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micromachines MDPI

Precise Layer Separation of Two-Dimensional Nanomaterials for Scalable Optoelectronics

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Introduction

Biography

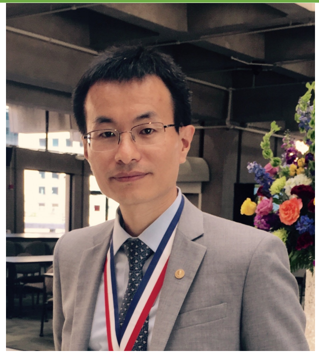
- BS and MS at Yonsei University (MSE)
- PhD at Northwestern University (MSE)
- Postdoc at UC Berkeley (Chemistry)
- Assistant Professor at SKKU (MSE)

Research Interests

- *Nanomaterials processing for optoelectronic devices*
- Nanomaterials: Carbon nanotubes, graphene-like 2D materials, perovskites
- Devices: Field effect transistor (FET), photodetector, light emitting diodes (LED)

Acknowledgement

Prof. Mark C. Hersam



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Hersam Group Members

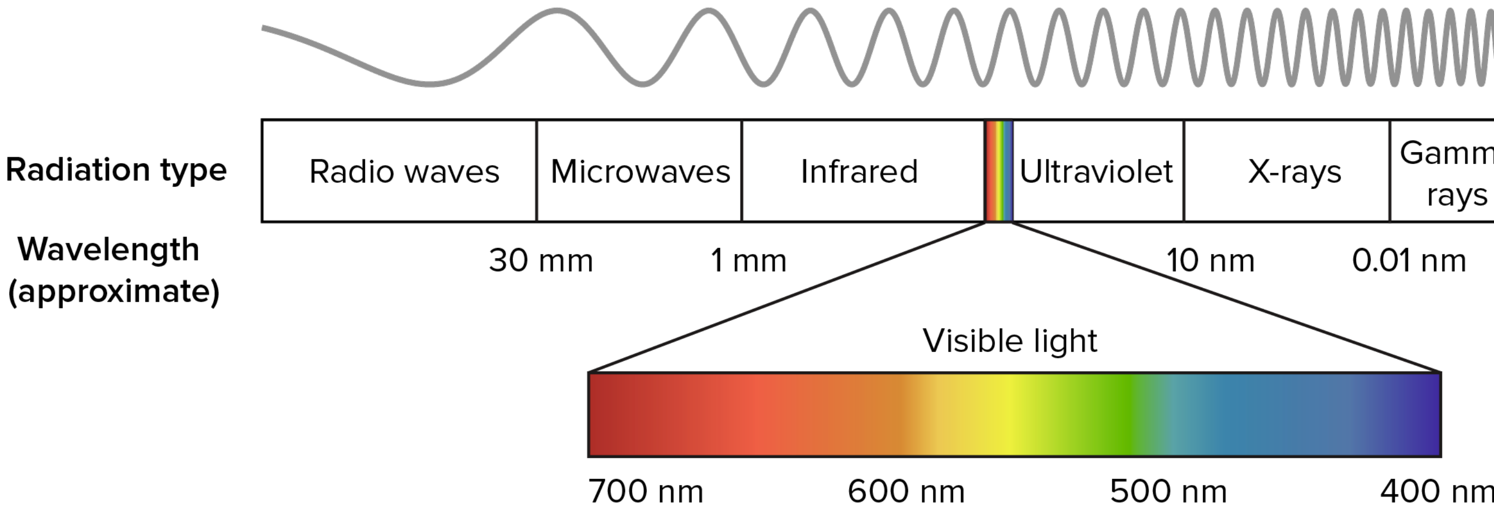
Yang Group Members

Hersam Group Members

Yang Group Members

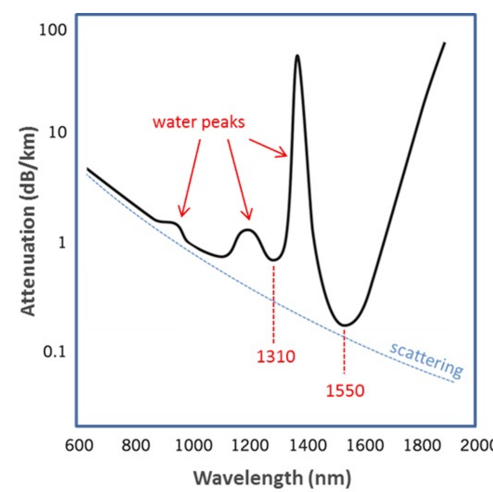
Wavelength of light

❖ Electromagnetic Spectrum



❖ Why 1550 nm?

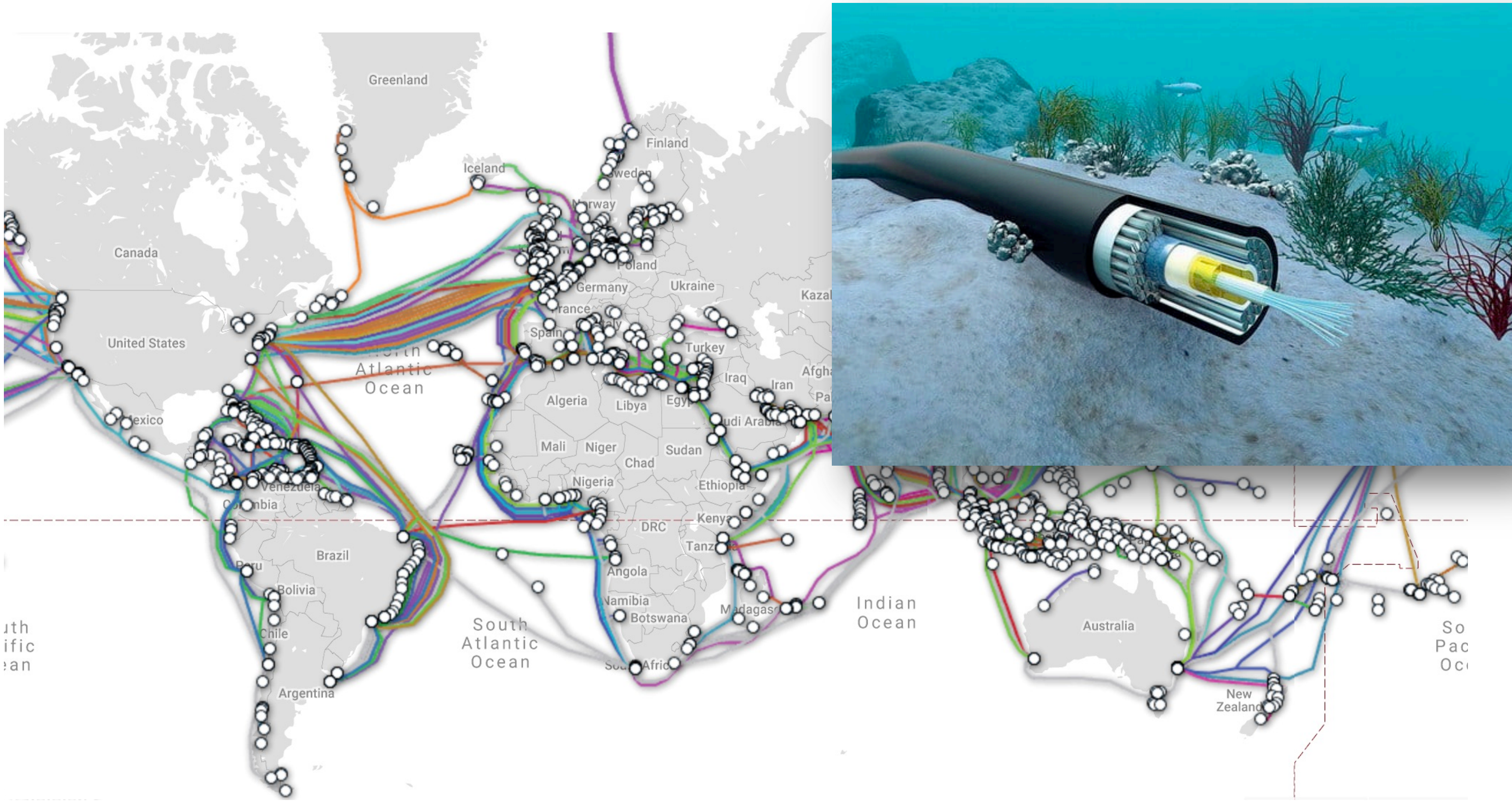
- Wavelength dependent optical loss in silica
- Minimum attenuation at 1550 nm
- "C-band" – 1530 nm to 1560 nm



Tamura, et al., *Optical Society of America* **Th5D.1** (2017)

Optical telecommunications

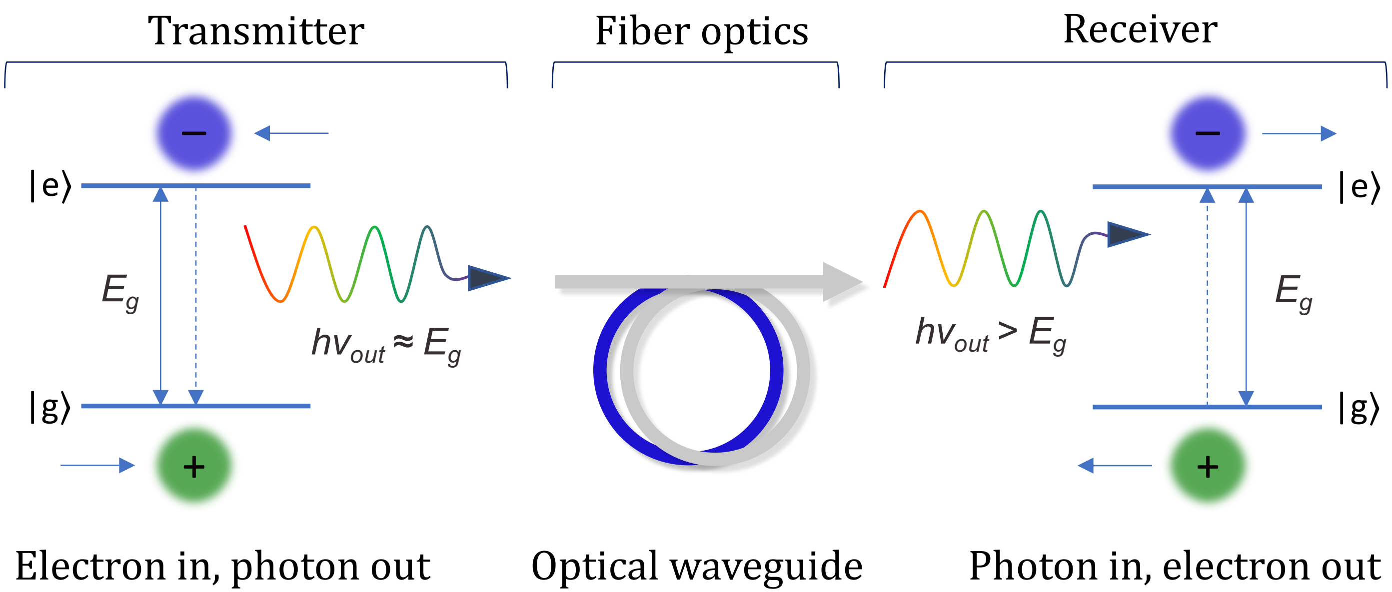
❖ Light delivers information through optical fiber



➢ The worldwide optical fiber network enables high-speed telecommunications

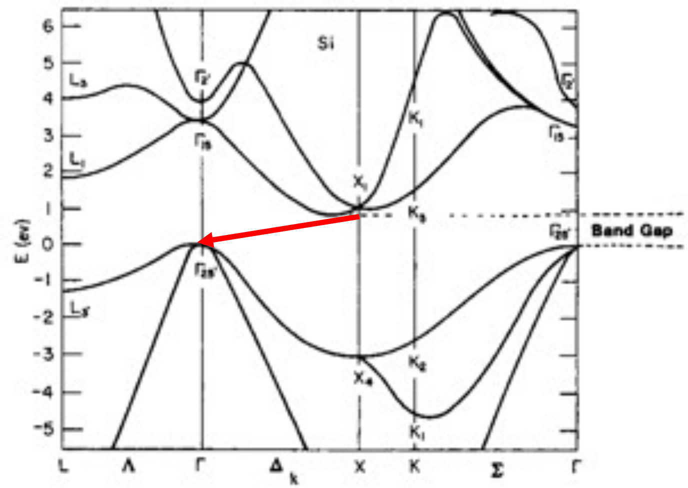
Optoelectronics

❖ Electron-photon interaction



Silicon for optoelectronics

❖ Optical properties of silicon



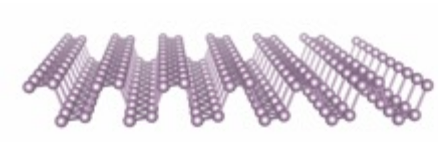
- Indirect bandgap – low photon-electron conversion efficiency
- Bandgap mismatch (1.12 eV at room temperature)
- *Requires gain medium*: direct bandgap III-V semiconductors (e.g., **InGaAs – 0.8 eV**)
- InGaAs – complicated process, ineffective production cost, fatal gases, etc.

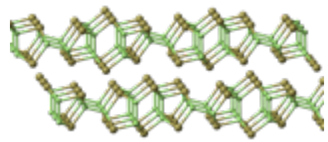
Kane, *J. Phys. Chem. Solids* **1**, 249 (1957)

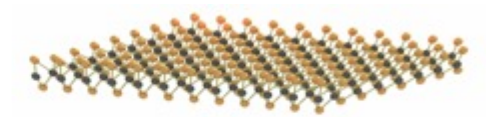
Two-dimensional semiconductors

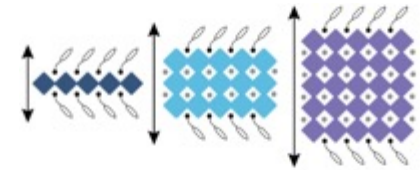
❖ Structure-dependent optical properties

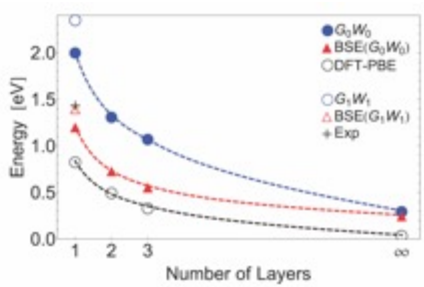
Phosphorene | III-VI compounds | TMDCs | 2D perovskites

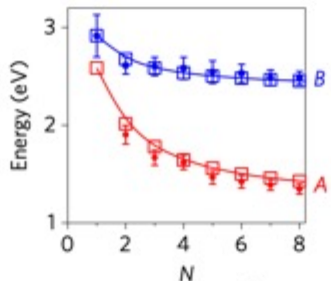


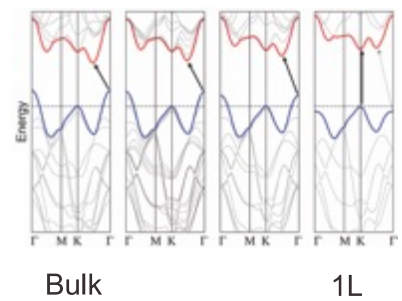


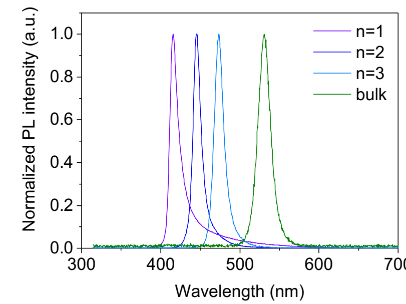










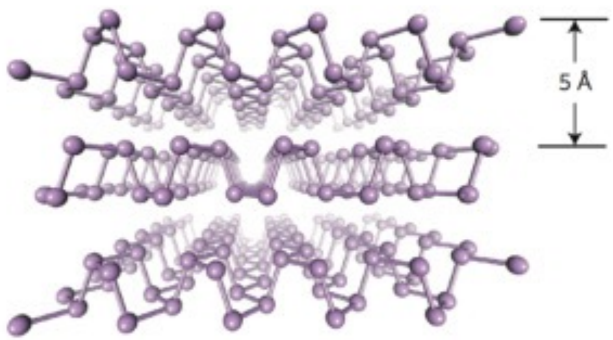


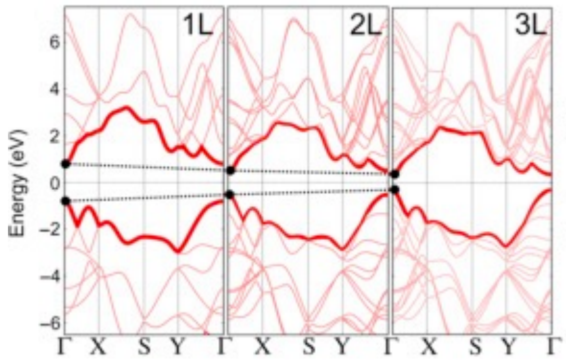
Materials	1L	2L	3L	Bulk
Phosphorene	1.88 eV (D)	1.3 eV (D)	**0.9 eV (D)**	0.3 eV (D)
III-VI (InSe)	2.6 eV (I)	1.9 eV (I)	1.7 eV (D)	1.3 eV (D)
TMDCs (MoS_2)	1.9 eV (D)	1.6 eV (I)	1.5 eV (I)	1.3 eV (I)
2D perovskites (CsPbBr)	3 eV (D)	2.7 eV (D)	2.5 eV (D)	2.3 eV (D)

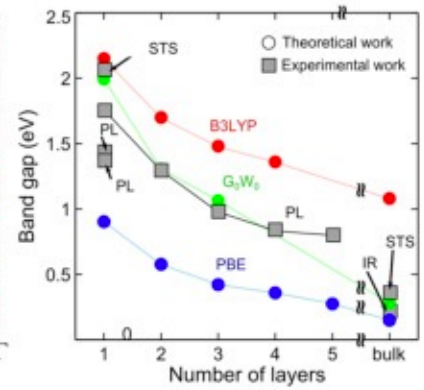
Kang et al., *Acc. Chem. Res.* **50**, 943 (2017); *Sci. Adv.* 6, eaay4045 (2020)

Black phosphorus

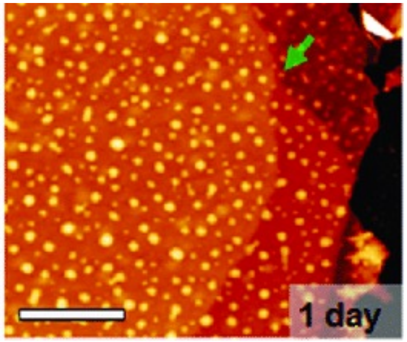
❖ Structure-dependent optical properties







- Ideal properties for optical communication
- 0.8 eV (3L - 5L), direct bandgap
- Except for 3L - 5L can be scattering sources
- Chemical degradation under ambient



- Goal: to produce large quantity 3L – 5L BP without chemical degradation

Kang et al., *Acc. Chem. Res.* **50**, 943 (2017)

Solution processing

❖ *Maximize* dispersion stability, *minimize* processing residue

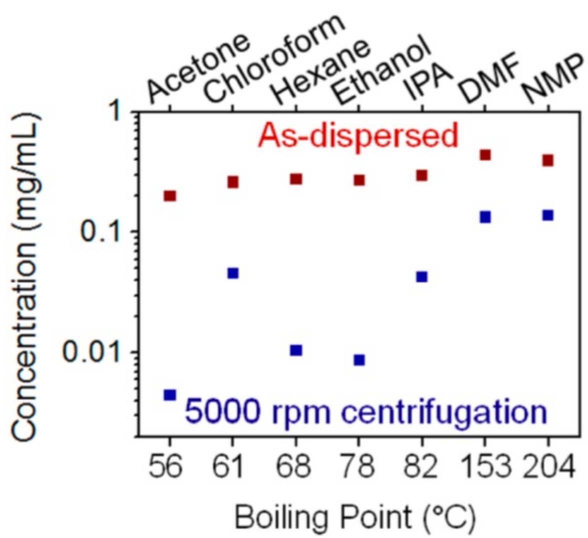
$$\frac{\Delta H_{mix}}{V} \approx \frac{2}{T_{2D}}\left(\sqrt{E_{S,solvent}} - \sqrt{E_{S,2D}}\right)^2 \phi_{2D}$$

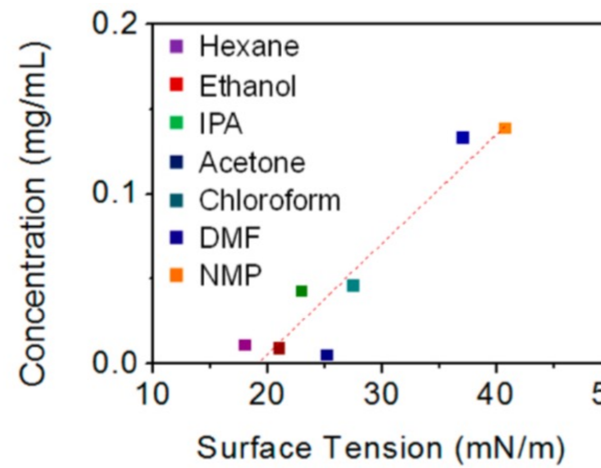
2D Materials

E_s (mJ/m^2) 10 20 30 40 50 60 70 80 90

Hexane, EtOH, IPA, acetone — NMP, DMF, CHP — Water

T_b (°C) 50 — 200





➢ Good to stabilize, but hard to remove residual solvent due to high boiling point

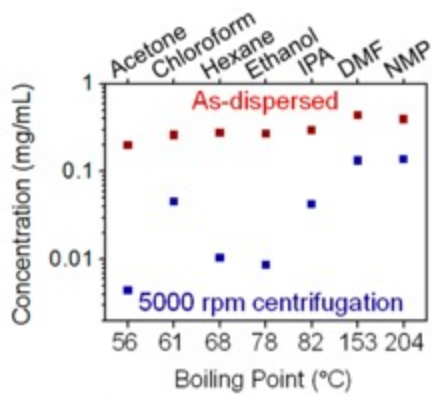
Kang et al., *ACS Nano* **9**, 3596 (2015)

Solution processing

❖ *Maximize* dispersion stability, *minimize* processing residue

(1) High T_b NMP (2015)

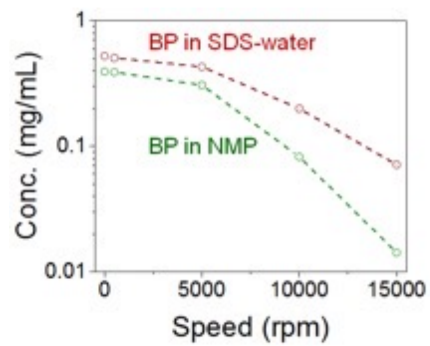
E_s matching



(2) Water + SDS (2016)

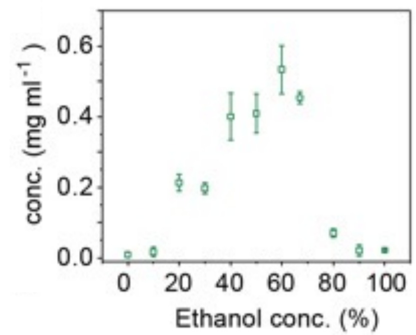
Amphiphilic surfactant

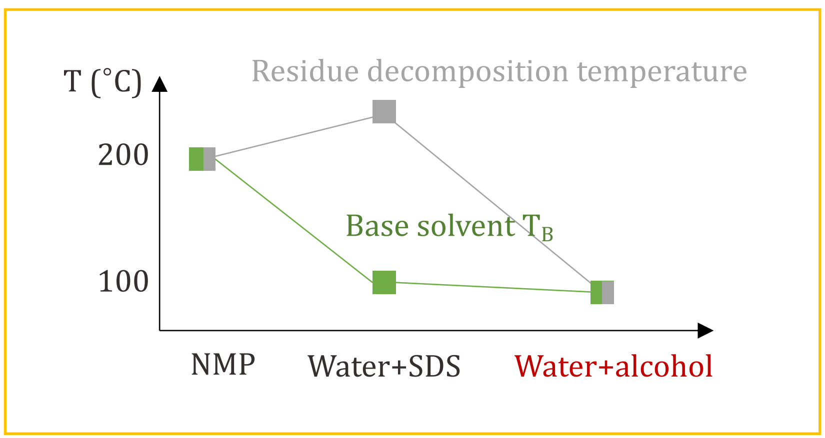
- Sodium dodecyl sulfate (SDS)



(3) Water + alcohol (2018)

High E_s + low E_s = Tunable E_s

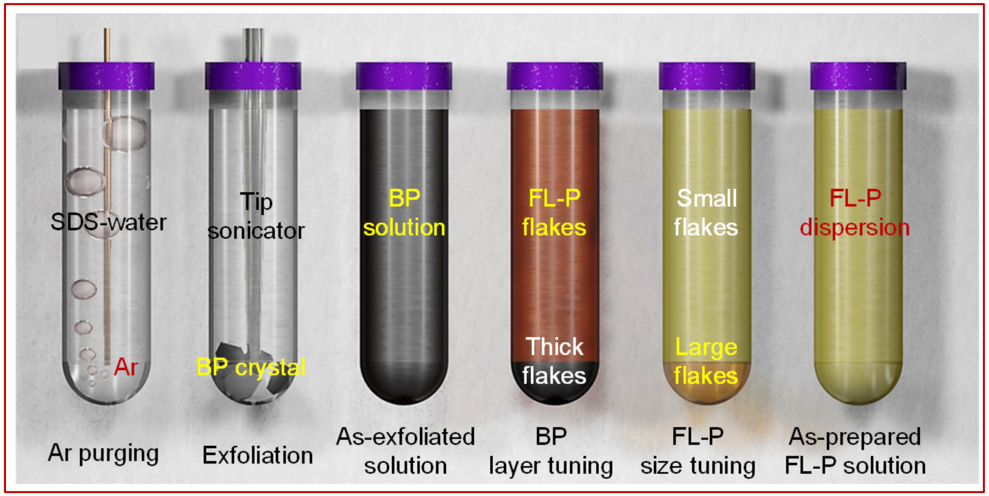


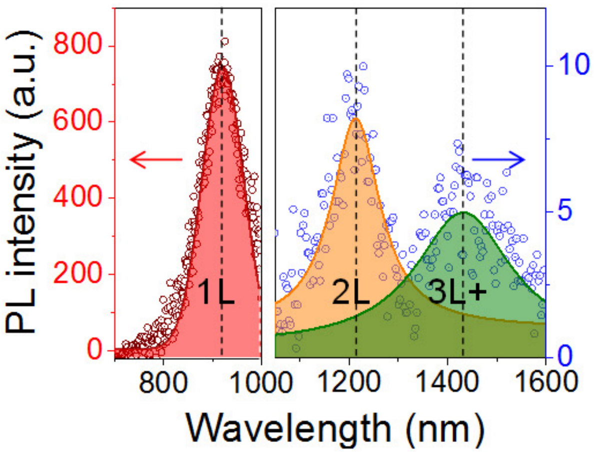


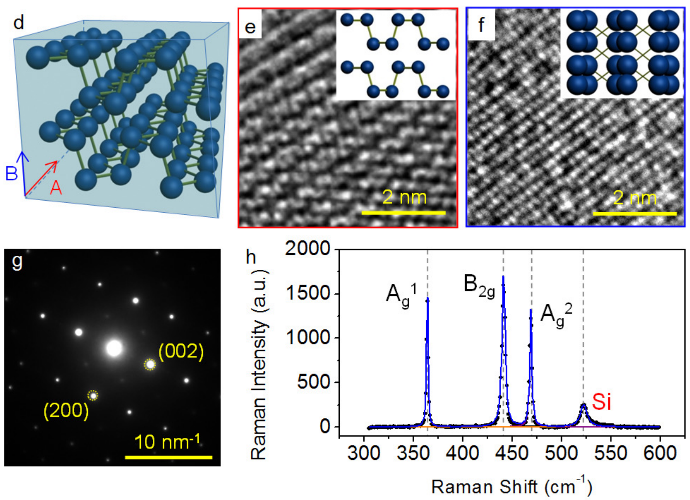
Kang et al., *ACS Nano* **9**, 3596 (2015); *PNAS* **113**, 11688 (2016); *Adv. Mater*. **30**, 1802990 (2018); *ACS Photonics* **5**, 3996 (2018)

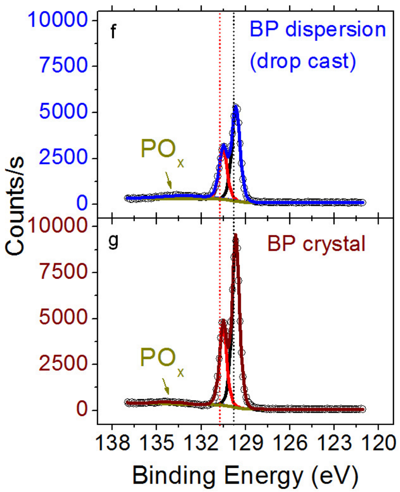
Oxidation during the process

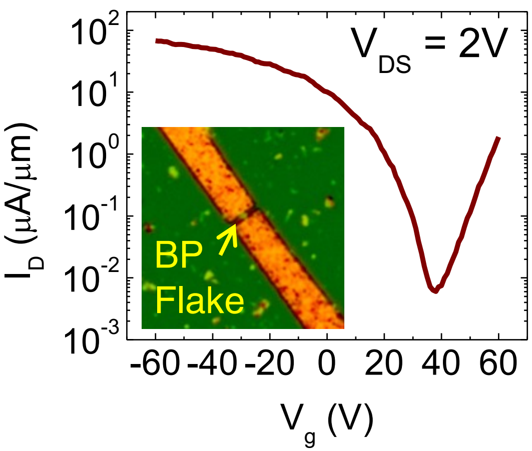
❖ *Minimize* oxygen exposure





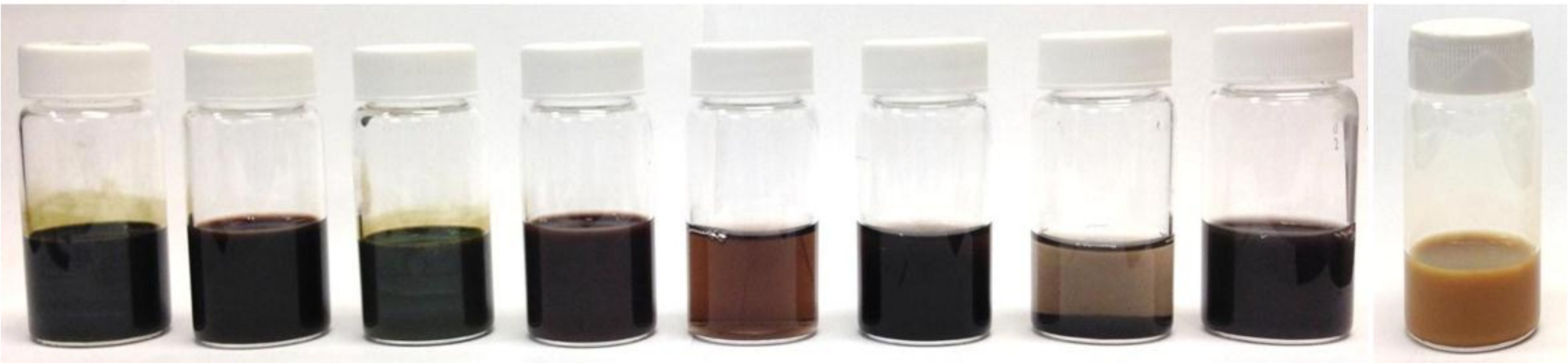






Solution processing

❖ *Maximize* dispersion stability, *minimize* processing residue



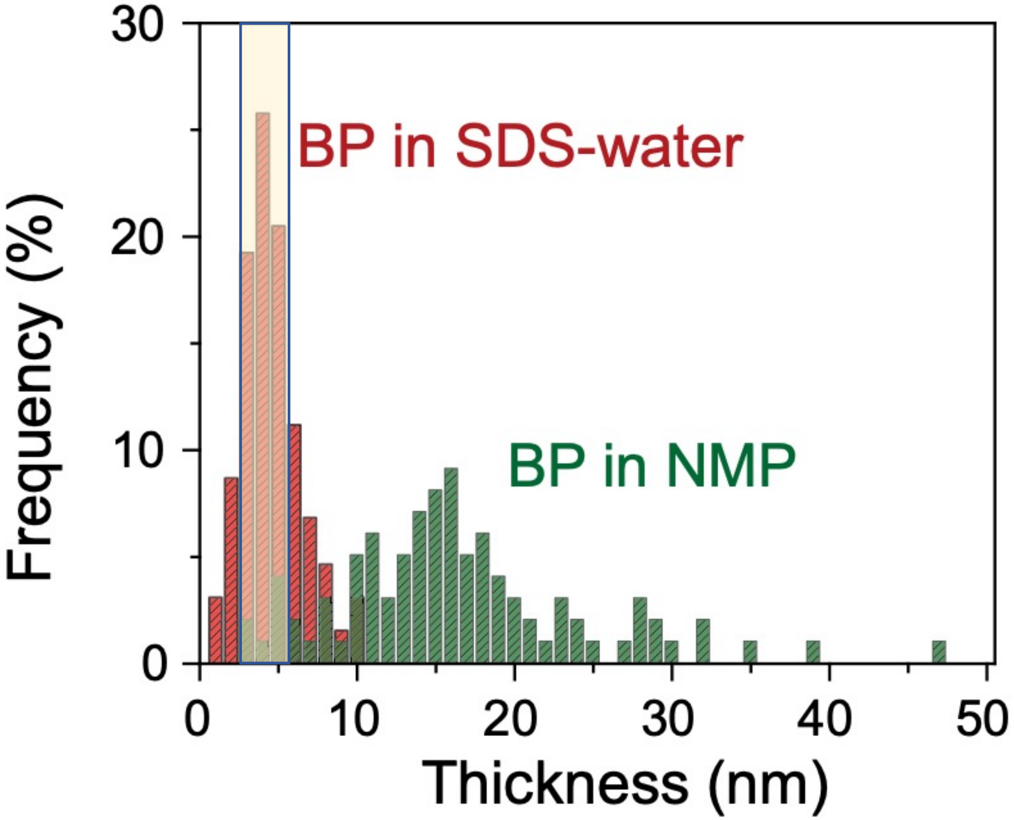
MoS_2 $MoSe_2$ WS_2 WSe_2 GaTe Bi_2Te_3 Bi_2O_2Se Bi_2Se_3 SnS_2

- Stable 2D semiconductor dispersions in largescale
- Co-solvent approach minimizes processing residues
- Monolayer to multilayer in each dispersion – *mixed layer-dependent properties*
- *How to extract targeted layer thickness in largescale?*

Kang et al., *ACS Nano* **9**, 3596 (2015); *PNAS* **113**, 11688 (2016); *Adv. Mater*. **30**, 1802990 (2018); *ACS Photonics* **5**, 3996 (2018)

Preferred sample thickness for telecommunications

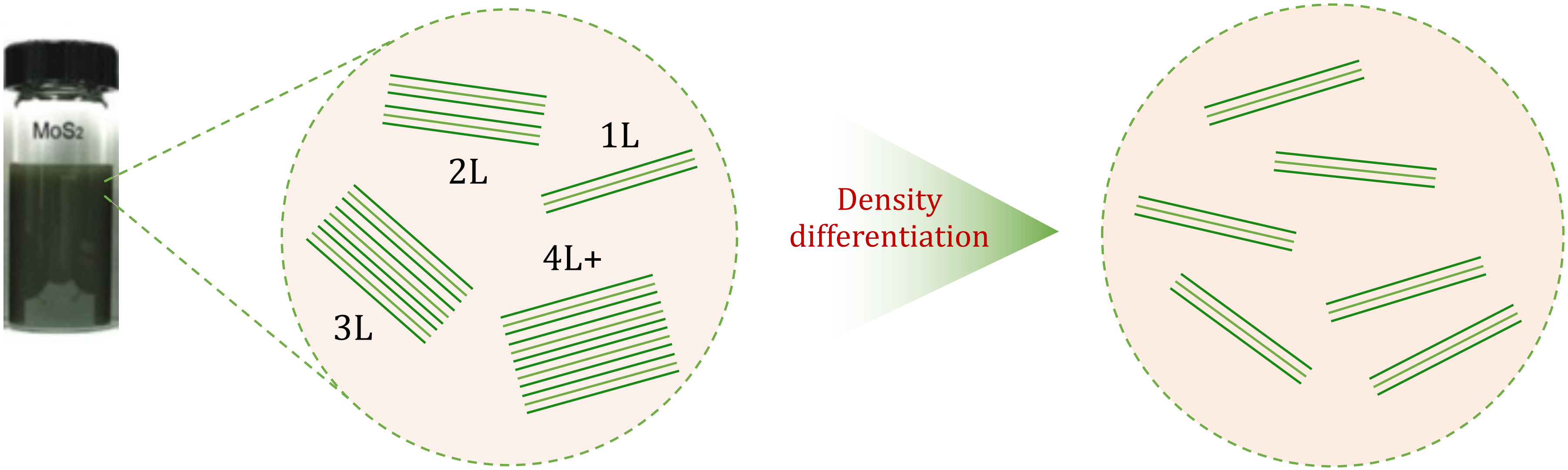
❖ Targeted thickness sorting from polydisperse solution



Kang et al., *PNAS* **113**, 11688 (2016)

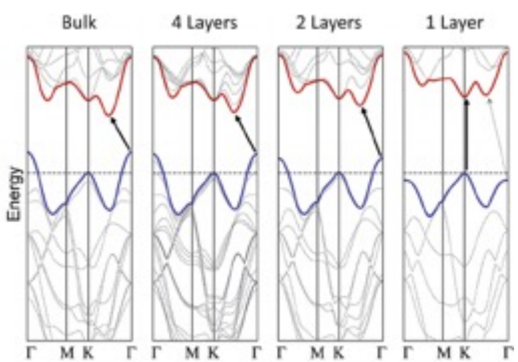
Layer sorting via density gradient ultracentrifugation

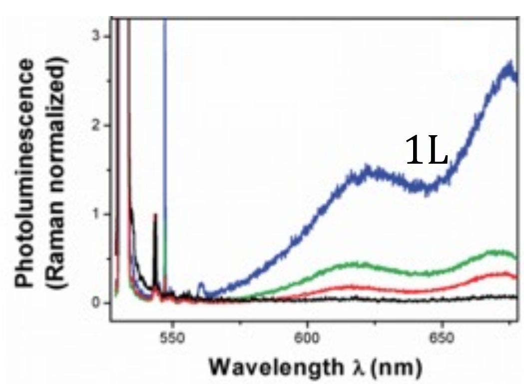
❖ Buoyant density differentiation



➢ Monodisperse MoS_2 dispersion (1L enrichment > 90%)

❖ Why monolayer?

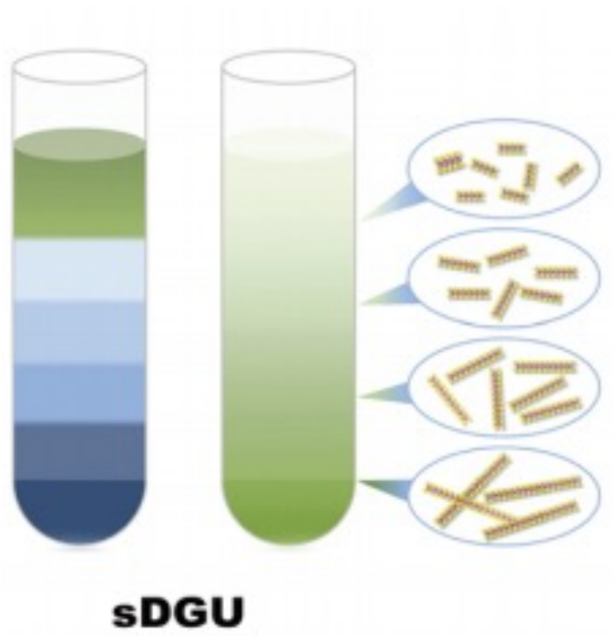




Kang et al., *Acc. Chem. Res.* **50**, 943 (2017); Splendiani et al., *Nano Lett.* **10**, 1271 (2010)

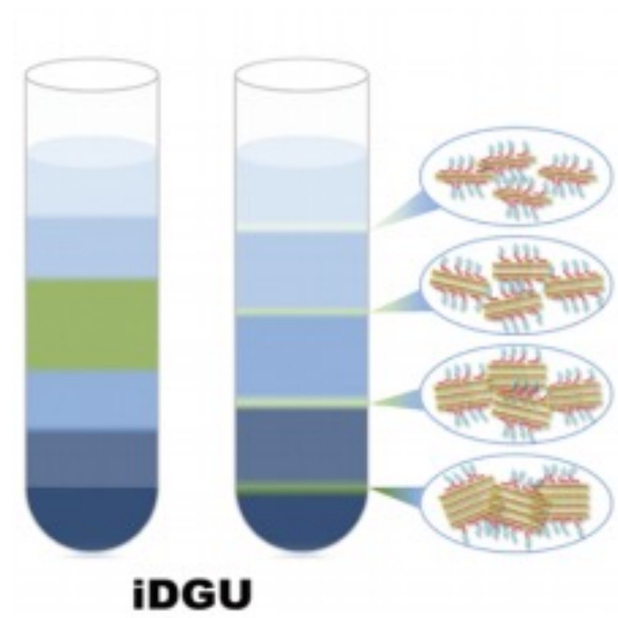
Density gradient ultracentrifugation (DGU)

❖ Sedimentation-based DGU



- Separation based on weight
- Lower speed
- Stop at proper time
- Not completely sedimented
- Suitable for size sorting

❖ Isopycnic DGU

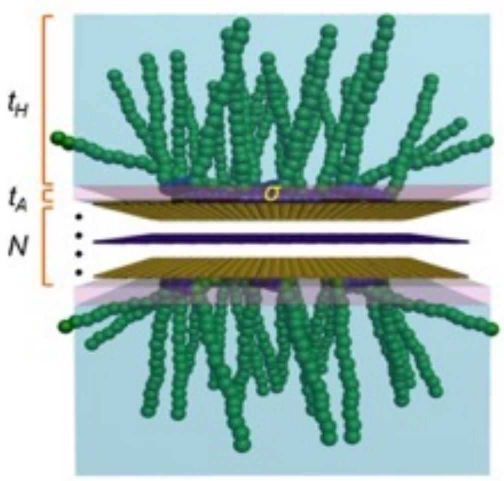


- Separation based on density
- High speed
- Long running time
- Completely sedimented
- Suitable for layer sorting

Introduction to Practical Biochemistry (2013); Hu, Kang et al., *Chem. Soc. Rev.* **47**, 3265 (2018)

Density gradient ultracentrifugation (DGU)

❖ Buoyant density of 2D-surfactant composite



$$\rho(N) = \frac{\rho_S N + 2m_{surf}\sigma + 2\rho_{H_2O}t_H}{(N+1)t_{MoS_2} + 2t_A + 2t_H}$$

ρ_s = sheet density

N = number of layers

m_{sc} = surfactant mass

σ = packing density

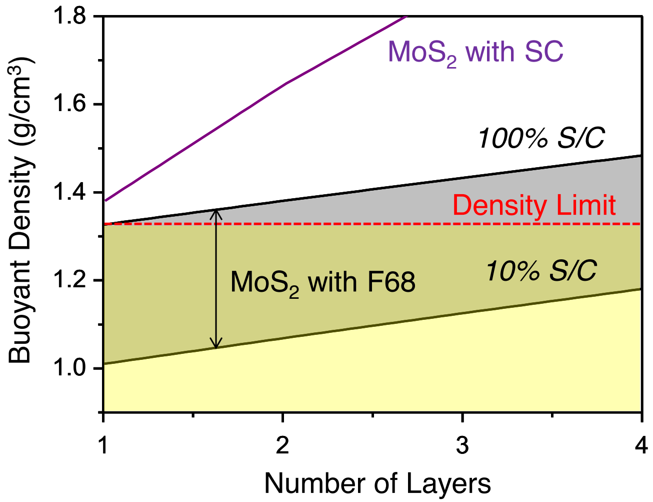
ρ_{H2O} = water density

t_H = hydration layer thickness

t_{MoS2} = MoS_2 thickness

t_A = anhydrous layer thickness

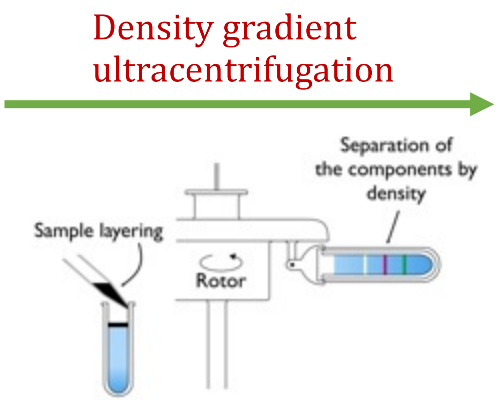
❖ Layer-dependent buoyant density

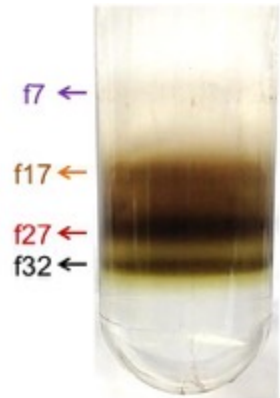


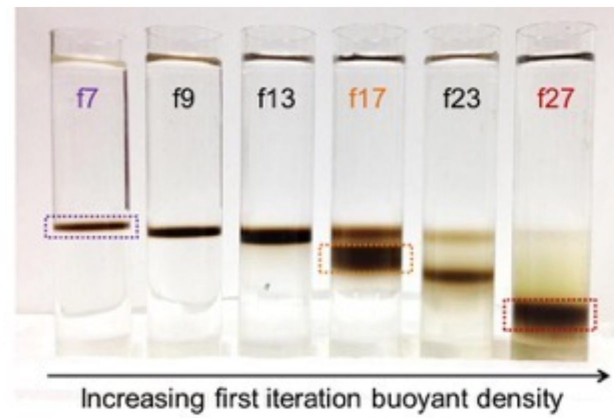
Kang et al., *Nat. Commun.* **5**, 5478 (2014); *Acc. Chem. Res.* **50**, 943 (2017)

Density gradient ultracentrifugation (DGU)

❖ MoS_2 layer separation







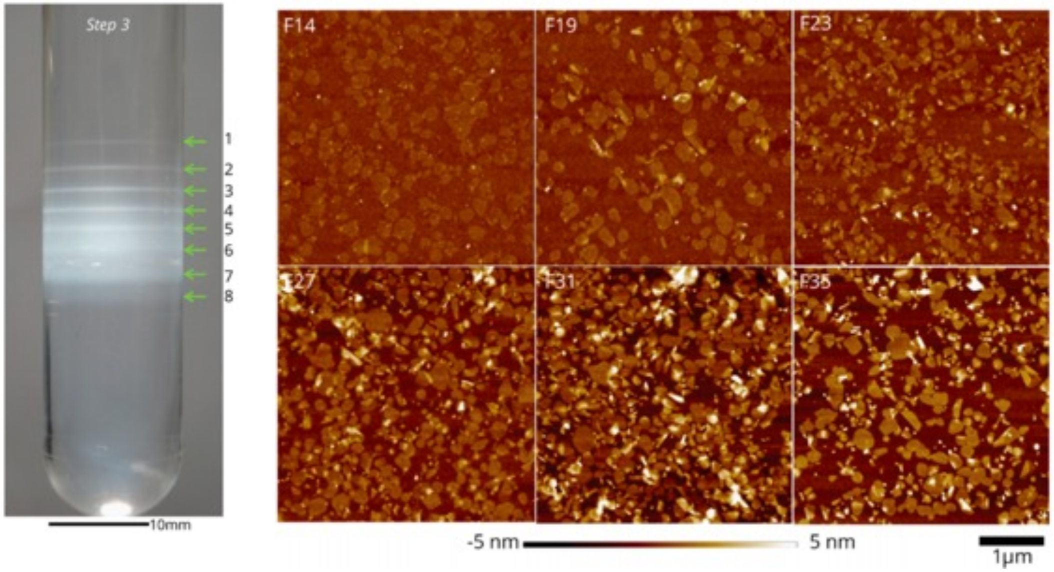
- Layer separation based on the buoyant density via DGU
- f7 – 90% 1L enriched (strong photoluminescence emission)

Kang et al., *Nat. Commun.* **5**, 5478 (2014); *Acc. Chem. Res.* **50**, 943 (2017)

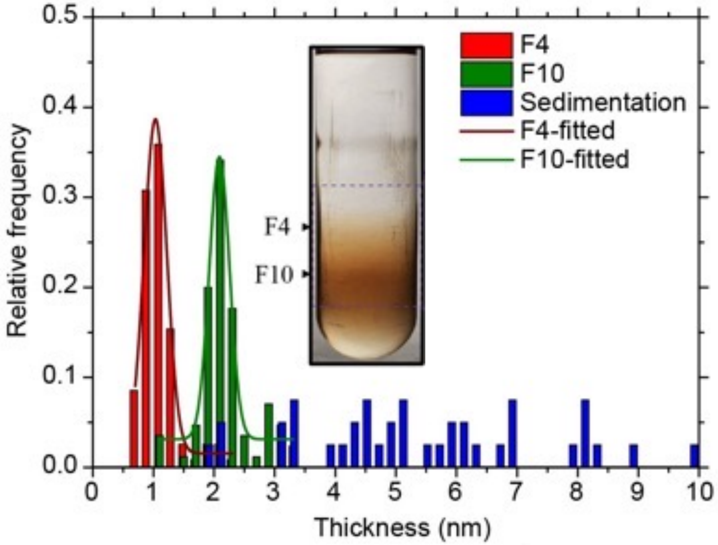
Density gradient ultracentrifugation (DGU)

❖ Other examples

Insulating hexagonal boron nitride (h-BN)



Heaviest TMDCs (ReS_2)



- ➢ Layer separation based on the buoyant density via DGU
- ➢ Graphene (metal), hexagonal boron nitride (insulator), transition metal dichalcogenides (semiconductors) including MoS_2, WS_2, $MoSe_2$, WSe_2, and ReS_2
- ➢ Enabling layer-dependent studies/uniform thin-film formation in largescale

Kang et al., *Nat. Commun.* **5**, 5478 (2014); *Nano Lett.* **15**, 7029 (2015); *Nano Lett.* **16**, 7216 (2016); *Acc. Chem. Res.* **50**, 943 (2017)

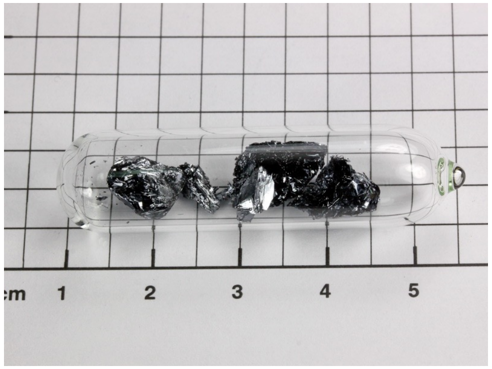
Processing BP for NIR light generator

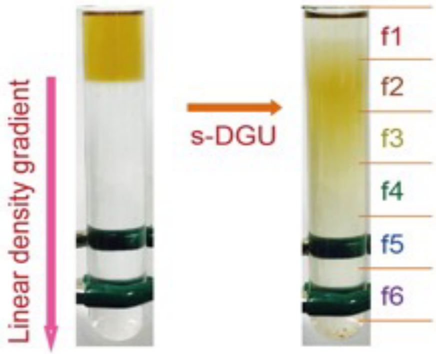
❖ Mass production of targeted material

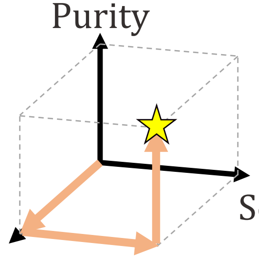
Material choice
- Black phosphorus crystal

Materials synthesis
- Oxygen-free processing

Materials processing
- High quality/purity







Kang et al., *Nat. Commun.* **5**, 5478 (2014); *Nano Lett.* **15**, 7029 (2015); *Nano Lett.* **16**, 7216 (2016); *Acc. Chem. Res.* **50**, 943 (2017)

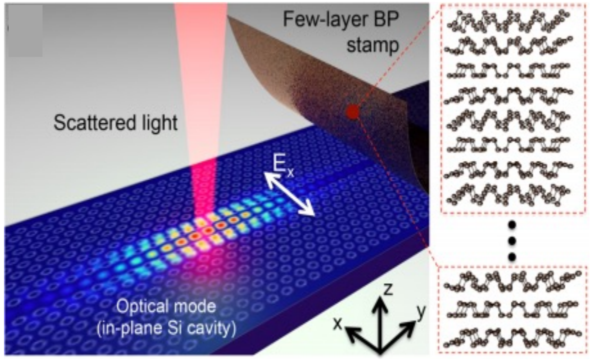
Processing BP for NIR light generator

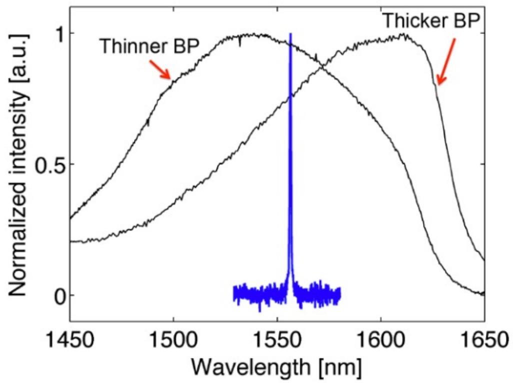
❖ Transfer and device evaluation

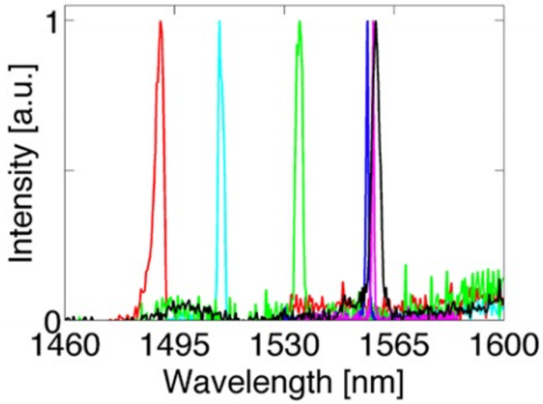
Dry transfer
- Si nanocavity

Device evaluation
- Emission at NIR wavelength

Tunability
- Tunable wavelength



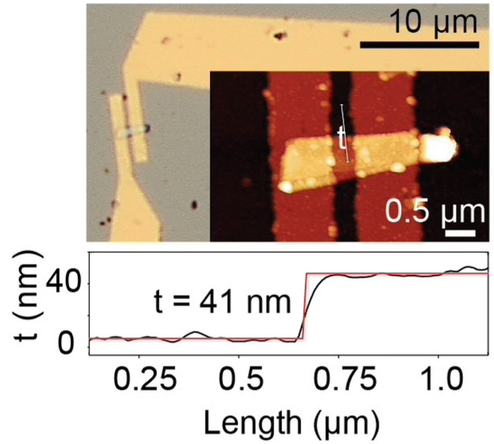


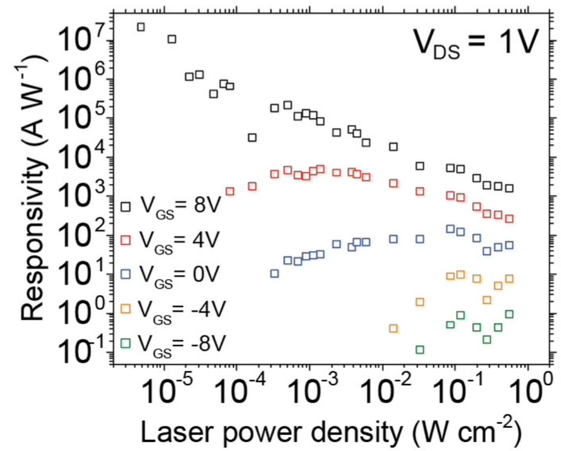


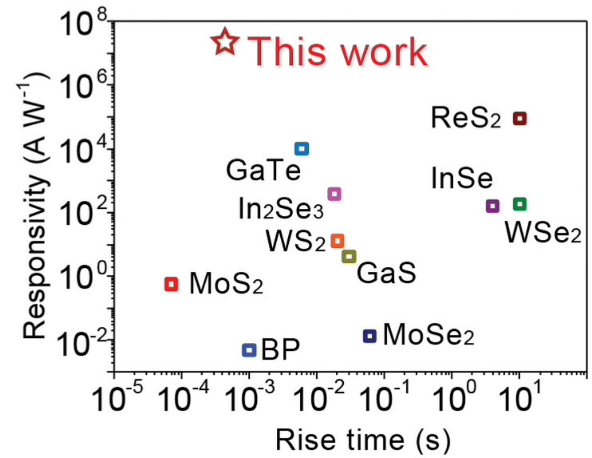
- ➢ Strong light amplification in the ideal range of NIR applications
- ➢ Tunable wavelength based on the Si nanocavity structure
- ➢ **Optically pumped light generation**

Husko (ANL) & Kang et al., *Nano Lett.* **18**, 6515 (2018)

High-performance phototransistor





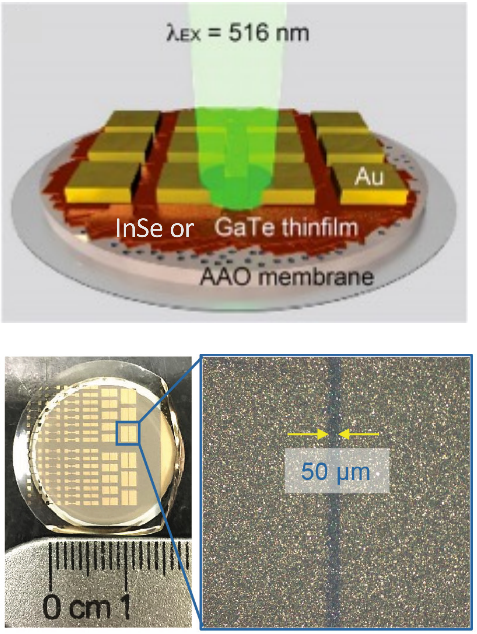


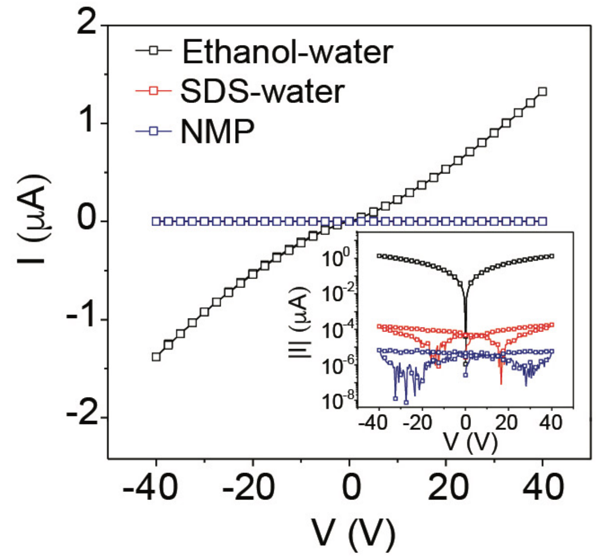
- Residue-free, solution-processed InSe-based phototransistor.
- The device exhibits the *highest* photoresponsivity (>10^7 A/W) and among the *fastest* photoresponse time.
- FLATFORM formation for scaling up.

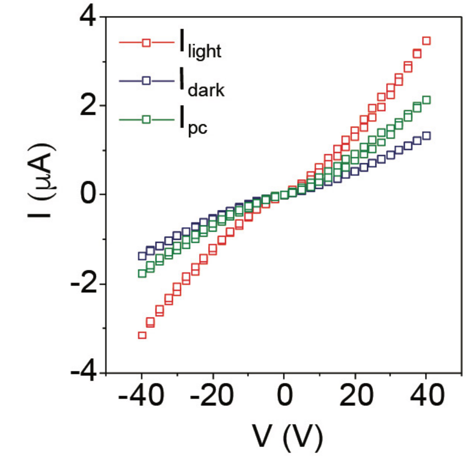
Kang et al., *Adv. Mater*. **30**, 1802990 (2018)

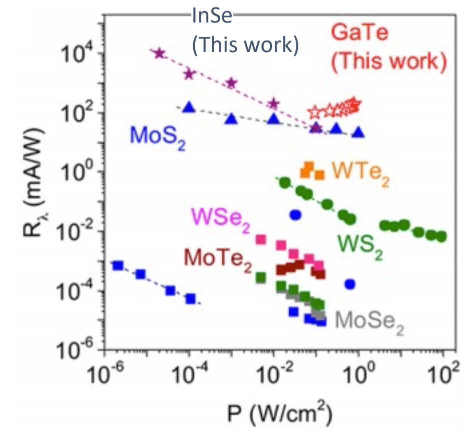
Thin-film photodetector

"III-VI FLATFORM"





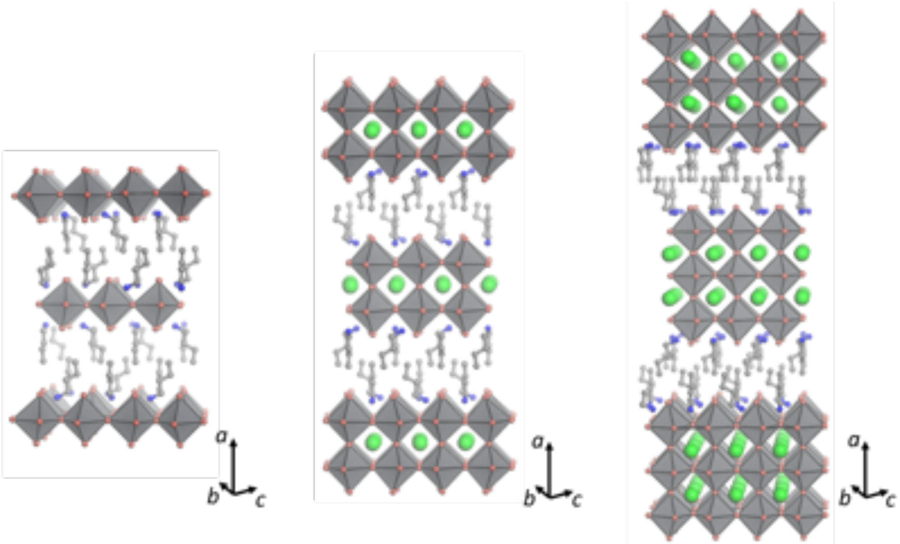




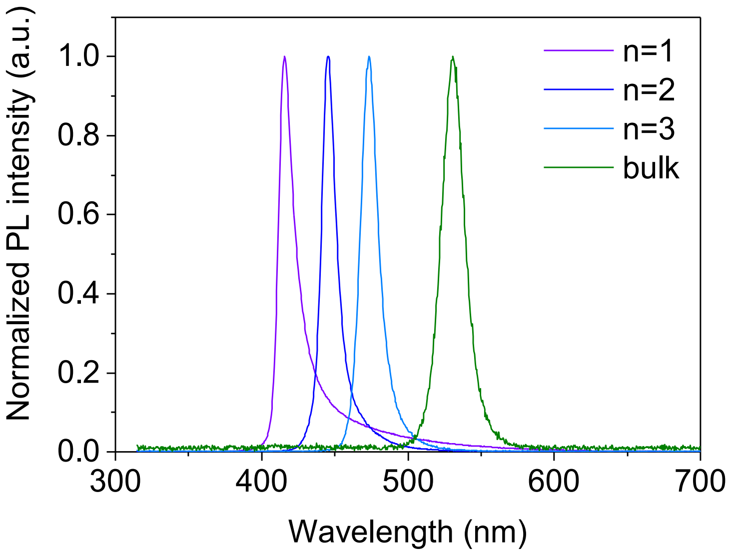
- III-VI FLATFORM-based photodetector
- Co-solvent process enables high-quality thin-film (4 orders improved electrical conductivity)
- *Best* thin-film based photoresponsivity

Electrically-pumped light generation

❖ Single-crystalline Ruddlesden-Popper phase perovskites



n=1: 2.94 eV n=2: 2.73 eV n=3: 2.54 eV

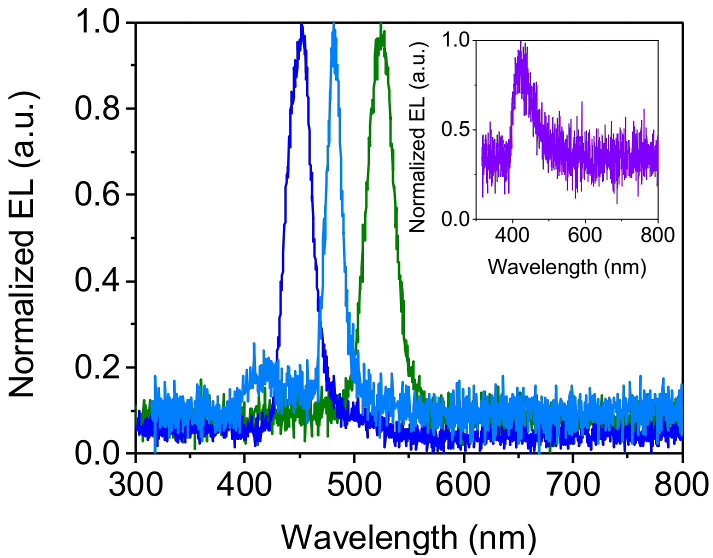


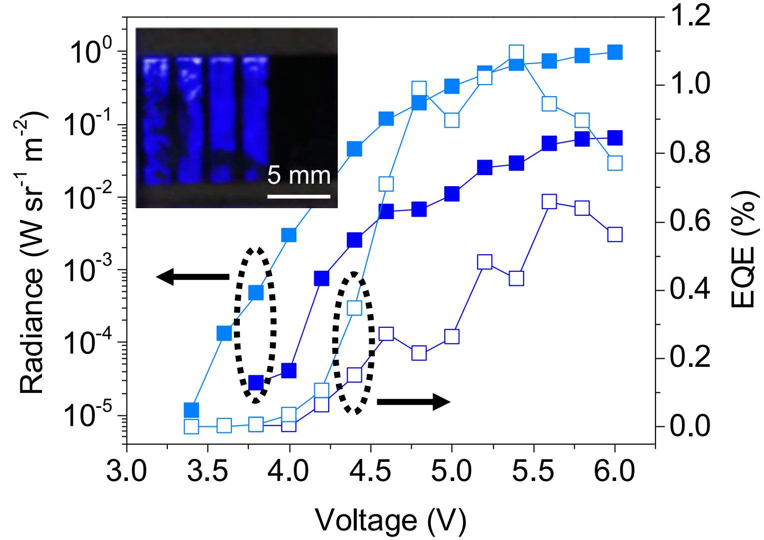
➢ Ruddlesden-Popper phase quasi-2D layered perovskite– (BA)CsPbBr

➢ Layer-dependent optical properties from violet, blue, to skyblue emission

Electrically-pumped light generation

❖ LED emitting intrinsic bandgap wavelengths





- Direct exfoliation of RP perovskite unlike the conventional spin-coating based approach
- Avoiding the energy funneling behavior (Green emission from blue emitters)
- Electrically-pumped bandgap wavelength emission
- **Applicable for electrically-driven BP-based NIR emitter (ongoing)**

Summary

- Scalable production of electronically- and optically-active nanomaterials via solution-based processing.
- Deoxygenated processing minimizes chemical reaction during the solution-based processing
- Density gradient ultracentrifugation originated from biochemistry allows to maximize monodispersity of nanomaterials in structure.
- Solution-processed high-purity semiconducting materials directly applied to photonic device applications.

Thank you for your attention

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