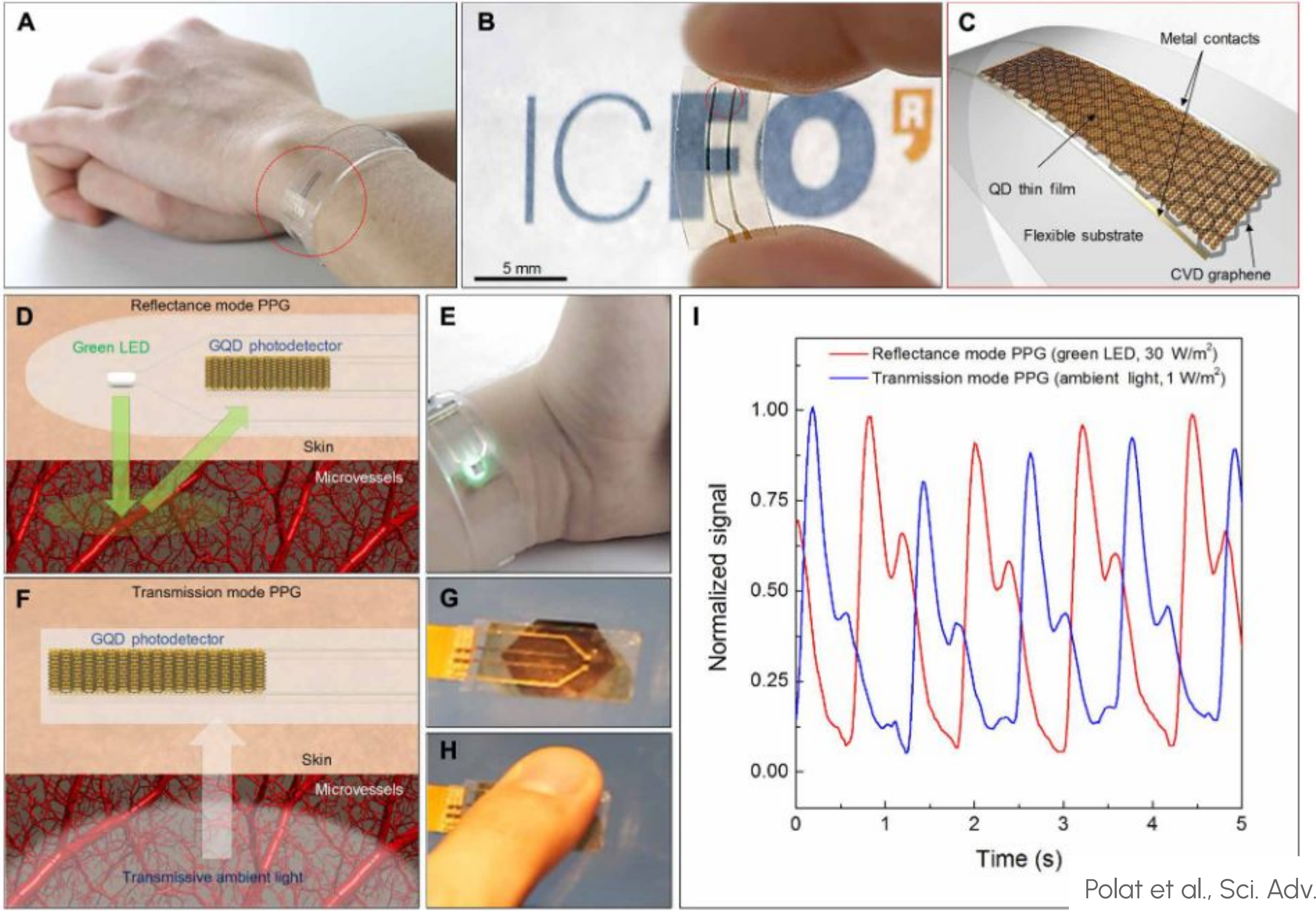
Light-sensitive quantum dots (QDs) made of PbS on the graphene layer.



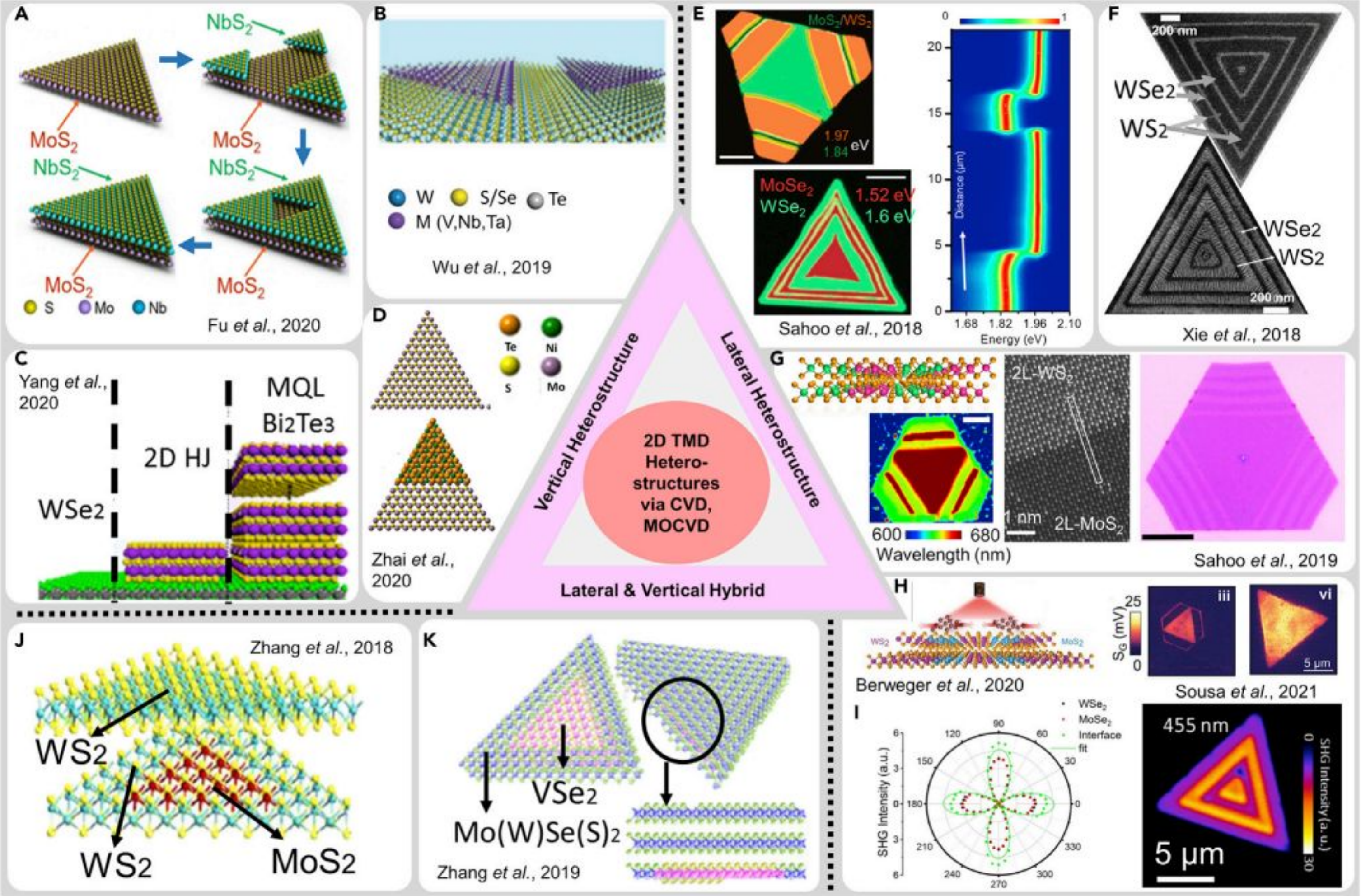
Wearable technology



Polat et al., Sci. Adv., 5, eaaw7846, 2019 / Phuong V. Pham et. al., Chem. Rev., 122, 6514, 2022.



Polat et al., Sci. Adv., 5, eaaw7846, 2019



S. K. Chakraborty, iScience 25, 103942, 2022

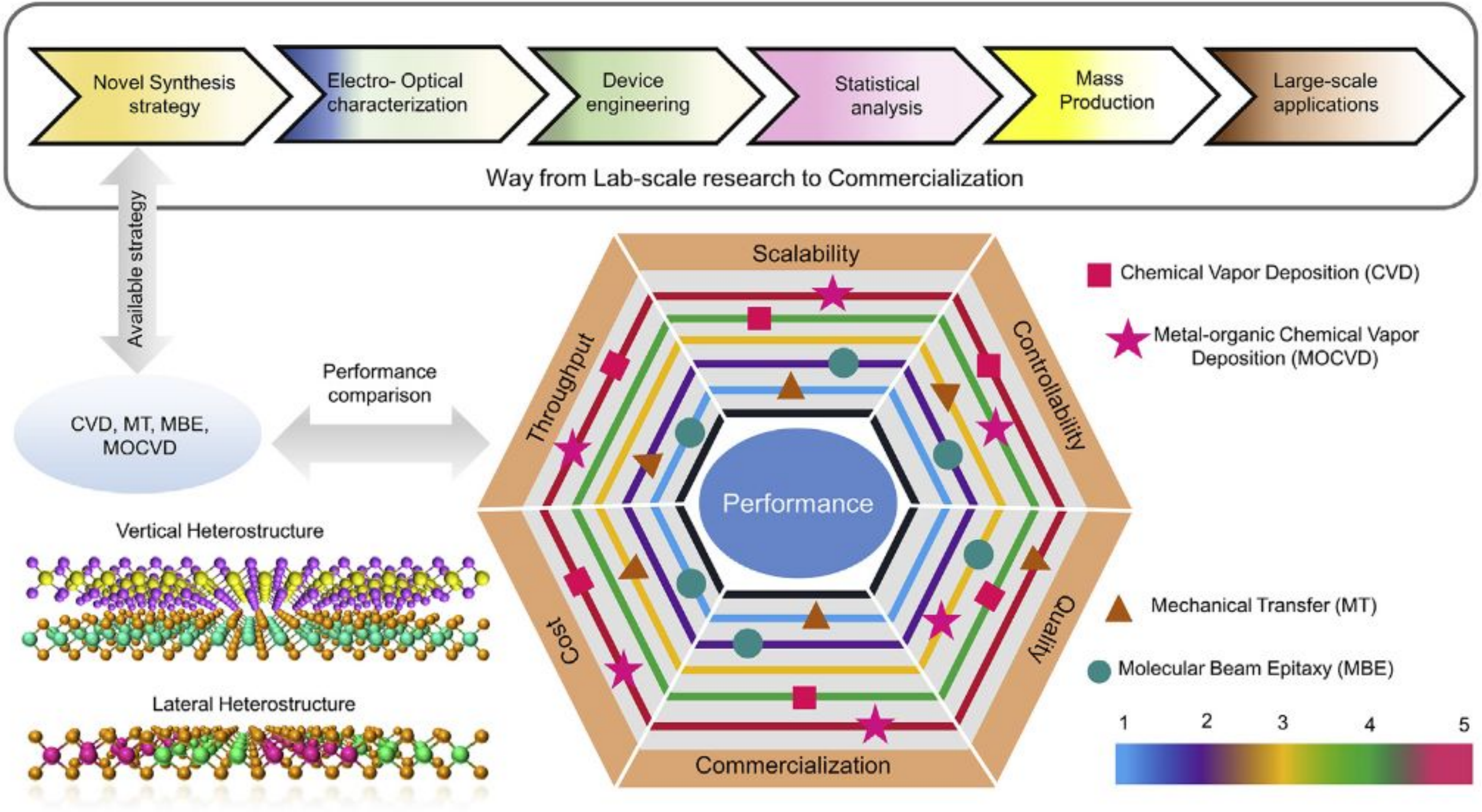
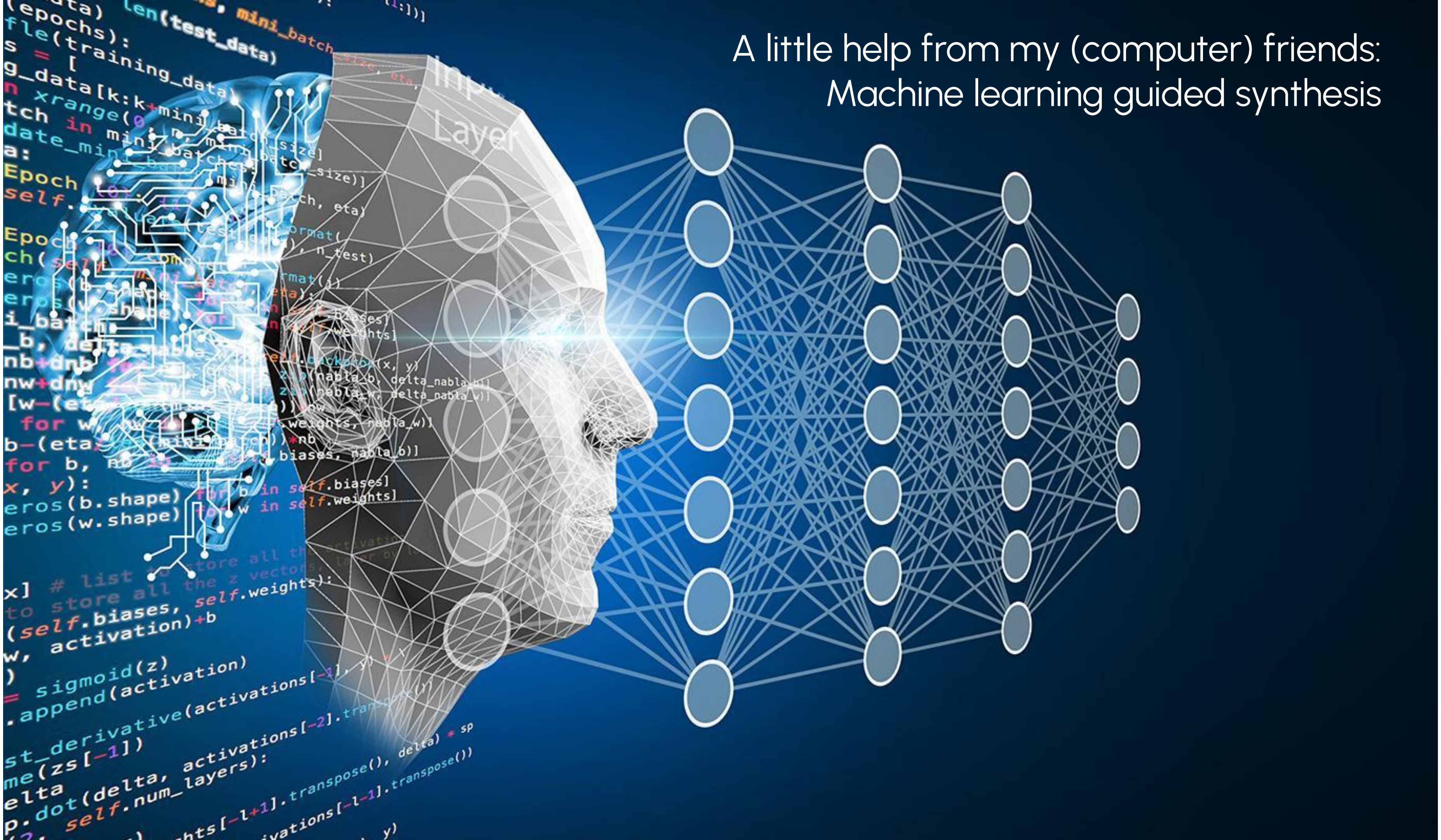


Figure 1. Roadmap toward commercialization

S. K. Chakraborty, iScience 25, 103942, 2022

A little help from my (computer) friends: Machine learning guided synthesis

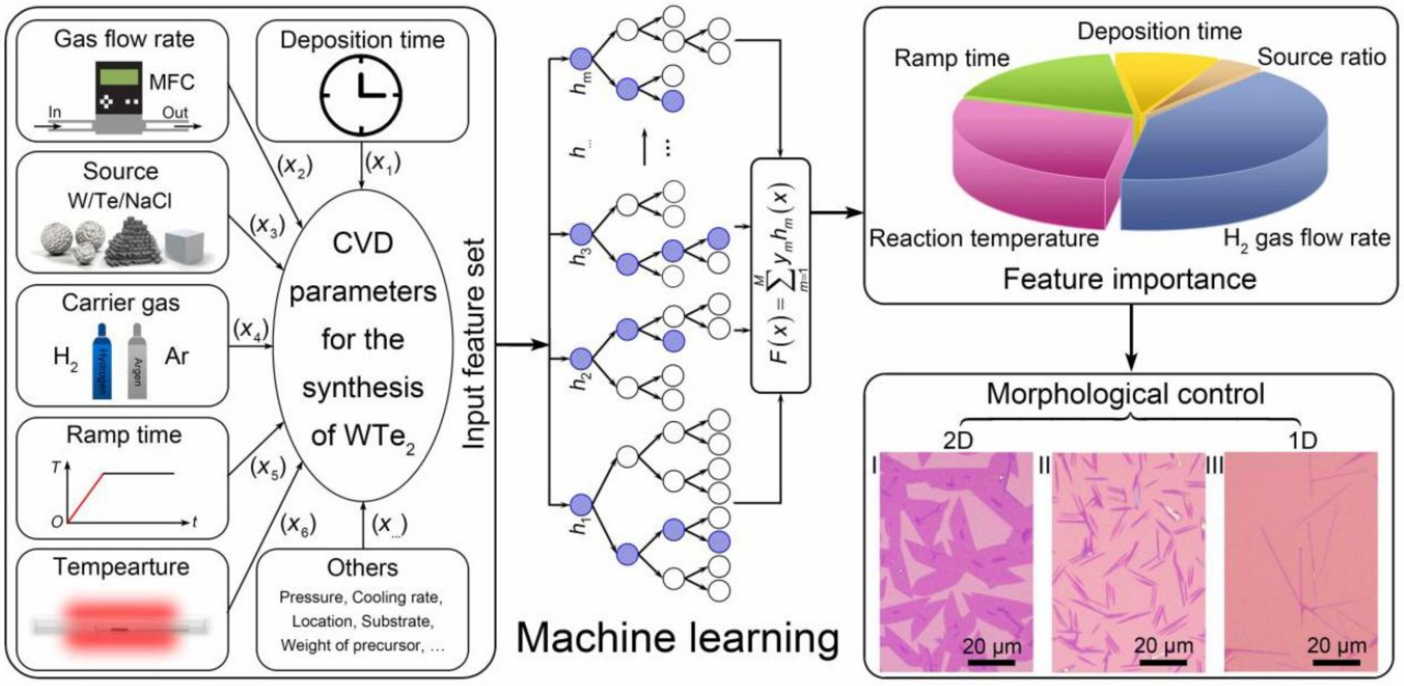



@teenybiscuit

Machine Learning Driven Synthesis of Few-Layered WTe_2 with Geometrical Control

Manzhang Xu, Bijun Tang, Yuhao Lu, Chao Zhu, Qianbo Lu, Chao Zhu, Lu Zheng, Jingyu Zhang, Nannan Han, Weidong Fang, Yuxi Guo, Jun Di, Pin Song, Yongmin He, Lixing Kang, Zhiyong Zhang*, Wu Zhao, Cuntai Guan, Xuewen Wang*, and Zheng Liu*

Cite this: *J. Am. Chem. Soc.* 2021, 143, 43, 18103–18113
Publication Date: October 4, 2021
https://doi.org/10.1021/jacs.1c06786

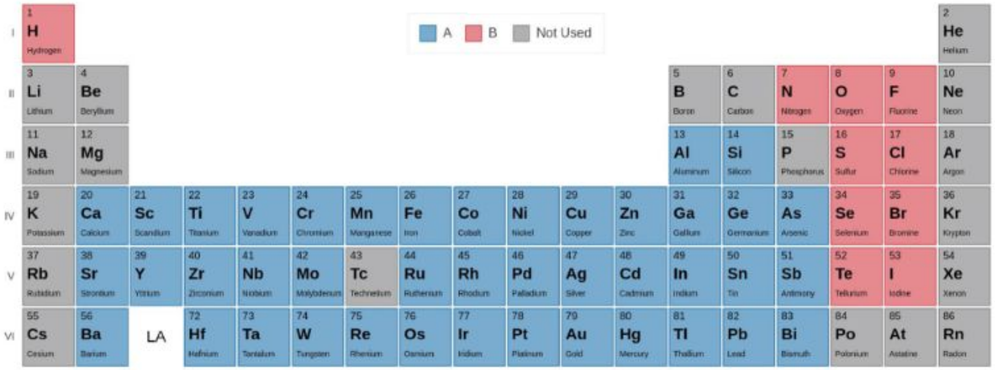


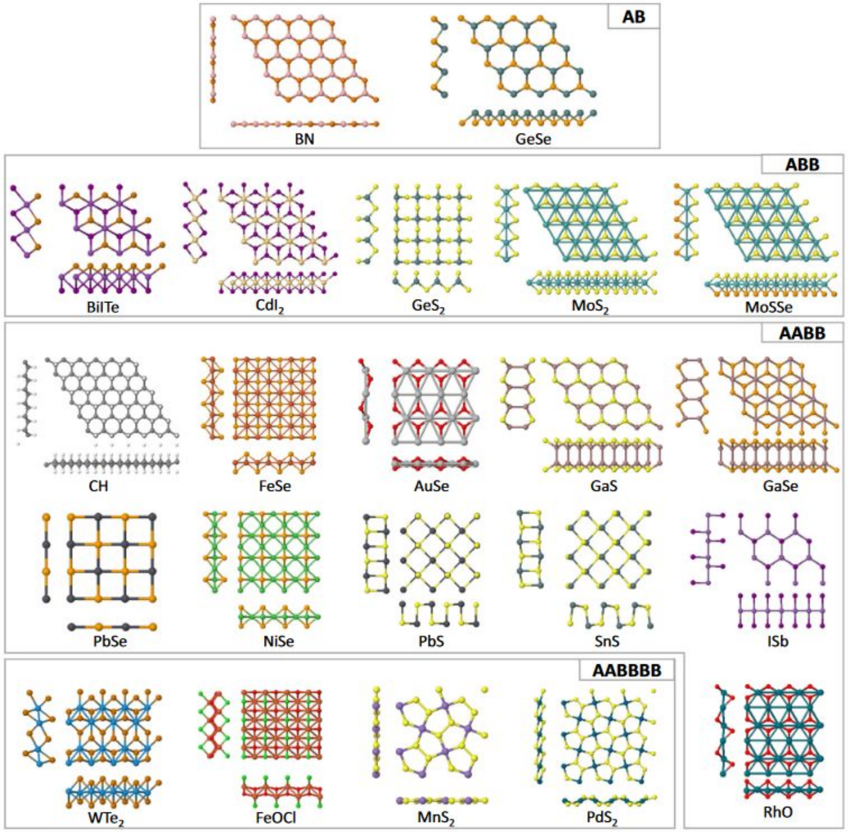
ARTICLE OPEN

An artificial intelligence-aided virtual screening recipe for two-dimensional materials discovery

Murat Cihan Sorkun[1,2,3], Séverin Astruc[1,2], J. M. Vianney A. Koelman[2,3] and Süleyman Er[1,2]✉

In recent years, artificial intelligence (AI) methods have prominently proven their use in solving complex problems. Across science and engineering disciplines, the data-driven approach has become the fourth and newest paradigm. It is the burgeoning of findable, accessible, interoperable, and reusable (FAIR) data generated by the first three paradigms of experiment, theory, and simulation that has enabled the application of AI methods for the scientific discovery and engineering of compounds and materials. Here, we introduce a recipe for a data-driven strategy to speed up the virtual screening of two-dimensional (2D) materials and to accelerate the discovery of new candidates with targeted physical and chemical properties. As a proof of concept, we generate new





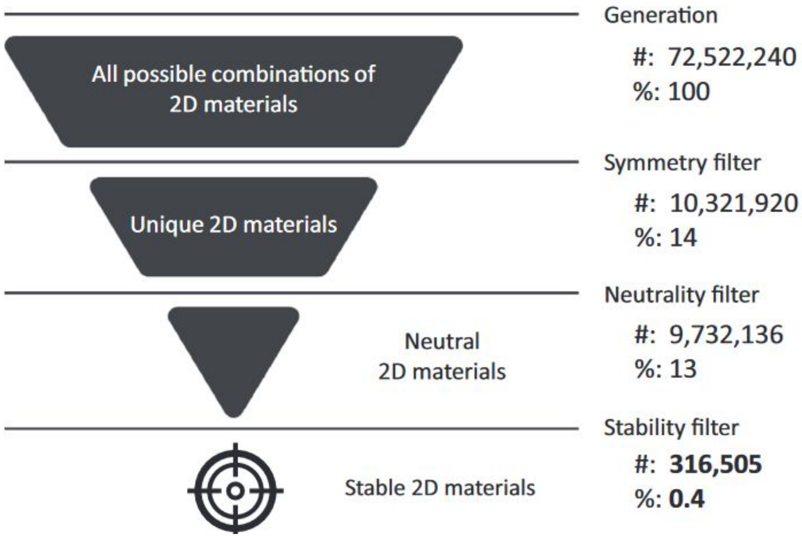
ARTICLE OPEN

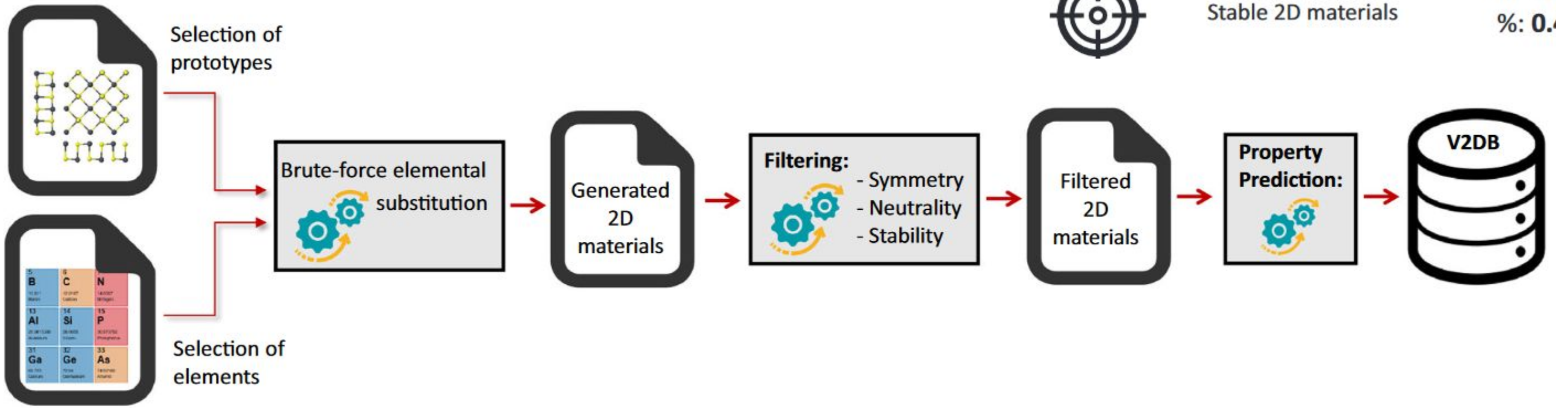
Check for updates

An artificial intelligence-aided virtual screening recipe for two-dimensional materials discovery

Murat Cihan Sorkun[1,2,3], Séverin Astruc[1,2], J. M. Vianney A. Koelman[2,3] and Süleyman Er[1,2]✉

In recent years, artificial intelligence (AI) methods have prominently proven their use in solving complex problems. Across science and engineering disciplines, the data-driven approach has become the fourth and newest paradigm. It is the burgeoning of findable, accessible, interoperable, and reusable (FAIR) data generated by the first three paradigms of experiment, theory, and simulation that has enabled the application of AI methods for the scientific discovery and engineering of compounds and materials. Here, we introduce a recipe for a data-driven strategy to speed up the virtual screening of two-dimensional (2D) materials and to accelerate the discovery of new candidates with targeted physical and chemical properties. As a proof of concept, we generate new





Article https://doi.org/10.1038/s41467-023-44236-5

Universal machine learning aided synthesis approach of two-dimensional perovskites in a typical laboratory

Received: 23 April 2023

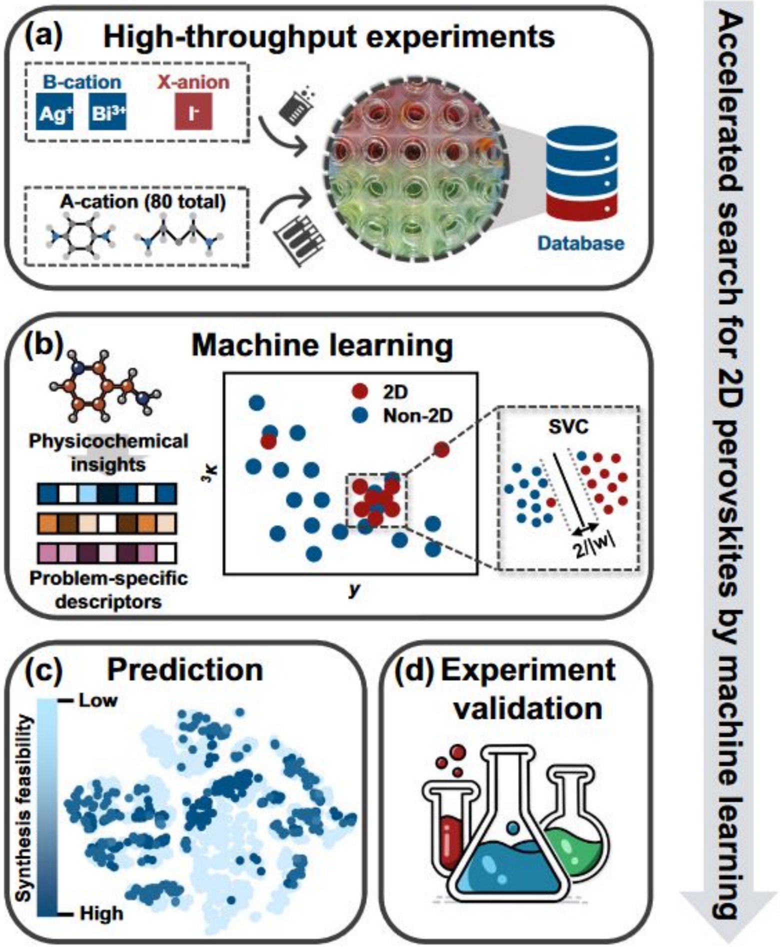
Accepted: 5 December 2023

Published online: 02 January 2024

Check for updates

Yilei Wu[1,4], Chang-Feng Wang[2,4], Ming-Gang Ju[1,4], Qiangqiang Jia[2], Qionghua Zhou[1], Shuaihua Lu[1], Xinying Gao[1], Yi Zhang[2] & Jinlan Wang[1,3]

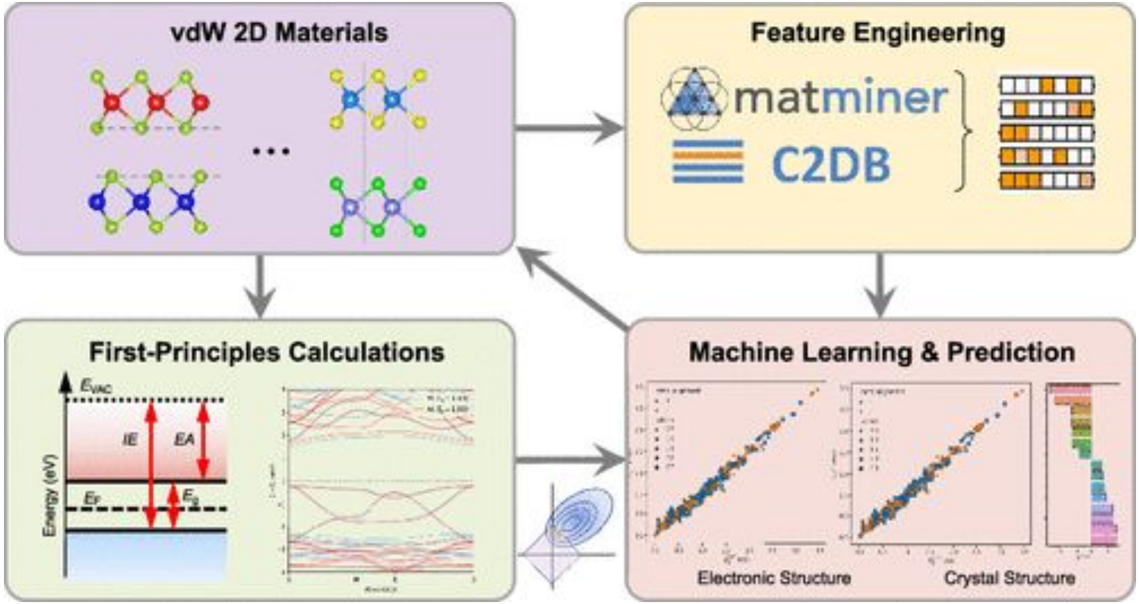
The past decade has witnessed the significant efforts in novel material discovery in the use of data-driven techniques, in particular, machine learning



Predicting Van der Waals Heterostructures by a Combined Machine Learning and Density Functional Theory Approach

Daniel Willhelm, Nathan Wilson, Raymundo Arroyave, Xiaoning Qian, Tahir Cagin*, Ruth Pachter*, and Xiaofeng Qian*

Cite this: *ACS Appl. Mater. Interfaces* 2022, 14, 22, 25907–25919
Publication Date: May 27, 2022
https://doi.org/10.1021/acsami.2c04403

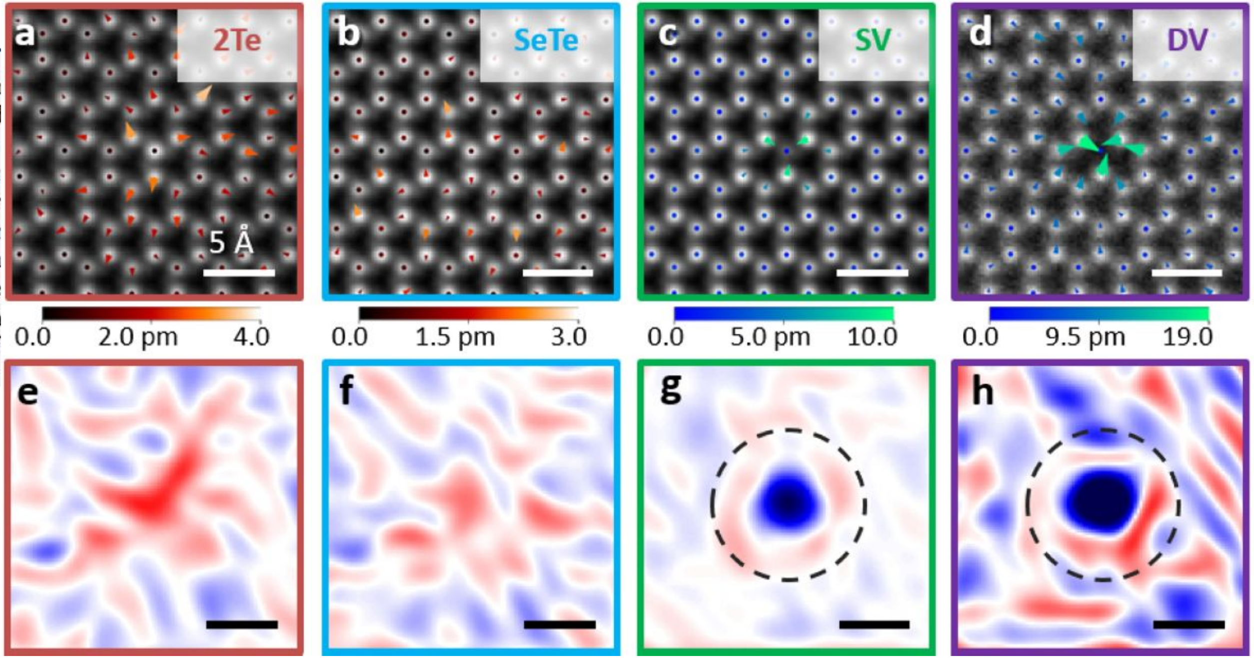


Deep Learning Enabled Strain Mapping of Single-Atom Defects in Two-Dimensional Transition Metal Dichalcogenides with Sub-Picometer Precision

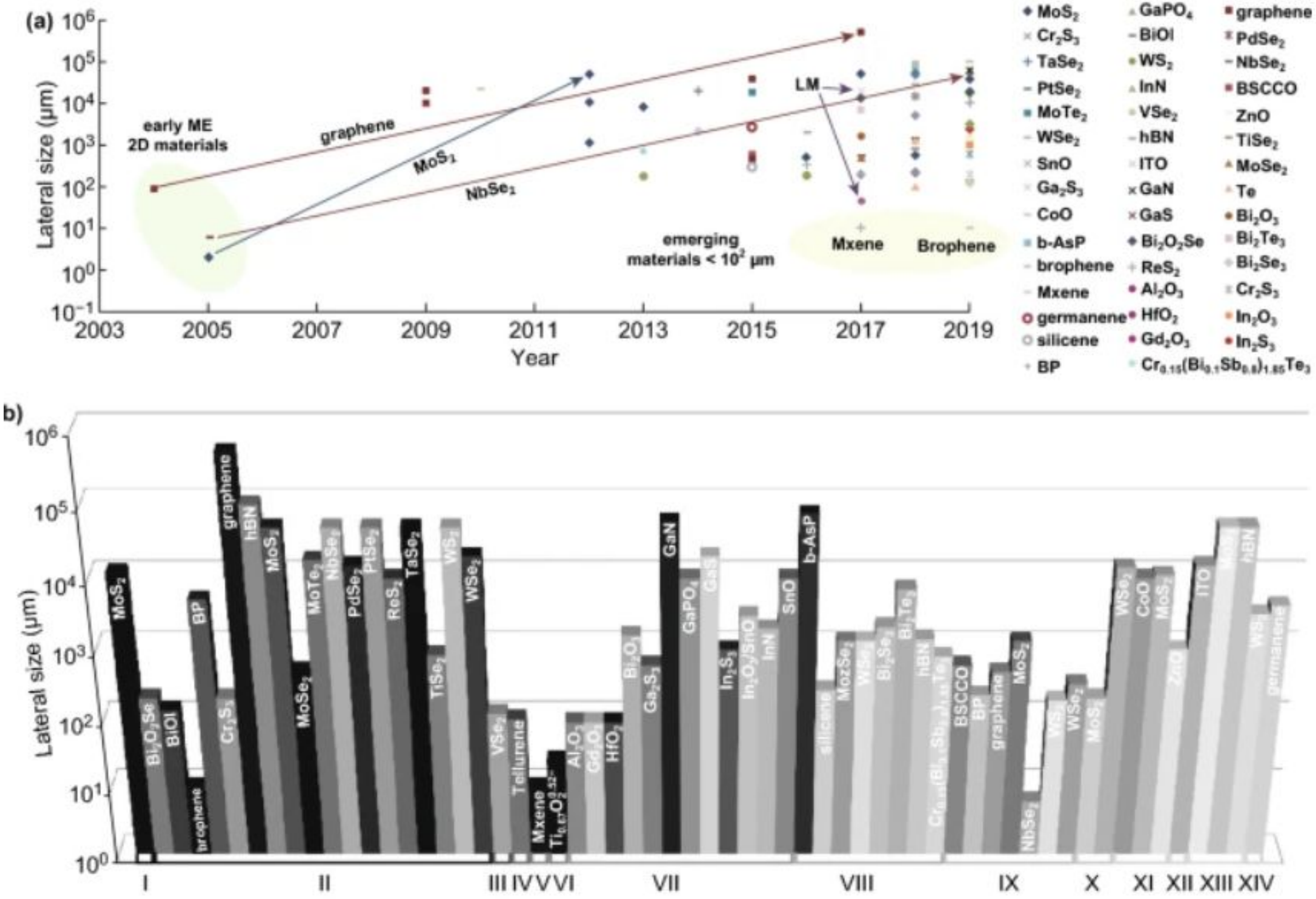
Chia-Hao Lee, Abid Khan,# Di Luo,# Tatiane P. Santos, Chuqiao Shi, Blanka E. Janicek, Sangmin Kang, Wenjuan Zhu, Nahil A. Sobh, André Schleife, Bryan K. Clark, and Pinshane Y. Huang*

Cite This: *Nano Lett.* 2020, 20, 3369–3377

ABSTRACT: Two-dimensional (2D) materials offe platform to study the strain fields induced by individ defects, yet challenges associated with radiation damage limited electron microscopy methods to probe these a strain fields. Here, we demonstrate an approach to pr atom defects with sub-picometer precision in a mor transition metal dichalcogenide, $WSe_{2-2x}Te_{2x}$. We u learning to mine large data sets of aberration-correcte transmission electron microscopy images to locate a point defects. By combining hundreds of images of identical defects, we generate high signal-to-noise class




Zinc-Titanium White
Yellow Ochre
Vermillion
Naphthol Red
Chromium Oxide
Burnt Sienna
Burnt Umber
Raw Umber
Titanium White
Cadmium Yellow Hue
Cadmium Yellow Deep Hue
Cadmium Red Hue
Alizarin Crimson
Cerulean Blue
Cobalt Blue
Ivory Black
ZEN ART SUPPLIES
INFINITY
PALETTE SERIES



(a)
Lateral size (μm)
Year
early ME
2D materials
graphene
MoS1
NbSe1
LM
emerging
materials < 10² μm
Mxene
Brophene
MoS2
Cr2S3
TaSe2
PtSe2
MoTe2
WSe2
SnO
Ga2S3
CoO
b-AsP
brophene
Mxene
germanene
silicene
BP
GaPO4
BiOI
WS2
InN
VSe2
hBN
ITO
GaN
GaS
Bi2O2Se
ReS2
Al2O3
HfO2
Gd2O3
Cr0.15(Bi0.1Sb0.9)1.85Te3
graphene
PdSe2
NbSe2
BSCCO
ZnO
TiSe2
MoSe2
Te
Bi2O3
Bi2Te3
Bi2Se3
Cr2S3
In2O3
In2S3
b)
Lateral size (μm)
MoS2
Bi2O2Se
BiOI
brophene
BP
Cr2S3
graphene
hBN
MoS2
MoSe2
MoTe2
NbSe2
PdSe2
PtSe2
ReS2
TaSe2
TiSe2
WS2
WSe2
VSe2
Tellurene
Mxene
Al2O3
Gd2O3
HfO2
Bi2O3
Ga2S3
GaN
GaPO4
GaS
In2S3
In2O3/SnO
InN
SnO
b-AsP
silicene
MoSe2
WSe2
Bi2Se3
Bi2Te3
hBN
BSCCO
BP
graphene
MoS2
NbSe2
WS2
WSe2
MoS2
WSe2
CoO
MoS2
ZnO
ITO
MoS2
hBN
WS2
germanene
I
II
III IV V VI
VII
VIII
IX
X
XI
XII
XIII
XIV