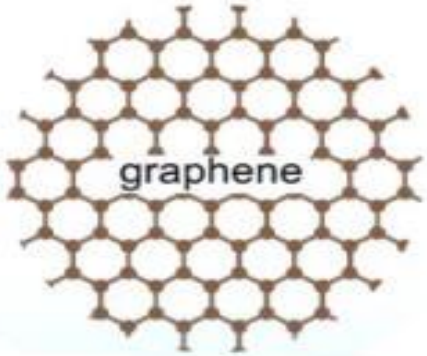
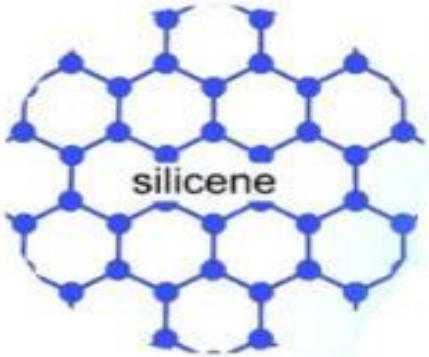
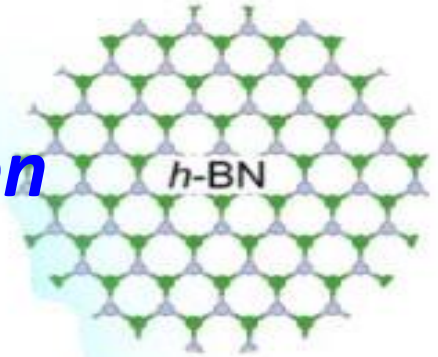


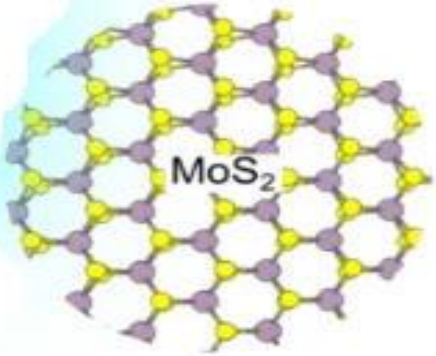


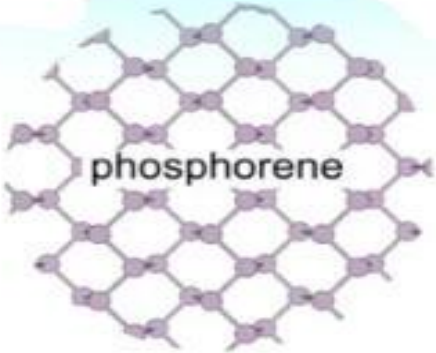


VUV Spectroscopy on 2D Materials

吳宇中

NSRRC





2D Materials

black phosphorus

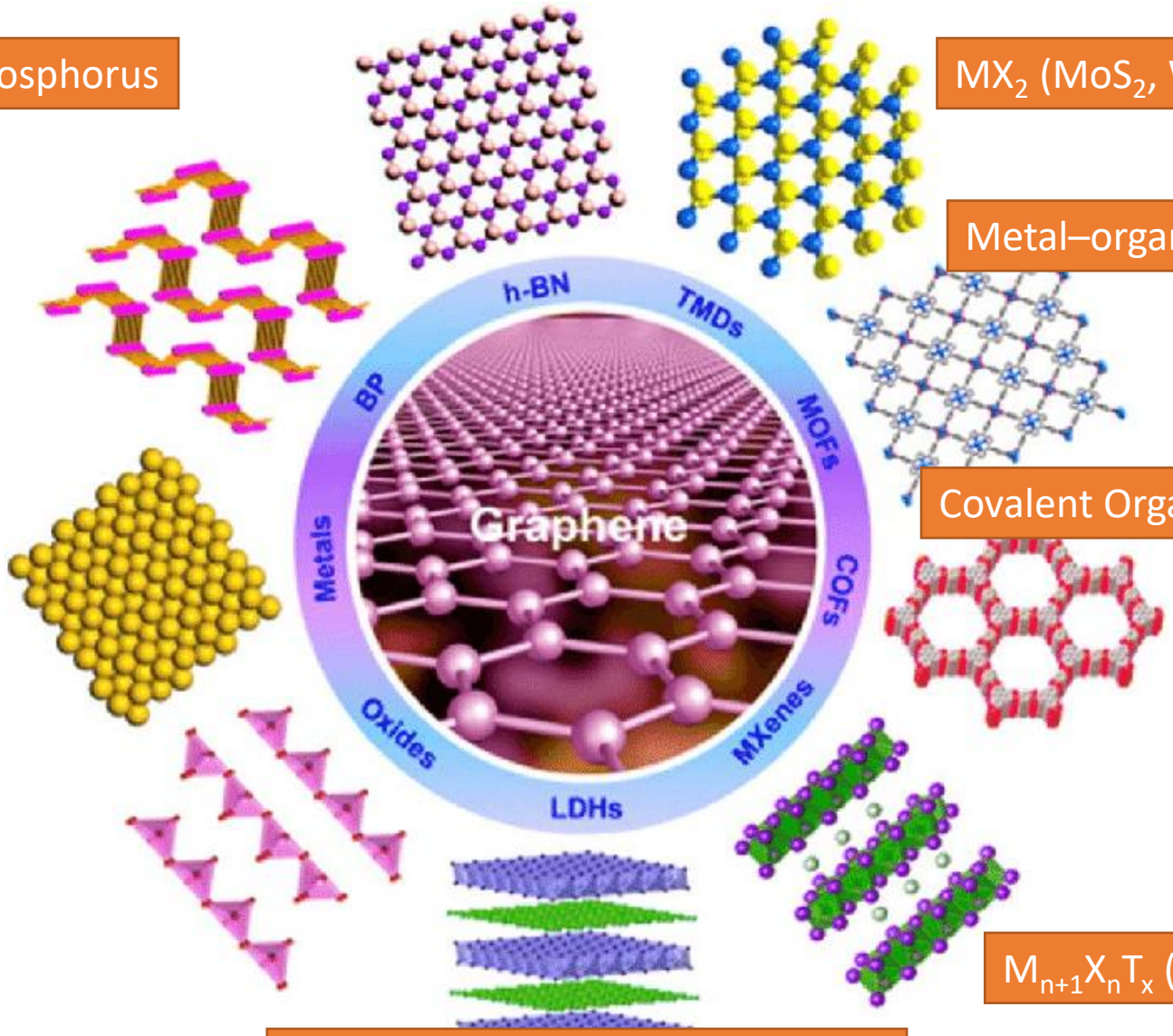
MX_2 (MoS_2, WS_2, $MoSe_2$ …)

Metal–organic framework

Covalent Organic Frameworks

$M_{n+1}X_nT_x$ (T = O, F, OH, Cl)

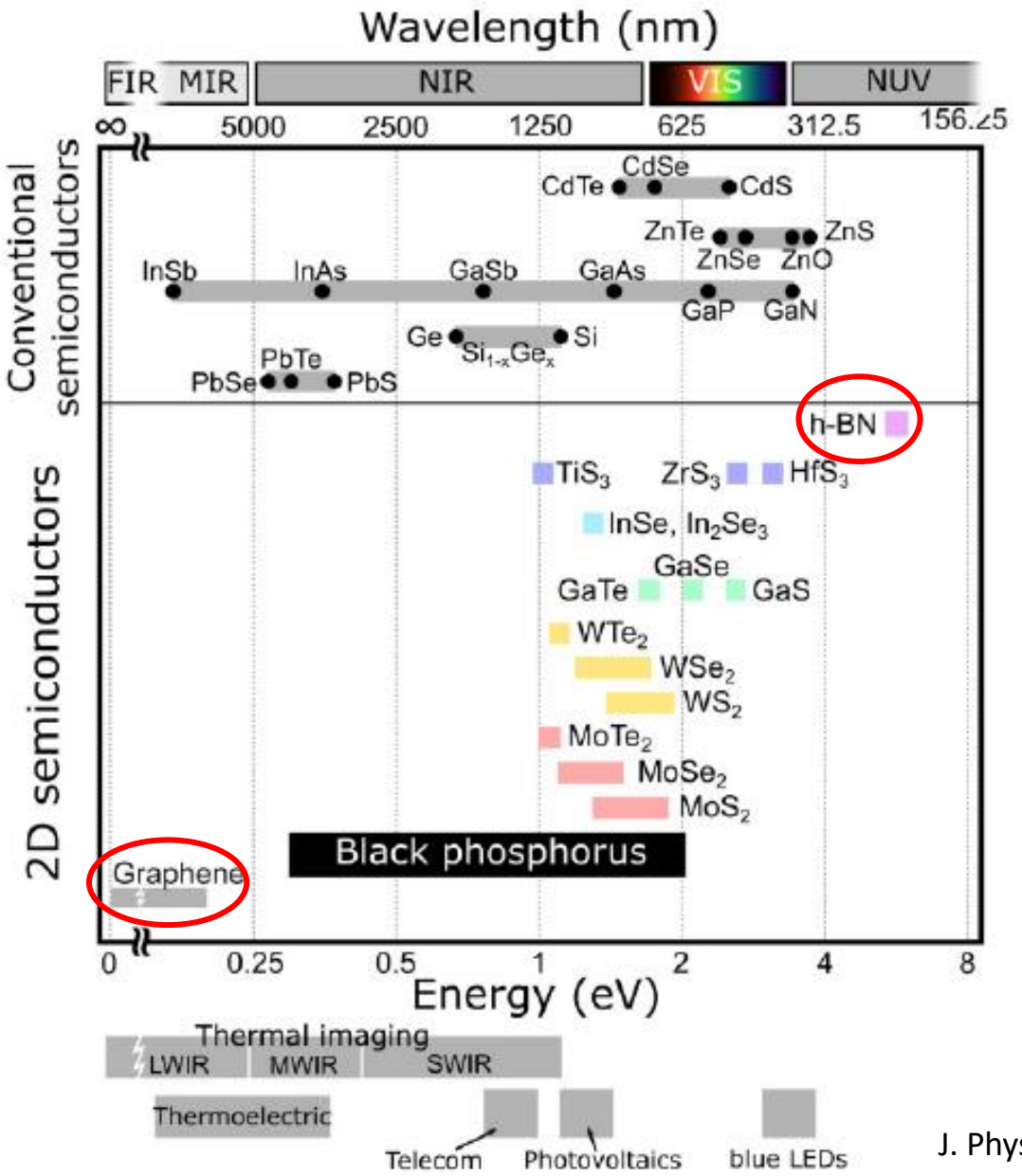
Layered double hydroxides (LDHs)



Chin. Opt. Lett. 16, 020004 (2018)

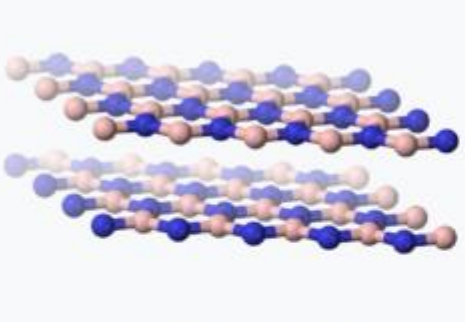
Far-UV Spectroscopy of Hexagonal Boron Nitrides (hBN)

Band Gap

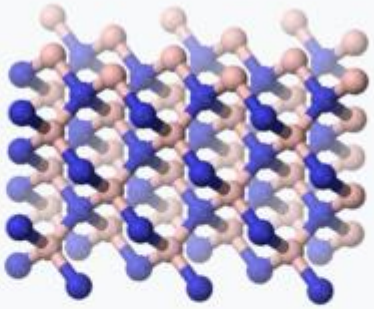


J. Phys. Chem. Lett., 6, 4280 (2015)

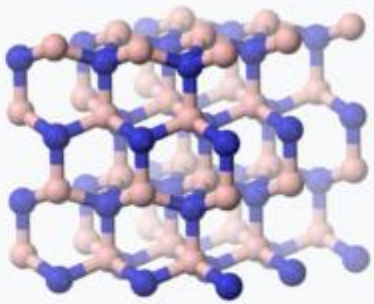
Boron Nitride



Hexagonal form (h-BN)
hexagonal
analogous to graphite



Cubic form (c-BN)
sphalerite structure
analogous to diamond



Wurtzite form (w-BN)
wurtzite structure
analogous to lonsdaleite

Properties of amorphous and crystalline BN, graphite and diamond.

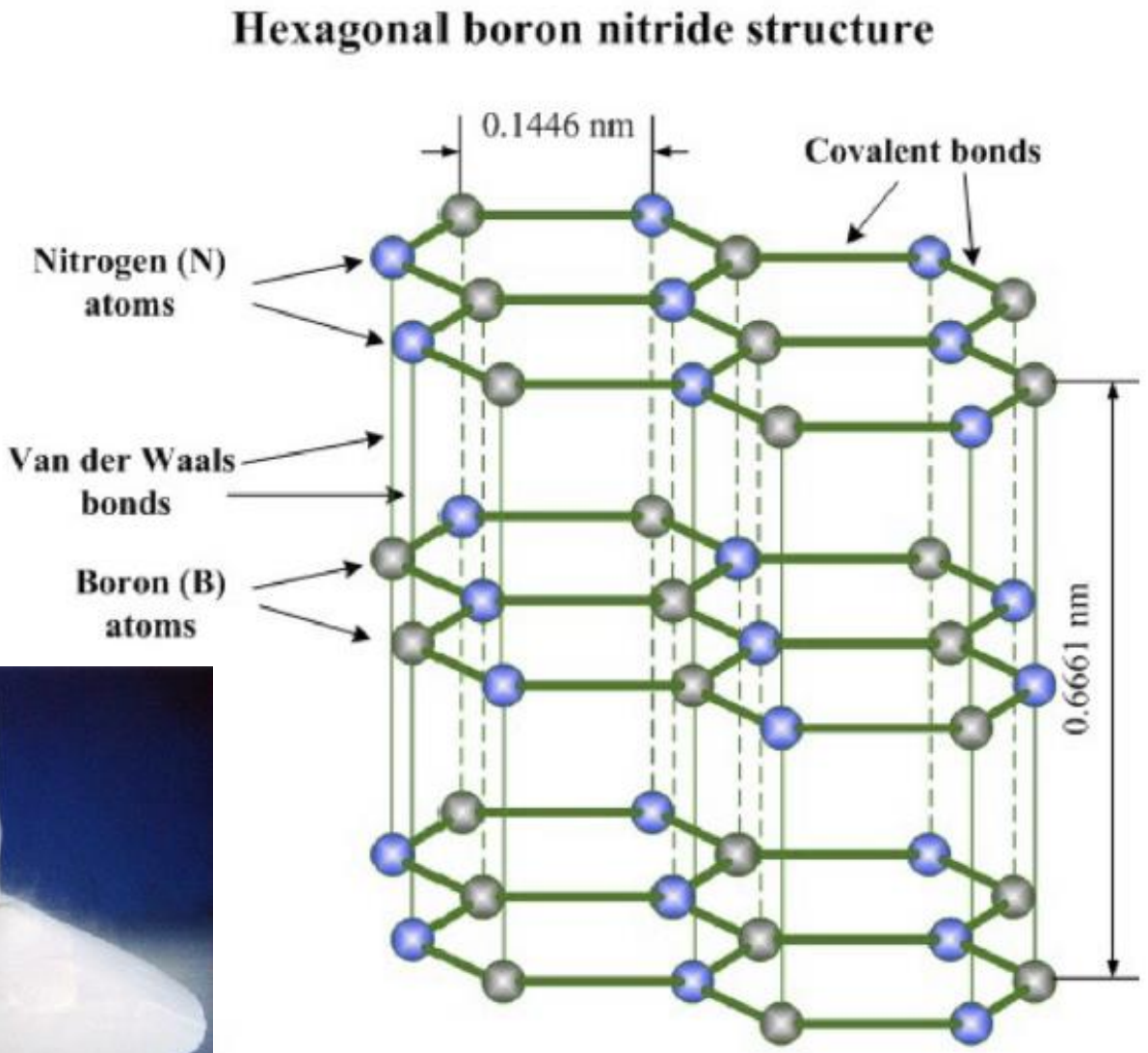
Some properties of h-BN and graphite differ within the basal planes (∥) and perpendicular to them (□)

Material	a-BN	h-BN	c-BN	w-BN	graphite	diamond
Density (g/cm^3)	2.28	~2.1	3.45	3.49	~2.1	3.515
Knoop hardness (GPa)	10		45	34		100
Bulk modulus (GPa)	100	36.5	400	400	34	440
Thermal conductivity (W/(m·K))	3	600 ∥, 30 □	740		200–2000 ∥, 2–800 □	600–2000
Thermal expansion (10^{-6}/°C)		−2.7 ∥, 38 □	1.2	2.7	−1.5 ∥, 25 □	0.8
Bandgap (eV)	5.05	5.2	6.4	4.5–5.5	0	5.5
Refractive index	1.7	1.8	2.1	2.05		2.4
Magnetic susceptibility (μemu/g)[6]		−0.48 ∥, −17.3 □			−0.2...−2.7 ∥, −20...−28 □	−1.6

Sources: amorphous BN,[7][8][9] *crystalline BN,*[10][11] *graphite,*[12] *diamond.*[11]

Wiki: boron nitride

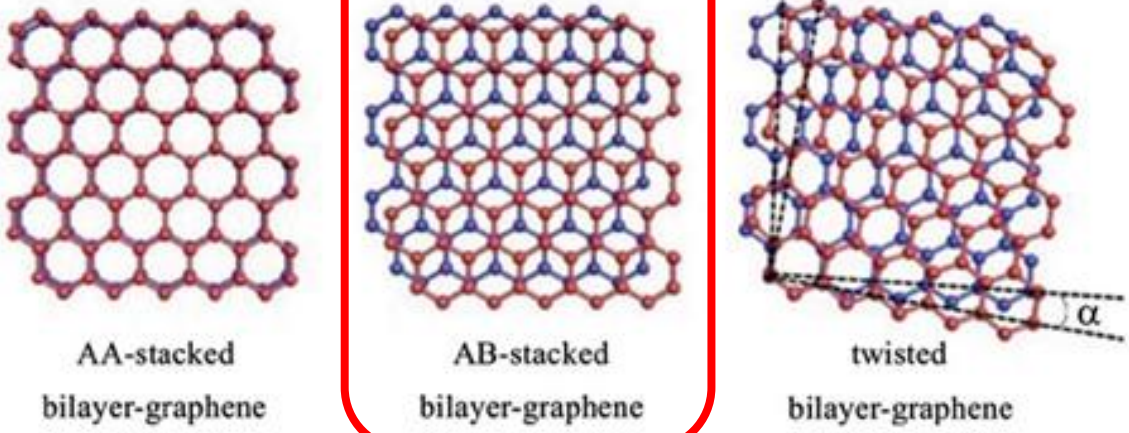
White Graphite : Hexagonal Boron Nitride (*h*-BN)

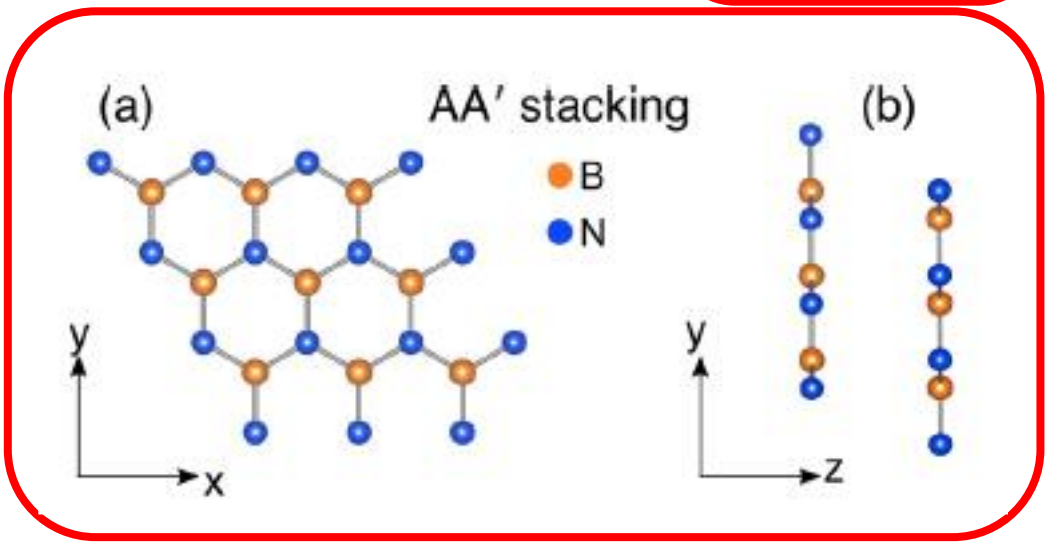


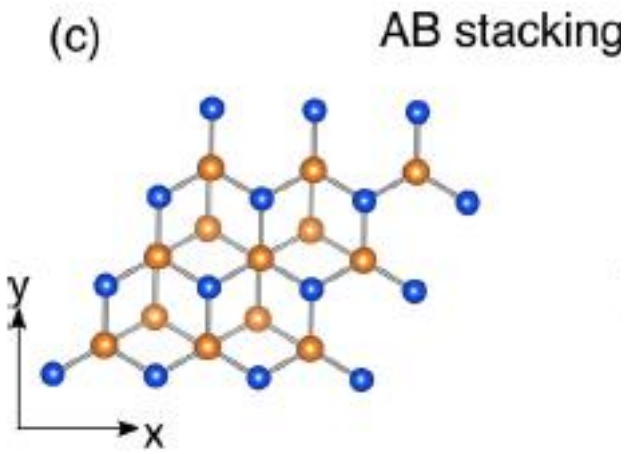
Stacking, Isoelectronic, Isostructural

Current Graphene Science **2**, 97 (2018)

B: $1S^2\ 2S^2\ 2P^1$
C: $1S^2\ 2S^2\ 2P^2$
N: $1S^2\ 2S^2\ 2P^3$



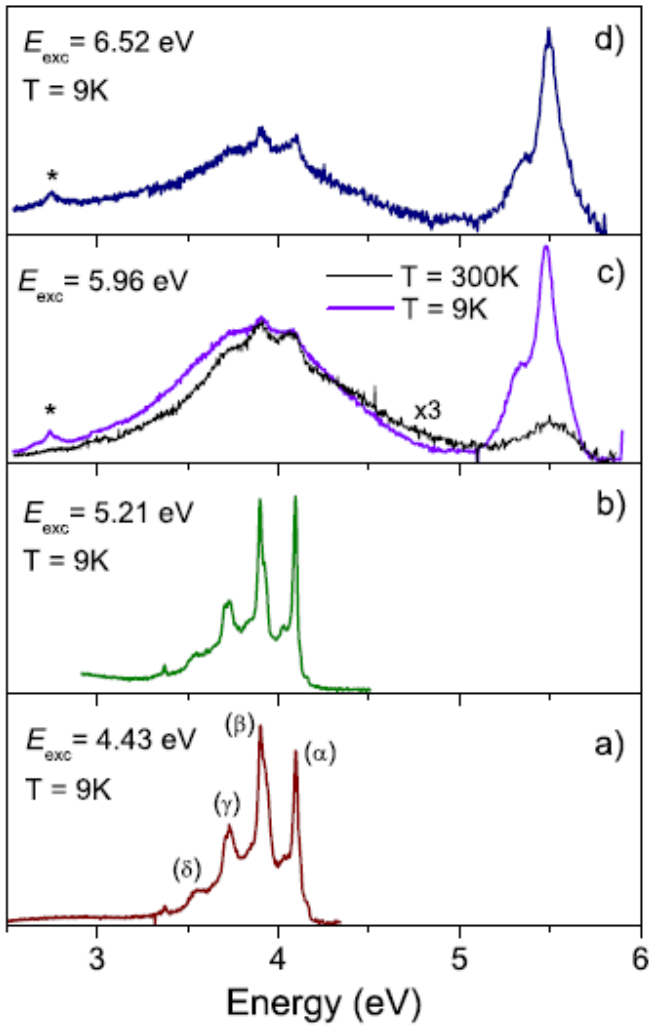


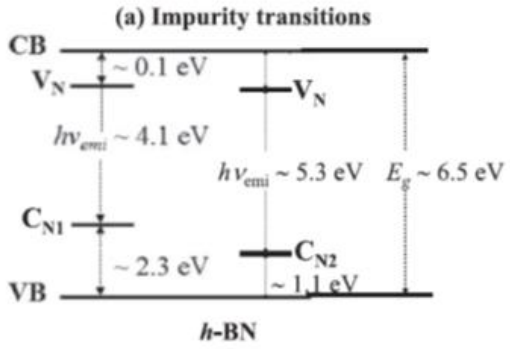


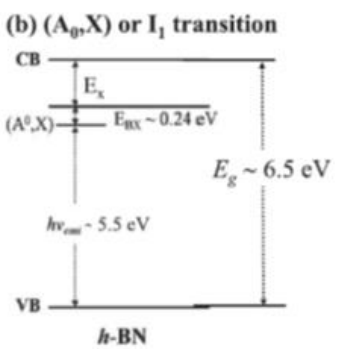
JPCC. **122**, 25524 (2018)

Photoluminescence of Bulk hBN

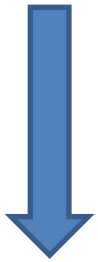
(5.5 eV, 225



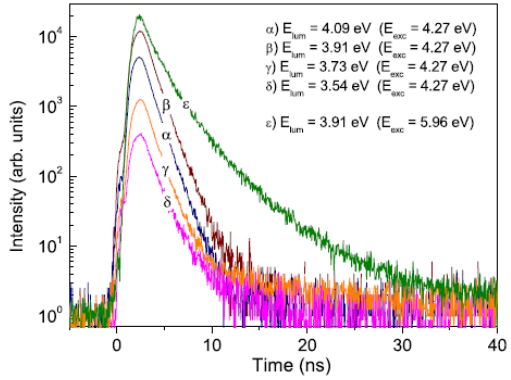


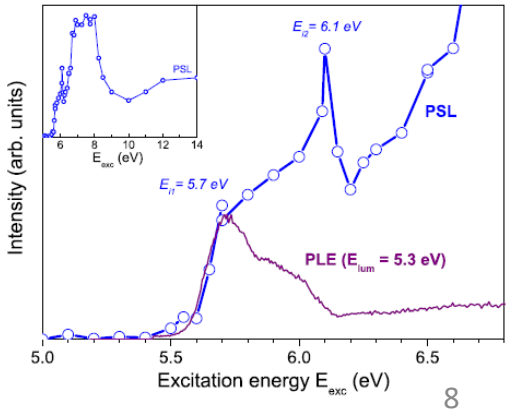


τ ~ ns
Frenkel-type excitons
Large Stoke Shift



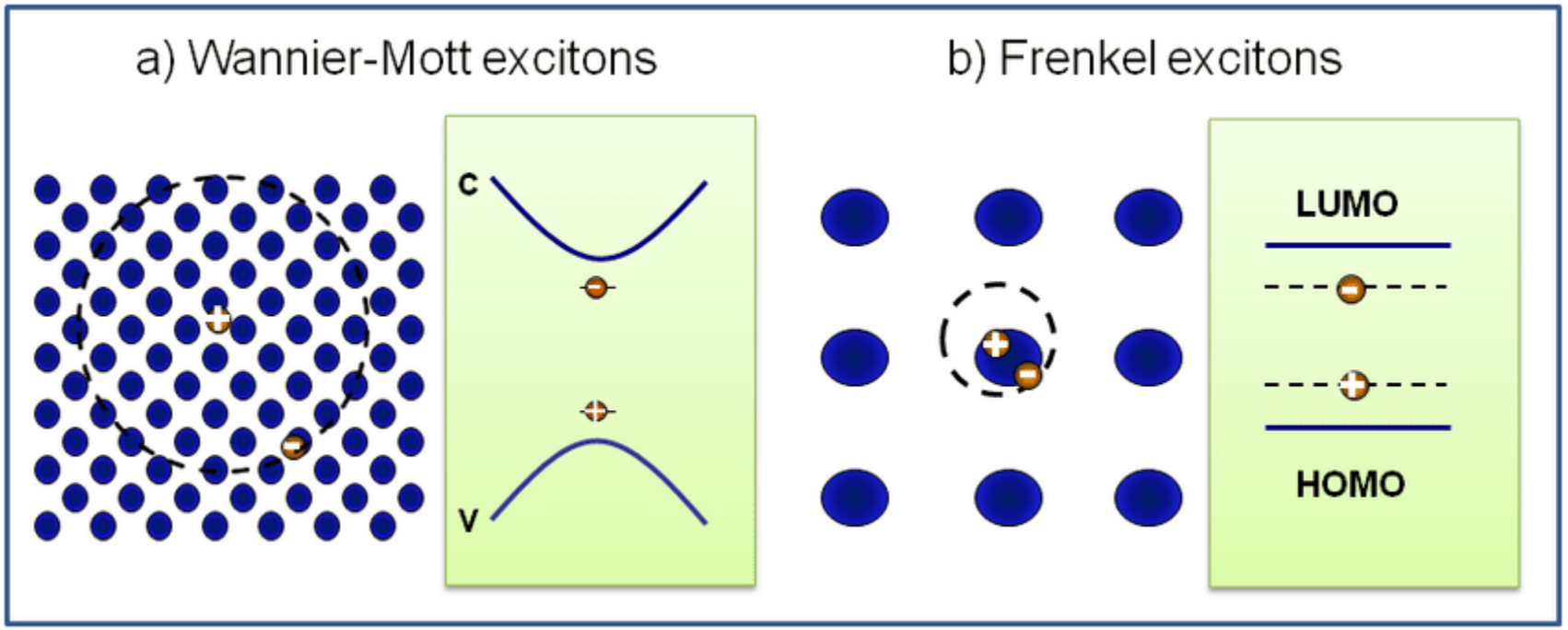
Indirect band-gap





PRB 78, 155204 (2008)
APL 106, 021110 (2015)

Exciton Type

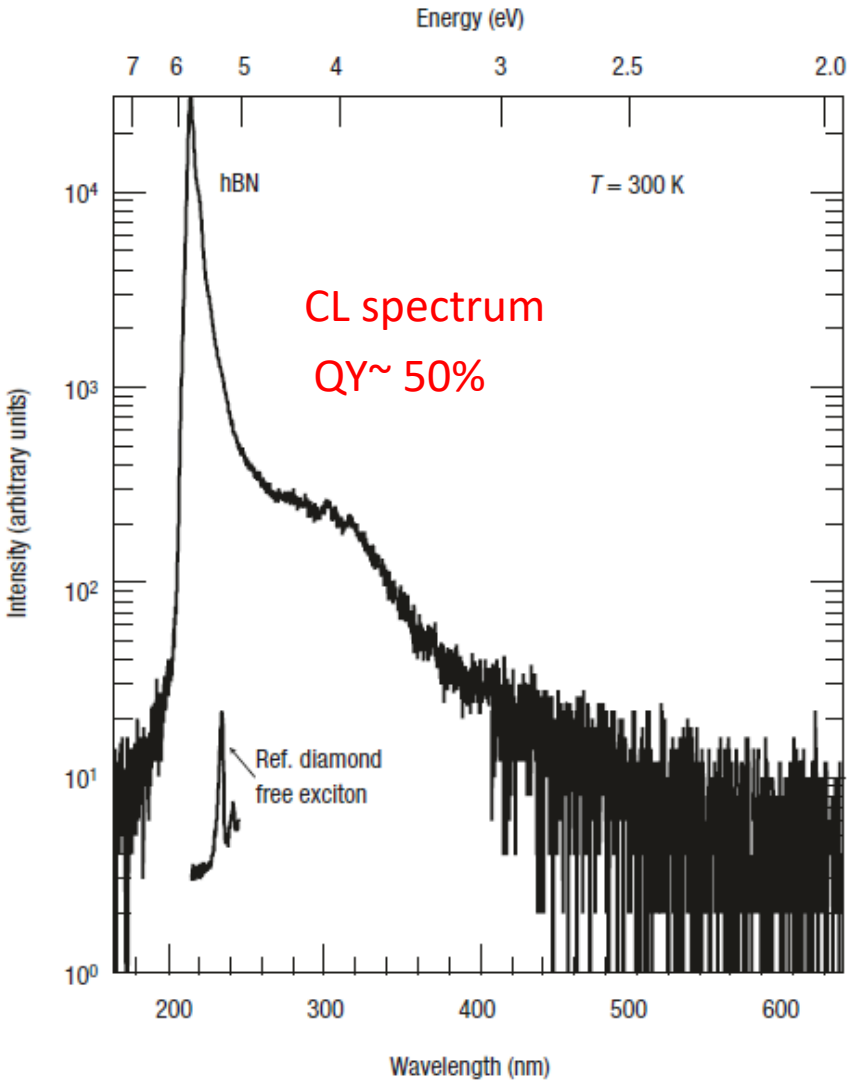


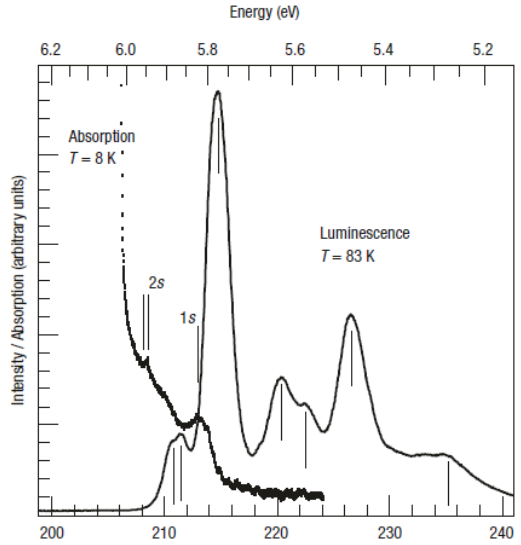
Binding energy ~0.01 eV
Semiconductor, inorganic materials

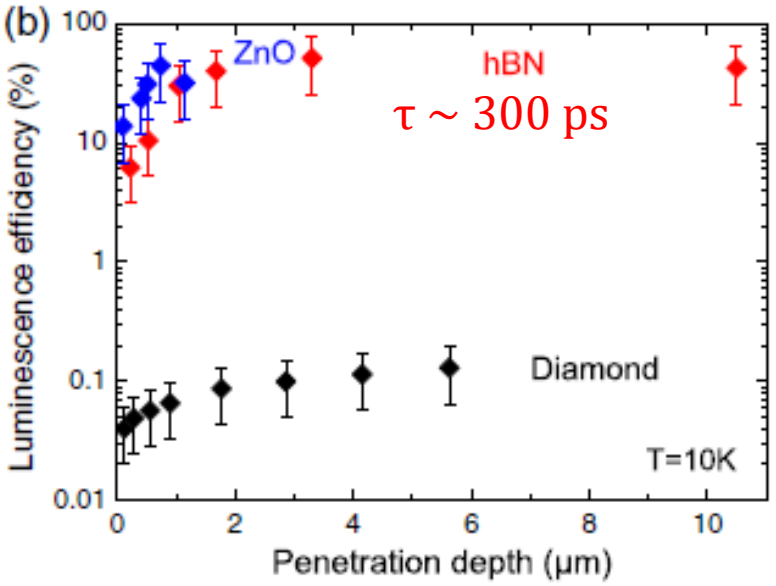
Binding energy 0.1~1 eV
organic materials

Kena-Cohen thesis

Direct Bandgap of Single h-BN Crystal (HP/HT)







Nat. Mat. **3**, 404 (2004)

PRL 122, 067401 (2019)

DUV Lasing of h-BN Synthesized at AP/HT

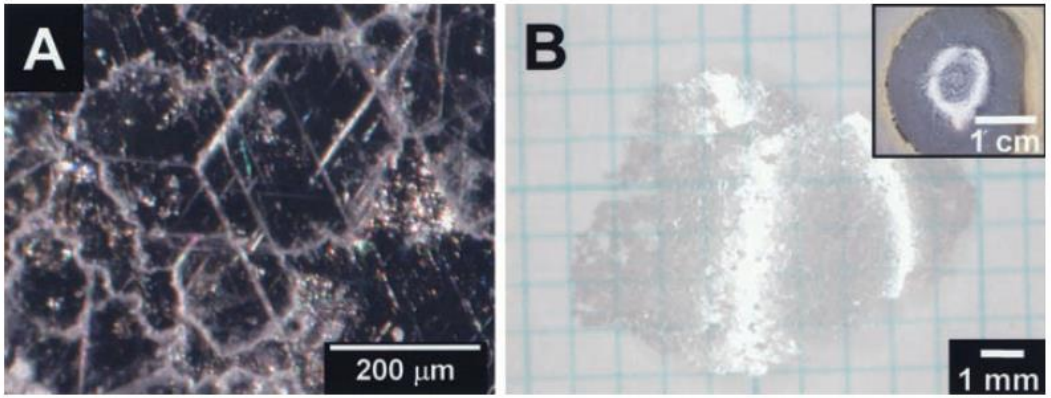
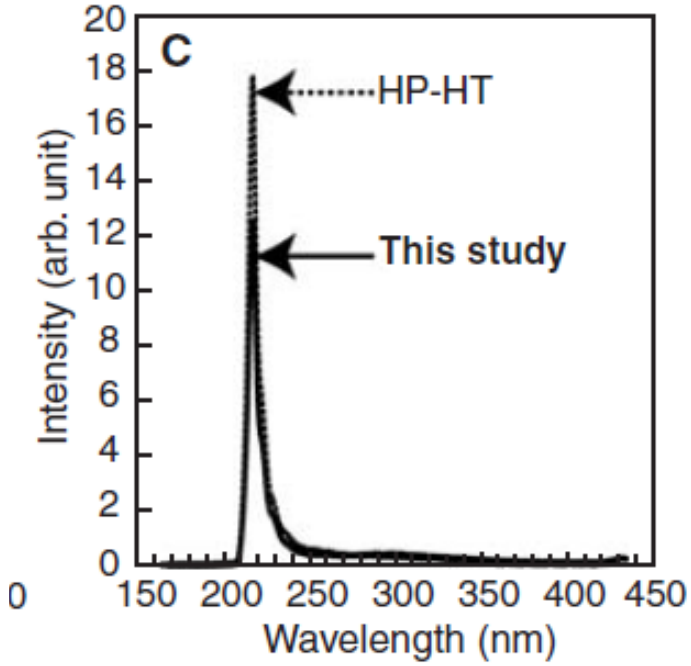


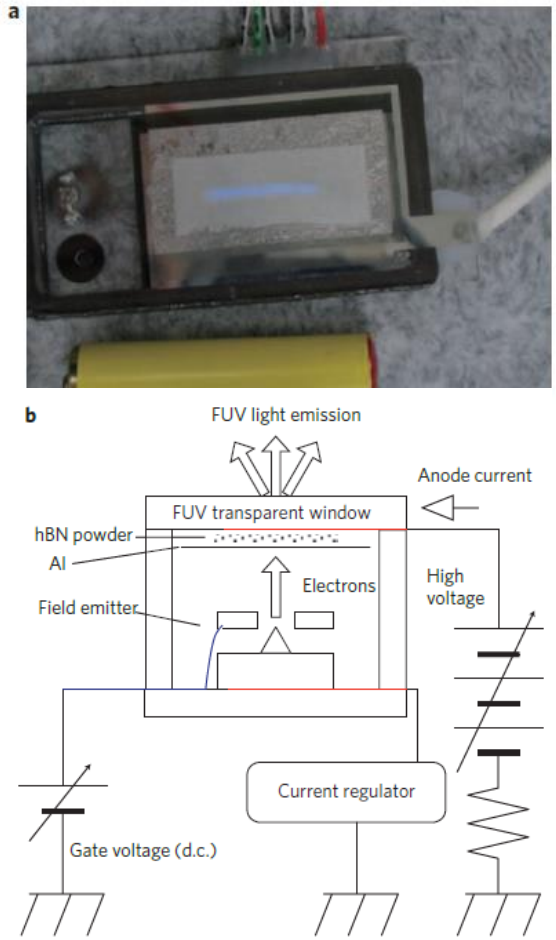
Fig. 1. Optical micrographs of recrystallized hBN obtained with a Ni-Mo solvent. (**A**) Typical hBN crystal on the solidified solvent (as grown). (**B**) A fragment of aggregate hBN crystals after acid treatment (the inset is an optical micrograph of a recovered sample). The shiny white regions are reflected light.

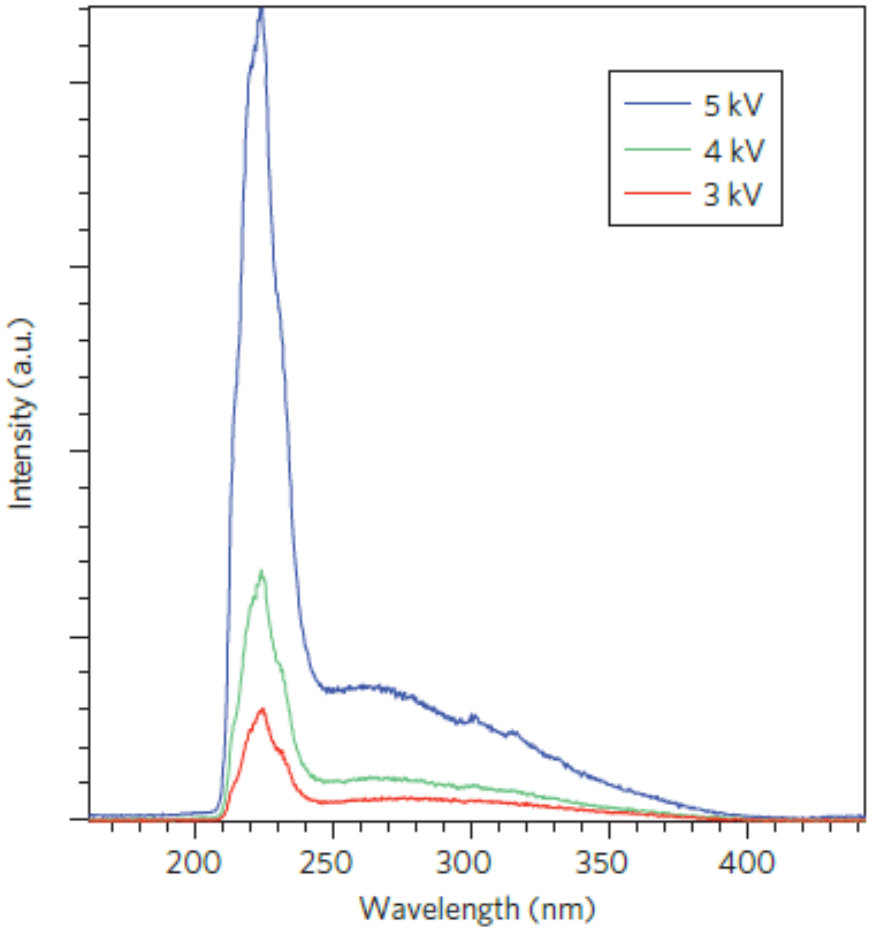


Science **317**, 932 (2007)

Far-ultraviolet plane-emission handheld device based on hexagonal boron nitride

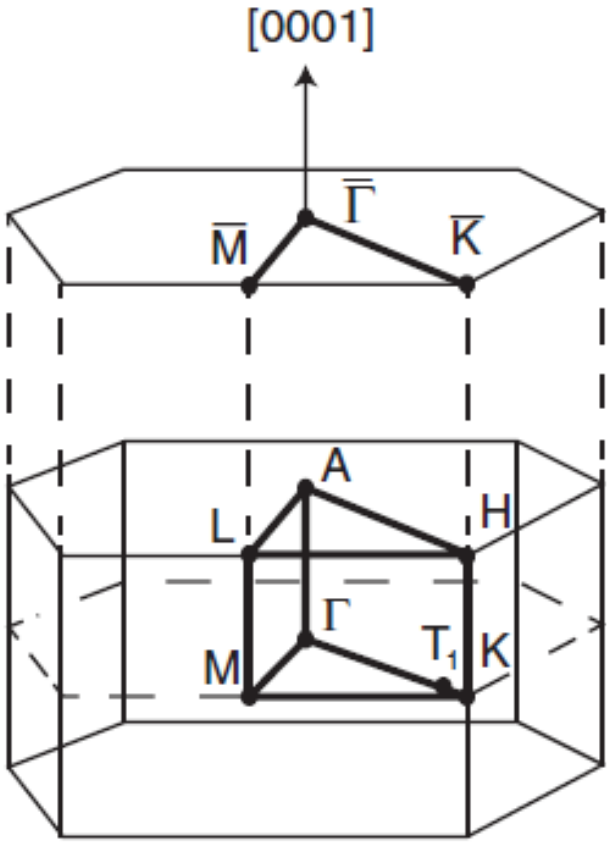
Kenji Watanabe[1]*, Takashi Taniguchi[1], Takahiro Niiyama[2], Kenta Miya[2] and Masateru Taniguchi[2]

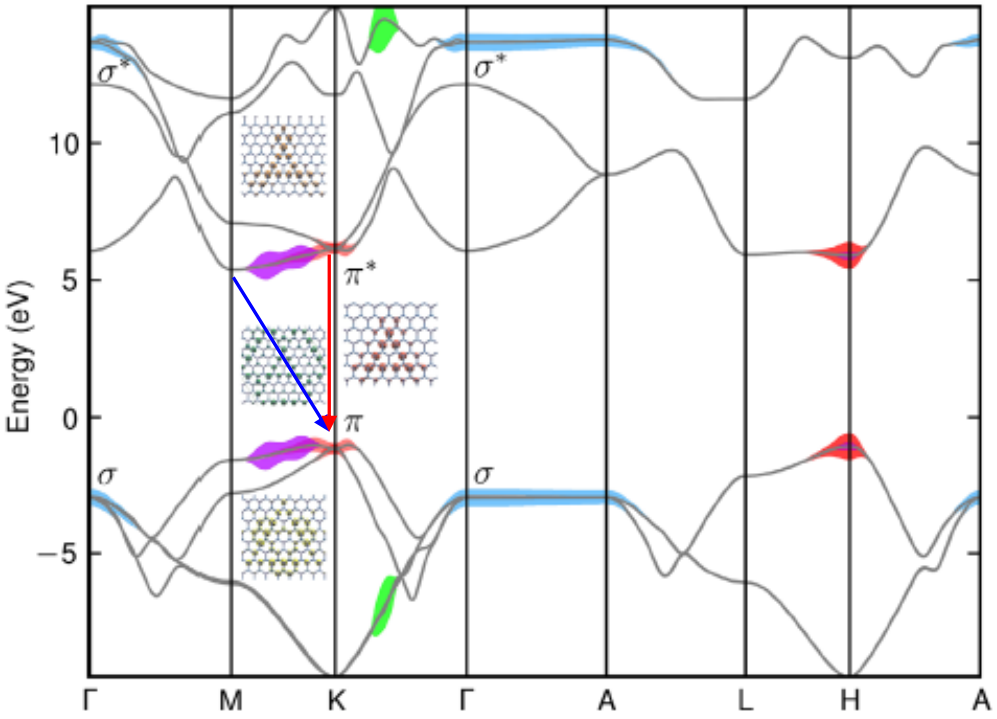




Nat. Photon. 3, 591 (2009)

Predicted Electronic Structures Indicate Indirect Band gap of hBN





M→K 6.03 eV

K → K 6.69 eV

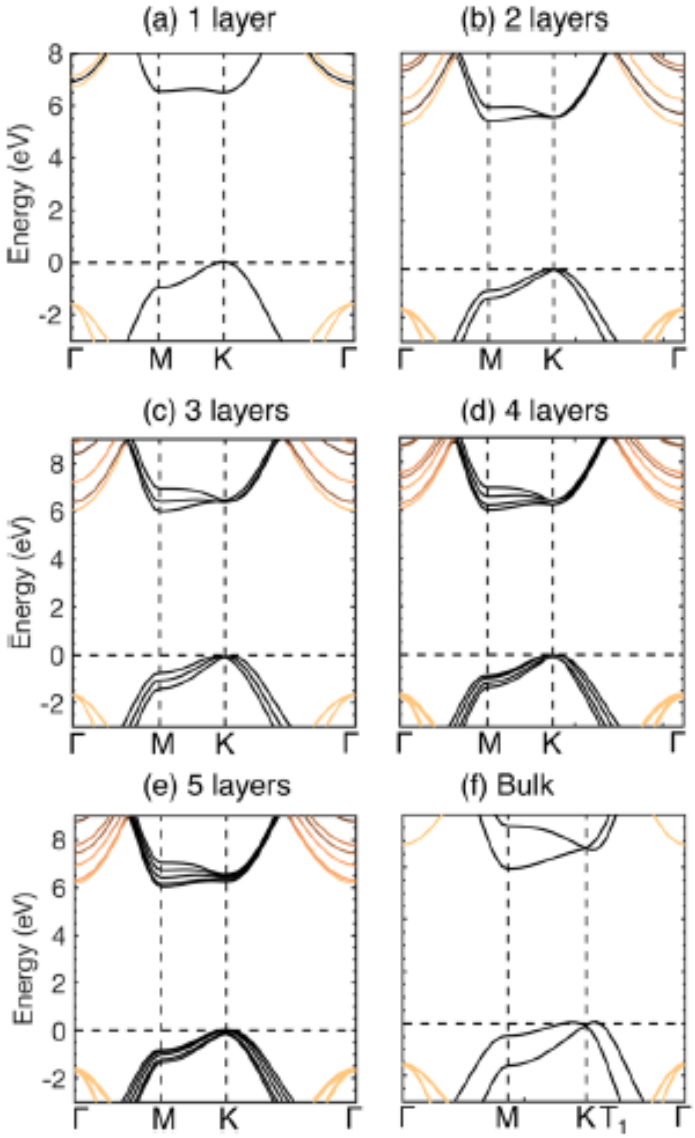
PRL 96, 026402 (2006)

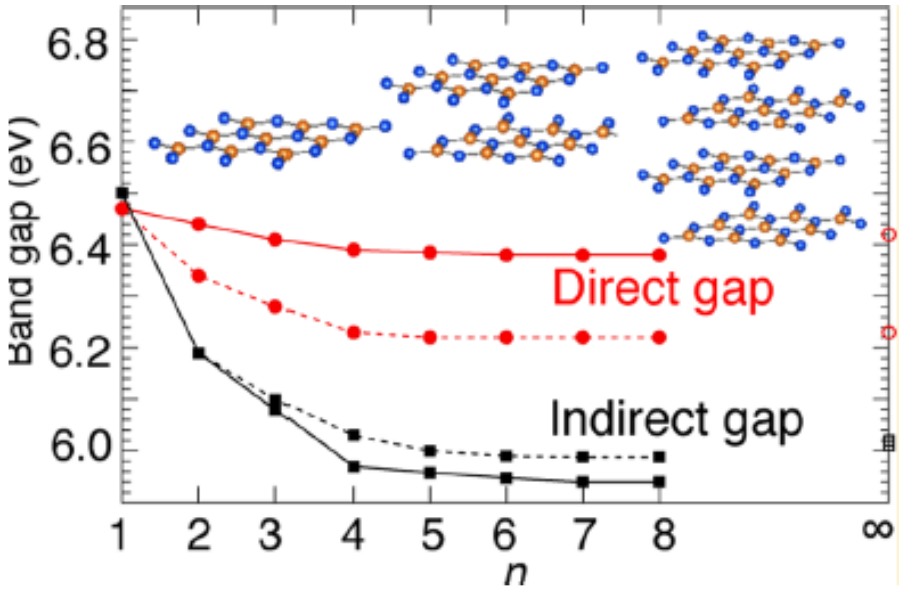
Adv. Photon. Res. 2, 2000101 (2021)

Monolayer to Bulk Properties of Hexagonal Boron Nitride

Darshana Wickramaratne,* Leigh Weston, and Chris G. Van de Walle

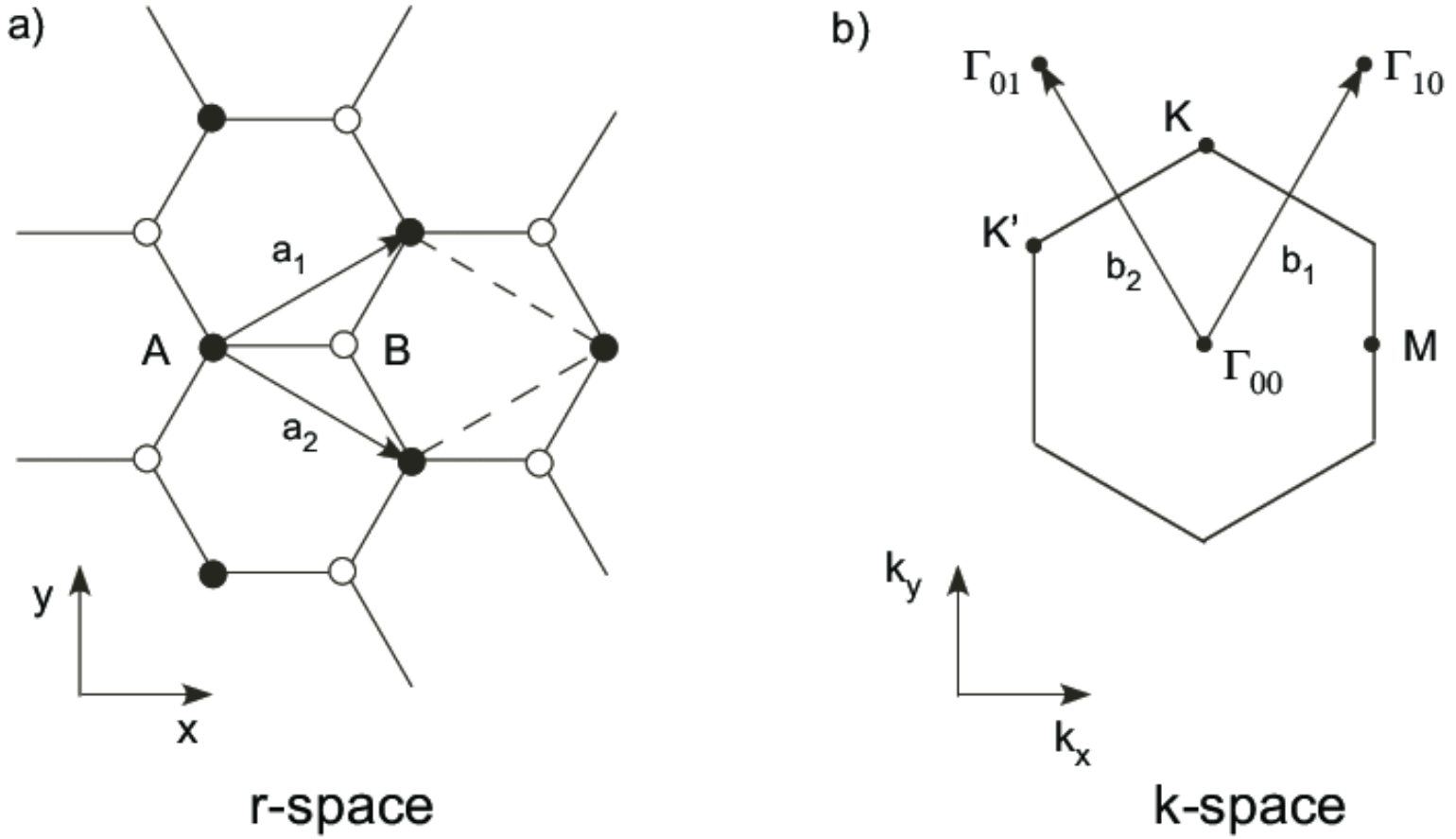
Materials Department, University of California, Santa Barbara, Santa Barbara, California 93106-5050, United States



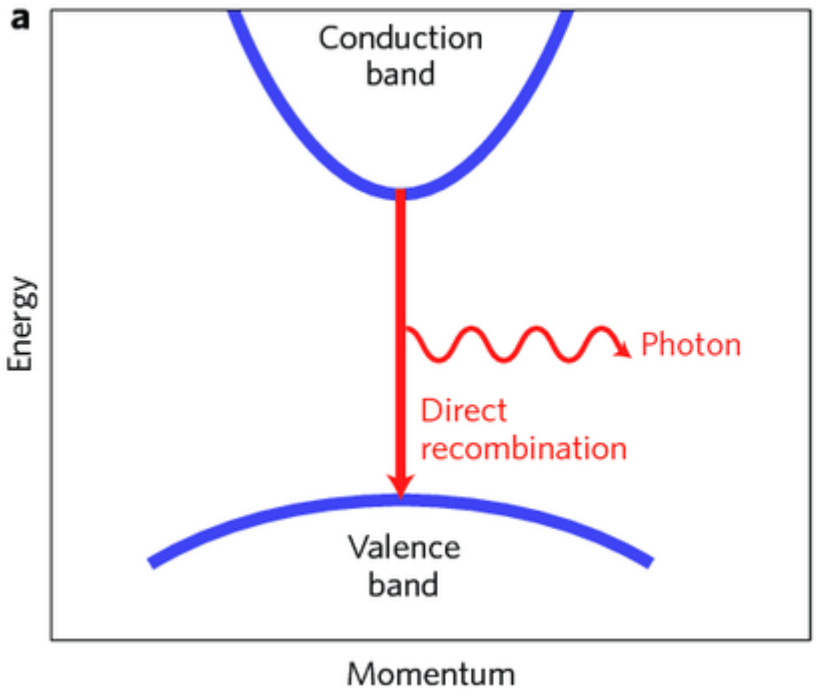


JPCC. **122**, 25524 (2018)

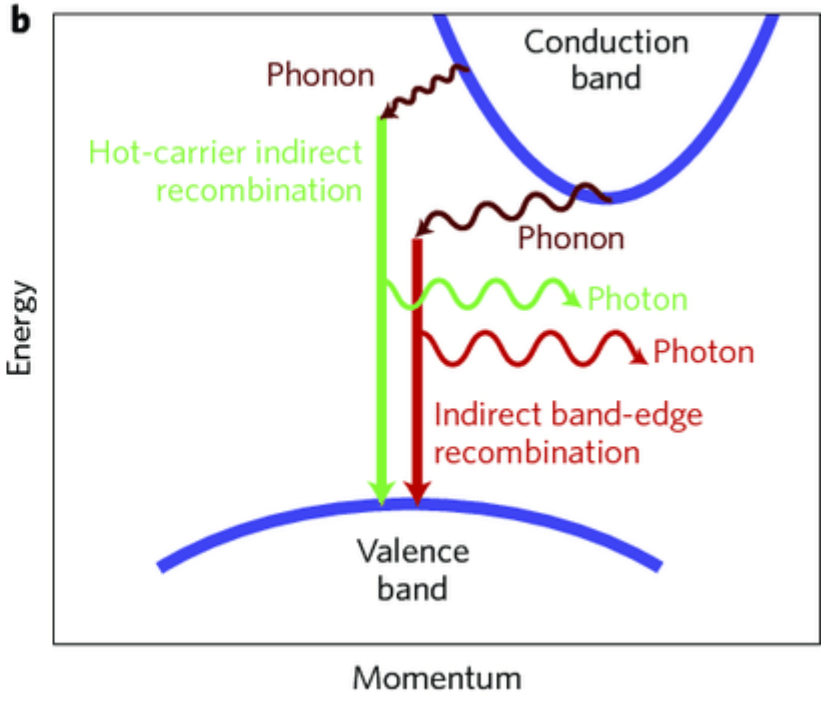
Real Space & K Space in Hexagonal System



Direct and Indirect Transitions: Fluorescence and Phosphorescence



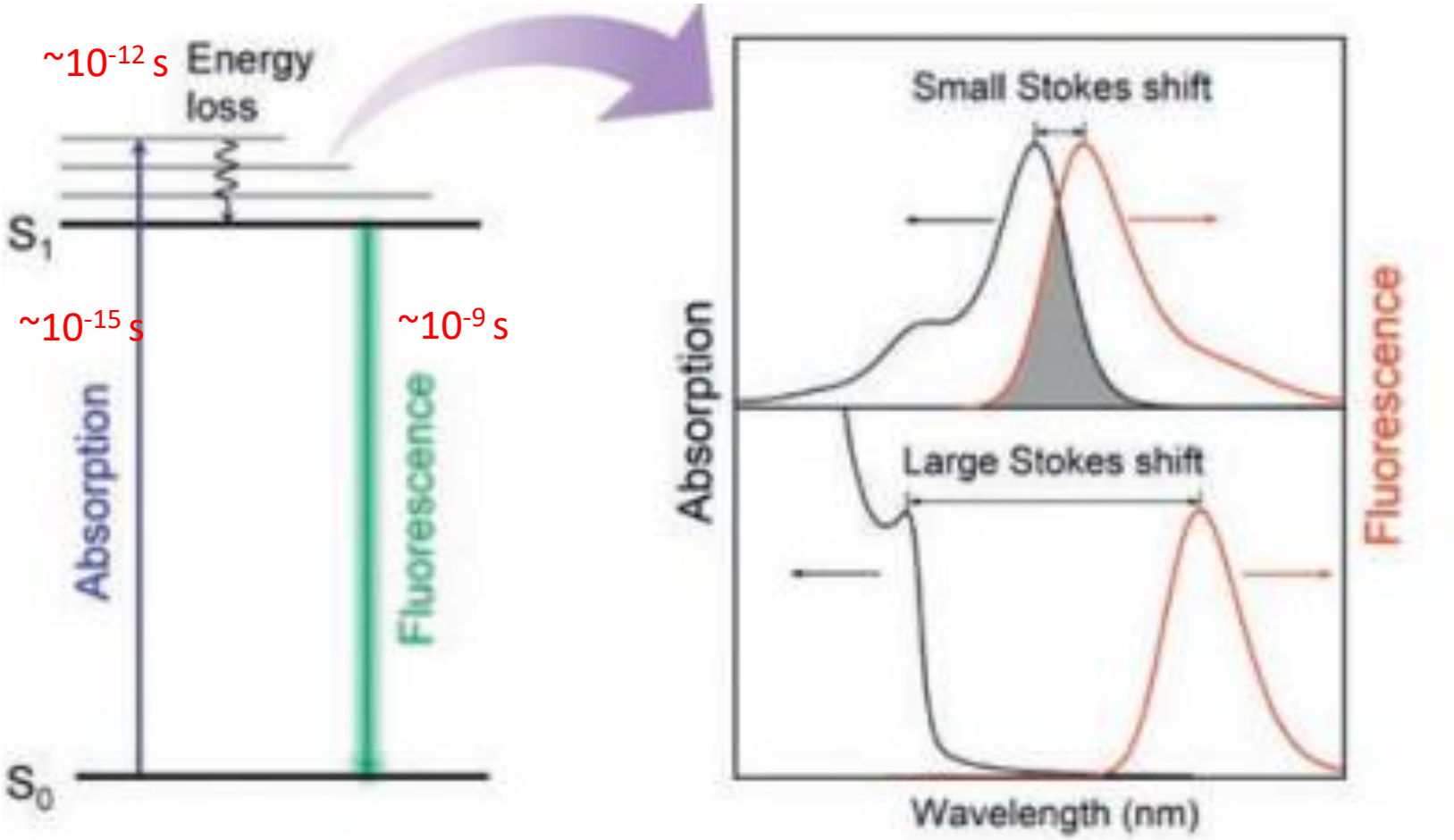
GaAs, InP and GaN



Silicon, diamond

Nat. photon. 7, 265 (2013)

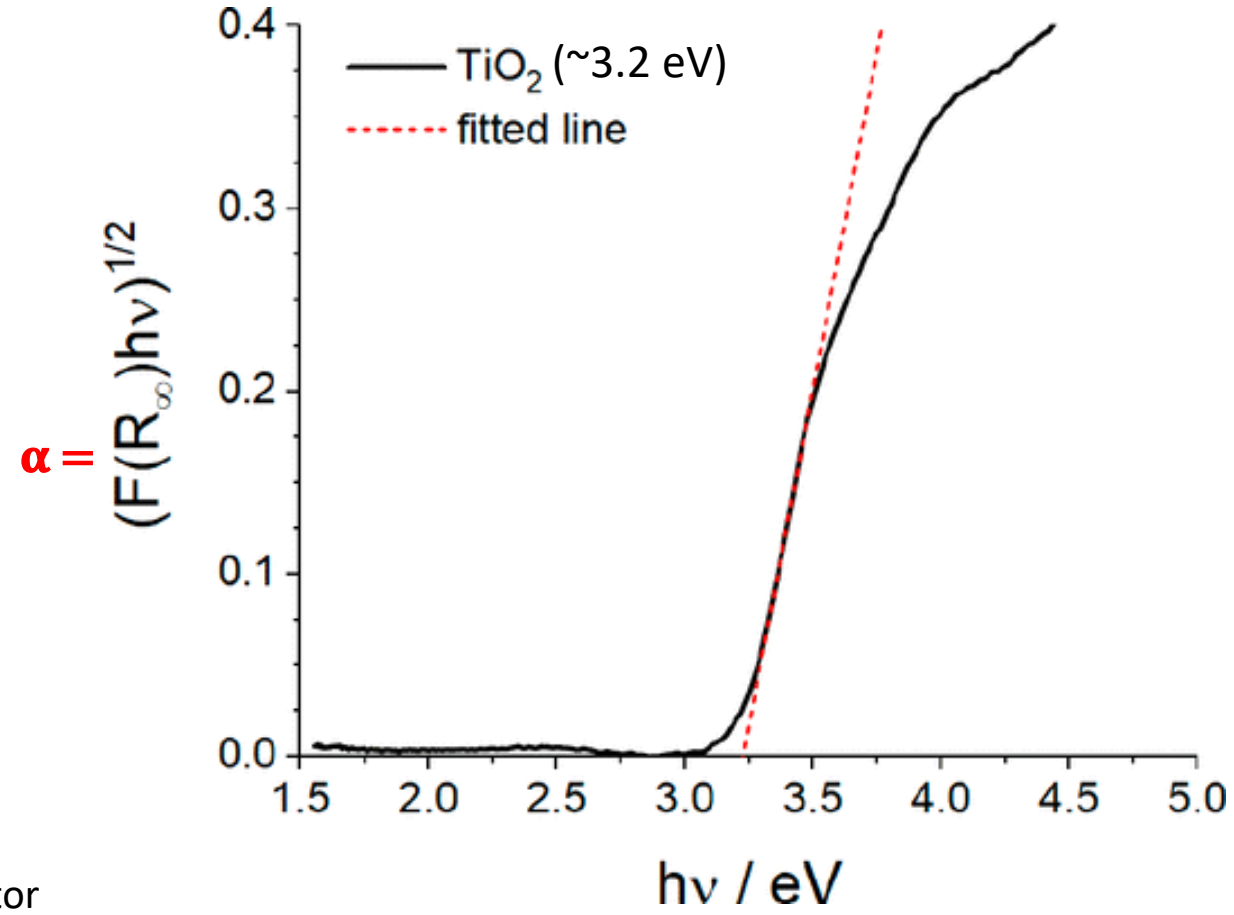
Stoke Shift: Absorption and PL



Quantum Yield (Φ)= Photons emitted / Photons absorbed

Chin. Chem. Lett., 30, 1843 (2019)

Tauc Plot for Determining Optical Bandgap

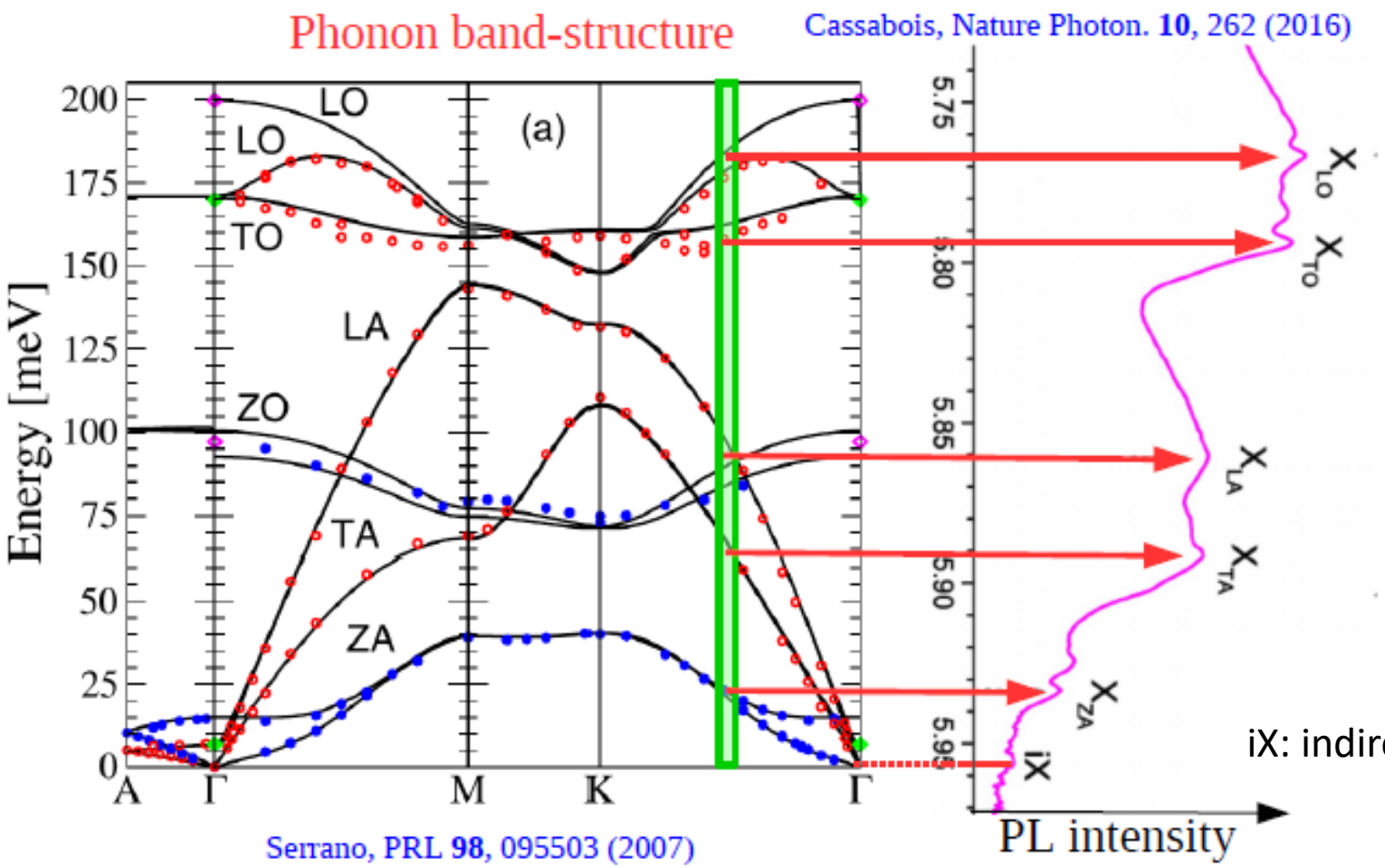


Semiconductor
r = 1/2 for direct allowed transitions
r = 3/2 for direct forbidden transitions.
r = 2 for indirect allowed transitions
r = 3 for indirect forbidden transitions

J. Tauc et al. Phys. Status Solidi B 15, 627 (1966)
P. Makuta et al. J. Phys. Chem. Lett. 9, 6814 (2018)

Bulk hBN is a Indirect Bandgap Materials

Identification of phonon replicas



iX: indirect exciton

Bright Luminescence from Indirect and Strongly Bound Excitons in h-BN

Léonard Schué,[1,2] Lorenzo Sponza,[1] Alexandre Plaud,[1,2] Hakima Bensalah,[2] Kenji Watanabe,[3] Takashi Taniguchi,[3] François Ducastelle,[1] Annick Loiseau,[1,*] and Julien Barjon[2,†]

[1]*Laboratoire d'Etude des Microstructures, ONERA-CNRS, Université Paris-Saclay, BP 72, 92322 Châtillon Cedex, France*

[2]*Groupe d'Etude de la Matière Condensée, UVSQ-CNRS, Université Paris-Saclay, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France*

[3]*National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan*

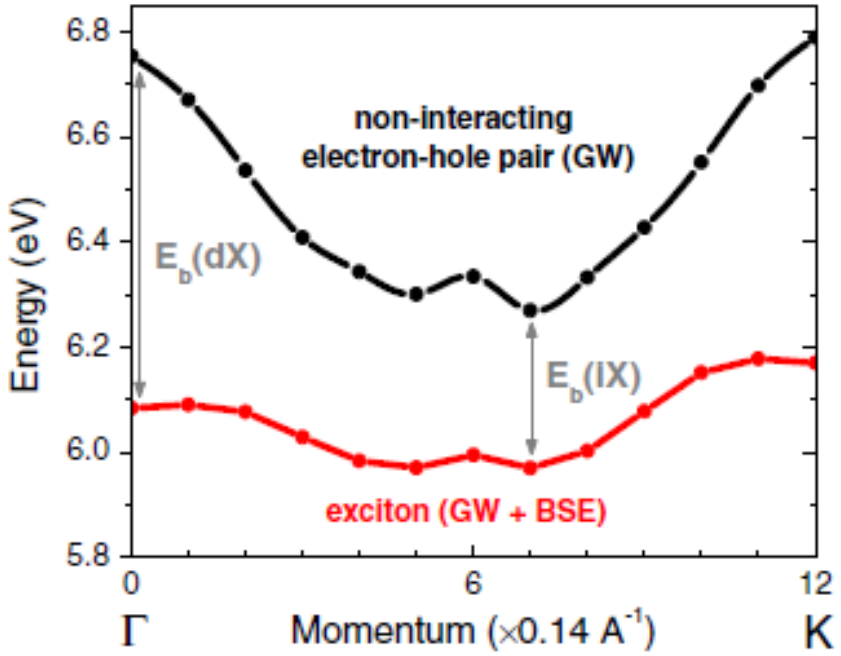
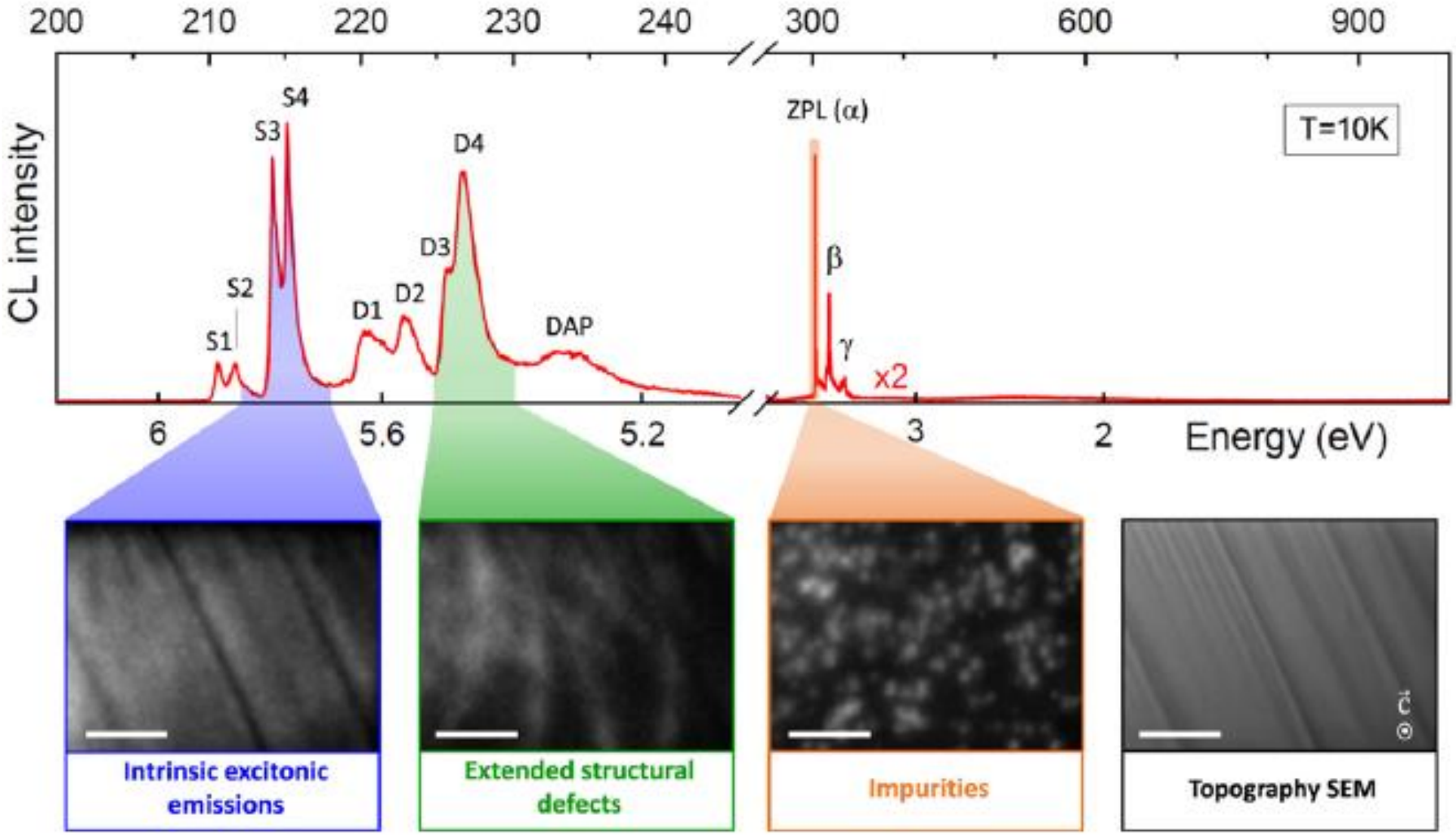


FIG. 3. Dispersion of excitons in h-BN compared to the non-interacting electron-hole pair along the ΓK direction. The vertical arrows indicate the binding energy E_b for the direct (dX) and indirect (iX) excitons. Adapted from Ref. [45].

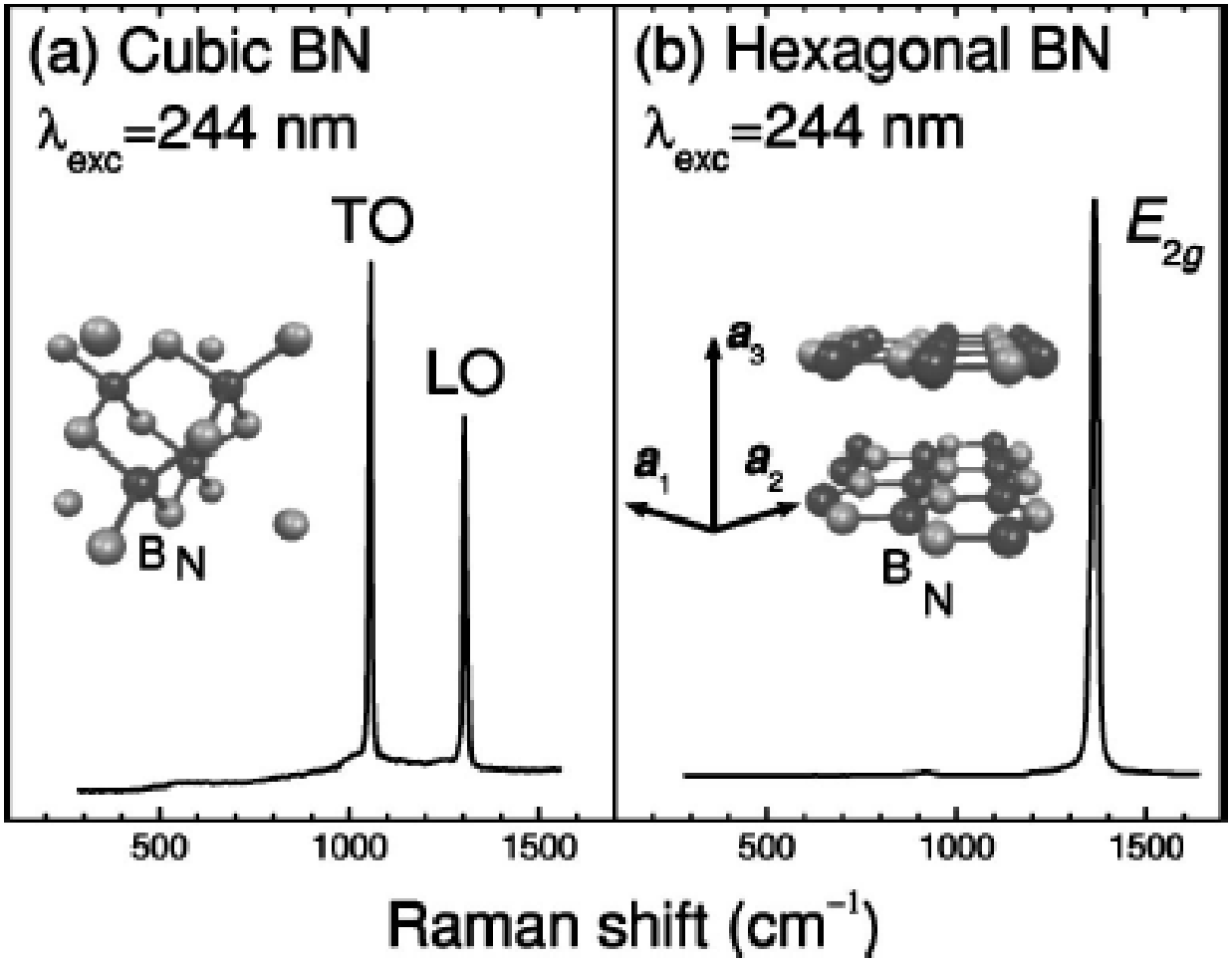
PRL 122, 067401 (2019)

Emission in Bulk hBN



2DM 4, 015028 (2016)
ECS JSST 6, Q3012 (2017)

Raman Spectra of Bulk cBN & hBN

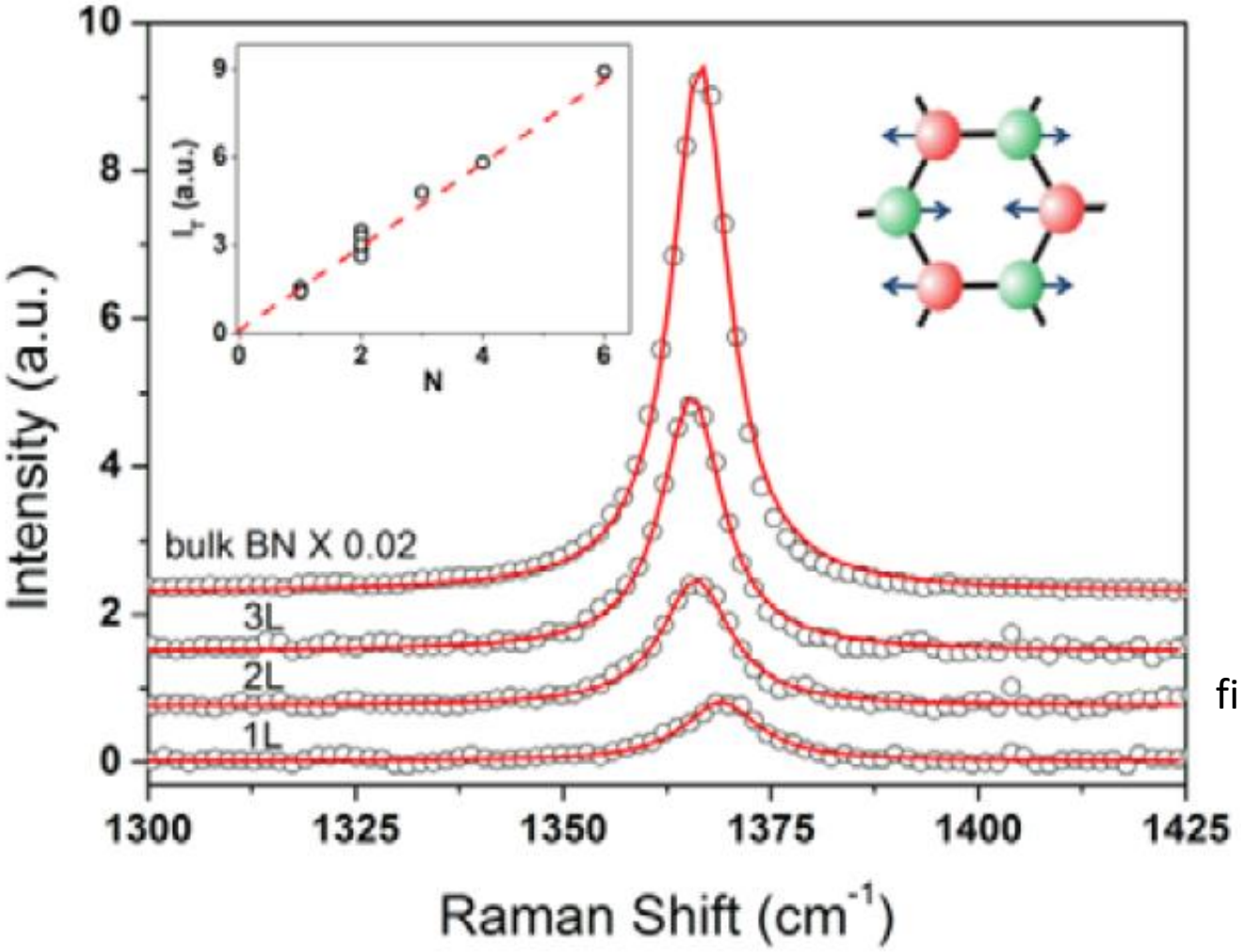


PRB 71, 205201 (2005)

Hunting for Monolayer Boron Nitride: Optical and Raman Signatures

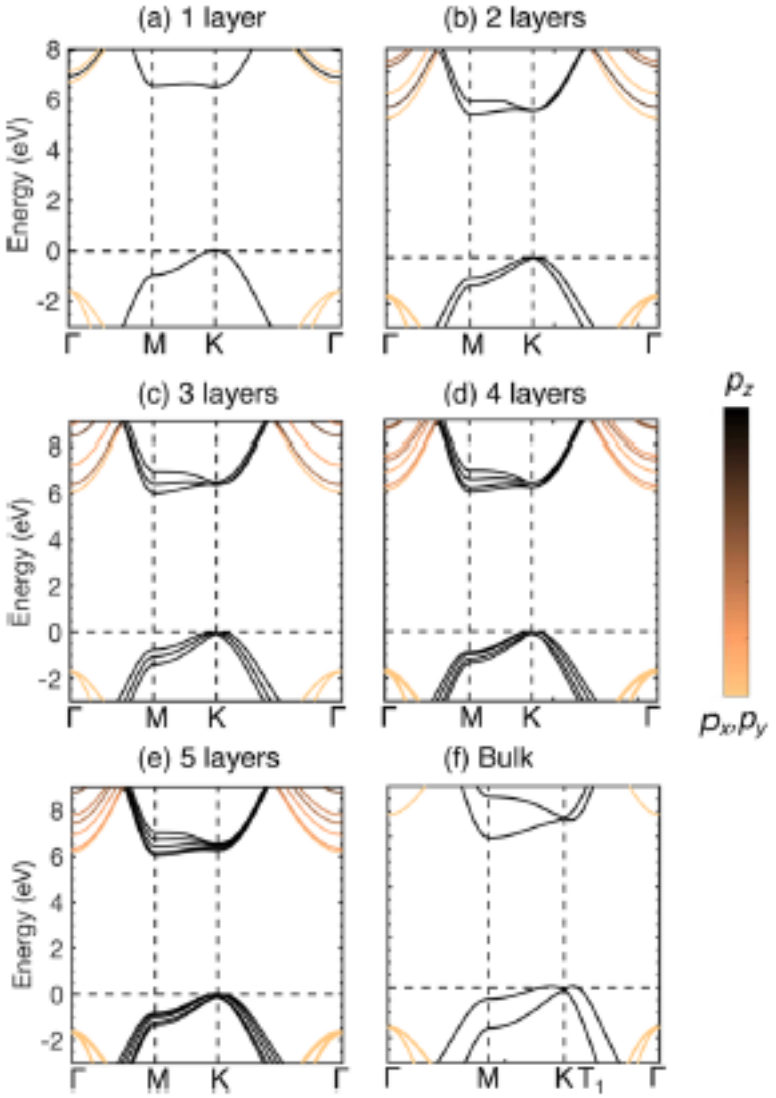
R. V. Gorbachev[1*], I. Riaz[1], R. R. Nair[1], R. Jalil[1], L. Britnell[1], B. D. Belle[1], E. W. Hill[1], K. S. Novoselov[1], K. Watanabe[2], T. Taniguchi[2], A. K. Geim[1], P. Blake[1*]

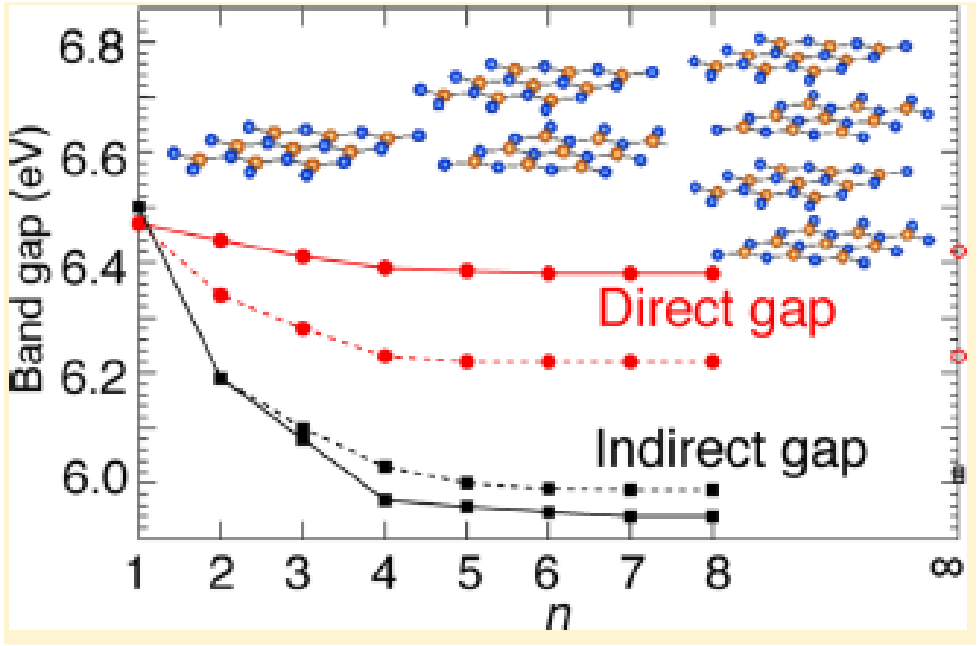
[1]Manchester Centre for Mesoscience & Nanotechnology, University of Manchester, Manchester M13 9PL, UK
[2]National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044 Japan



films on SiO_2

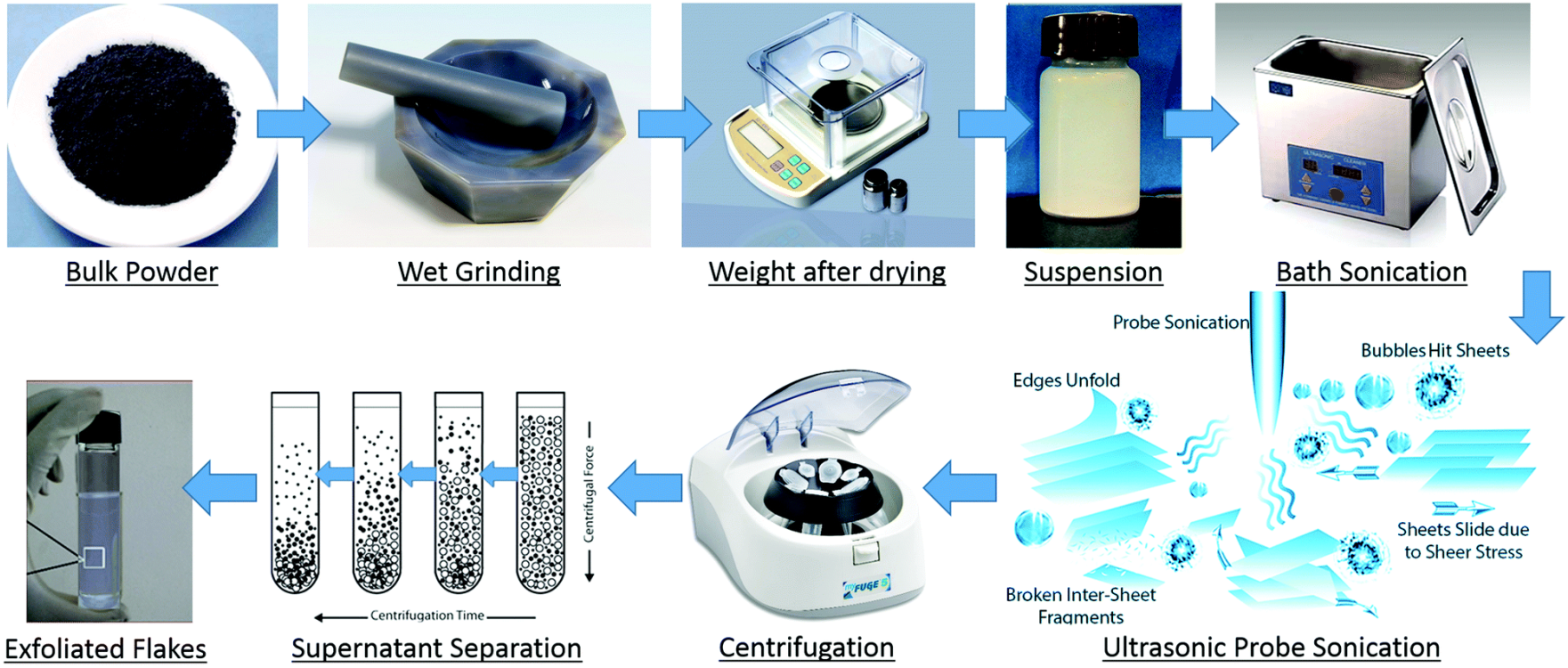
From Monolayer to Bulk, from Direct to Indirect Bandgap





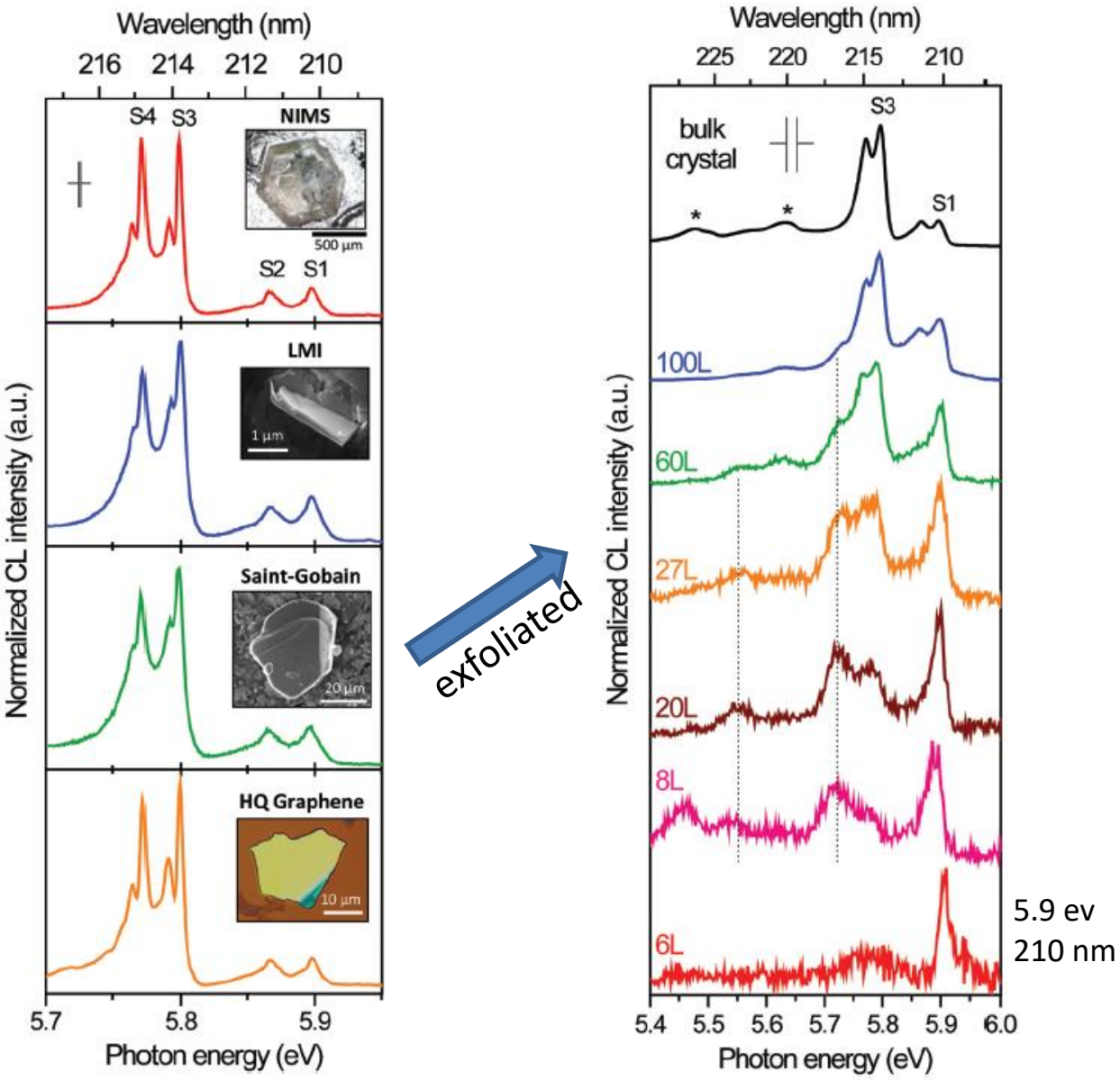
JPCC 122, 255524 (2018)

Exfoliation of Bulk hBN to form hBN flakes



J. Mater. Chem. C 6, 1421 (2018)

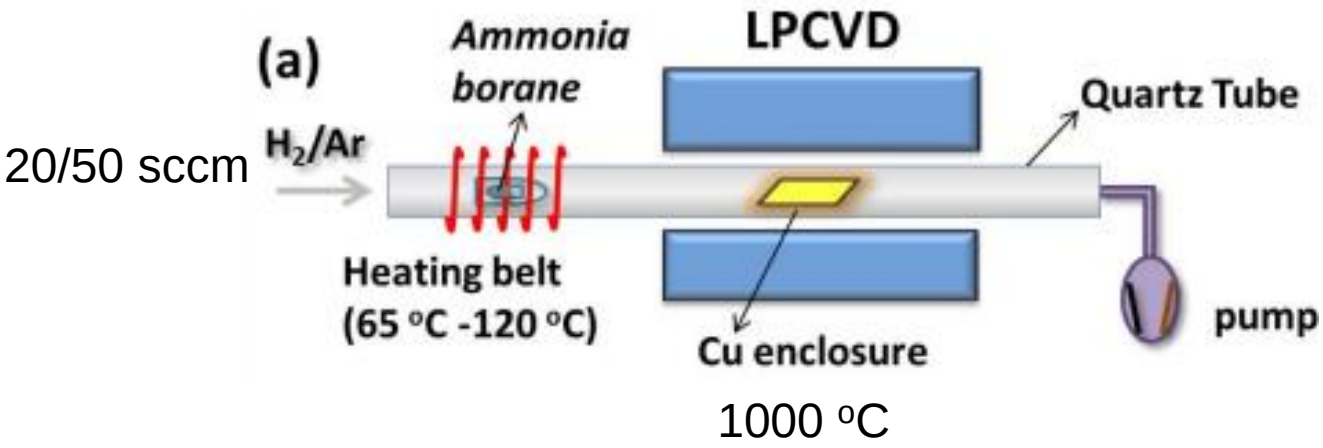
Luminescence from Bulk to Thin Films

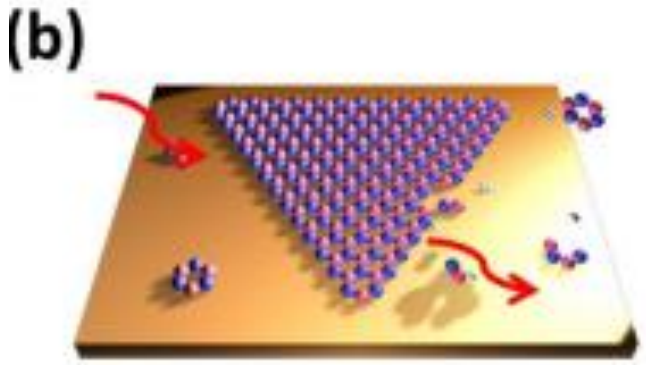


Nanoscale 8, 6986 (2016)

LPCVD hBN Growth & Transfer

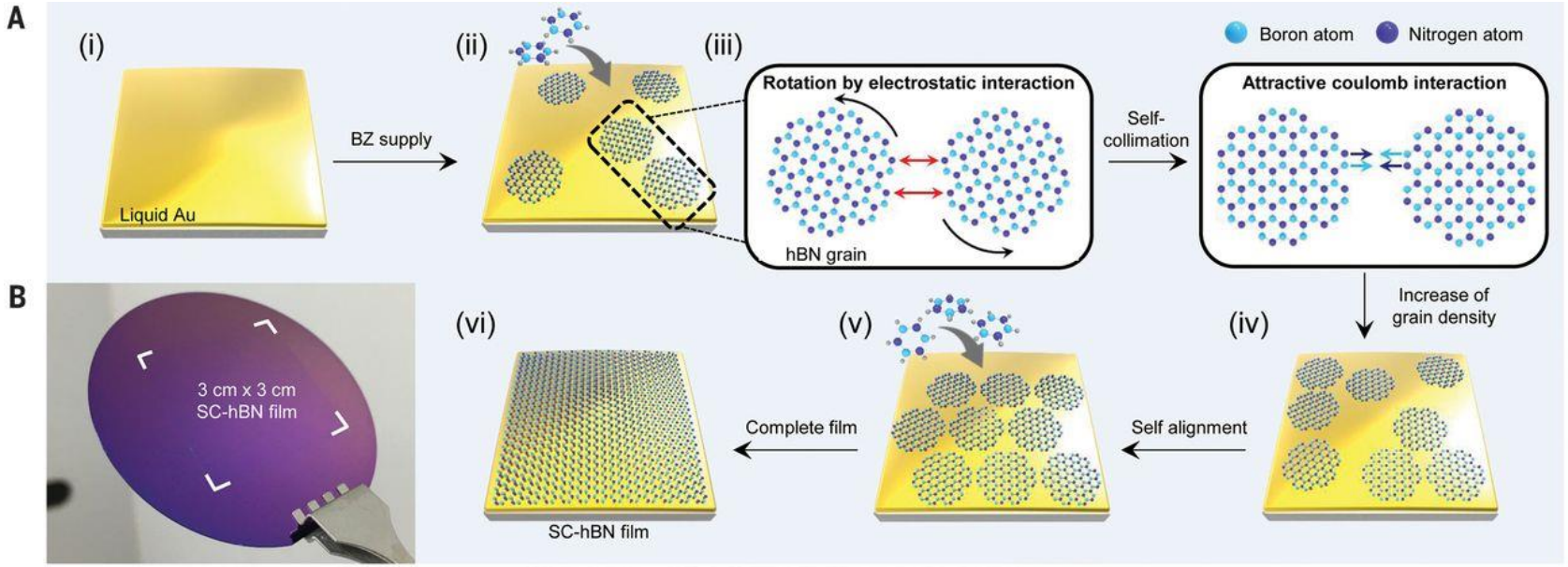
$$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$$

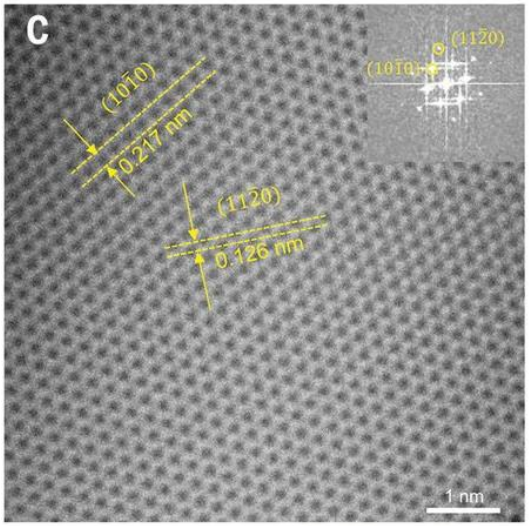




Nano Research, **8**, 3164 (2015)

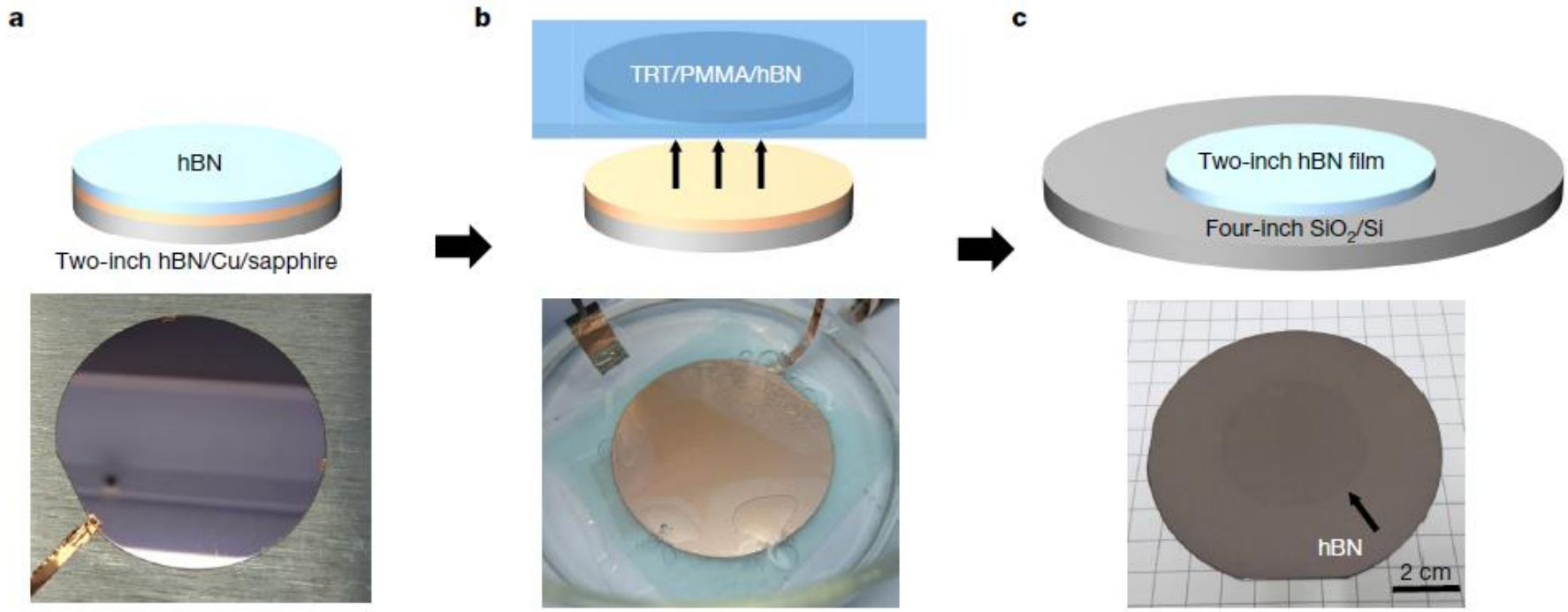
Wafer-scale single-crystal hexagonal boron nitride film via self-collimated grain formation (KIST, Korea)





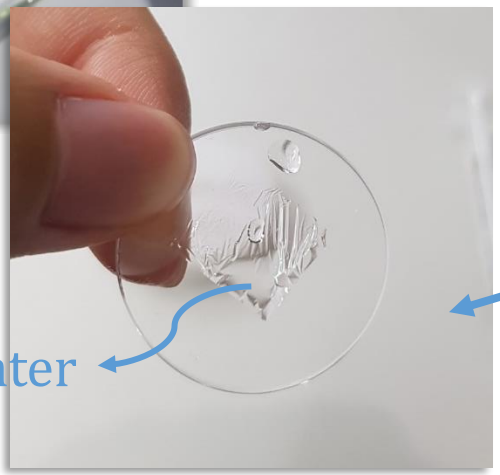
Science **362**, 817 (2018)

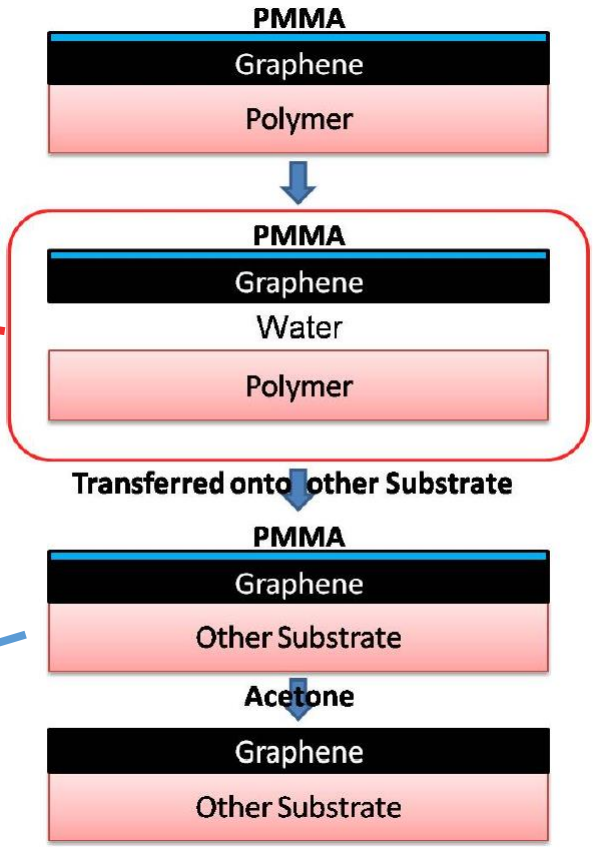
Wafer-scale single-crystal hexagonal boron nitride monolayers on Cu (111), (tsmc, NCTU)



Nature **579**, 219 (2020)

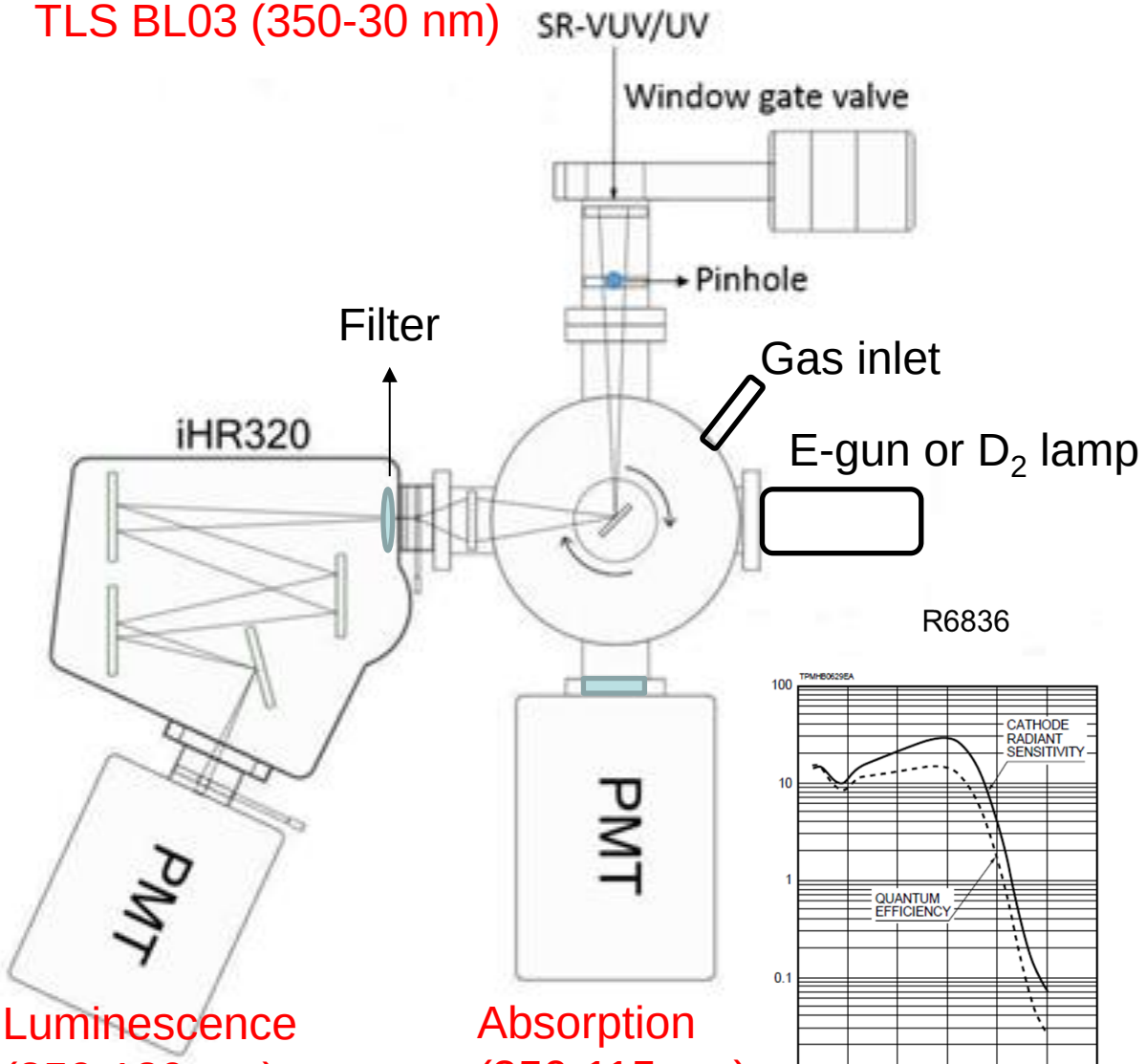
Wet Transfer Process



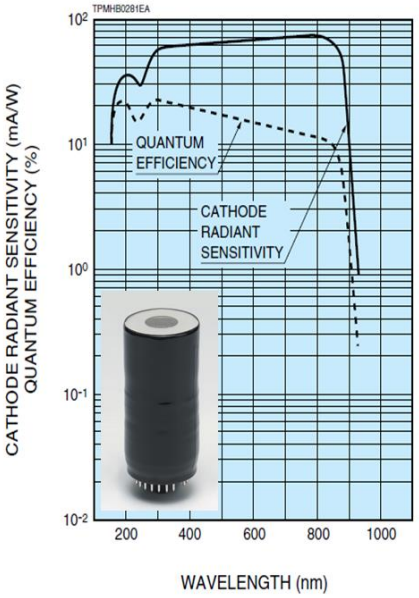


Experimental Setup

TLS BL03 (350-30 nm)



R943-02

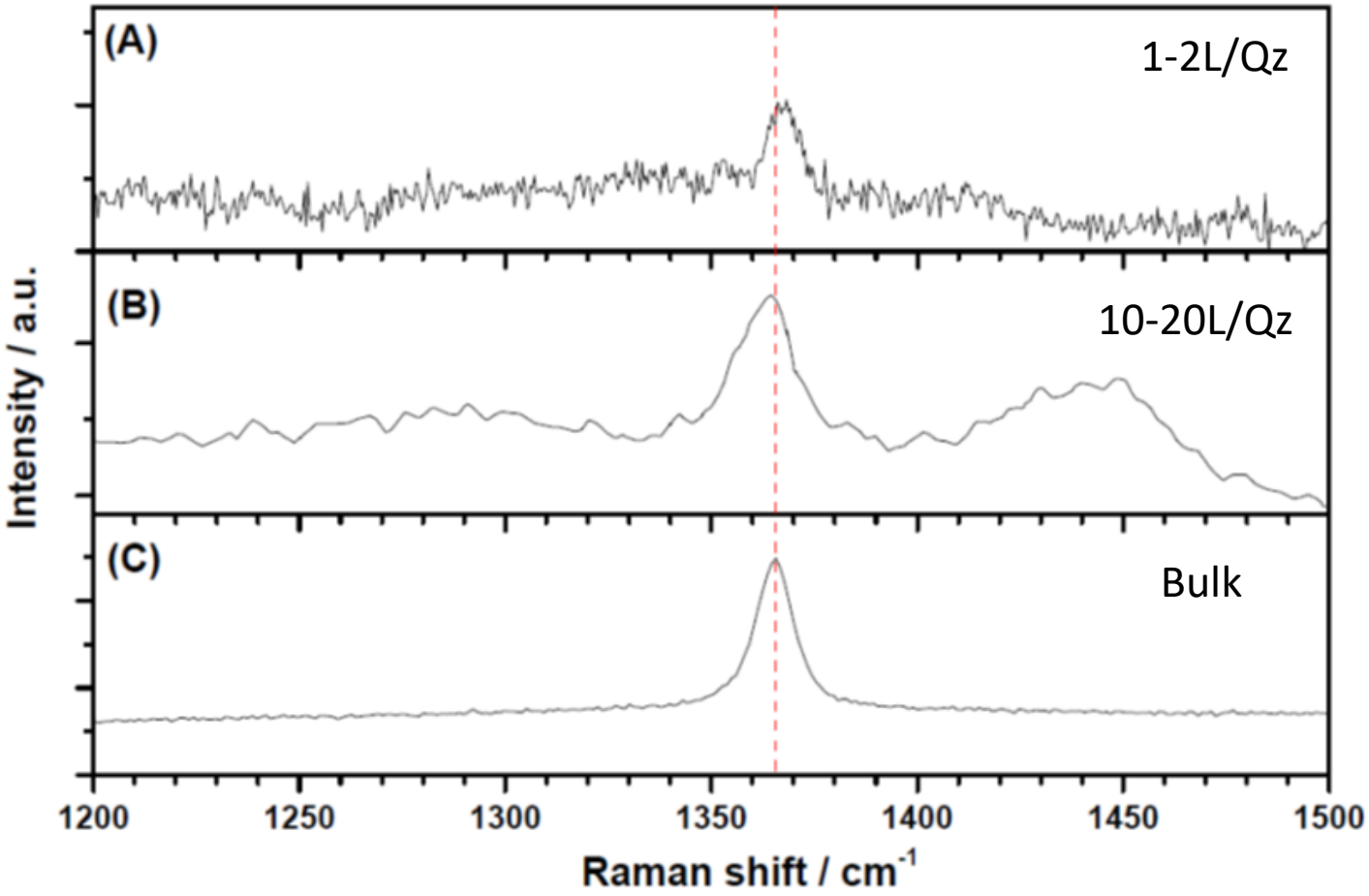


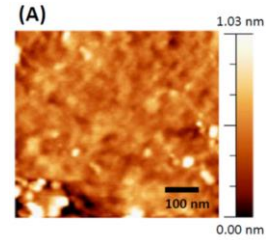
R6836

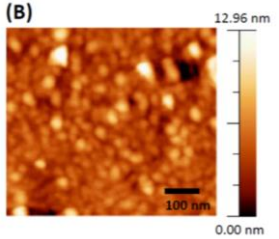
Luminescence (850-180 nm)

Absorption (350-115 nm)

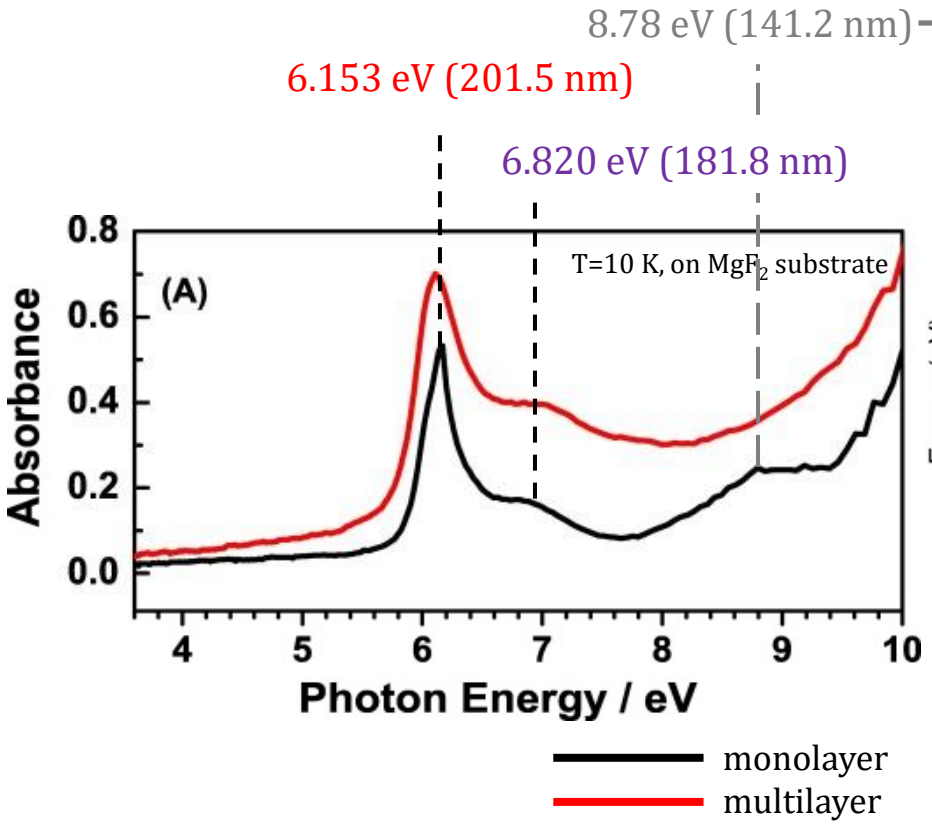
Raman Spectra & AFM Images of hBN Samples

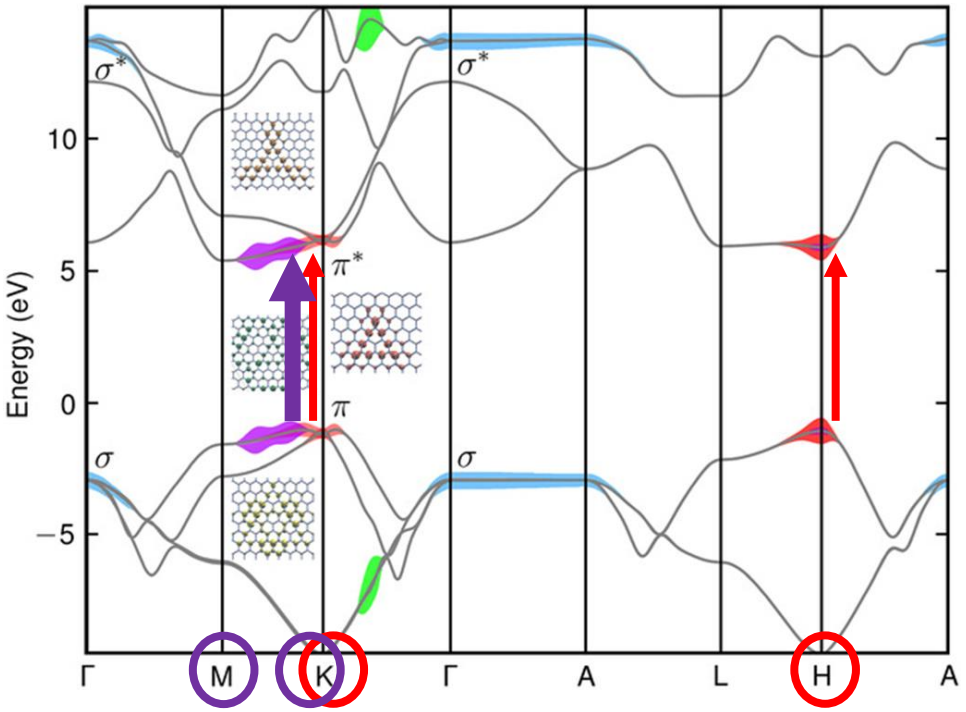






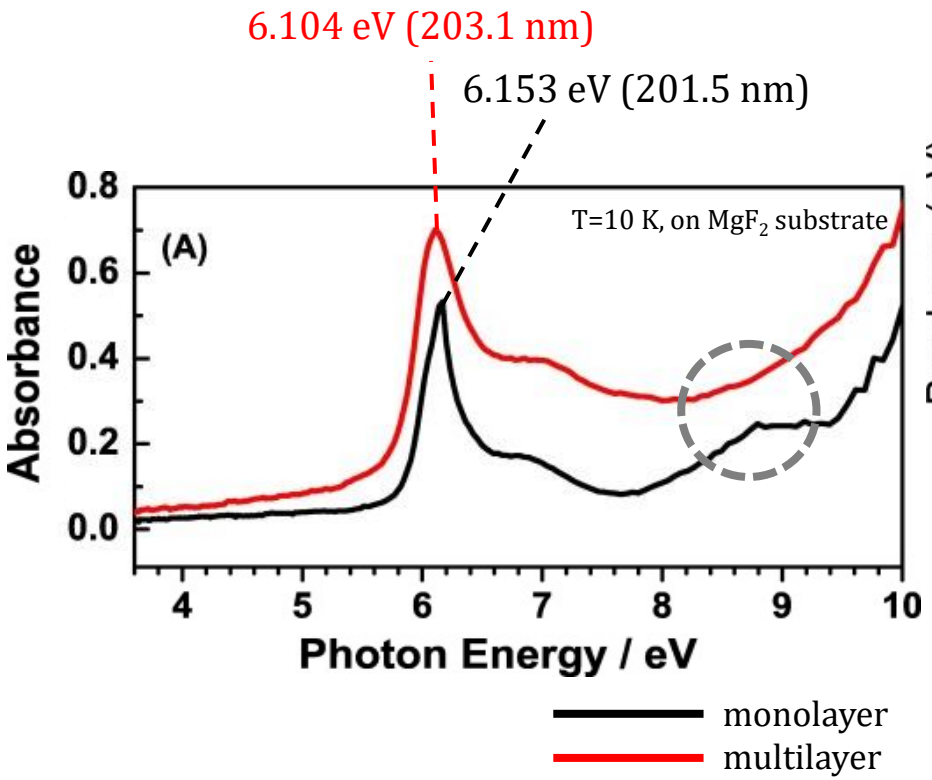
Photoabsorption

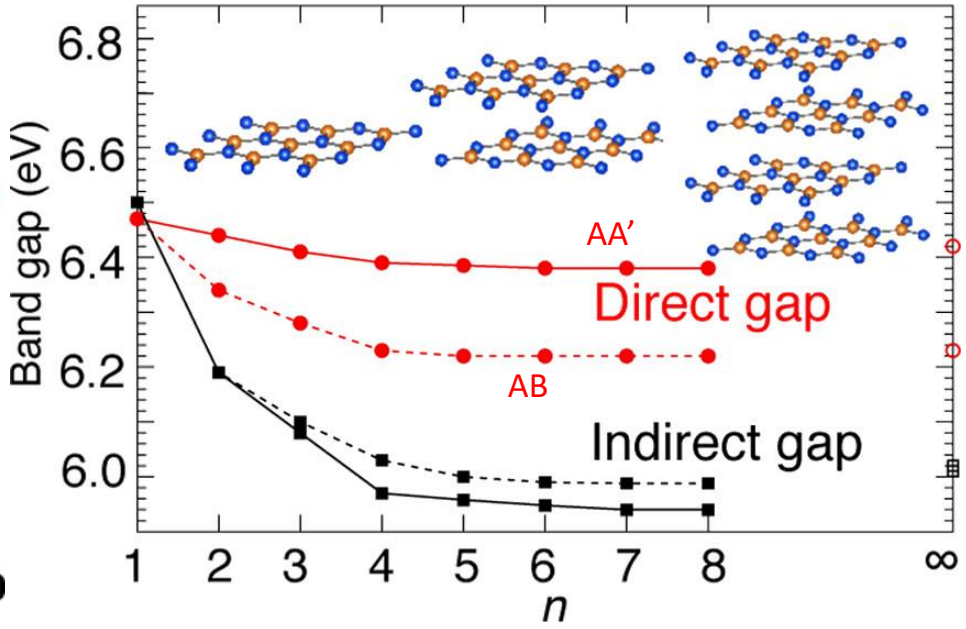




Adv. Photonics Res.2021,2, 2000101

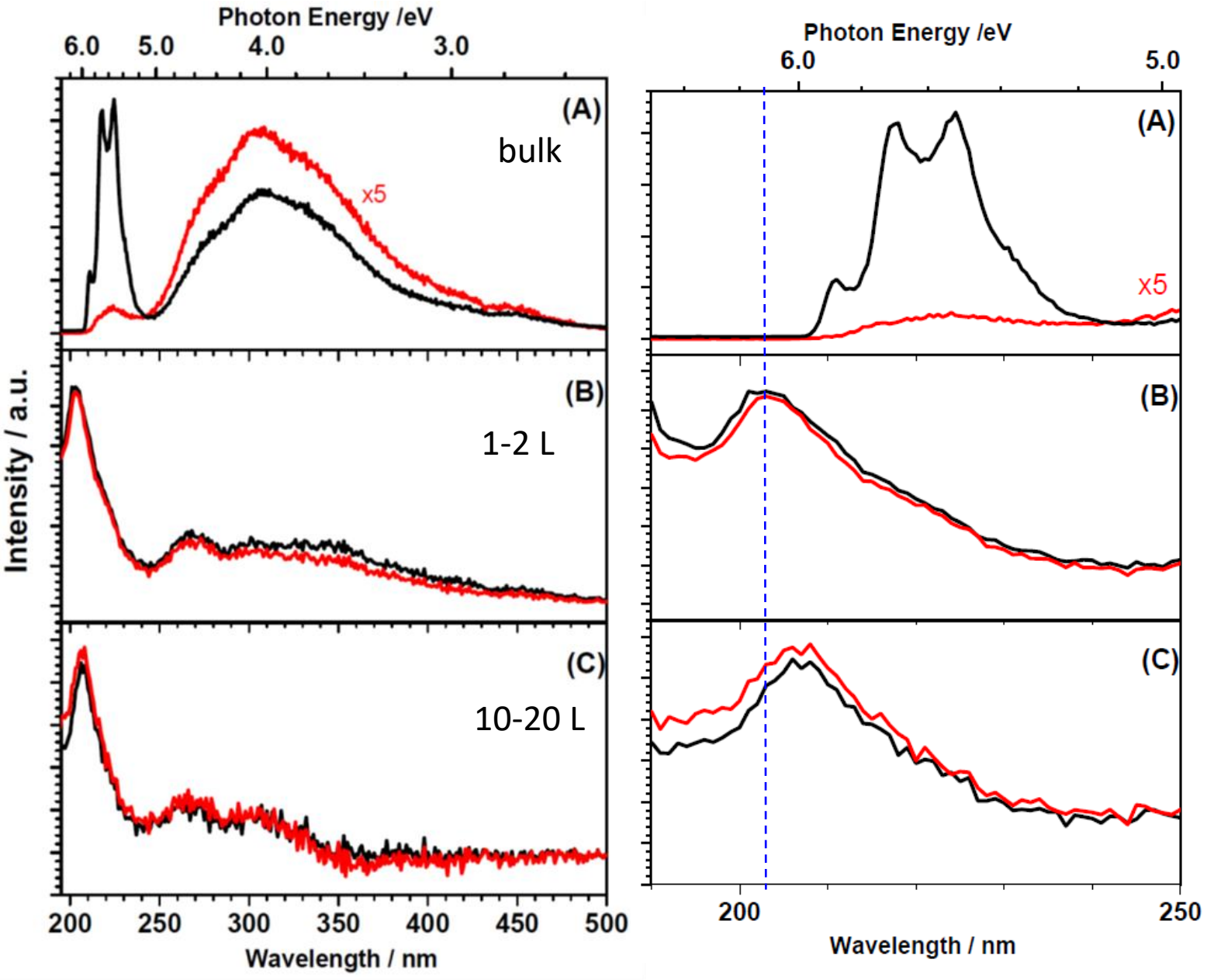
Photoabsorption



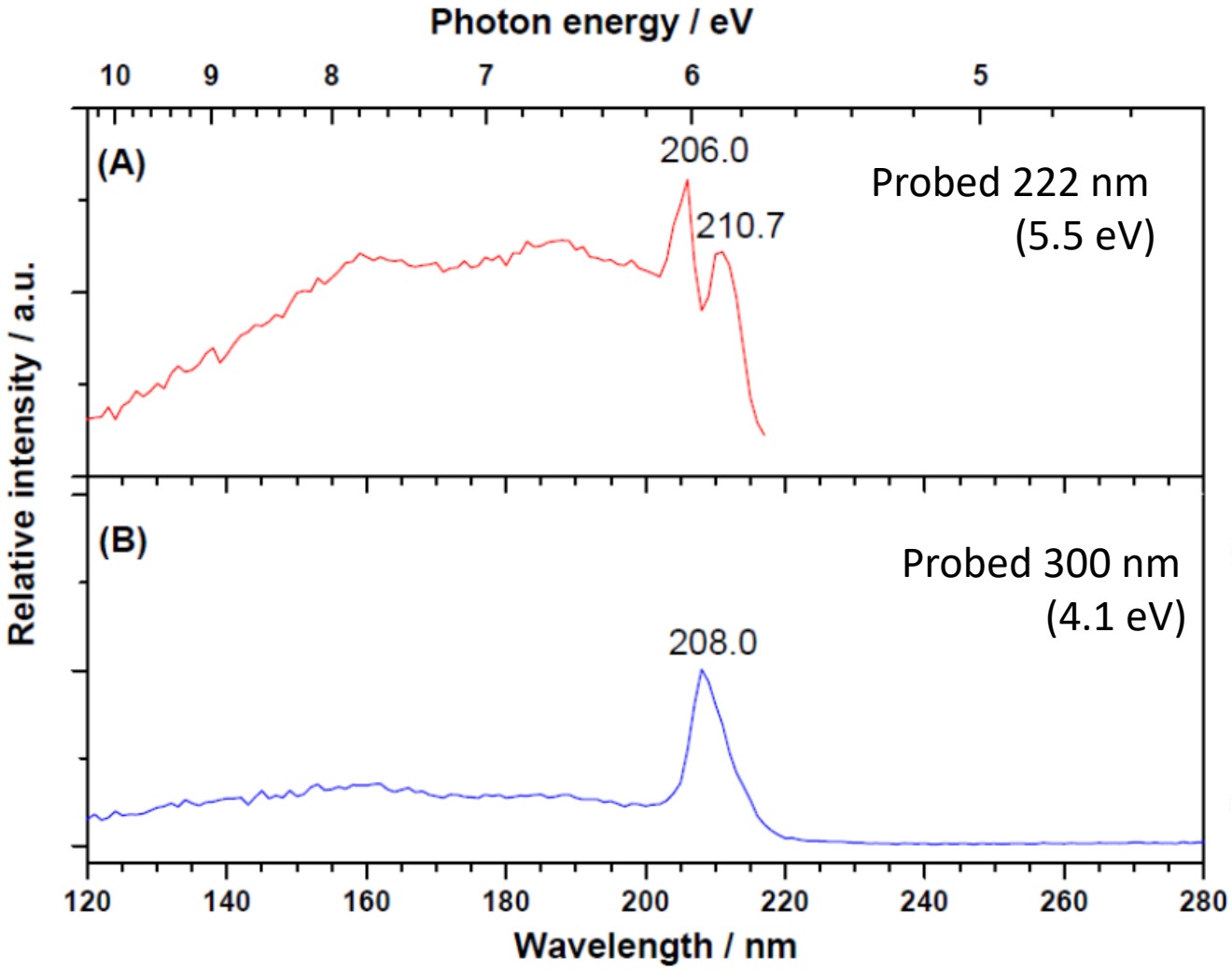


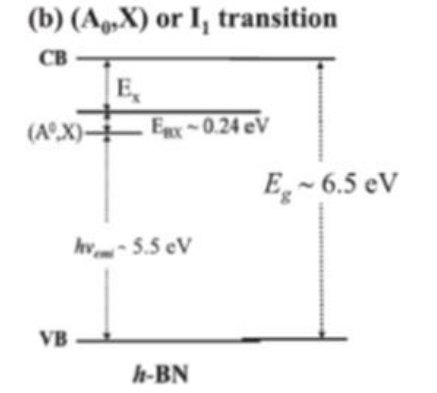
J. Phys. Chem. C 2018, 122, 44, 25524-25529

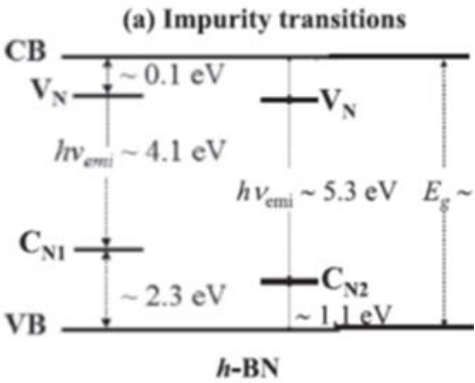
PL Spectra of Thin-film and Bulk hBN Excited at 180 nm



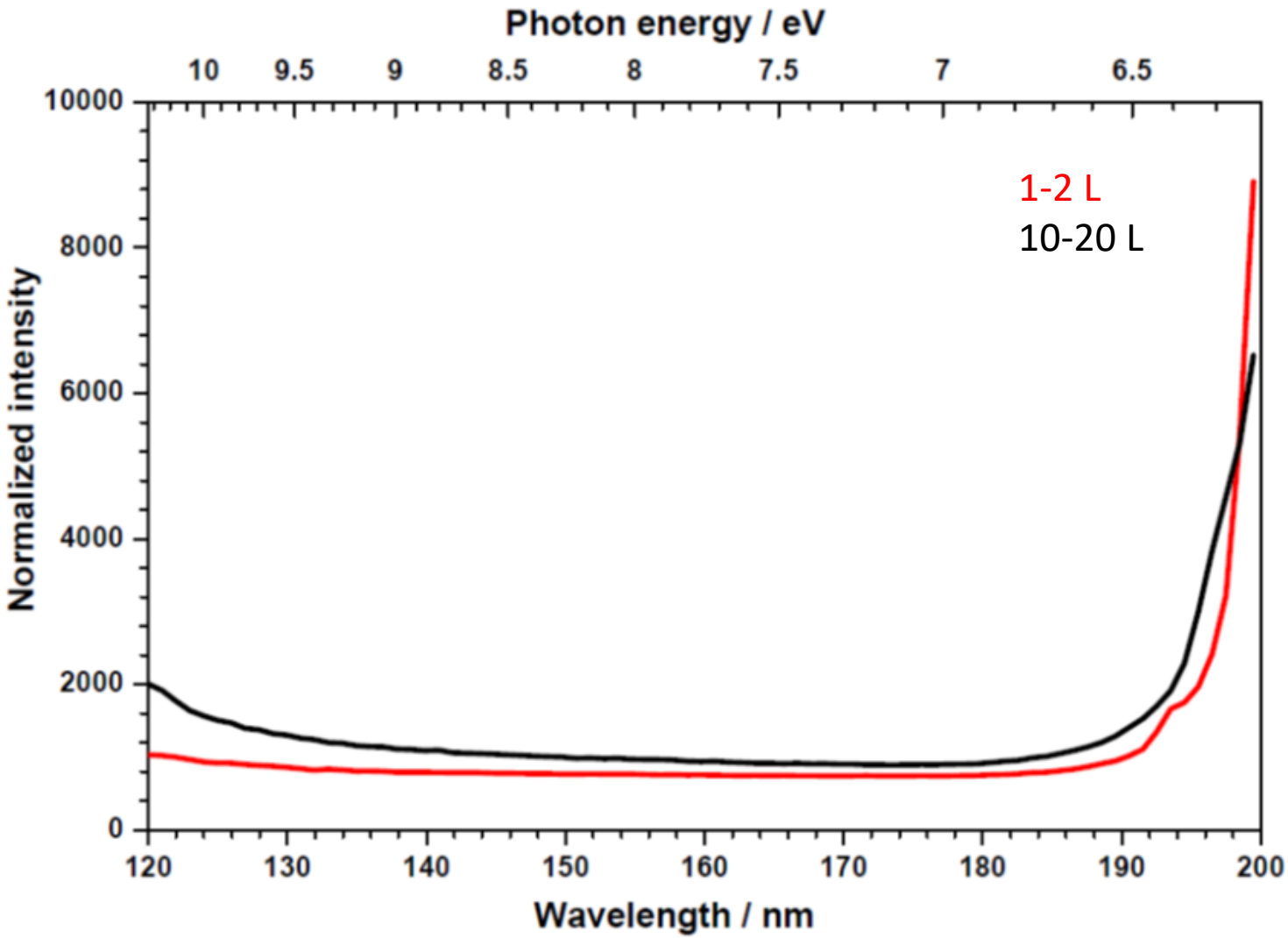
PL Excitation Spectra of Bulk hBN



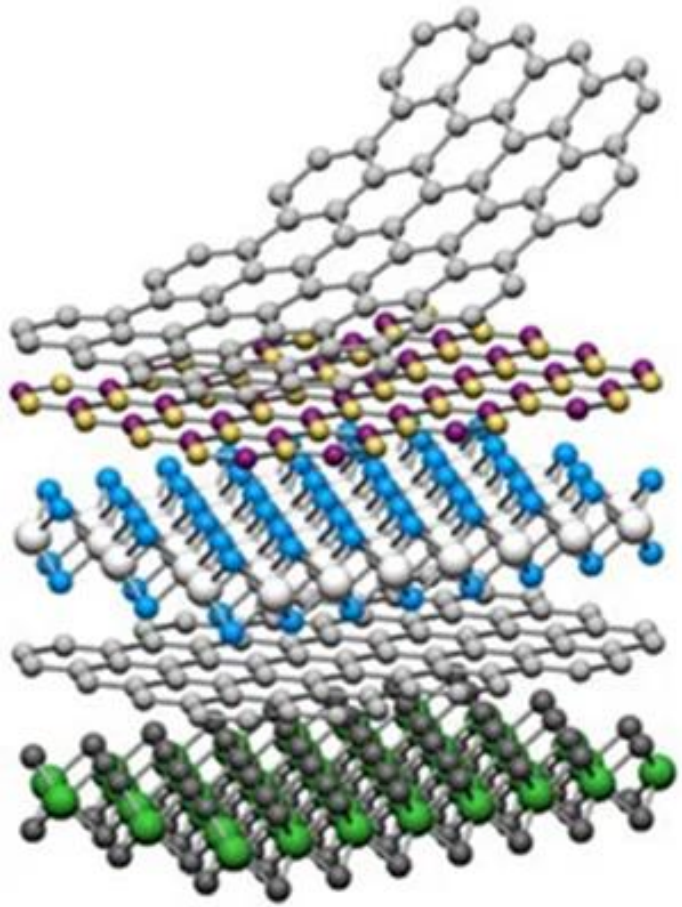


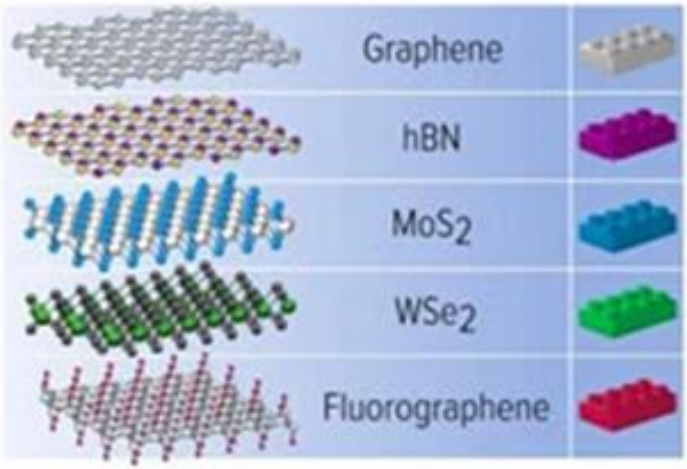


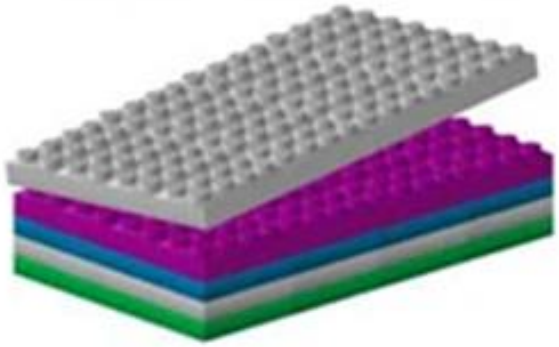
PL Excitation Spectra of hBN Thin Films



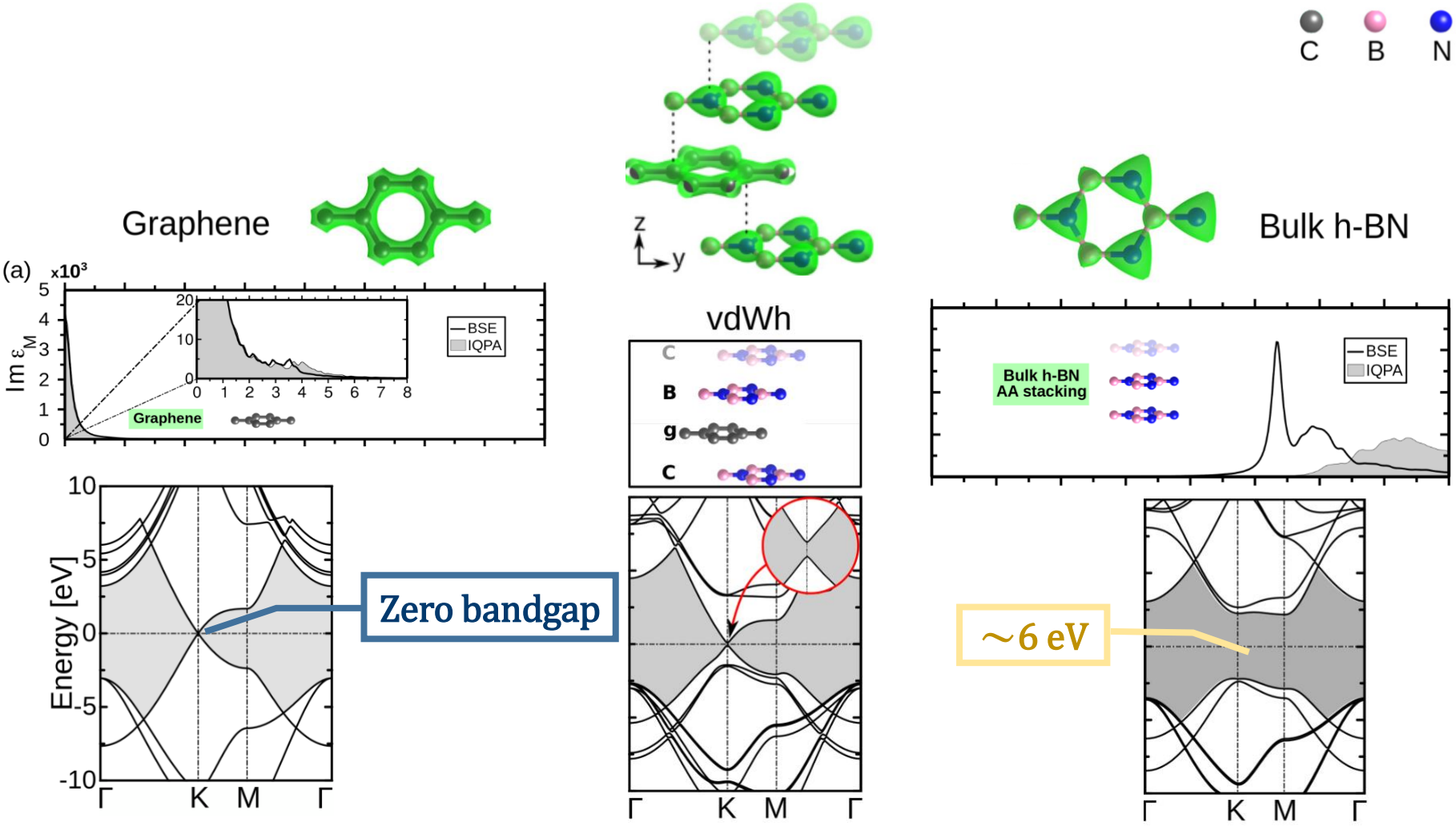
Heterostructured 2D-Materials (vdw materials)



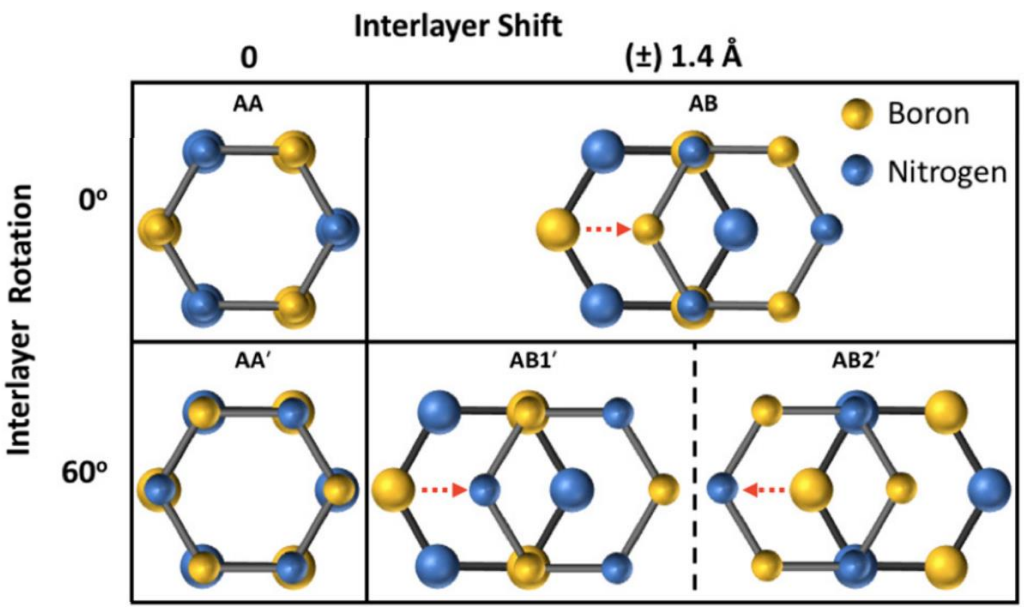




Gr/hBN vdW Materials



Stacking Order

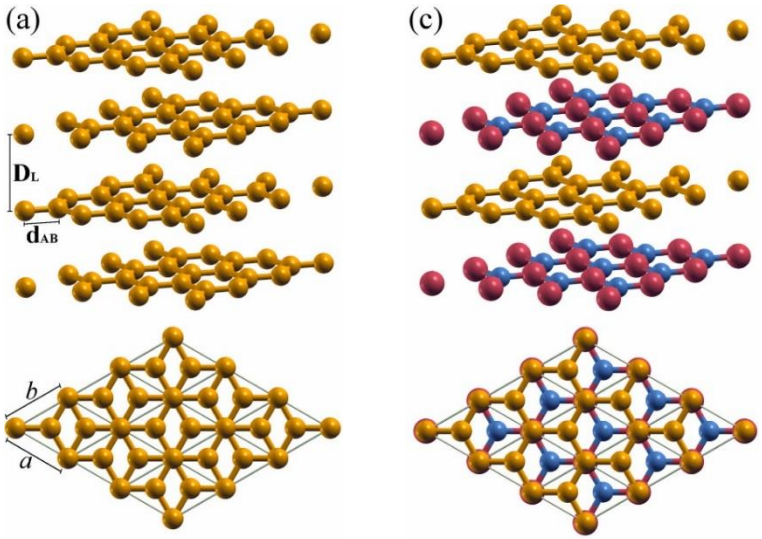


S Matt Gilbert *et al* 2019 *2D Mater.* **6** 021006

AA' Stacking

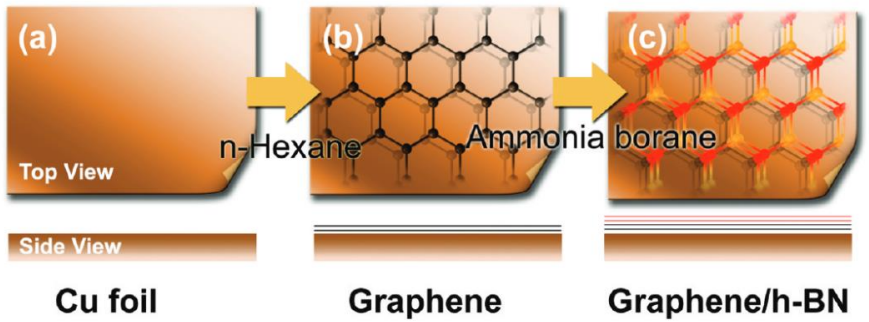
Graphene

Gr/hBN



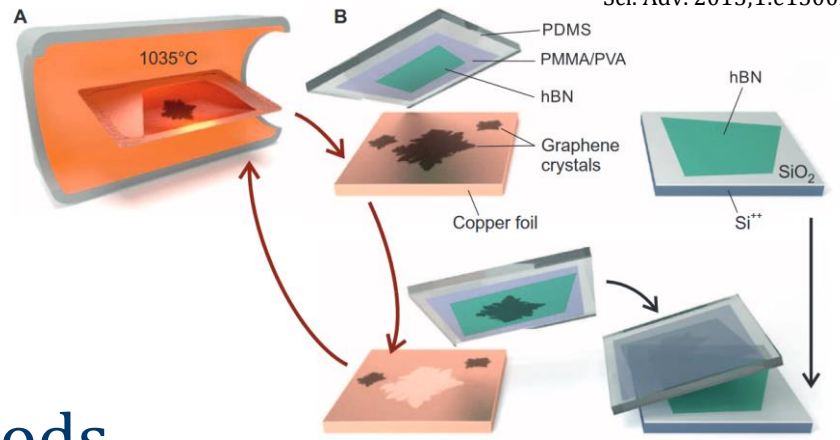
AB Stacking

Multistage deposition techniques on substrates



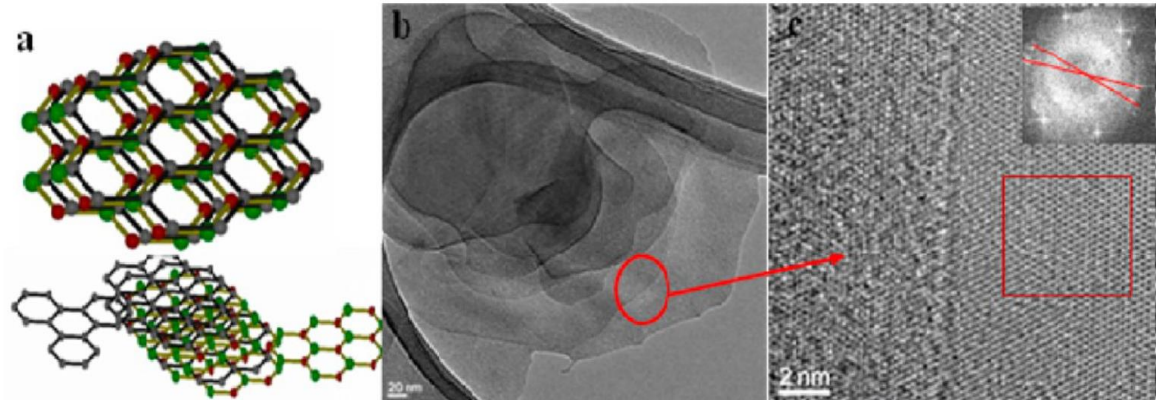
Nano Lett. 2011, 11, 2032–2037

Sci. Adv. 2015;1:e1500222



Liquid phase exfoliation methods

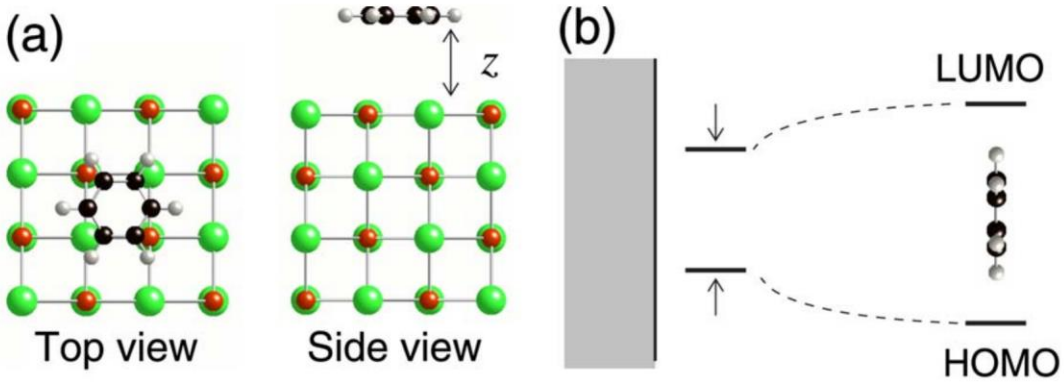
stack randomly



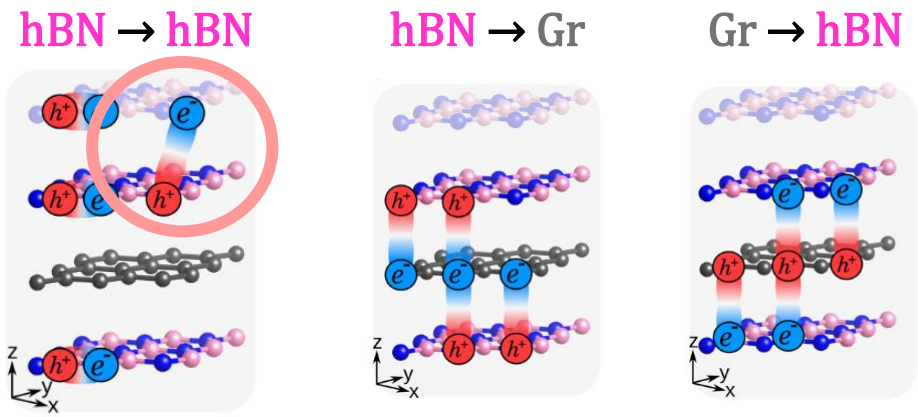
Nano Lett. 2012, 12, 3518−3525

New Properties in Gr/hBN vdWh

Polarization effect

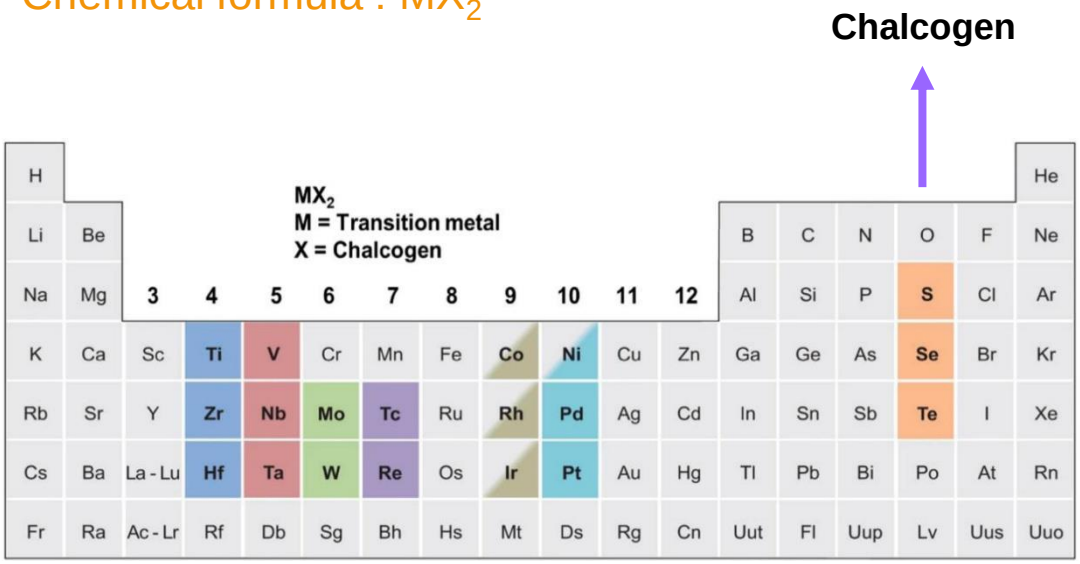


Charge-Transfer

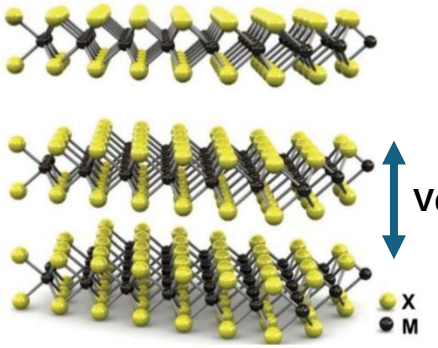


Transition metal dichalcogenide (TMDCs)

Chemical formula : MX_2



Coordination Chemistry Reviews **2022**, *472*, 214765.



Insulator: HfS_2

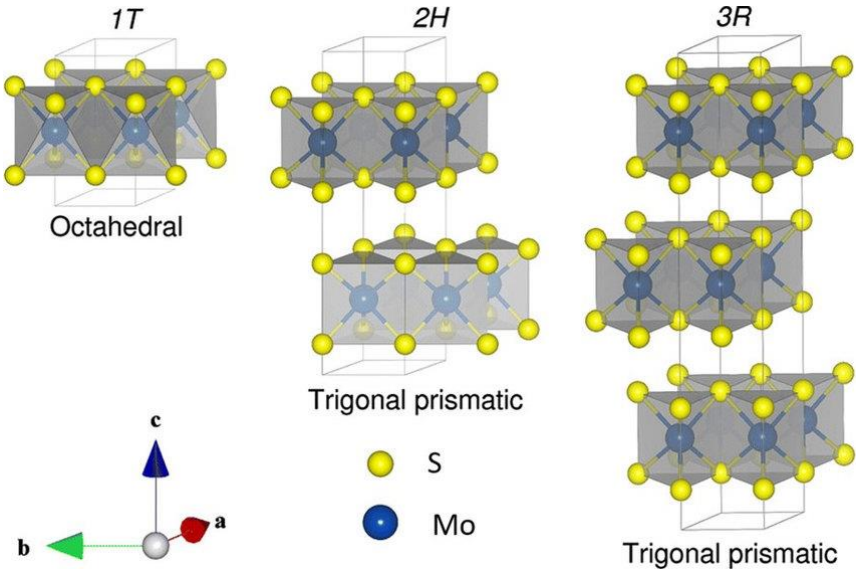
Semiconductor: MoS_2 / WS_2

Semi-metal: WTe_2

Metal: VSe_2

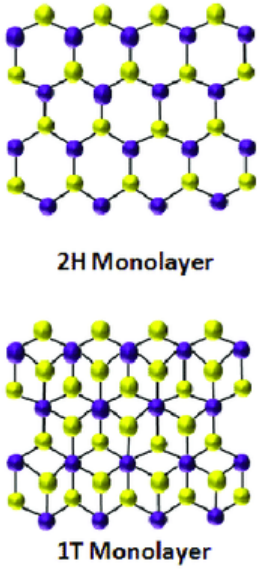
Crystal structures of MoS_2

Side view



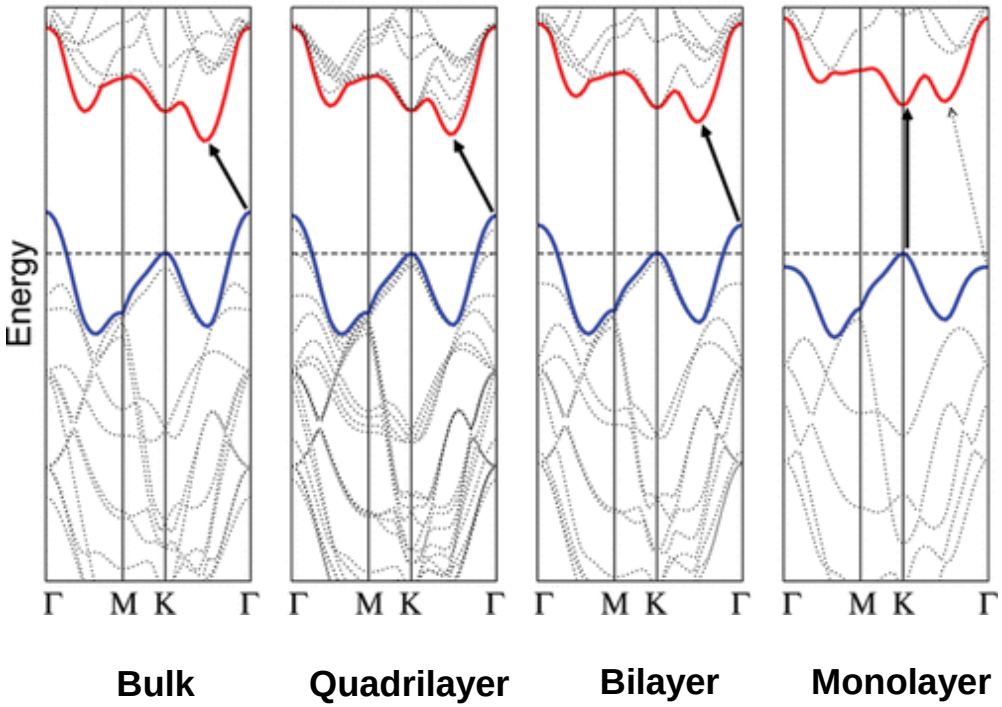
Energy Science & Engineering **2016**, *4* (5), 285–304.

Top view



Materials **2021**, *14* (12), 3283.

Band structure of MoS_2



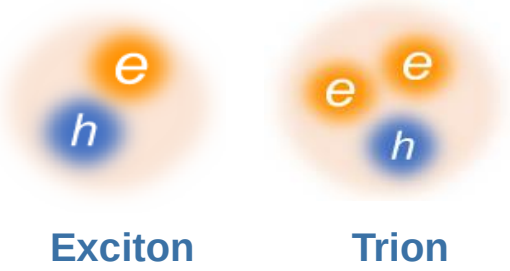
Bulk → Monolayer

Indirect → Direct

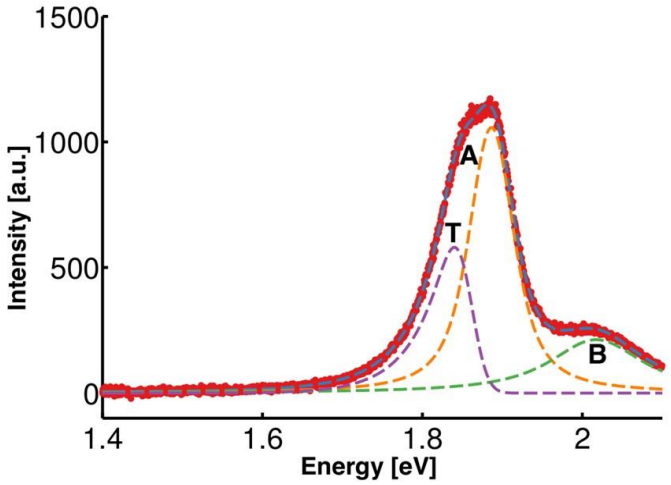
Nano Lett. **2010**, *10* (4), 1271–1275.

Exciton and trion

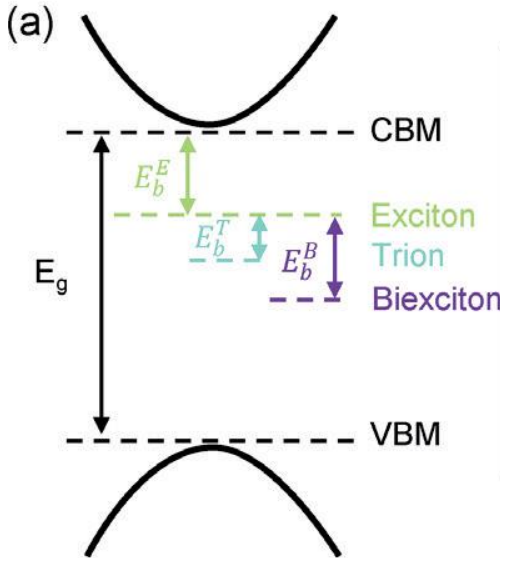
- **Characteristic property of 2D TMDCs**



Exciton **Trion**

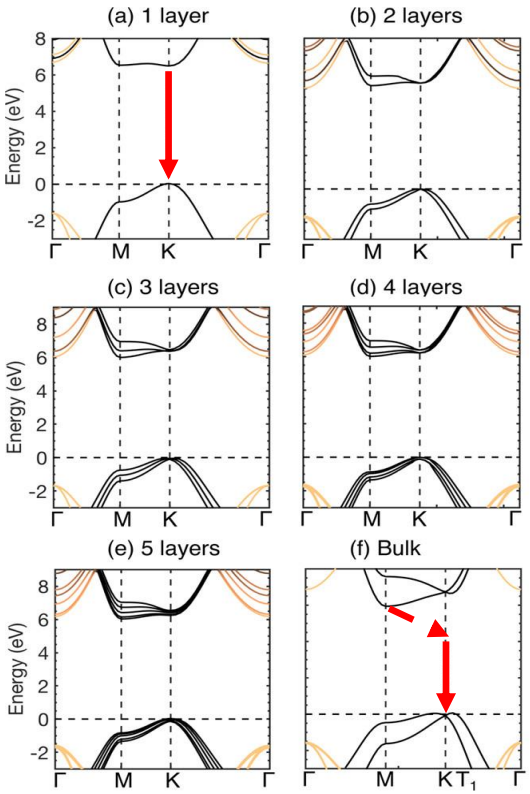


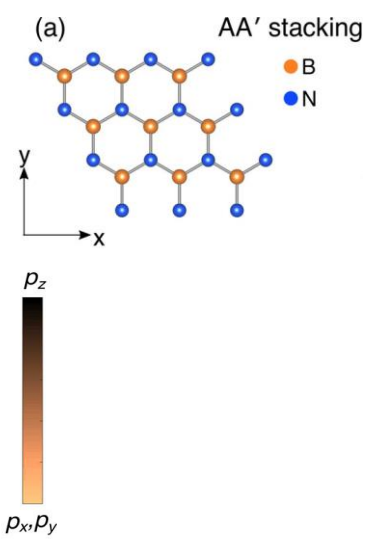
Nat Commun **2021**, *12* (1), 6131.

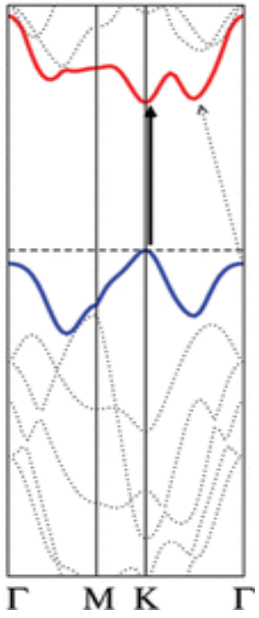


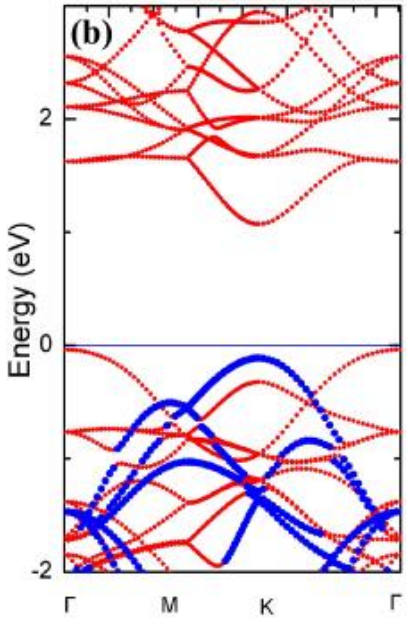
IntechOpen, **2020**.

Band structure of hBN and MoS_2 / hBN heterostructure









J. Phys. Chem. C 2018, 122, 44, 25524-25529

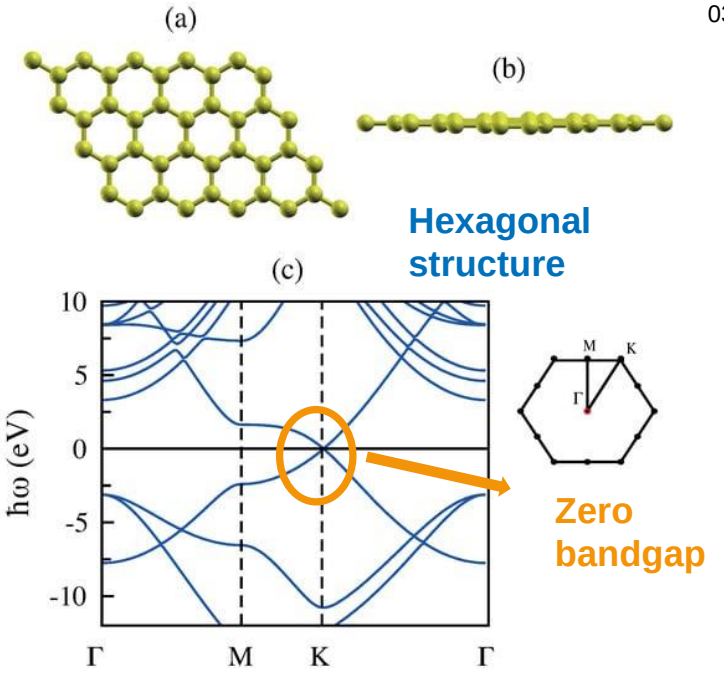
Bulk → **Monolayer**

Indirect → **Direct**

MoS_2 → **MoS_2 / hBN**

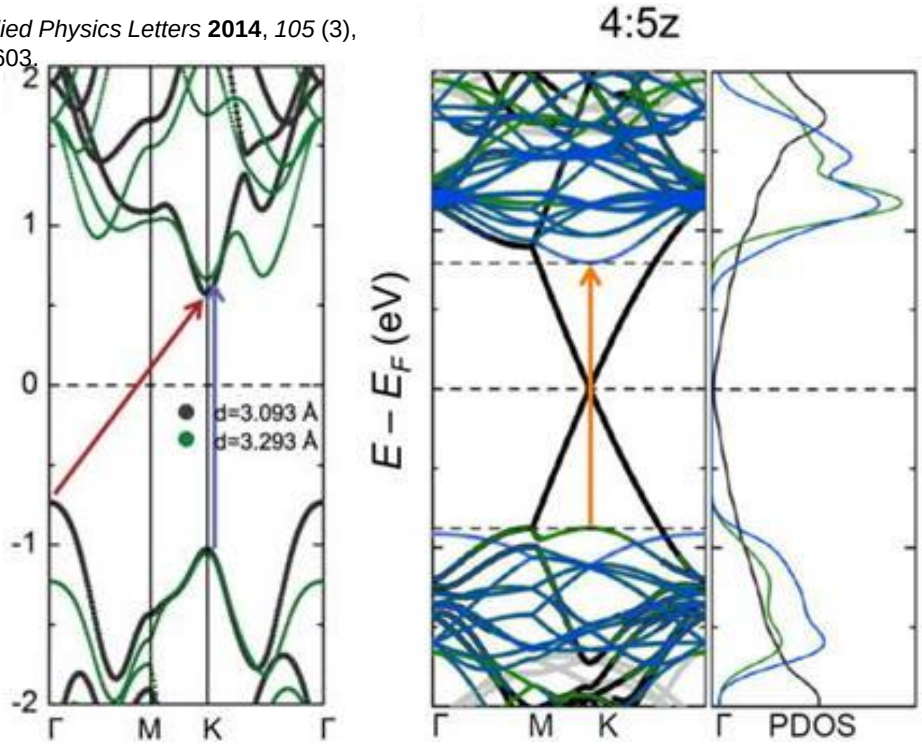
J. Phys. D: Appl. Phys. **2014**, *47* (7), 075301

Band structure of Gr and MoS_2 / Gr heterostructure



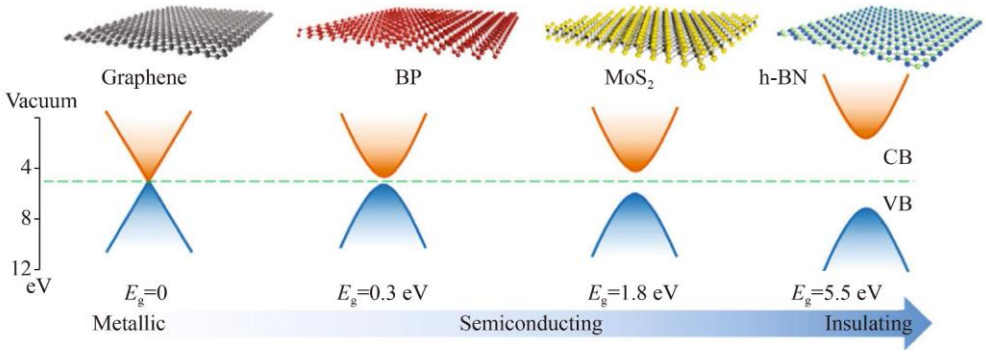
Applied Sciences **2018**, *8* (2), 238.

Applied Physics Letters **2014**, *105* (3), 031603.

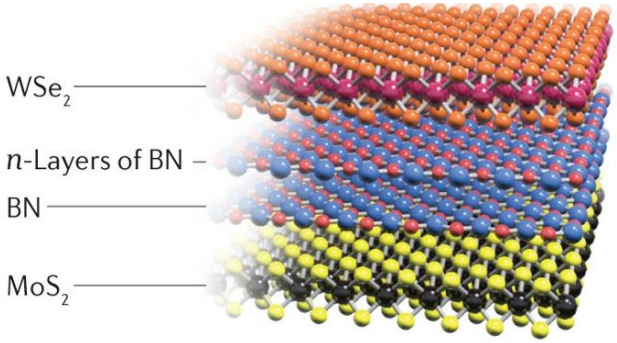


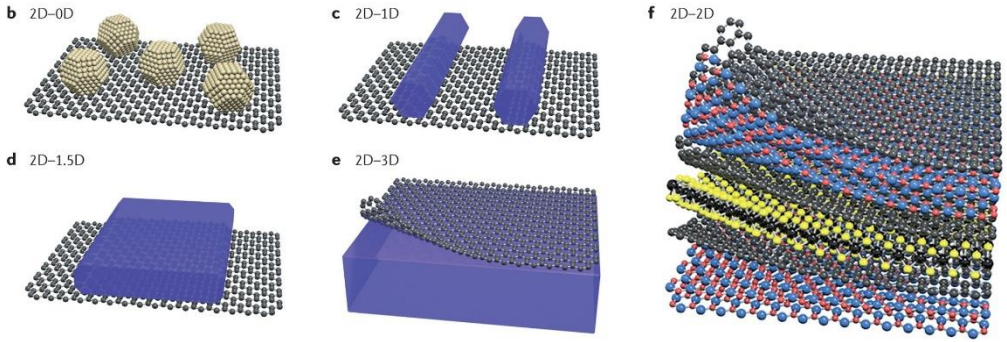
MoS_2 → **MoS_2 / Gr**

Van der Waals heterostructure



Front. Phys. **2022**, *17* (4), 43202.



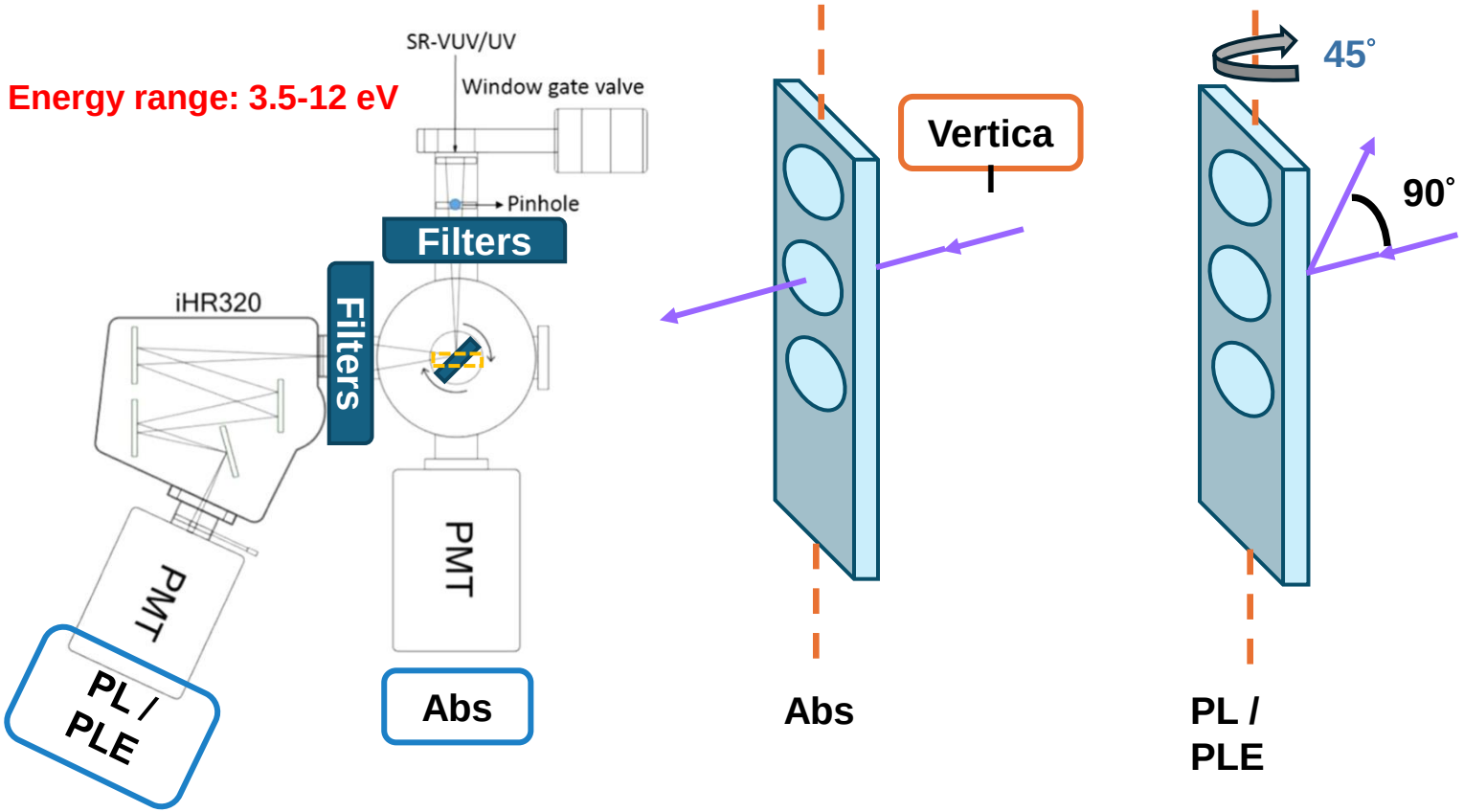


Nature Reviews Materials **2016**, *1* (9), 16042.

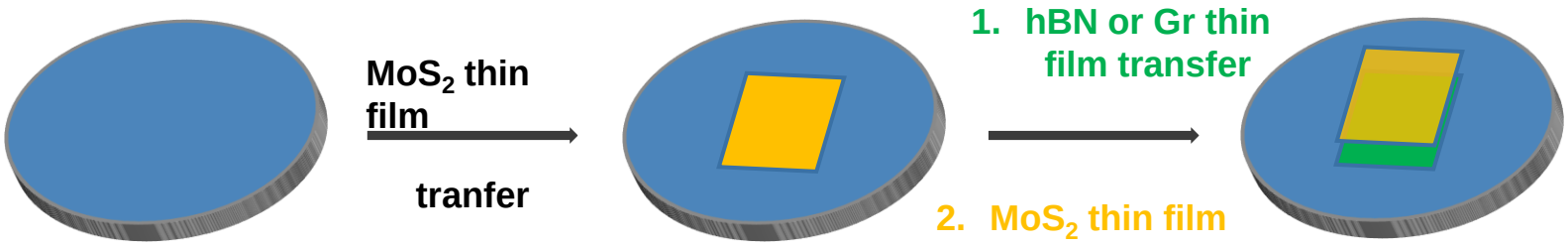
- **Van der Waals interactions allow the integration of highly disparate materials without the constraints of crystal lattice matching.**

TLS BL03 - Absorption and Photoluminescence measurements

Energy range: 3.5-12 eV



Sample preparation



MgF_2 substrate

MoS_2 on MgF_2

MoS_2 / hBN or Gr heterostructure

The aims of the study

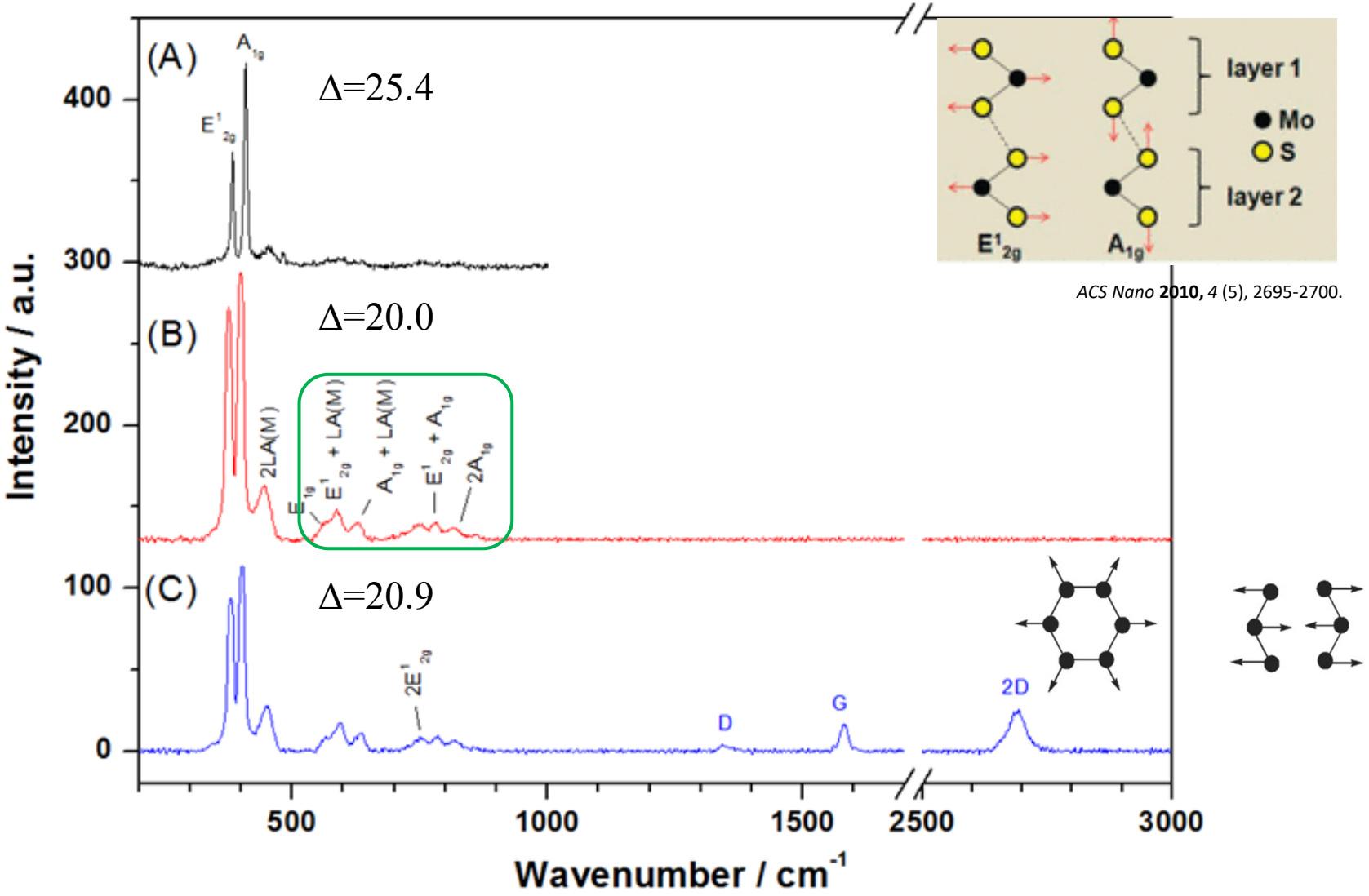
1. This study aims to provide information on the absorption and photoluminescence spectra of MoS_2 and its heterostructures, covering the range from VUV to the visible region.

2. This research investigates how different optical substrates influence the photoluminescence properties of MoS_2.

3. This study examines the differences in absorption and photoluminescence properties between MoS_2 and its heterostructures.

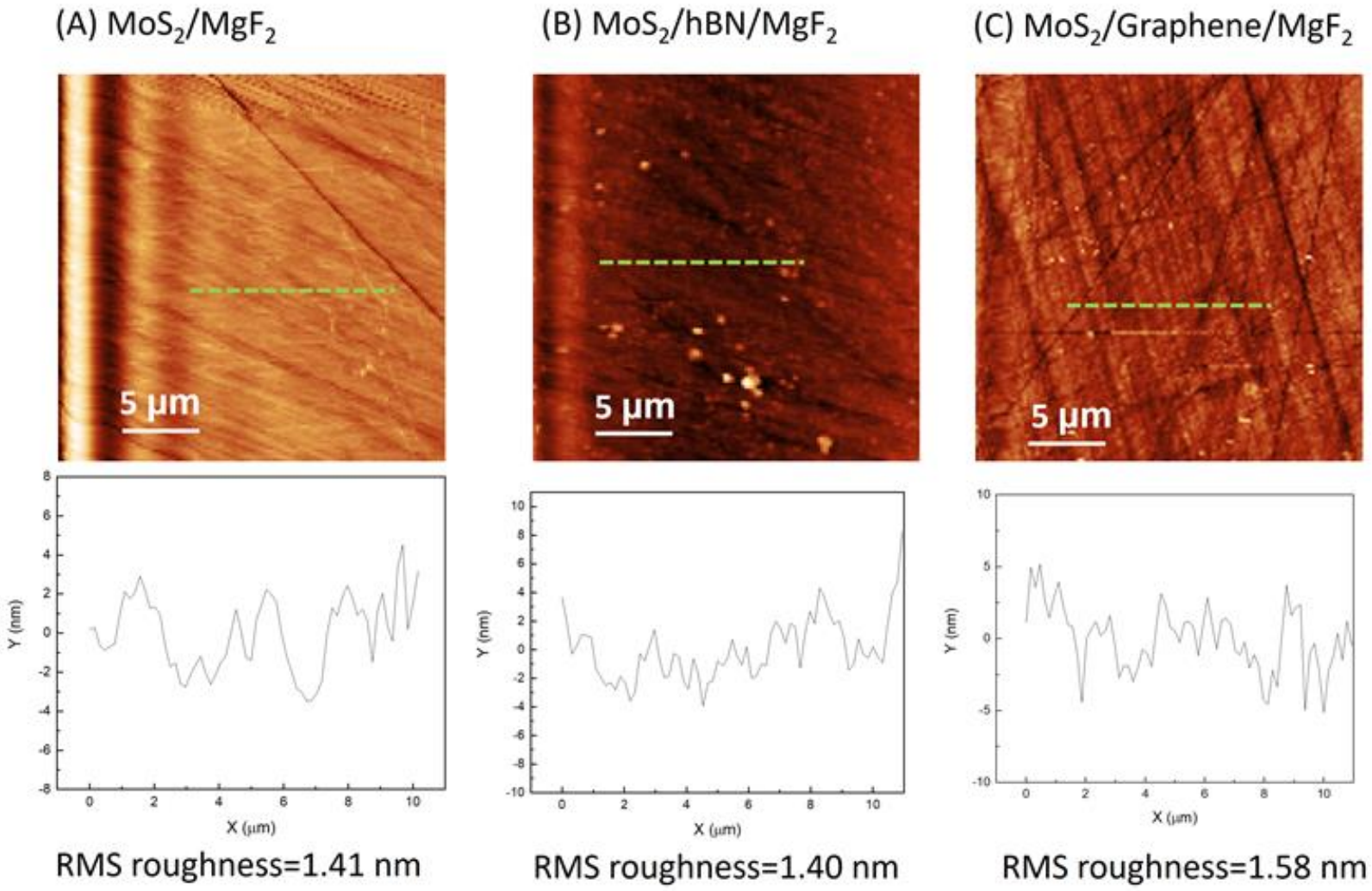
4. The study also investigates the characteristic photoluminescence properties of hBN or Gr layers.

Raman Spectra of MoS_2 and MoS_2 / hBN & MoS_2/Gr

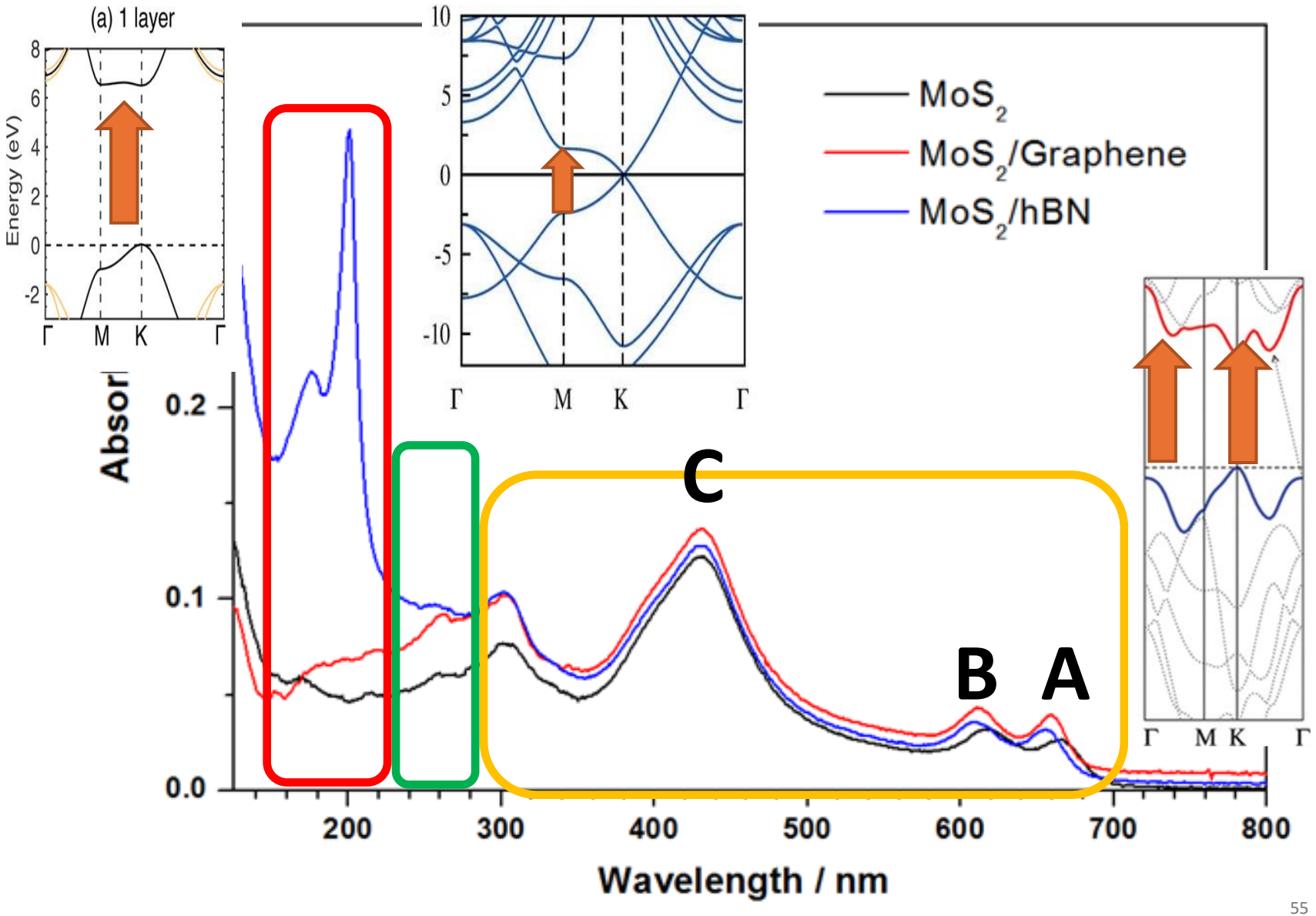


ACS Nano **2010,** *4* (5), 2695-2700.

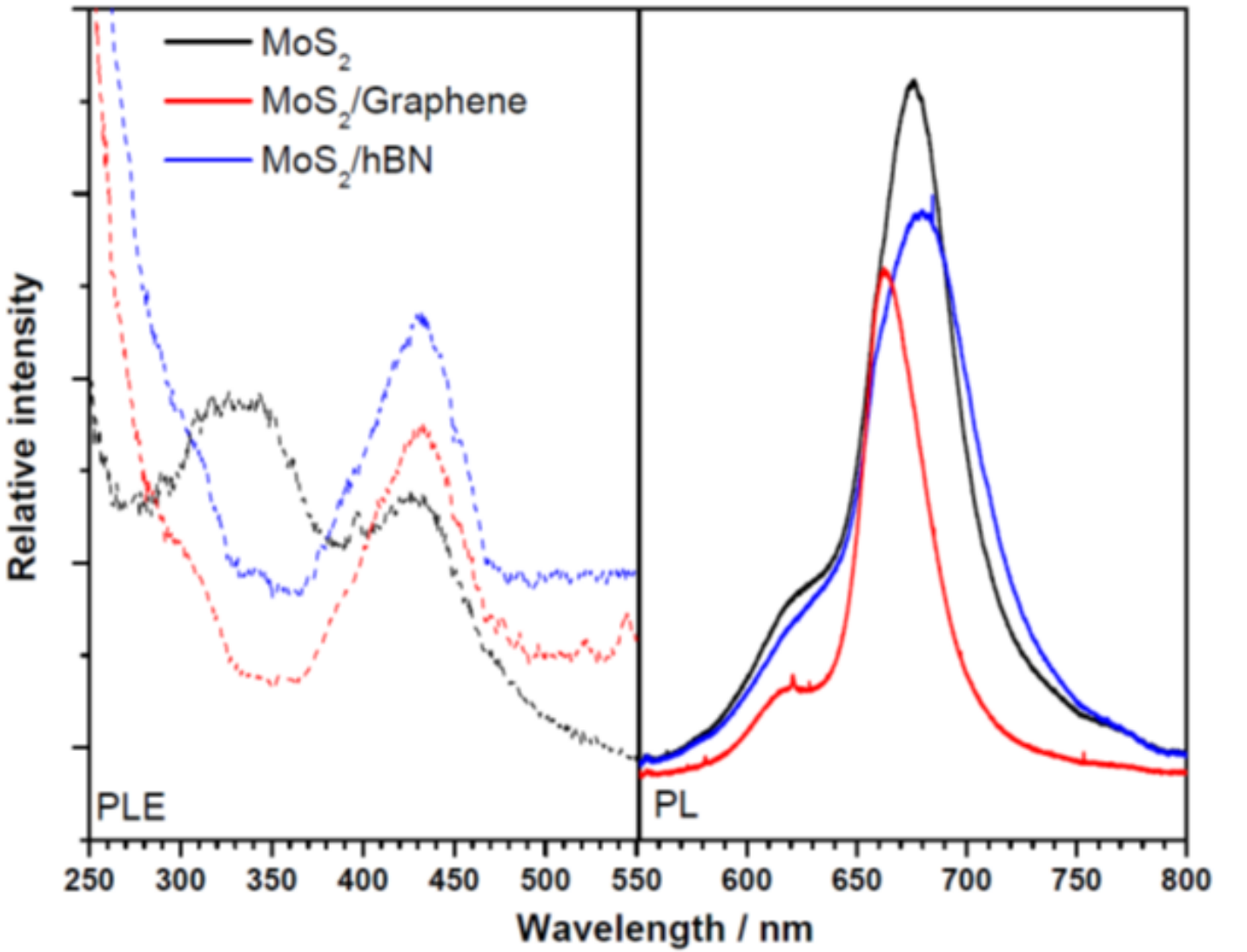
AFM images of MoS_2 and its heterostructures



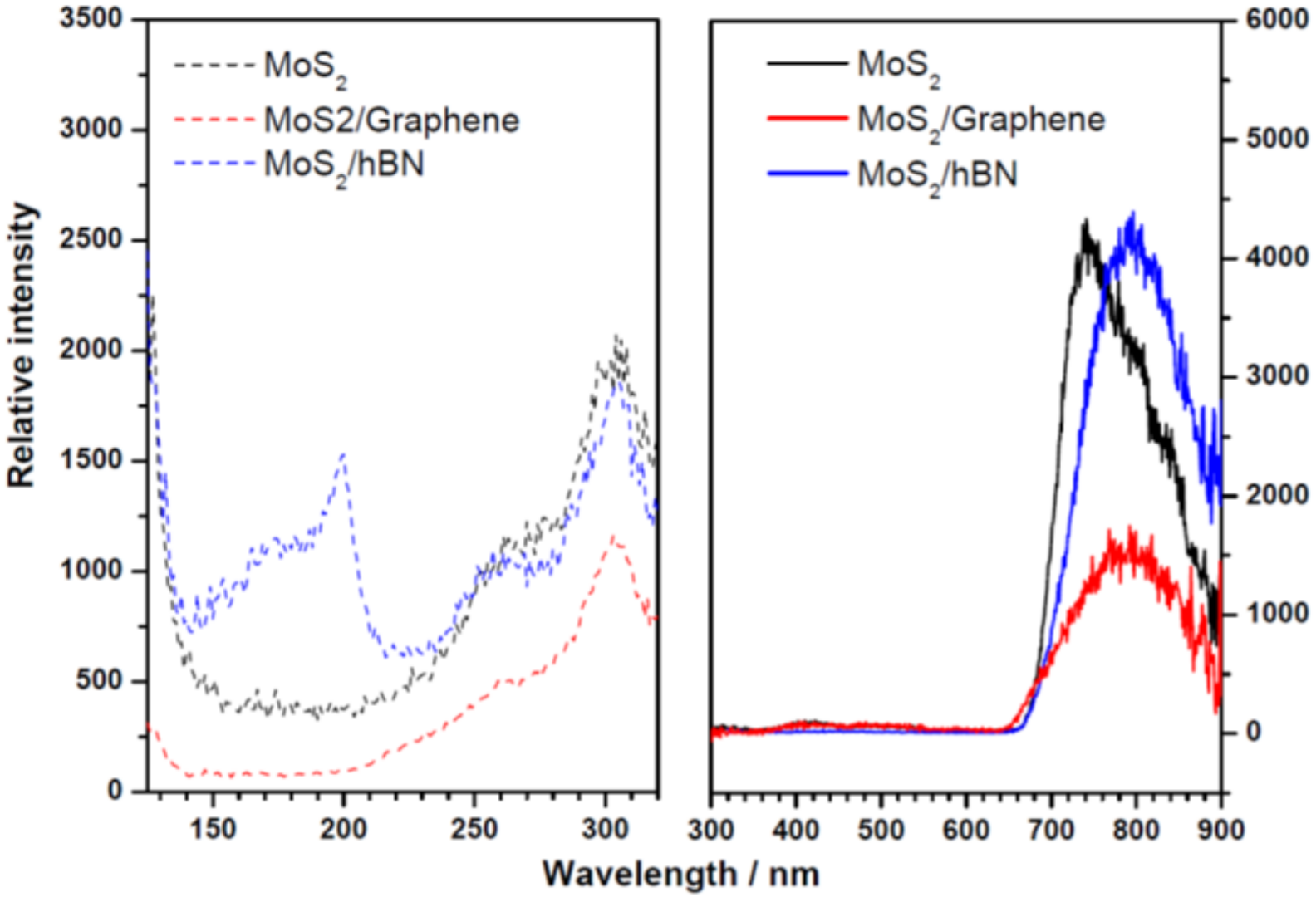
UV/VUV Absorption Spectra



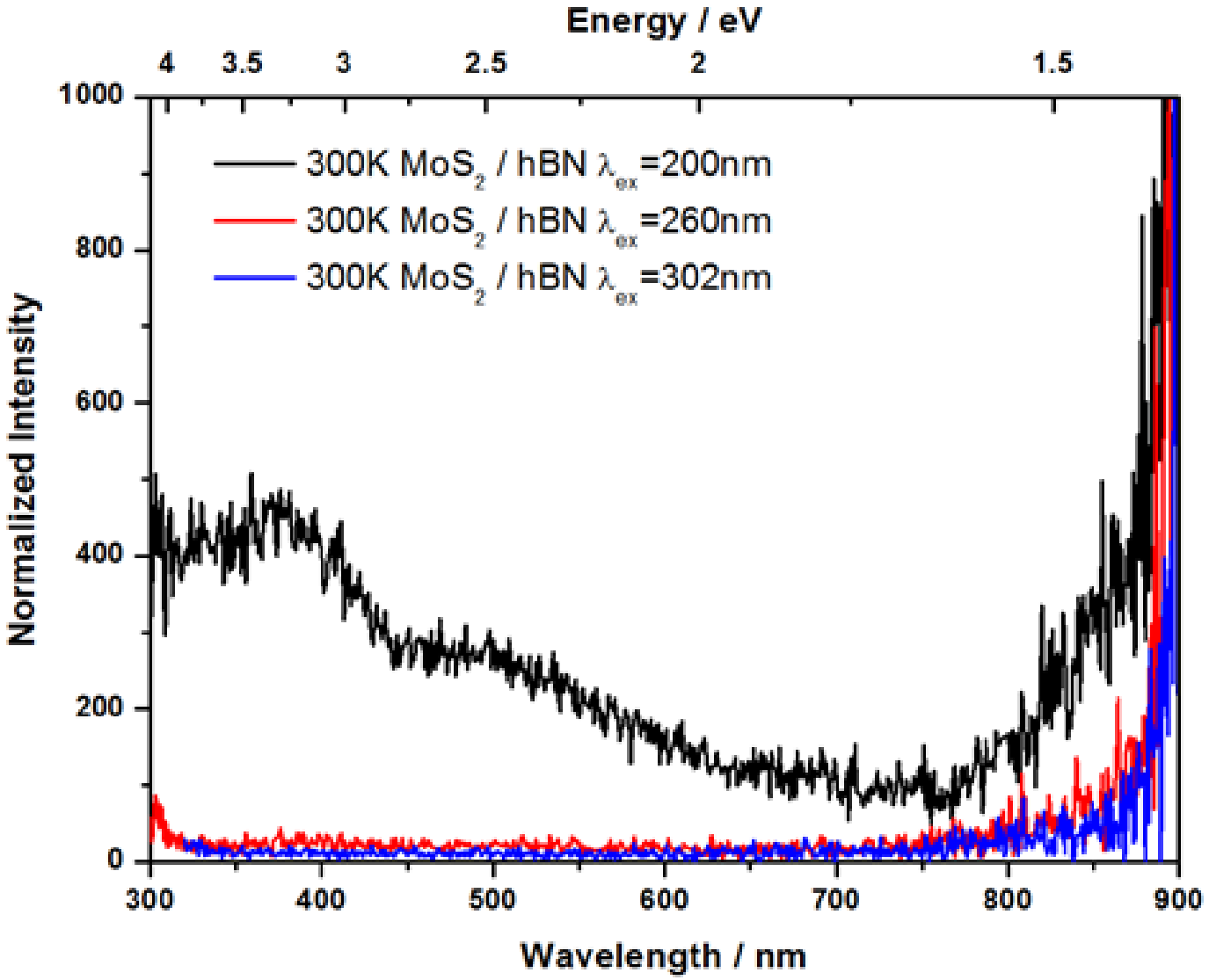
PL Spectra Excited with UV/vis @ RT



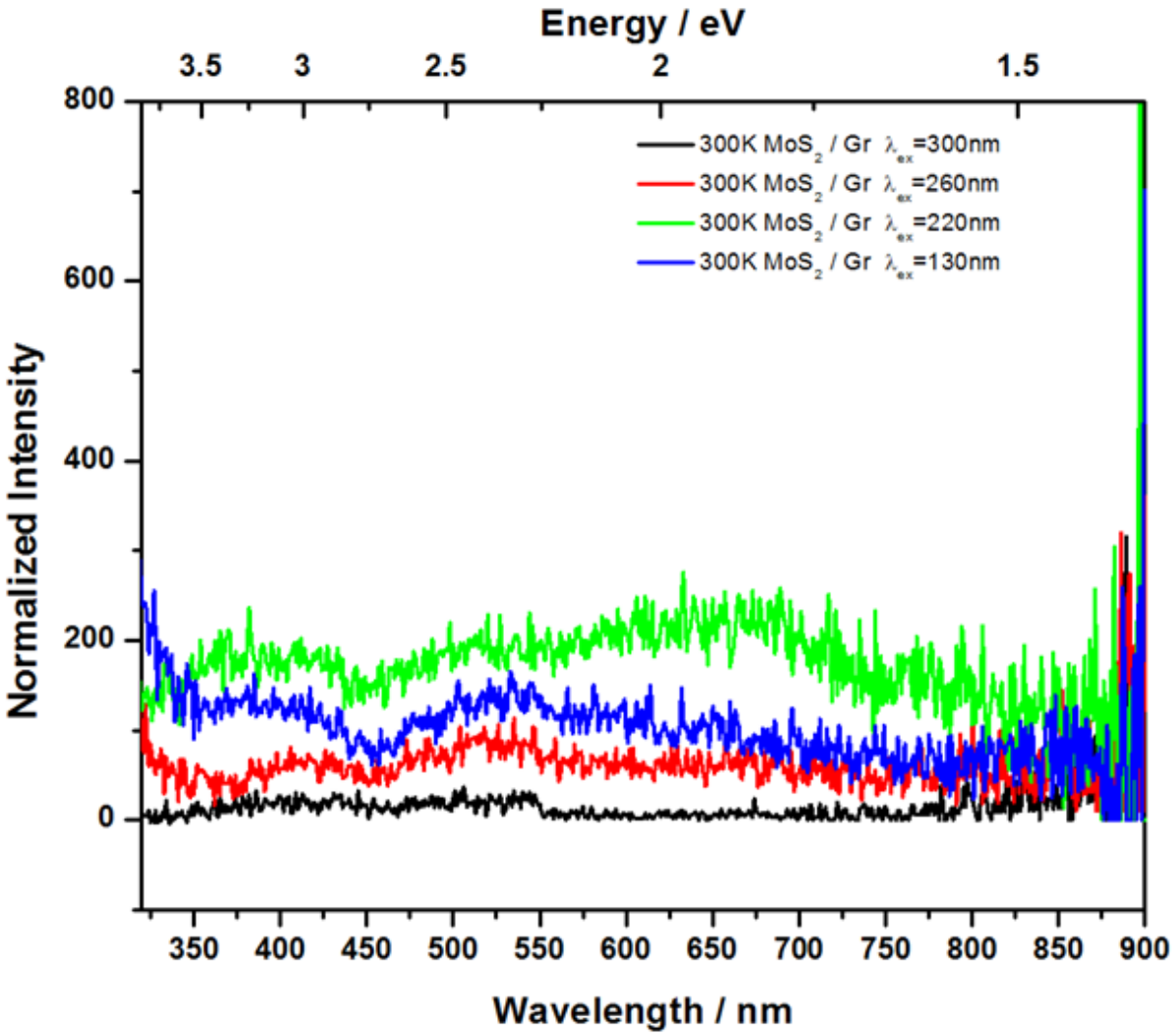
PL Spectra Excited with UV light @ 10 K



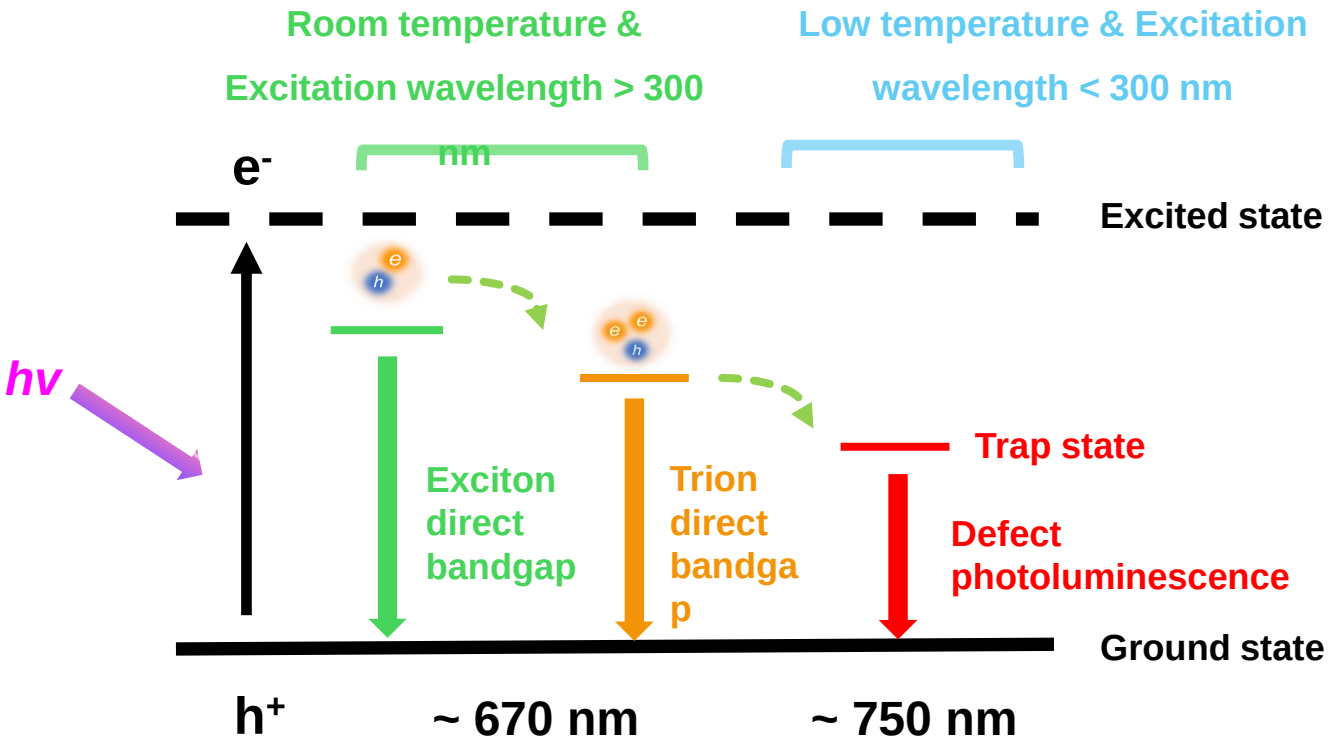
PL Spectra of MoS_2/hBN Excited with UV light @ RT : No A, B- excitonic emissions

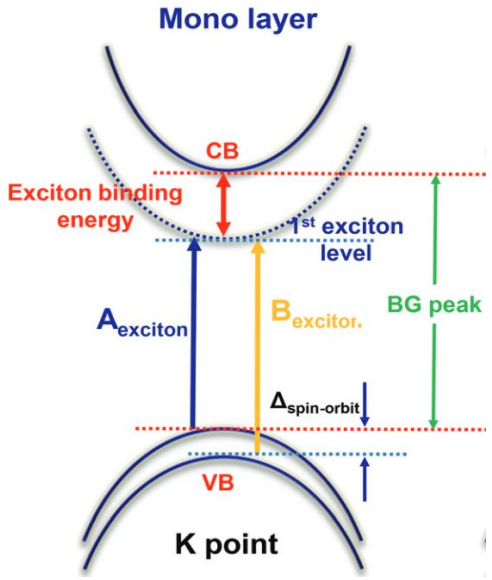


PL Spectra of MoS_2/Gr Excited with UV light @ RT : No A, B- excitonic emissions



Discussion – Part I





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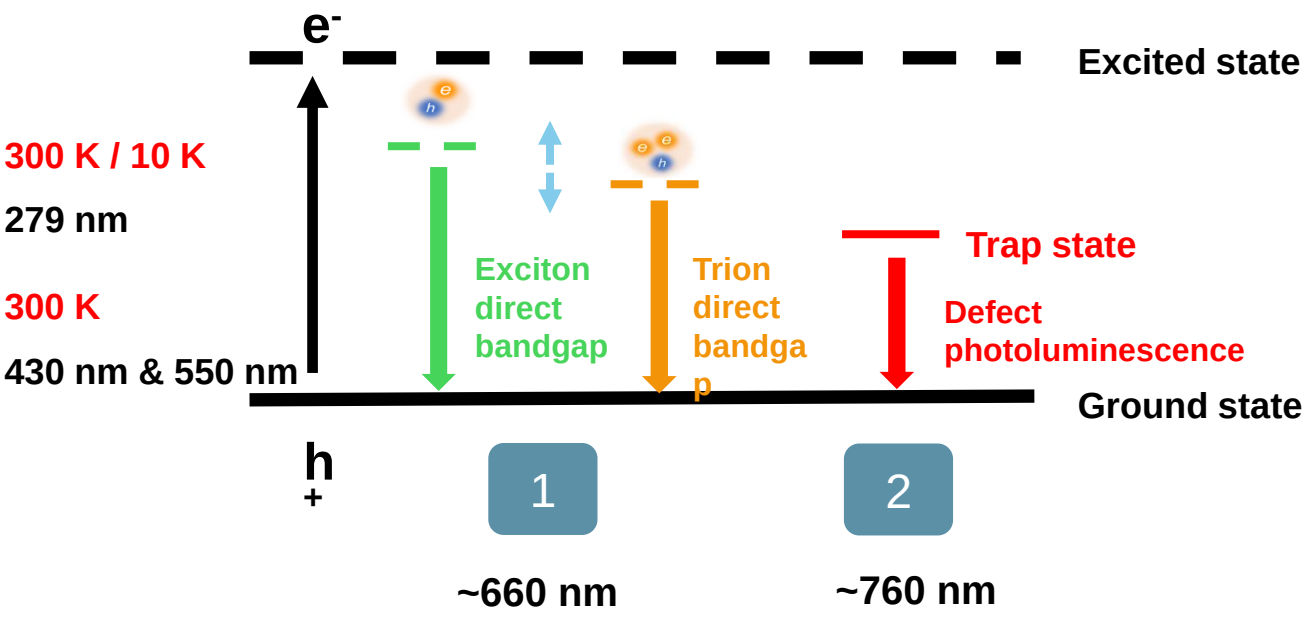
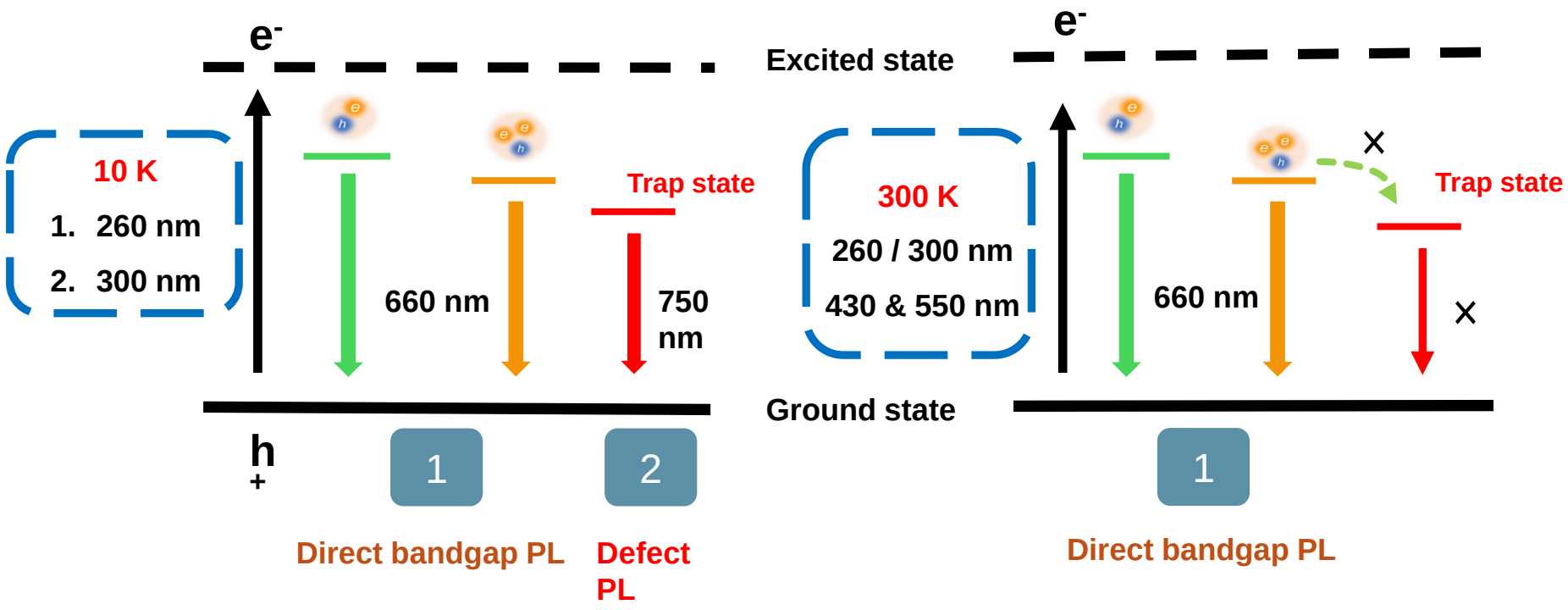
Discussion – Part II

➢ MoS_2 on Sapphire substrate



Discussion – Part II

- MoS_2 on Quartz substrate



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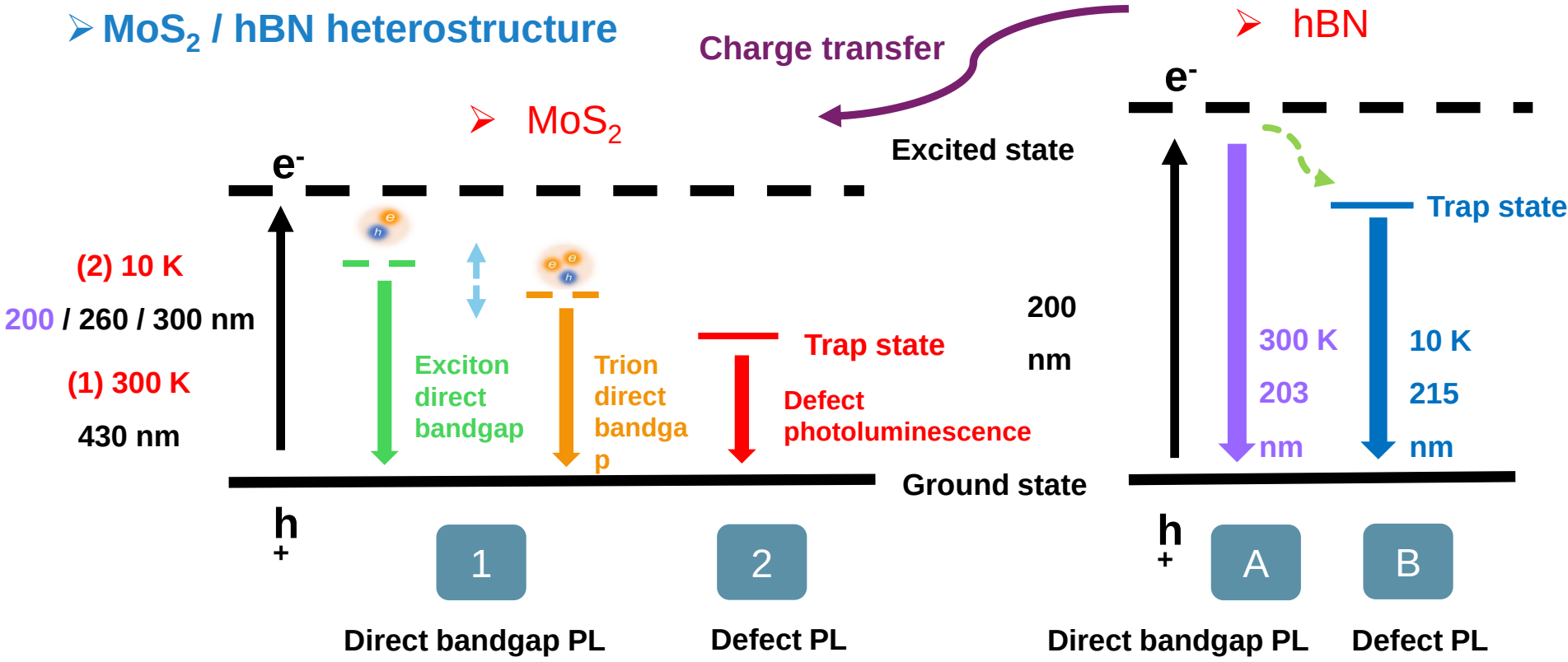
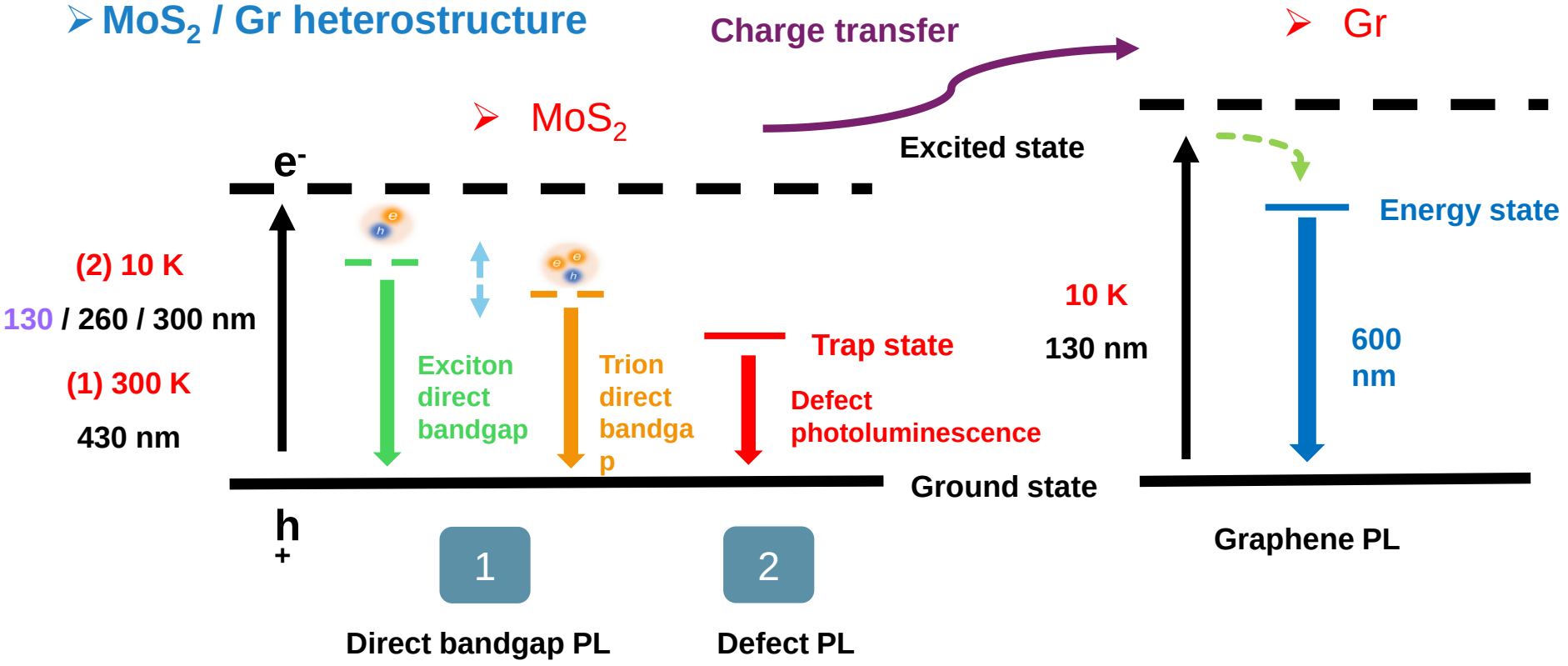
Discussion – Part III

➢ MoS_2 / hBN heterostructure



Discussion – Part III

- MoS_2 / Gr heterostructure



Conclusion

1. 新型光致發光通道的發現

單層 MoS_2 在可見光激發下只呈現典型的 A 激子發光（~660 nm）。然而，在深紫外（DUV, <300 nm）激發下，於低溫（~10 K）的 MoS_2/hBN 與 MoS_2/graphene 異質結構中，出現寬帶近紅外發光（750 – 900 nm）。

2. 界面能量轉移機制

hBN 層：在 ~200 nm 激發時，$\pi - \pi^*$ 過渡吸收能量可轉移至 MoS_2，觸發其寬帶發光。Graphene 層：在 ~260 nm 激發時，石墨烯的 π 電子吸收產生高能載子，部分可穿隧到 MoS_2 缺陷或局域態，進而產生紅外發光。

3. hBN 與 Graphene 的對比效應

hBN：絕緣性大能隙材料，避免界面電荷轉移，能有效保留並強化 MoS_2 的輻射復合。Graphene：導電性強，常在可見激發下淬熄 MoS_2 的發光，但在 DUV 激發時仍能經由熱載子注入 MoS_2 觸發紅外發光。整體而言，MoS_2/hBN 的發光較強，MoS_2/graphene 較弱。

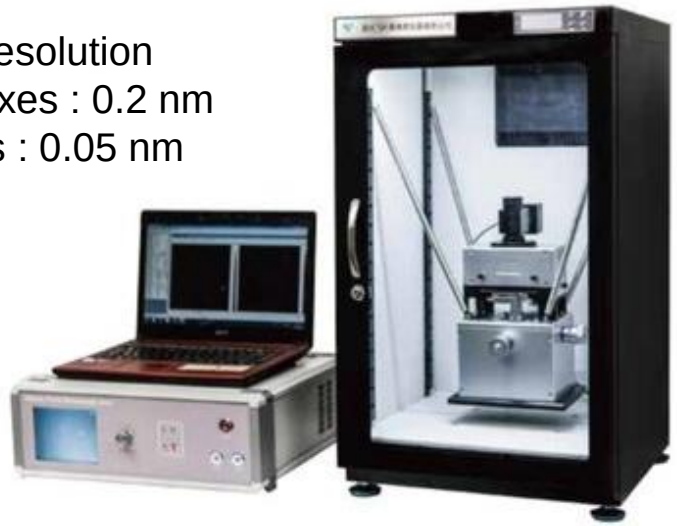
4. 科學與應用意涵

本研究證明了透過 異質結構設計與 DUV 光敏化，可開啟 MoS_2 原本無法展現的隱藏輻射通道。這提供了一種新策略來 調控 2D 材料的光學特性，對光電元件設計有潛在價值，例如：分光吸收與發光分離的裝置。

AFM and Raman system

Atomic Force Microscopy

Spatial resolution
- ✓ X/Y axes : 0.2 nm
- ✓ Z axis : 0.05 nm



Confocal micro-Raman spectroscopy system

- ✓ 532 nm laser source
- ✓ Liquid N_2-cooled CCD
- ✓ Resolution : 0.5 cm^{-1}

Commercial spectrofluorometer

Visible region information

- ✓ Light source: 150 W Xenon lamp
- ✓ Spectral coverage : 230-870 nm
- ✓ Scan mode: Absorption / photoluminescence
- ✓ Different filters