NC STATE UNIVERSITY

EFRC TUTORIAL

Part II:

Excitons in 2D TMDC Materials

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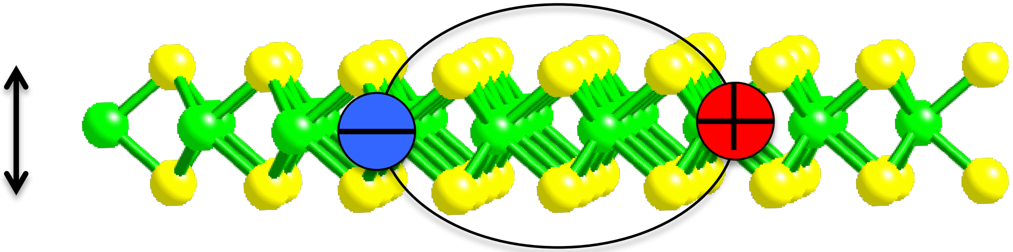
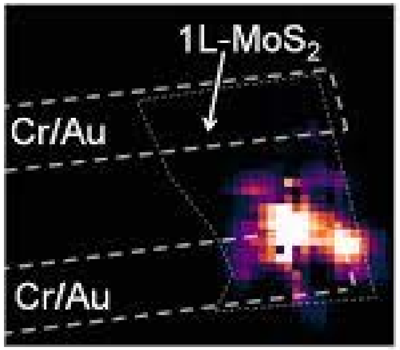
Temple University, July 29. 2016

2D TMDC Materials : A Remarkable Excitonic System

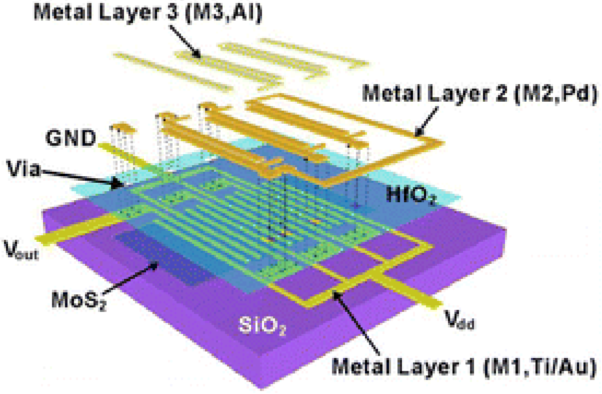
0.62 nm



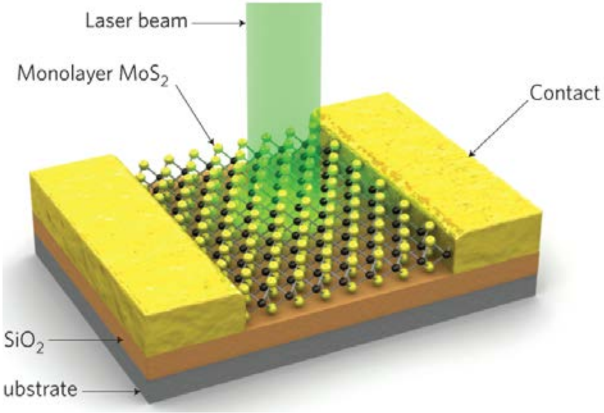
LEDs



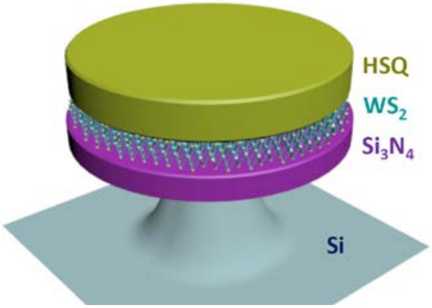
Integrated Circuits



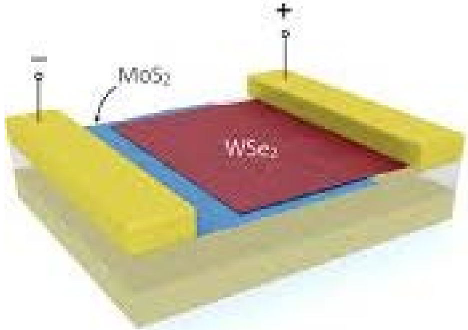
Photodetectors



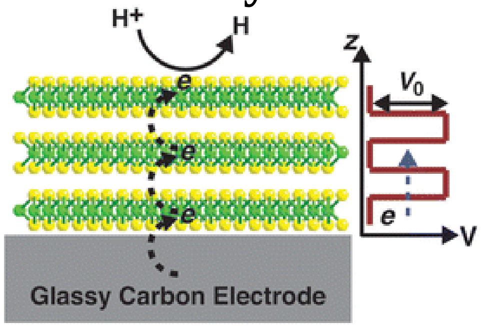
Lasers



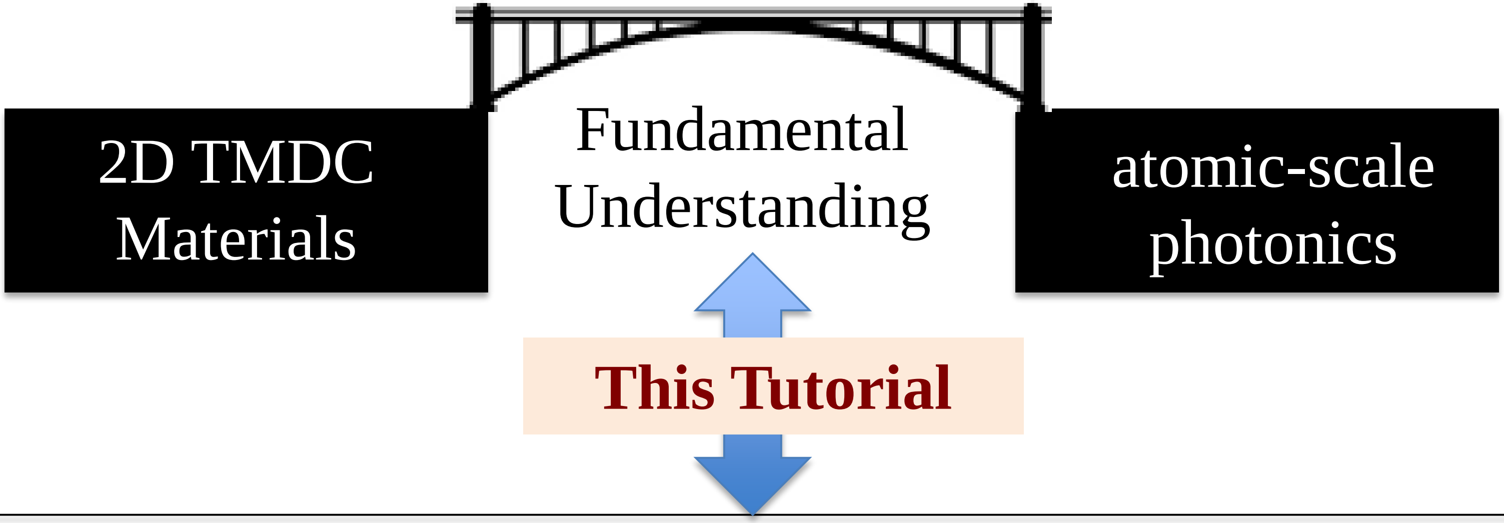
Chemical/bio Sensors



Catalysts



Key: Fundamental Understanding



2D TMDC Materials

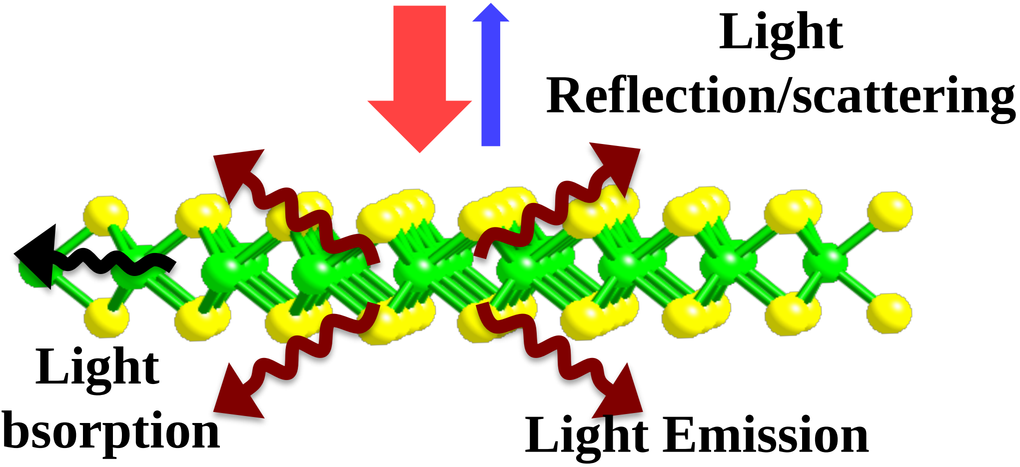
Fundamental Understanding

atomic-scale photonics

This Tutorial

Light-Matter Interactions

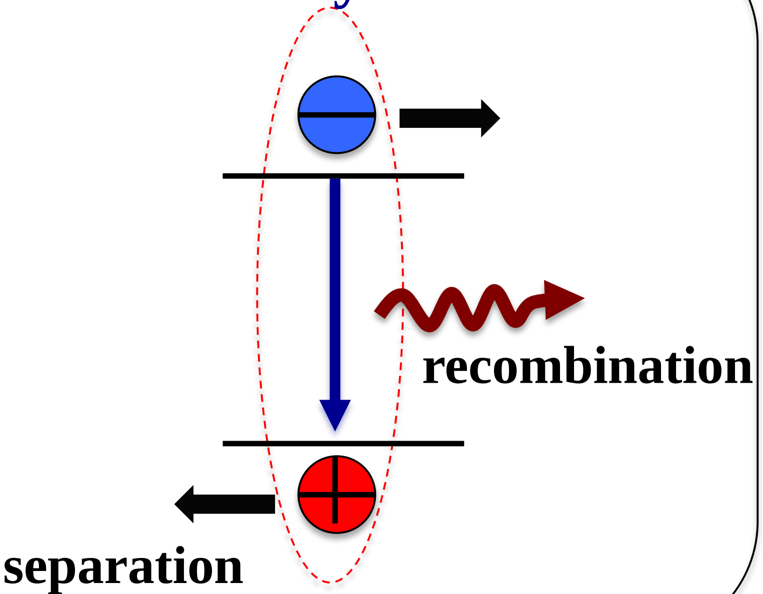
Exciton Dynamics



Light Reflection/scattering

Light absorption

Light Emission

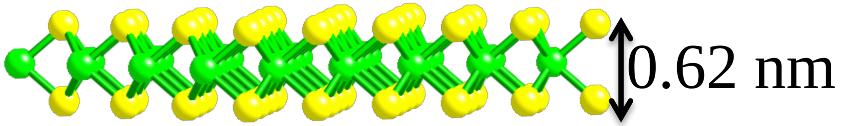


recombination

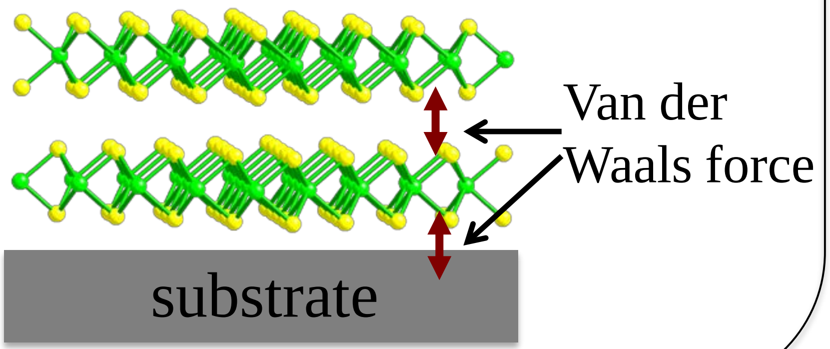
separation

Unique Physical Features ➔Exotic Excitonic Properties ?

Atomically thin



Weak interaction (vdW)



Strong exciton binding energy

Strong many-body interactions

High susceptibility to substrate effects

Dominating excitonic effects in light-matter interactions

Efficient interfacial transfer

Overview

1. **Excitonic States, Binding Energy, Exciton Radius**

2. **Many body interactions (Coulomb scattering)**

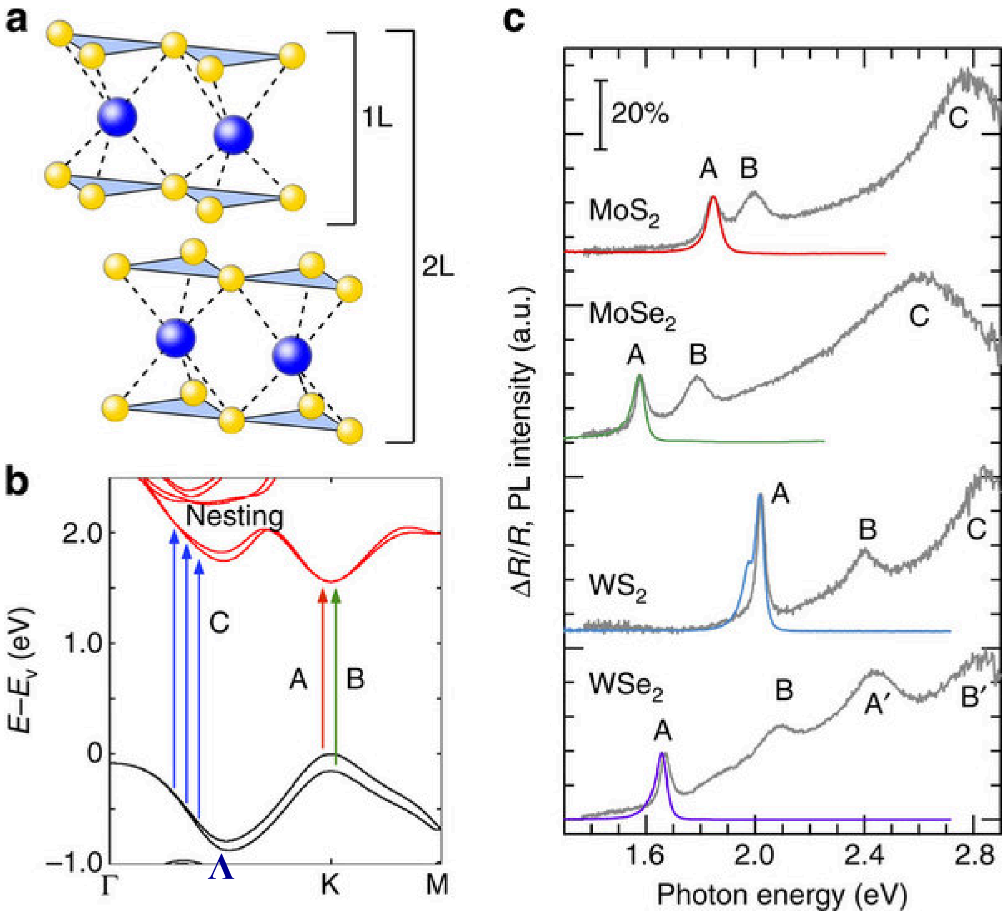
   Exciton-charge, exciton-exciton

3. **Effect of substrates**

4. **Exciton dynamics**

5. **Dominating excitonic effects in light-matter interactions**

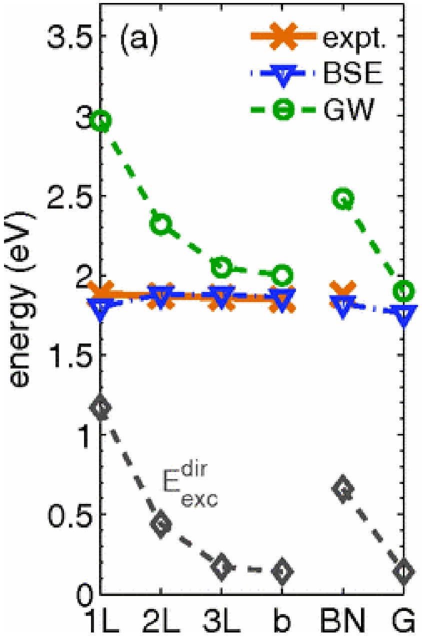
Excitonic States



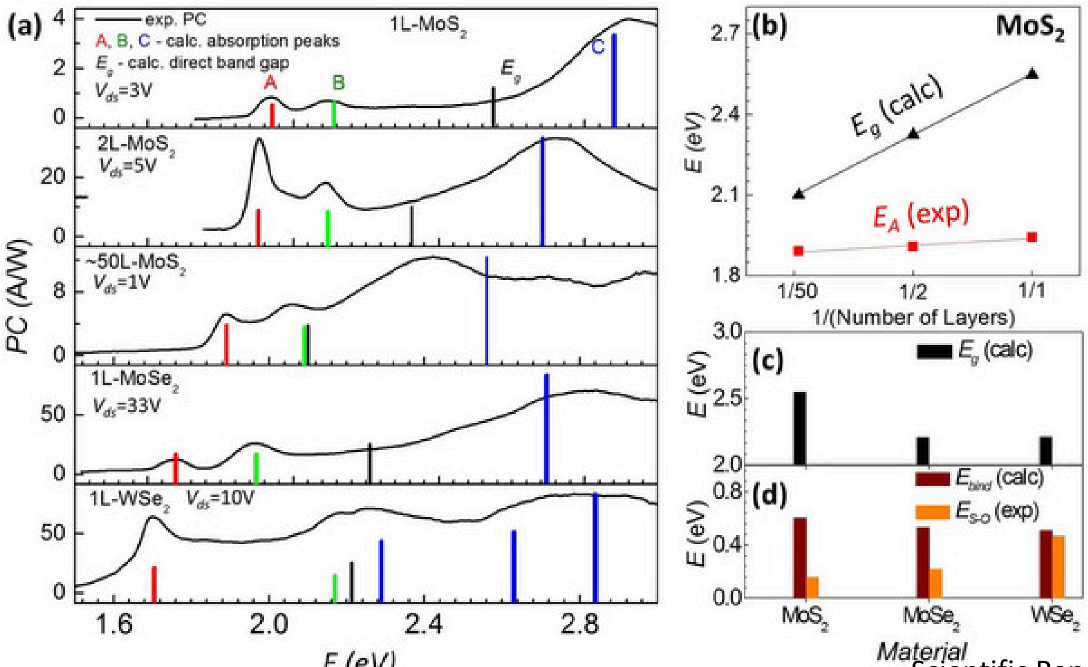
Nature Communications 5, 4543, (2014)

A and B from interband transtion of K/K’ points, and C from transition in the Brillouin zone between Γ and Λ

Extraordinarily Strong Binding Energy



Phys. Rev. B 86, 241201(R)

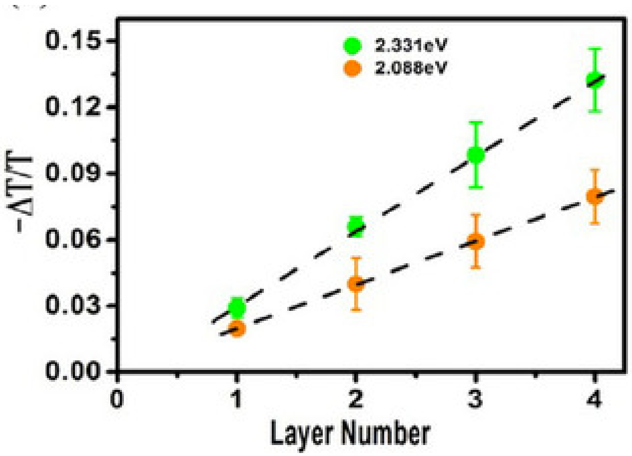


Scientific Reports 4, 6608, 2014

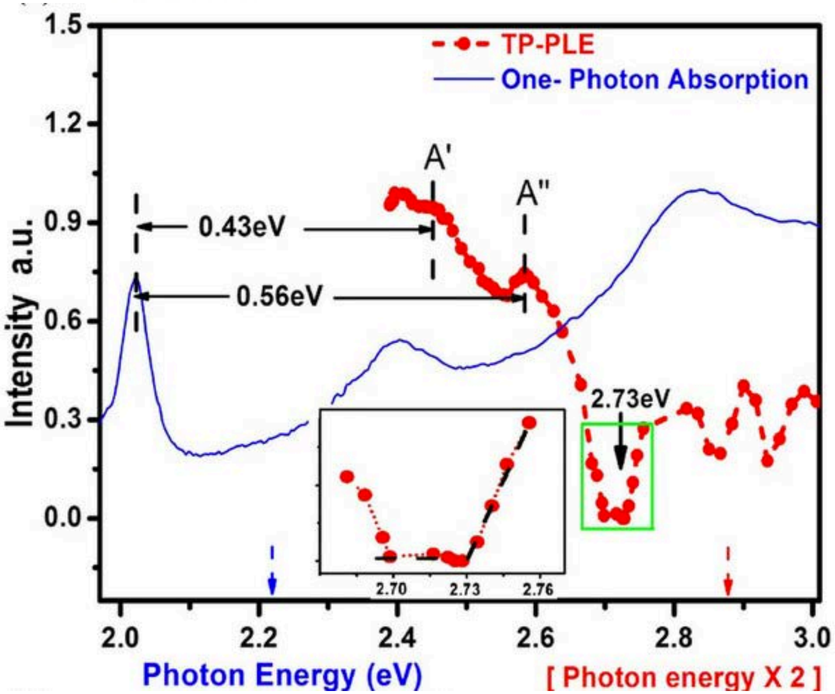
	Energy cutoffs	*k* point	E_g	E_g(optical)	Binding energy
Monolayer MoS$_2$ (3.160 Å)	400 and 200	6 × 6 × 1(SOC)	2.89	1.87	1.02
		6 × 6 × 1	2.99	1.96	1.03
		9×9×1	2.84	2.08	0.76
		12 × 12 × 1	2.78	2.16	0.62
		15 × 15 × 1	2.76	2.22	0.54
	600 and 300	12 × 12 × 1	2.80	2.17	0.63
Monolayer MoS$_2$ (3.190 Å)	600 and 300	12 × 12 × 1	2.66	2.04	0.62
Monolayer WS$_2$ (3.155 Å)	400 and 200	6 × 6 × 1(SOC)	3.02	1.97	1.05
		6 × 6 × 1	3.28	2.21	1.07
		9×9×1	3.12	2.34	0.78
		12 × 12 × 1	3.06	2.43	0.63
		15 × 15 × 1	3.05	2.51	0.54
	600 and 300	12 × 12 × 1	3.11	2.46	0.65
Monolayer WS$_2$ (3.190 Å)	600 and 300	12 × 12 × 1	2.92	2.28	0.64

The exciton binding energy in 1L MoS2 is reported ~ 0.4-1.1 eV (0.4-0.6 eV more reasonable)

Strong Binding Energy in WS2



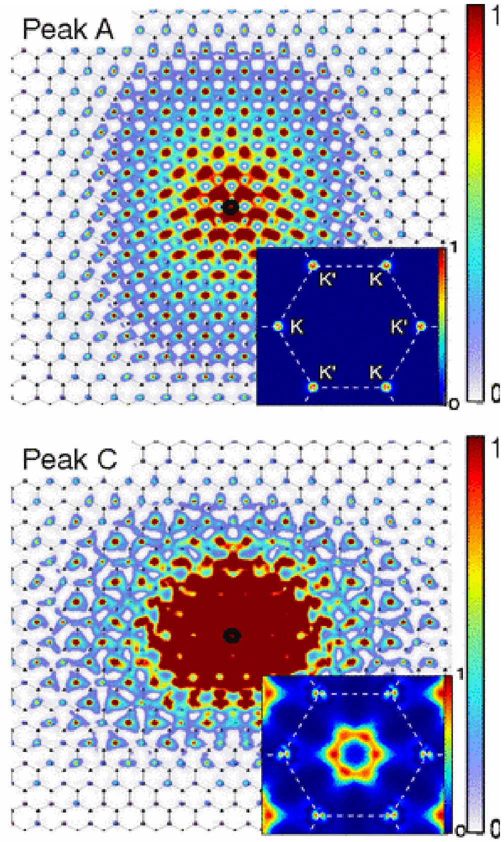
	1L(10K)	1L(300K)	2L(300K)	4L(300K)
A	2.123ev	2.020ev	1.987ev	1.981ev
B	2.505ev	2.403ev	2.366ev	2.380ev
C	2.884ev	2.825ev	2.737ev	2.702ev



Scientific Reports 5, 9218 (2015)

The exciton binding energy in WS2 monolayer is 0.71 ± 0.01 eV around K valley

Exciton Radius

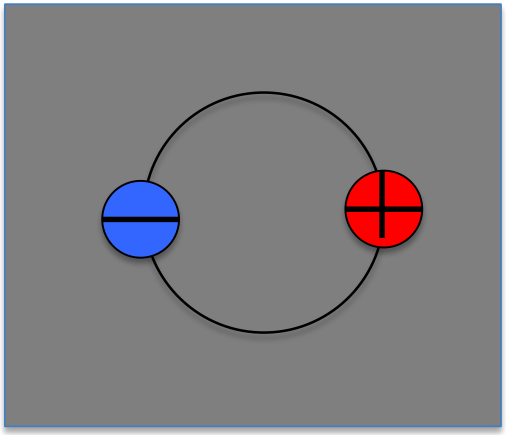


Phys. Rev. Lett. 111, 216805

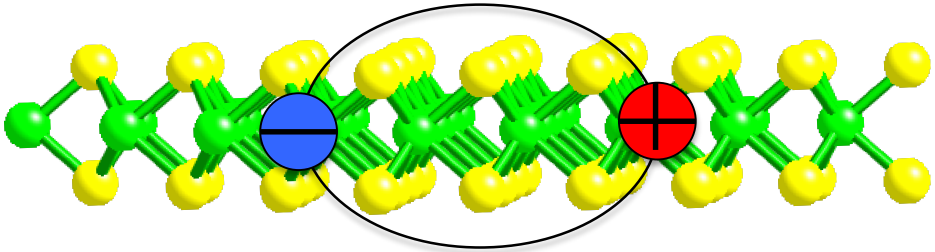
The exciton radius is estimated to be 0.5-2 nm

Anisotropy: Fractional Dimensional Space

Conventional materials: Isotropic



2D TMDC materials: Anisotropic



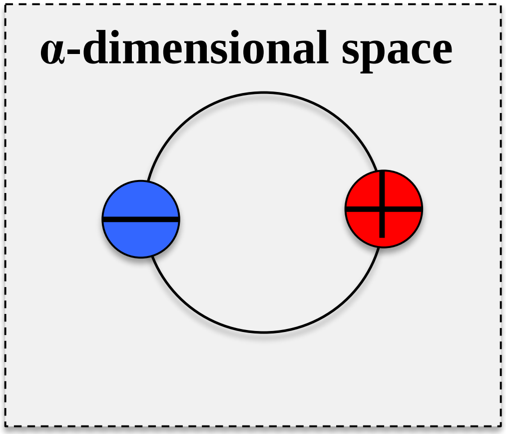
How should the concept developed for isotropic systems be adjusted for the extremely anisotropic excitons in 2D TMDC materials?

Fractional dimensional space model

$$\alpha = (E_{bulk}/E_{2D})^{1/2}+1$$

X.-F. He, Physical Review B **42**, 11751 (1990).
C. Tanguy, Physical Review Letters **75**, 4090 (1995).
C. Tanguy, P. Lefebvre, H. Mathieu, and R. J. Elliott, Journal of Applied Physics **82**, 798 (1997).

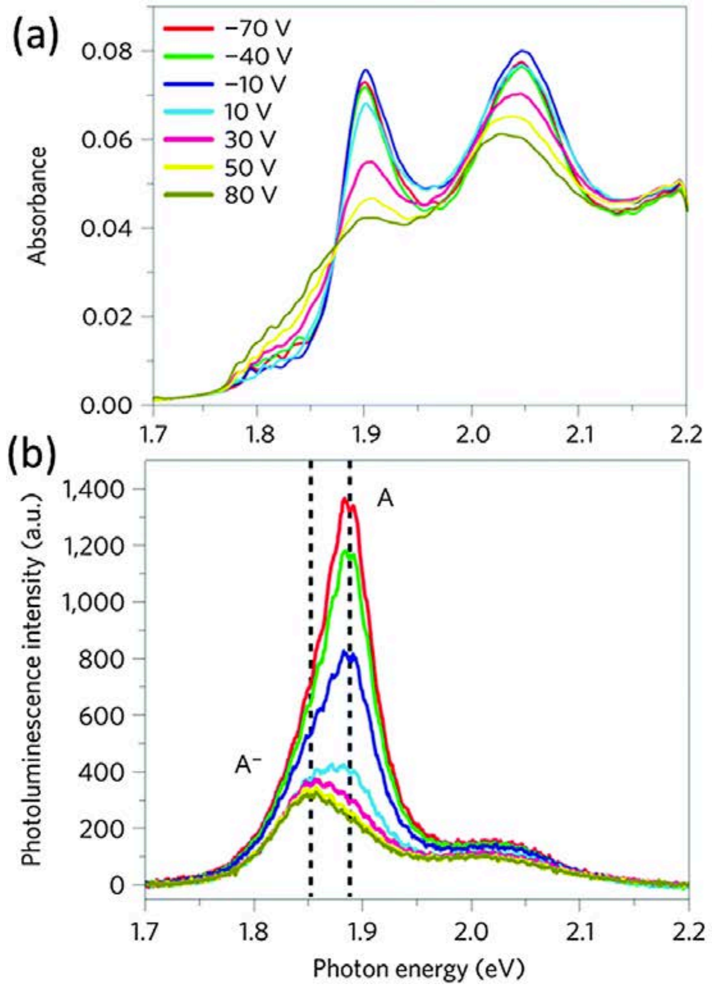
α-dimensional space



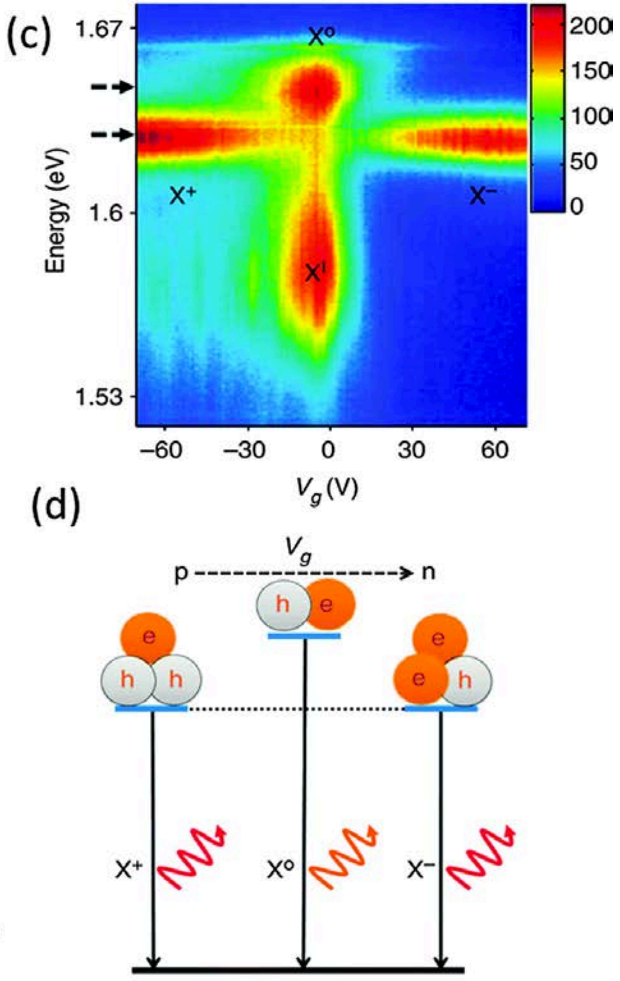
Many-body Interactions

- **Exciton-charge**
- **Exciton-exciton**

Exciton-Charge Interaction: Neutral and Charged Exictons



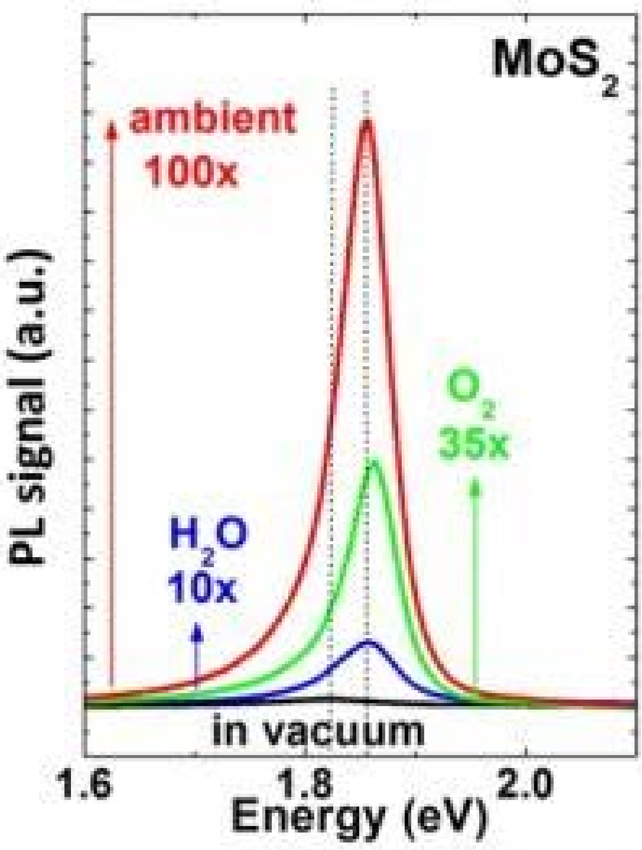
Nature Materials 12, 207–211 (2013)

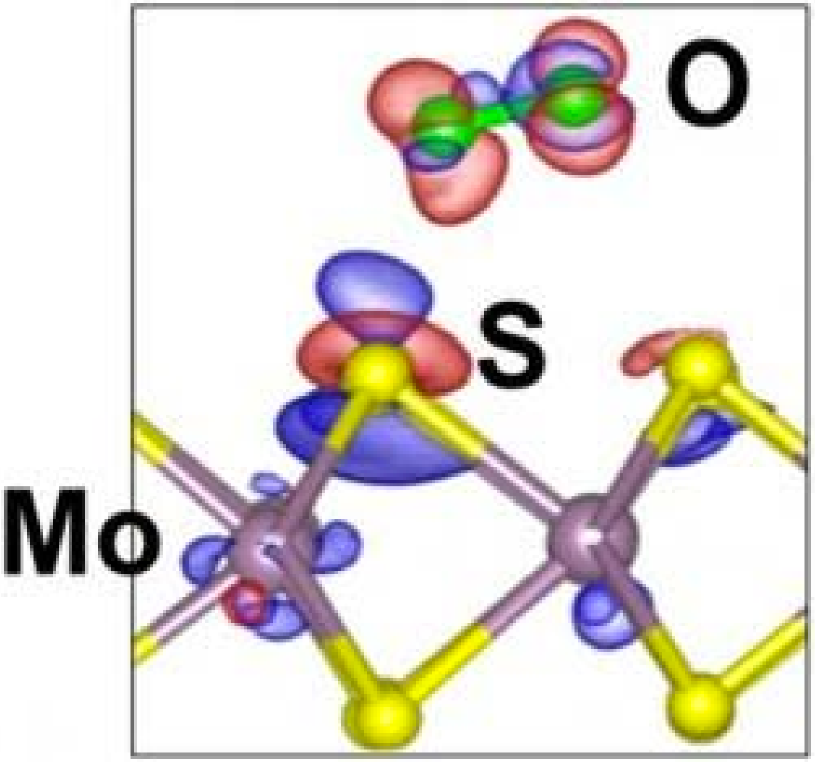


Nature communication, Xiaodong Xu’ groupd

Trions have a binding energy estimated to be ~20meV and much lower efficiency than neutral excitons

Effect of Doping on Luminescence Efficiency

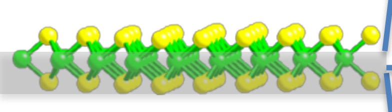




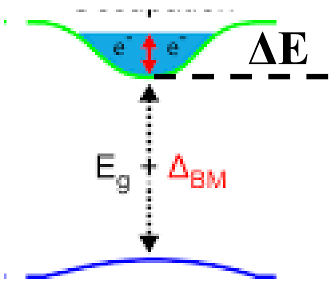
Nano Lett., 2013, 13 (6), pp 2831–2836

The PL intensity and position can be substantially affected by the doping level

Doping Effect: More than Coulomb Scattering



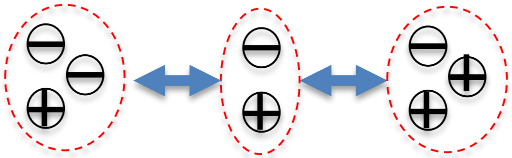
Phase Space Filling (Pauli principle)



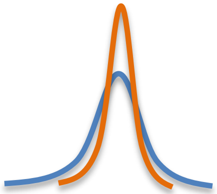
$\Delta E = \pi\hbar^2 n/2m$
m: effective mass
n: density of charge

Coulomb scattering

Interchange of charged and neutral excitons

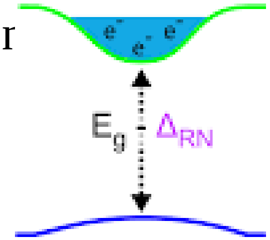


Dephasing: spectral broadening



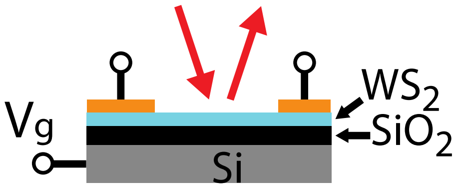
Dielectric screening scattering

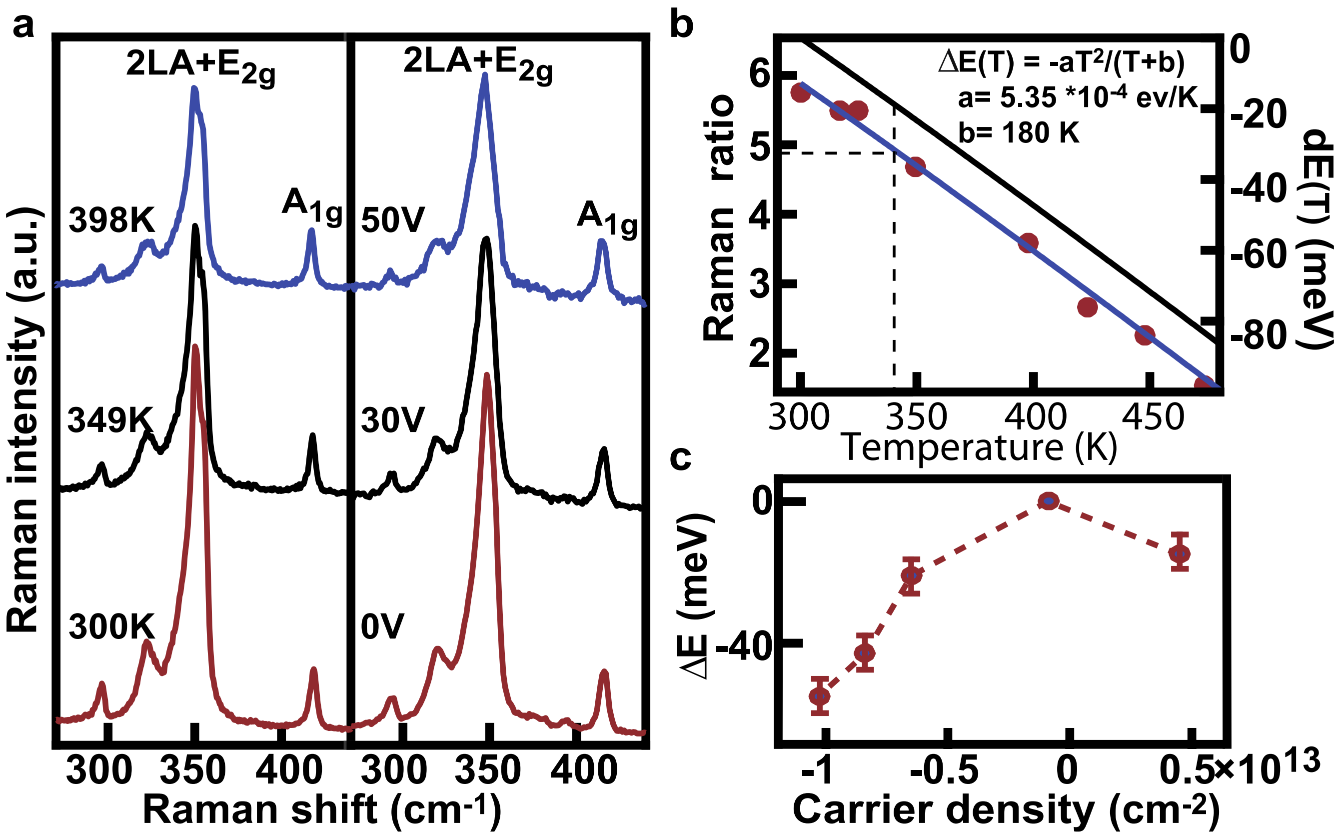
Bandgap renormalizatior



Change in exciton binding energy

Bandgap Renormalization by Dielectric Screening

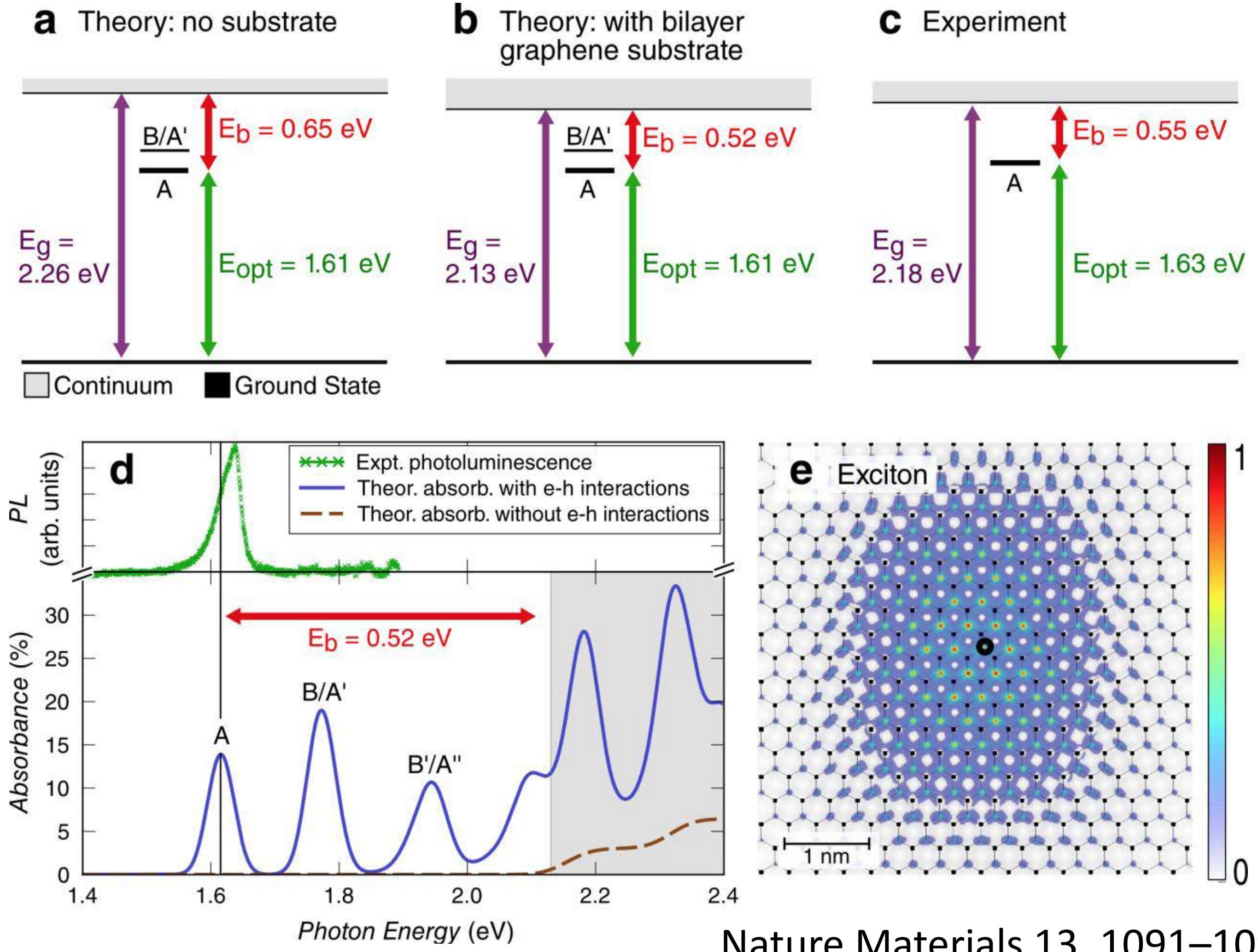




The electronic bandgap can be renormalized due to the dielectric screening effect of doping.

Yiling Yu, et al submitted

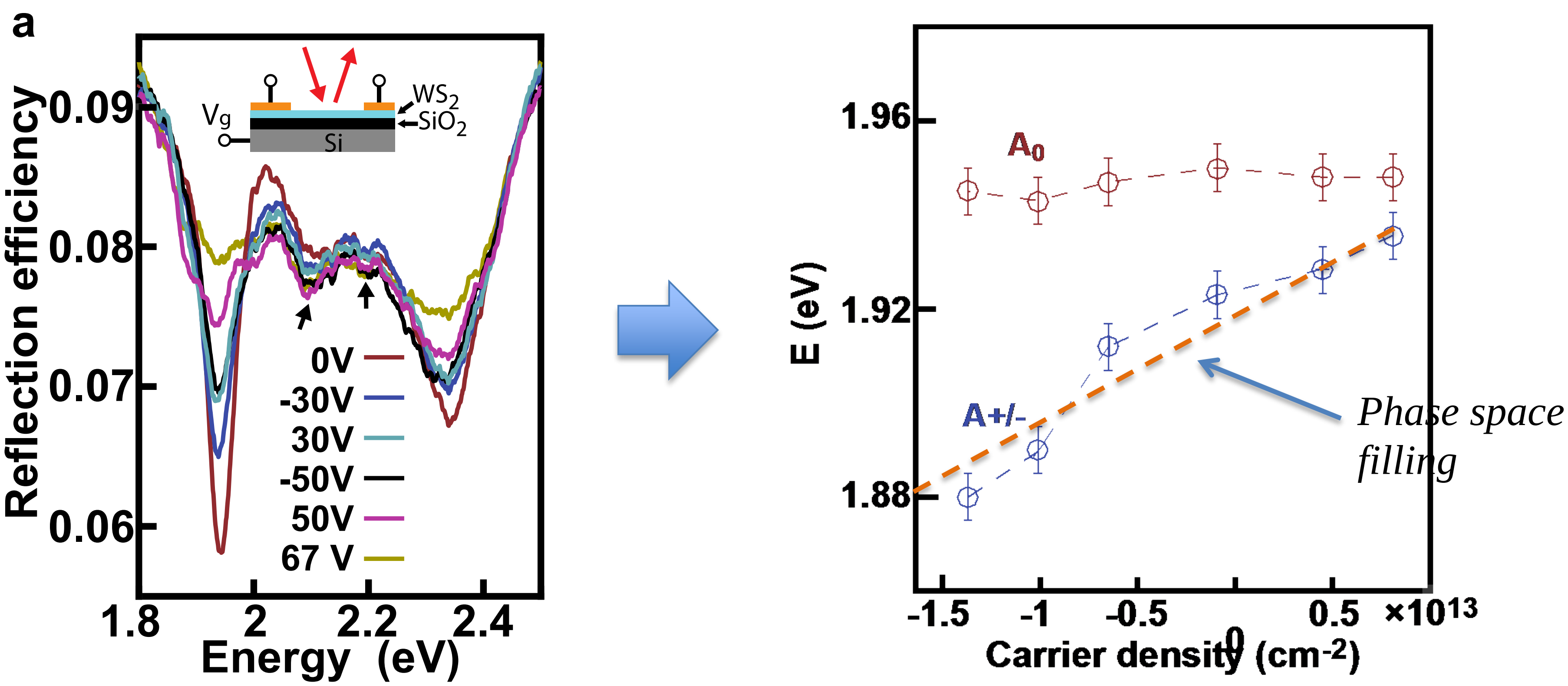
Bandgap Renormalization by Dielectric Screening



Nature Materials 13, 1091–1095 (2014)

The electronic bandgap can be renormalized due to the dielectric screening effect of substrates (but the value is most likely overestimated).

Change in Exciton Binding Energy by Dielectric Screening



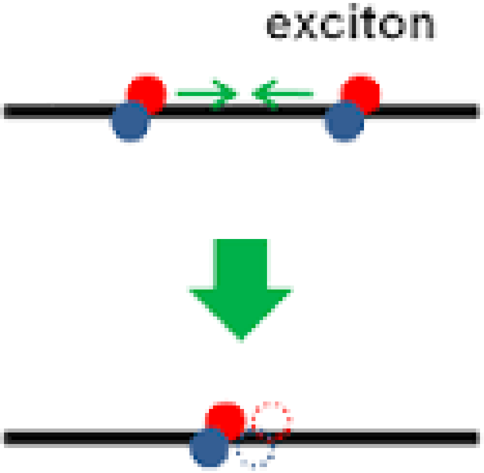
change in binding energy $\Delta E_{ex} = \Delta E_g - \Delta E_{opt}$,

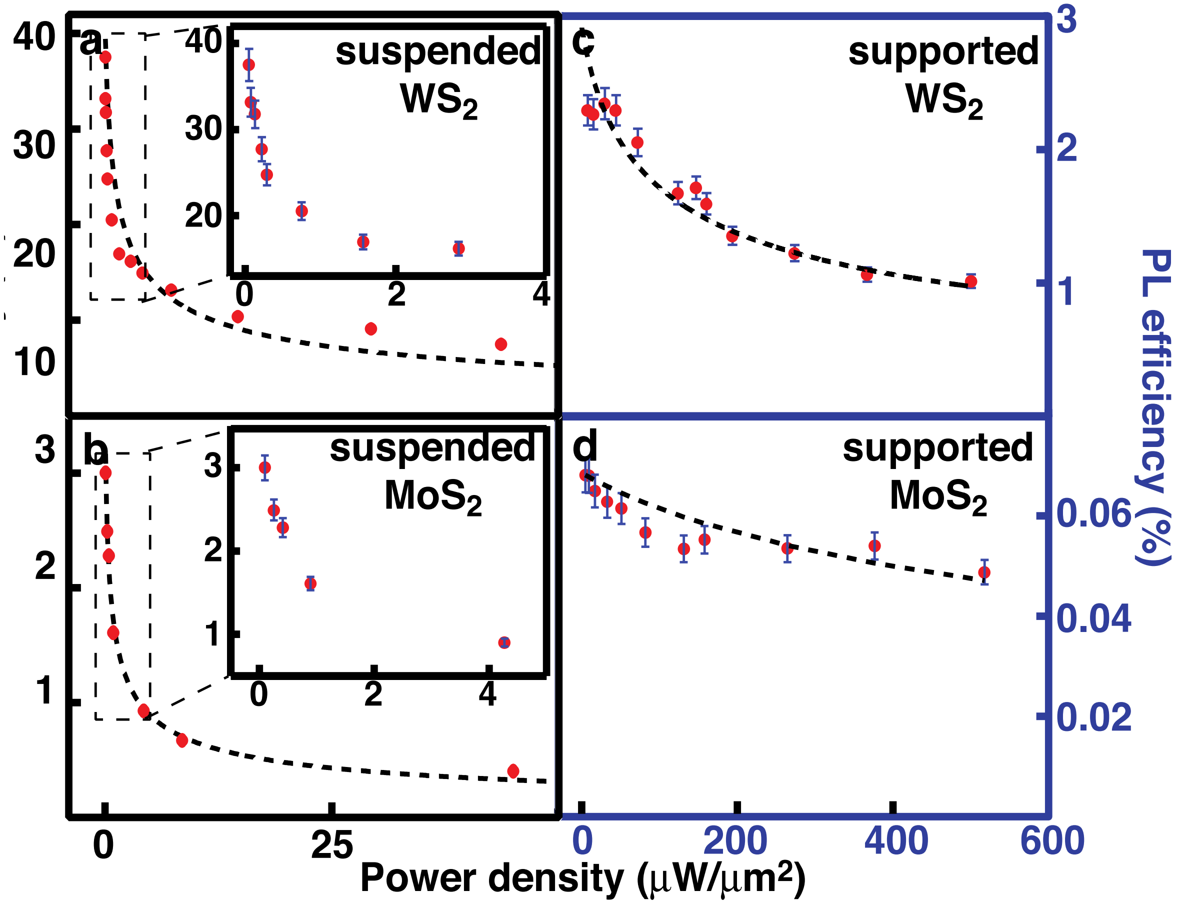
$\Delta E_{g:}$ bandgap renormalization, ΔE_{opt} change in optical bandgap

Change in exciton binding energy: 5- 25 meV

Yiling Yu , et al submitted

Exciton-Exictons Annihilation

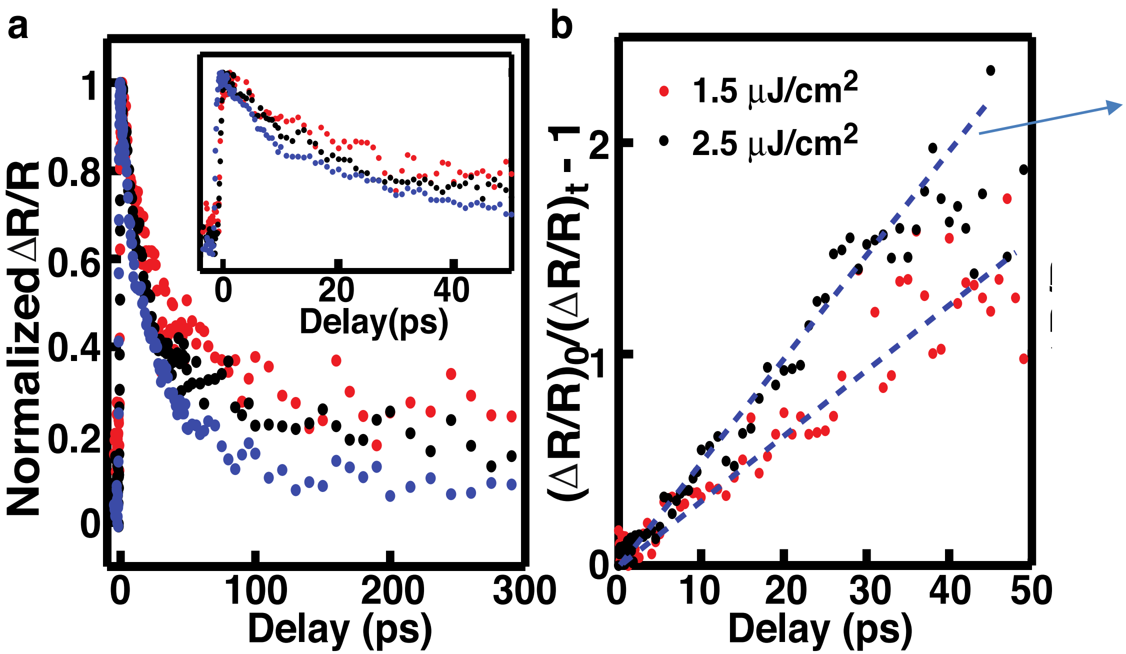




High exciton-exciton annihilation rate!

Yiling Yu[§], Yifei Yu[§], Chao Xu[§] et al, Phys. Rev. B **93**, 201111(R)

Exciton-Exicton Annihilation



Slope: $k_{ee}N_0$

$N_0 \propto$ Incident power fluence

$$dN/dt = -k_{ee}N^2$$

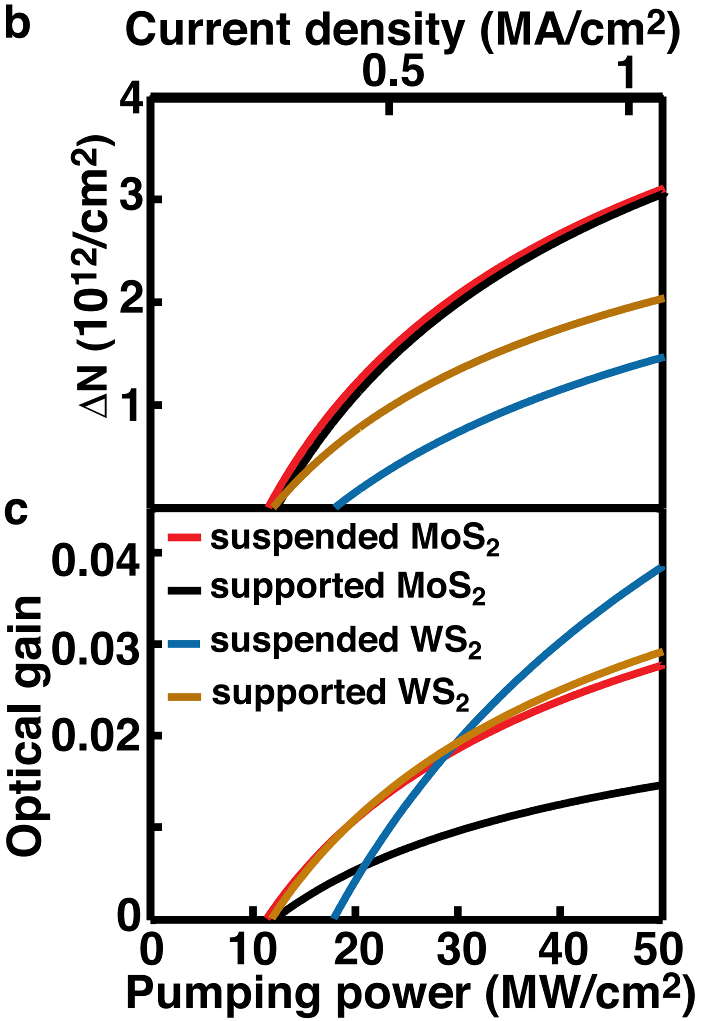
$$\frac{N_0}{N(t)} - 1 = k_{ee}N_0 t$$

	k_{ee} (cm^2/s)	τ_r (ns)	τ_{nr} (ns)
Suspended WS$_2$	0.3	1	0.76
As-grown WS$_2$	0.1	4.5	0.13
Suspended MoS$_2$	0.1	28	1
As-grown MoS$_2$	0.05	80	0.05

Dependence of exciton-exciton annihilation rate on substrates

Yiling Yu§, Yifei Yu§, Chao Xu§ et al, Phys. Rev. B **93**, 201111(R)

Pumping Threshold for Population Inversion

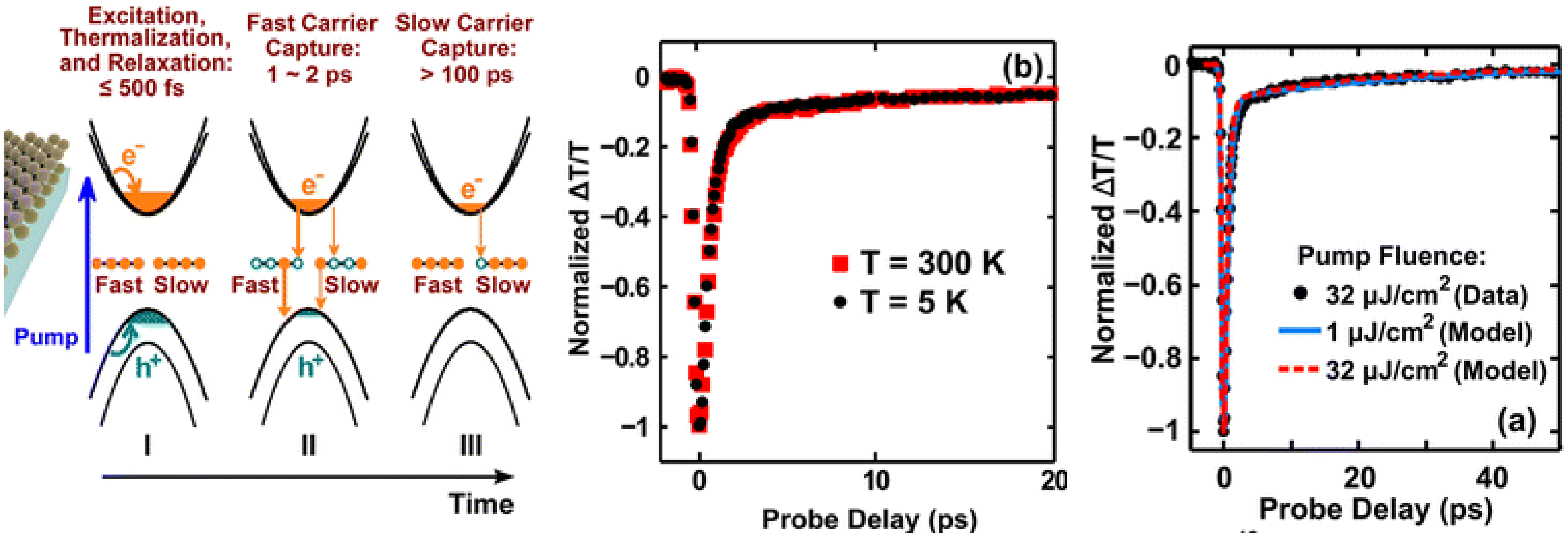


$$\frac{dN}{dt} = -\left(\frac{1}{\tau_r} + \frac{1}{\tau_{nr}}\right)N - k_{ee}N^2 + \alpha I_0$$

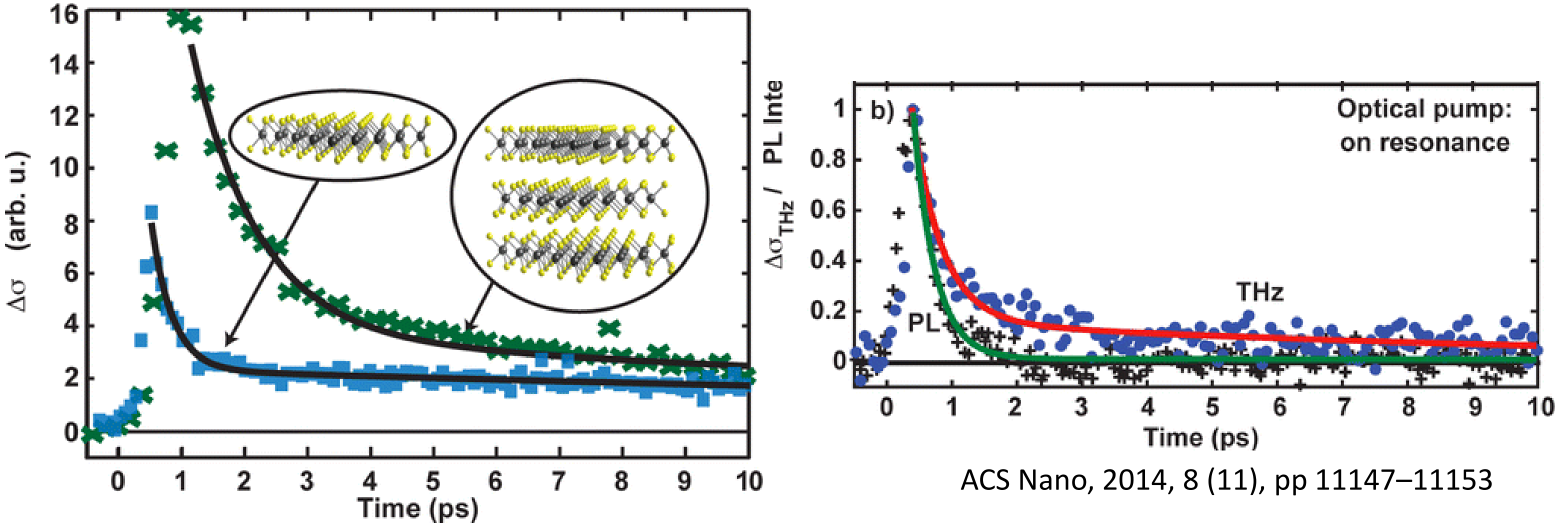
The pumping threshold is solely dictated by the exciton-exciton annihilation rate.

Yiling Yu§, Yifei Yu§, Chao Xu§ et al, Phys. Rev. B **93**, 201111(R)

Excicton Dynamics: Defect-assisted



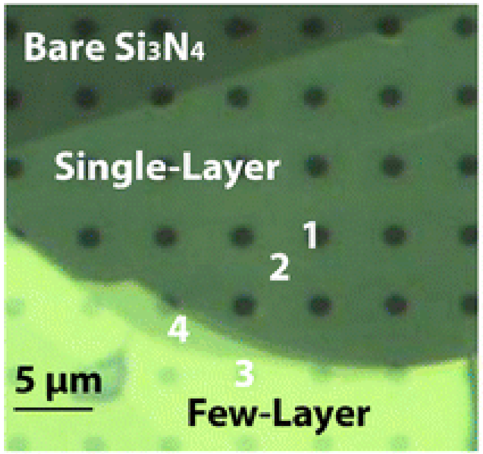
Nano Lett., 2015, 15 (1), pp 339–345

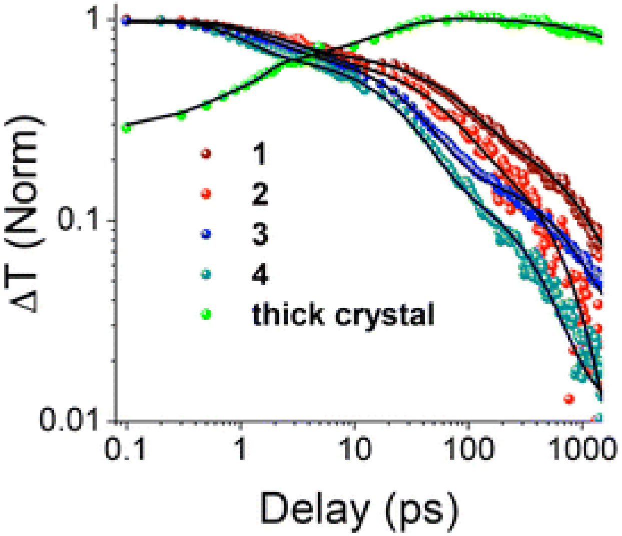


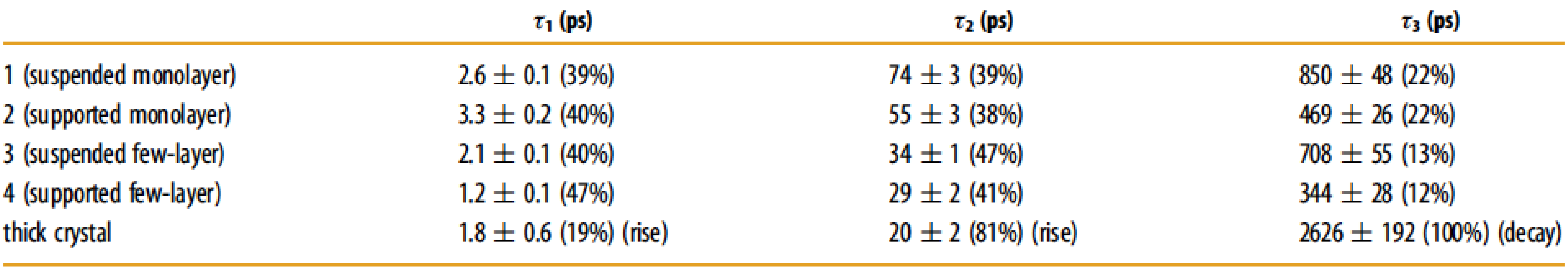
ACS Nano, 2014, 8 (11), pp 11147–11153

Defect-Assisted Electron–Hole Recombination

Exciton Lifetime







	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
1 (suspended monolayer)	2.6 ± 0.1 (39%)	74 ± 3 (39%)	850 ± 48 (22%)
2 (supported monolayer)	3.3 ± 0.2 (40%)	55 ± 3 (38%)	469 ± 26 (22%)
3 (suspended few-layer)	2.1 ± 0.1 (40%)	34 ± 1 (47%)	708 ± 55 (13%)
4 (supported few-layer)	1.2 ± 0.1 (47%)	29 ± 2 (41%)	344 ± 28 (12%)
thick crystal	1.8 ± 0.6 (19%) (rise)	20 ± 2 (81%) (rise)	2626 ± 192 (100%) (decay)

ACS Nano, 2013, 7 (2), pp 1072–1080

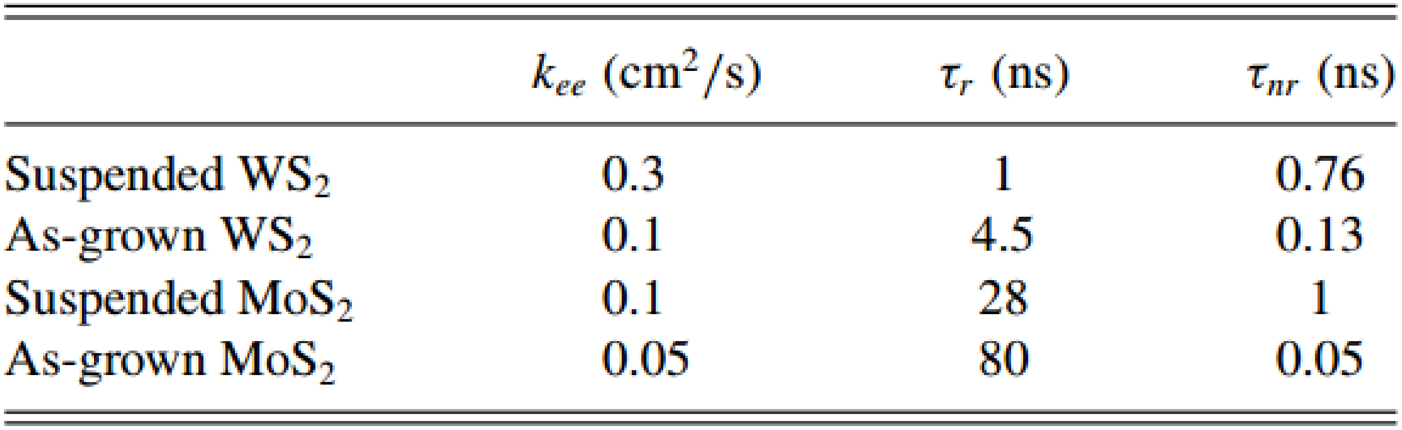
Exciton lifetime in many reports: 1-30ps.

Exciton Lifetime

In most of the current dynamics studies, the process of exciton-exciton annhilation is ignored.

This makes problems in the evaluation for the intrinsic lifetime of excitons

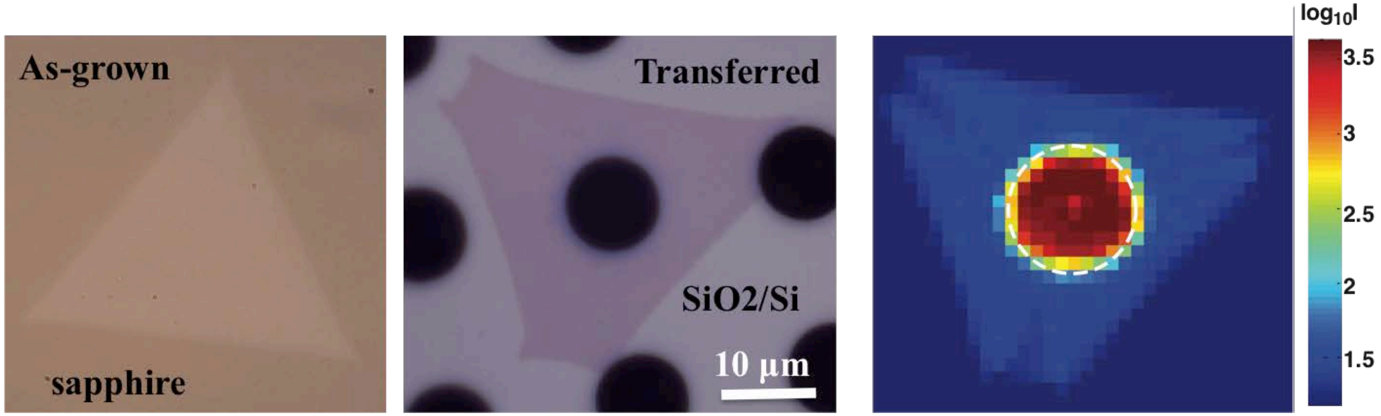
Our result

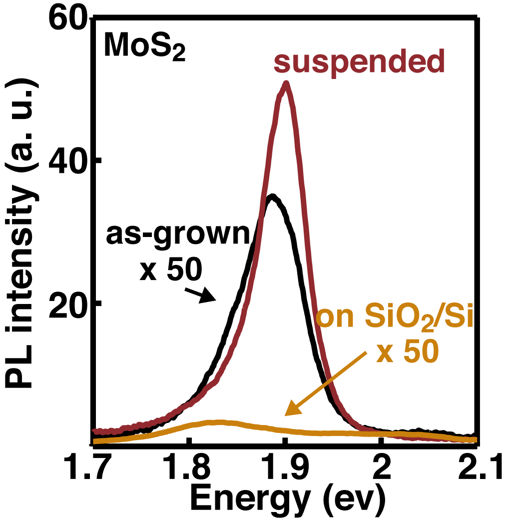


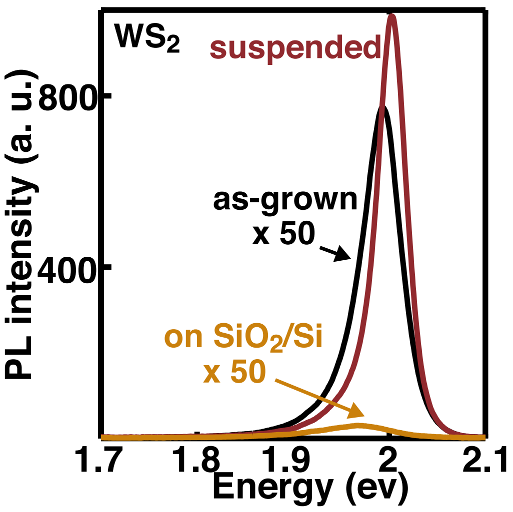
	k_{ee} (cm^2/s)	τ_r (ns)	τ_{nr} (ns)
Suspended WS_2	0.3	1	0.76
As-grown WS_2	0.1	4.5	0.13
Suspended MoS_2	0.1	28	1
As-grown MoS_2	0.05	80	0.05

Substrate Effects

Effects of Substrate







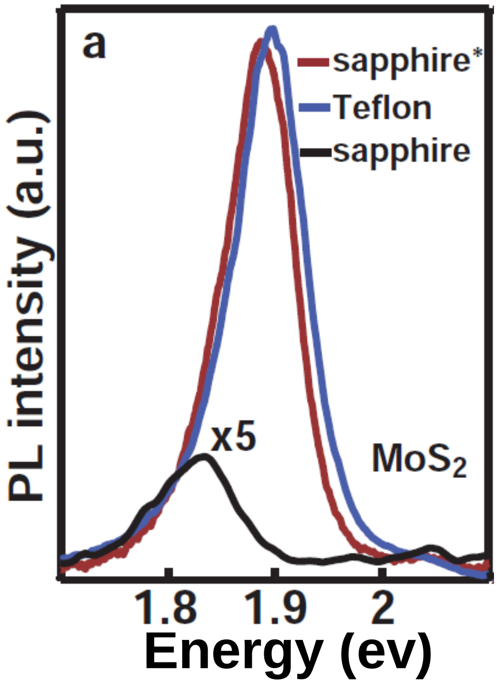
	PL efficiency
As-grown MoS2	0.1%
As-grown WS2	1.5%
Suspended MoS2	3%
Suspended WS2	35%

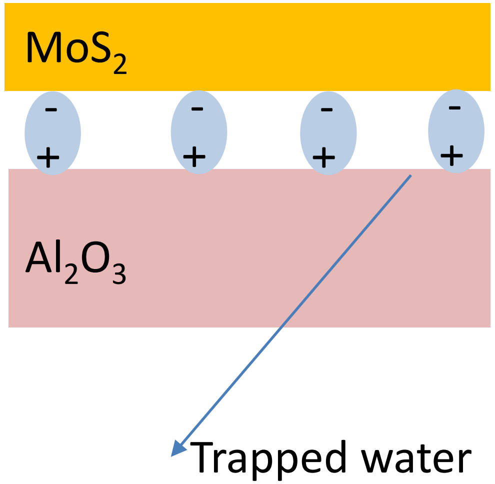
> 2 orders of magnitude improvement in the PL in suspended monolayers!

Yifei Yu [§], **Yiling Yu** [§], Chao Xu [§] et al, **Adv. Fun. Mat.** doi:10.1002/adfm.201600418. (2016)

Effect of Trapped Moisture on Hydrophilic Substrates

* denote as grown

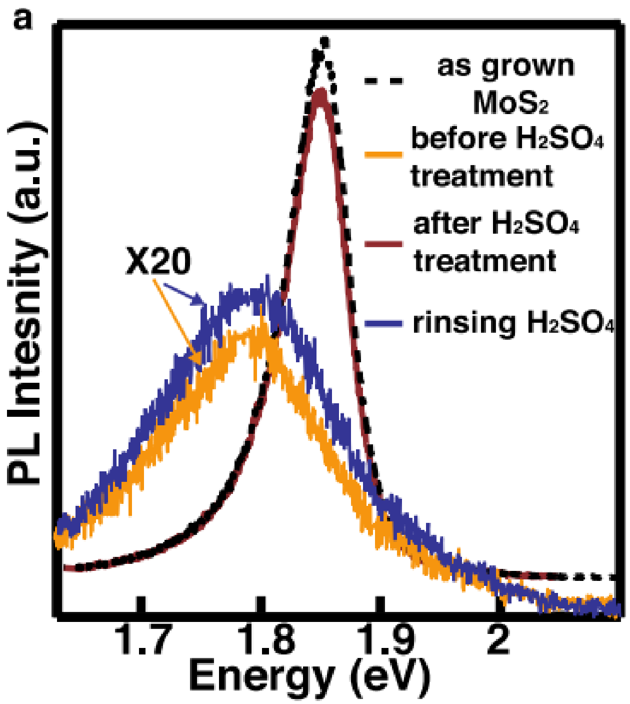




MoS_2

Al_2O_3

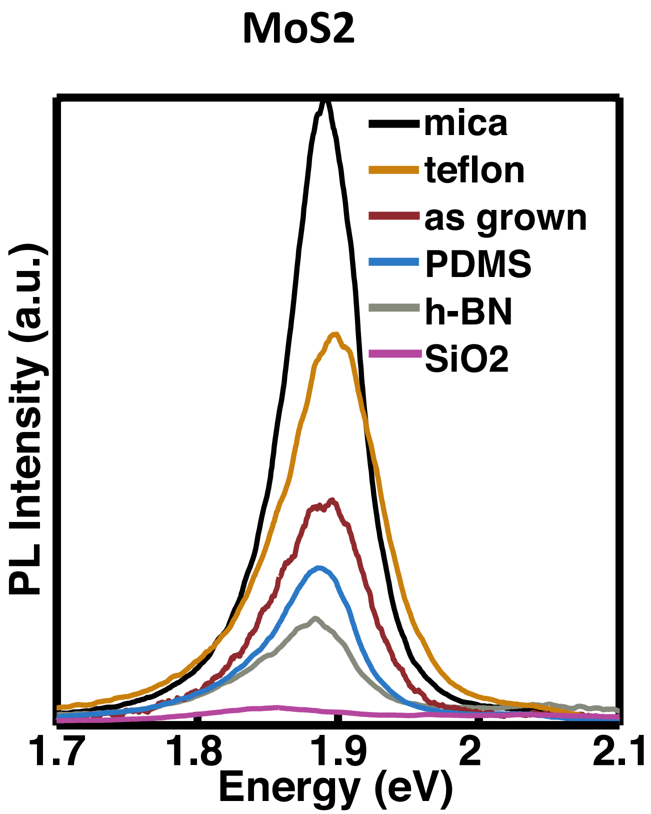
Trapped water



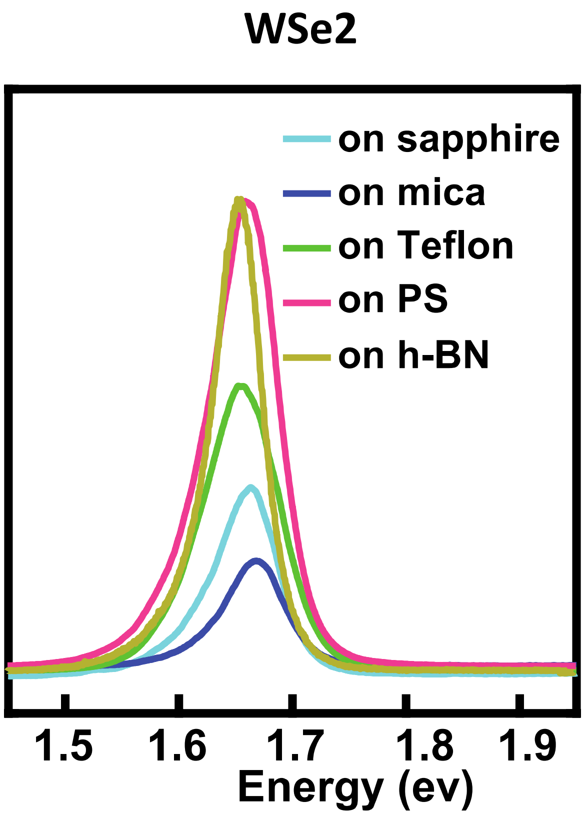
The doping effect of trapped moisture may cause more than one order of magnitude difference in PL.

Yifei Yu §, **Yiling Yu** §, Chao Xu § et al, **Adv. Fun. Mat.** doi:10.1002/adfm.201600418. (2016)

Intrinsic Doping Effect of Substrates


MoS2

mica and Teflon best for WS2 and MoS2

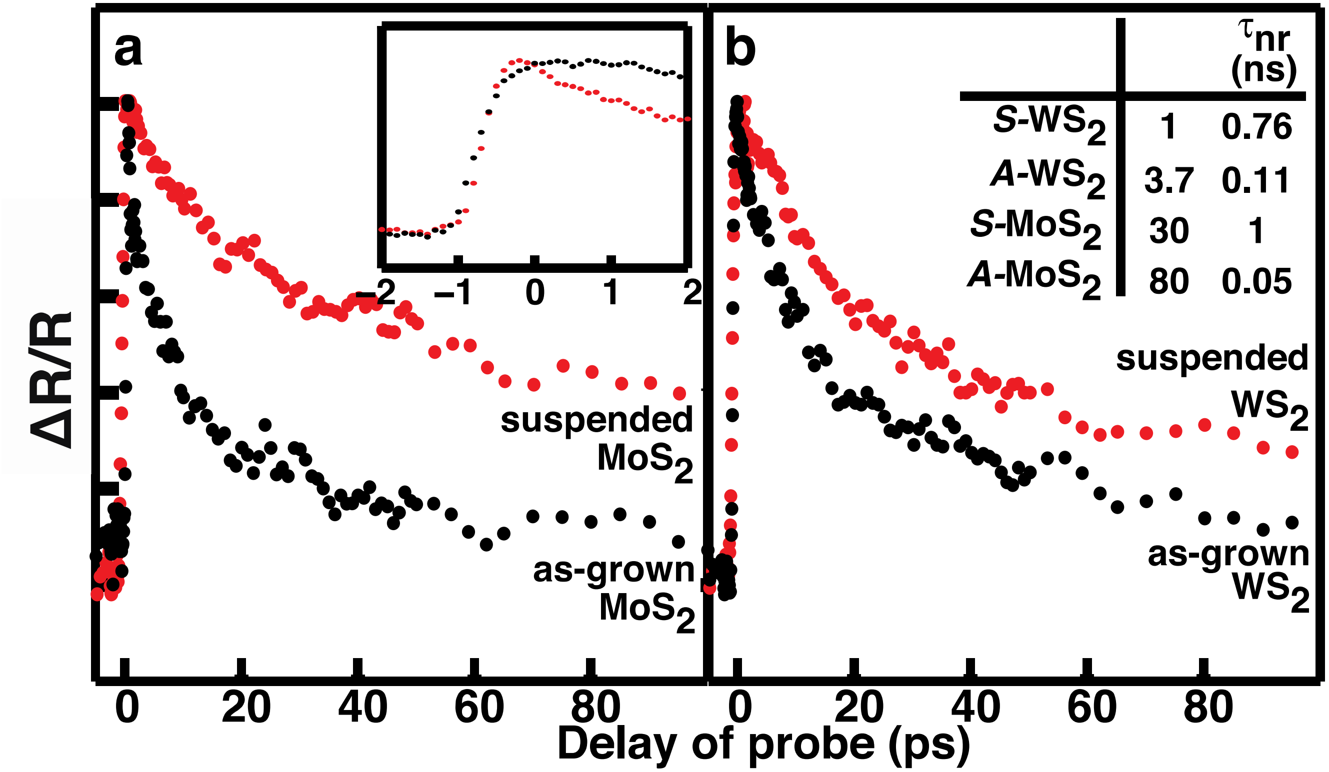

WSe2

Polystyrene and h-BN best for WSe2.

Substrates may also dope the monolayers, but much weaker than that of trapped moisture (by 2-4 times at maximum)

Yifei Yu[§], **Yiling Yu**[§], Chao Xu[§] et al, **Adv. Fun. Mat.** doi:10.1002/adfm.201600418. (2016)

Defects of Substrates: Effect on Exciton Dynamics

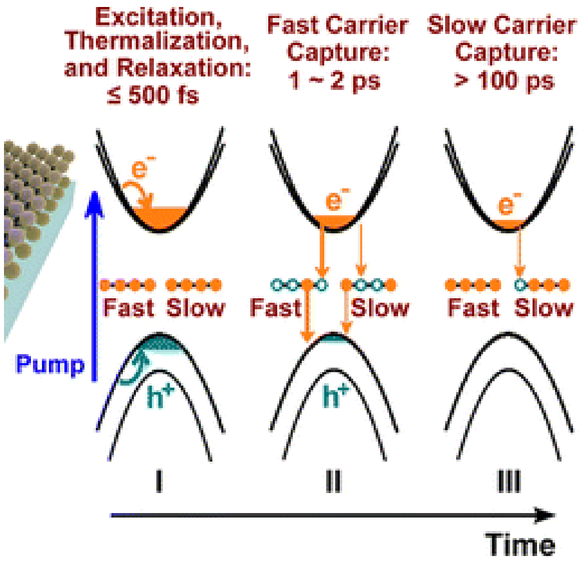


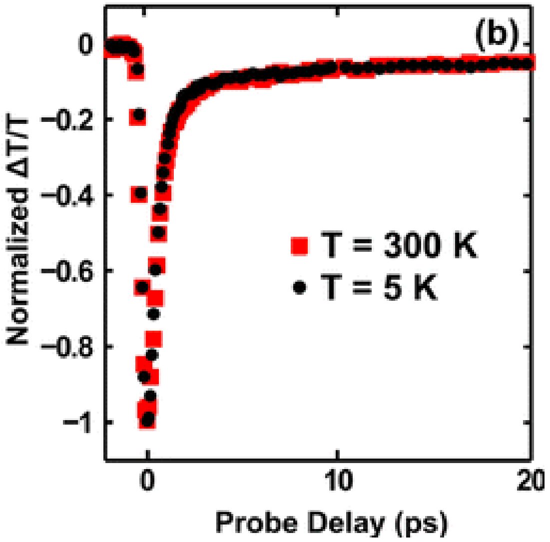
		τ_{nr} (ns)
S-WS$_2$	1	0.76
A-WS$_2$	3.7	0.11
S-MoS$_2$	30	1
A-MoS$_2$	80	0.05

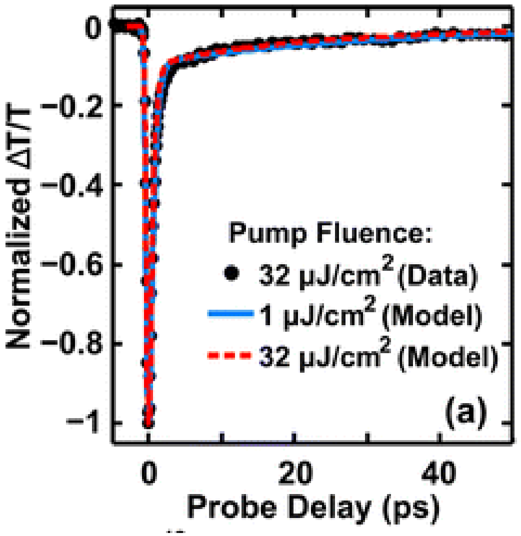
Substrate may facilitate non-radiative lifetime of excitons by providing defects to serve as recombination centers.

Yifei Yu [§], **Yiling Yu** [§], Chao Xu [§] et al, **Adv. Fun. Mat.** doi:10.1002/adfm.201600418. (2016)

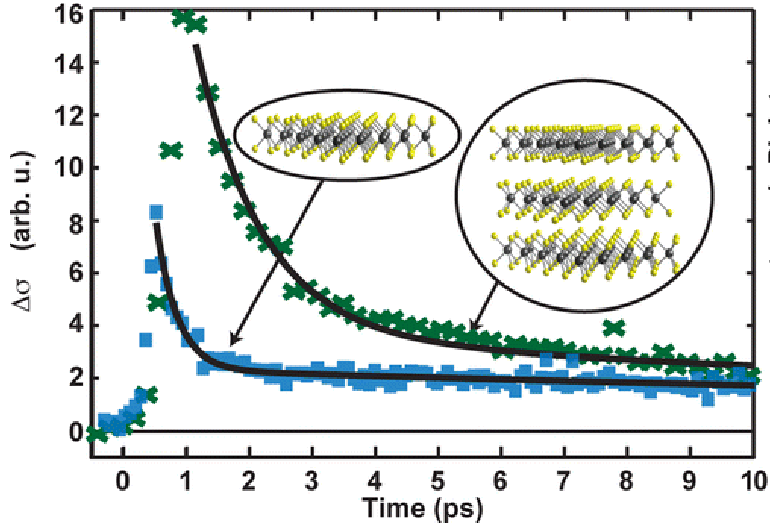
Exicton Dynamics: Defect-assisted

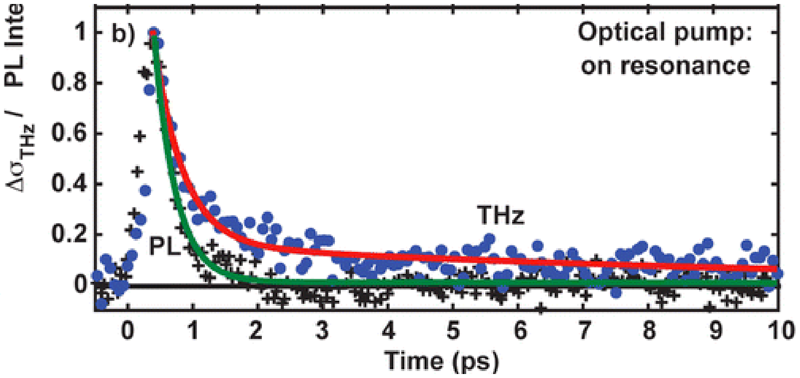






Nano Lett., 2015, 15 (1), pp 339–345

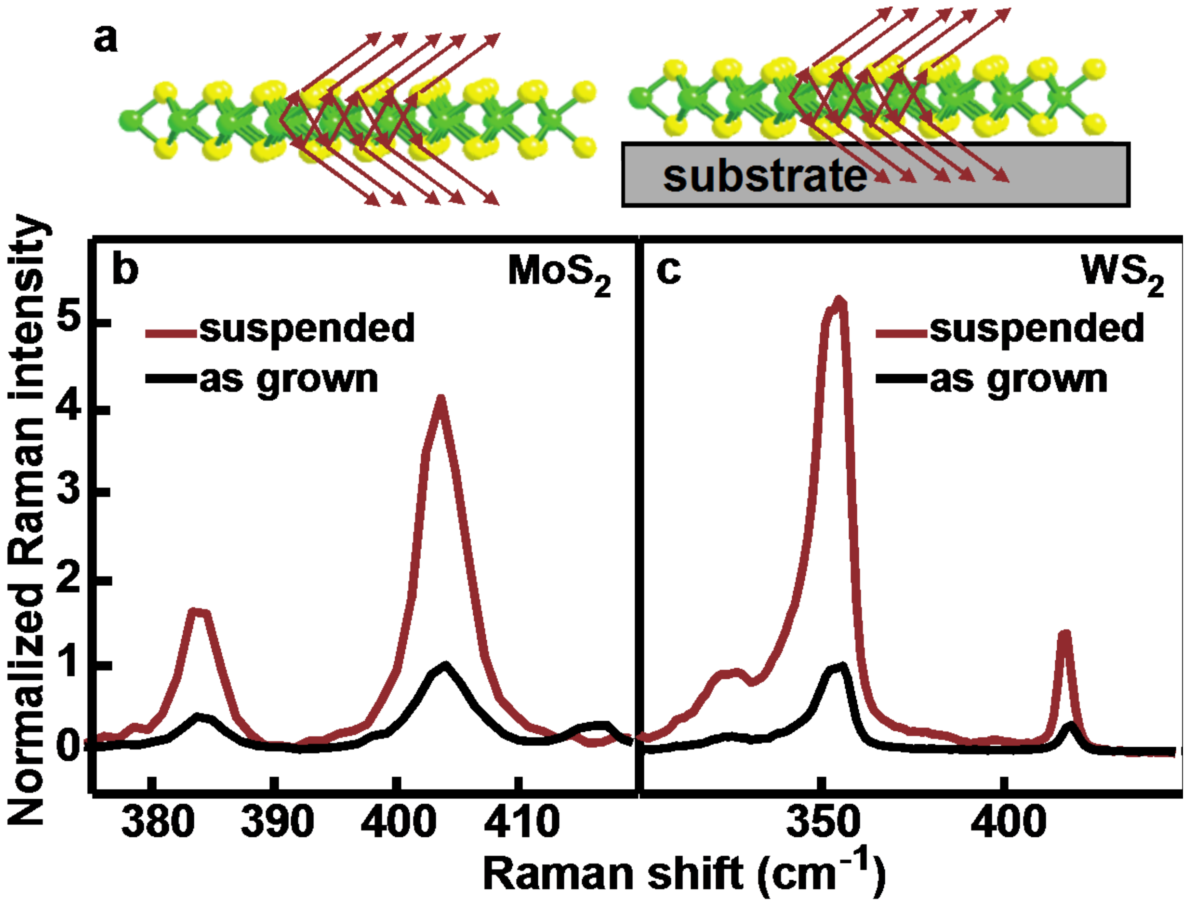




ACS Nano, 2014, 8 (11), pp 11147–11153

Defect-Assisted Electron–Hole Recombination

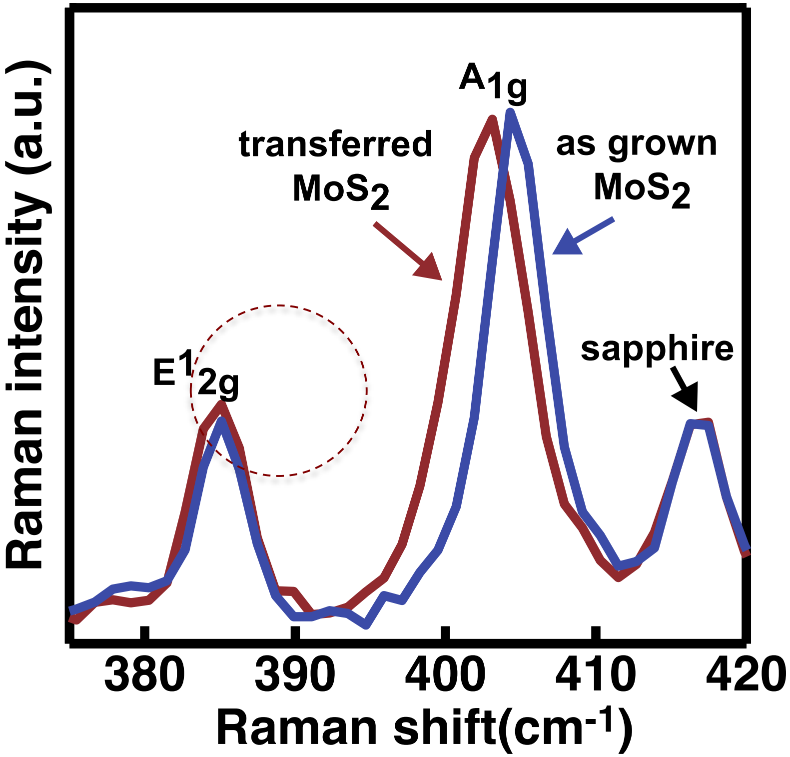
Index Contrast: Interference Effects

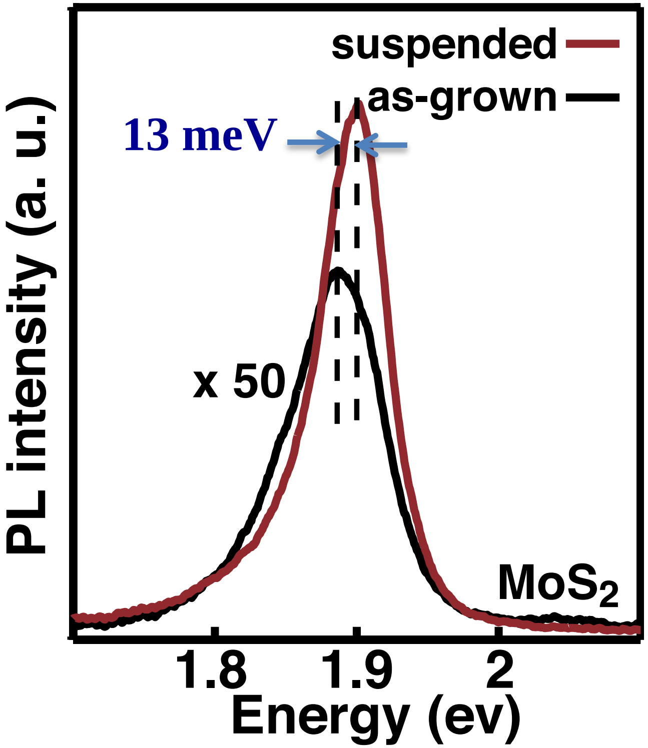


The interference effect of monolayers may affect the PL efficiency depending on the refractive index of the substrates.

Yifei Yu [§], **Yiling Yu** [§], Chao Xu [§] et al, **Adv. Fun. Mat.** doi:10.1002/adfm.201600418. (2016)

Substrate-induced Strains & Dielectric Screening





The substrate-induced strain is small, < 0.3%, affecting the PL efficiency <50%.

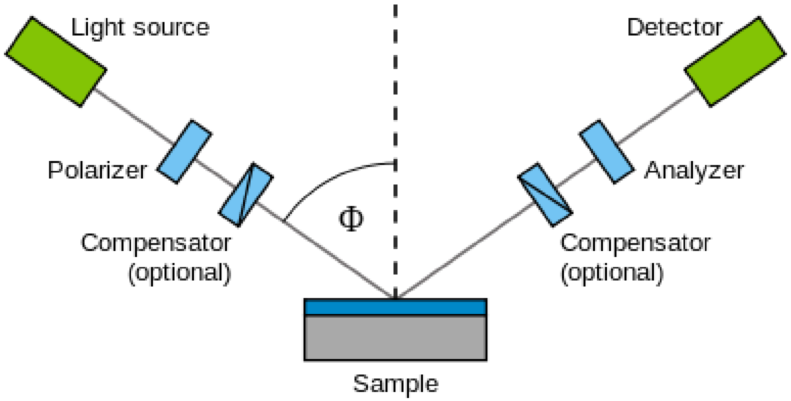
The effect of the substrate-induced dielectric screening on the PL < 2 times

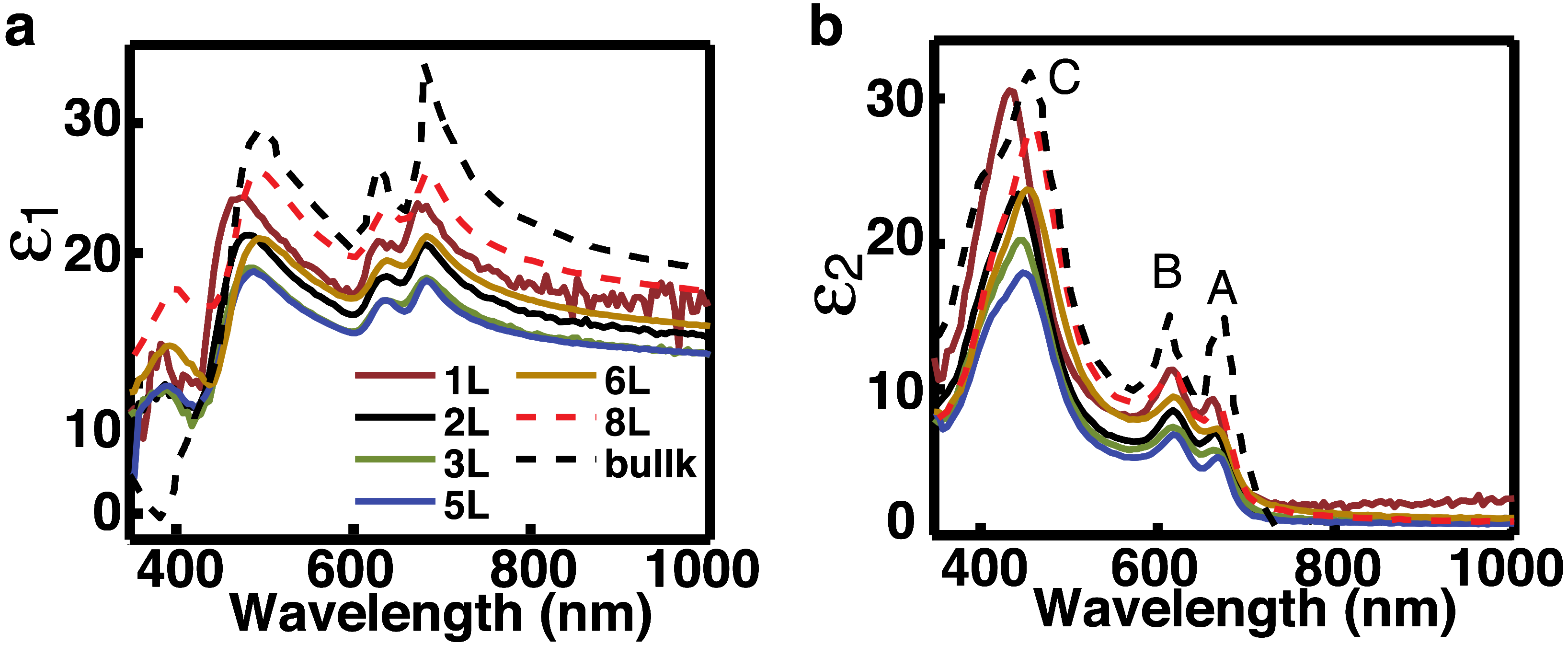
Yifei Yu [§], **Yiling Yu** [§], Chao Xu [§] et al, **Adv. Fun. Mat.** doi:10.1002/adfm.201600418. (2016)

Exciton-Dominated Light-Matter Interactions

Layer-dependent Optical Constants

Ellipsommetry
measurement

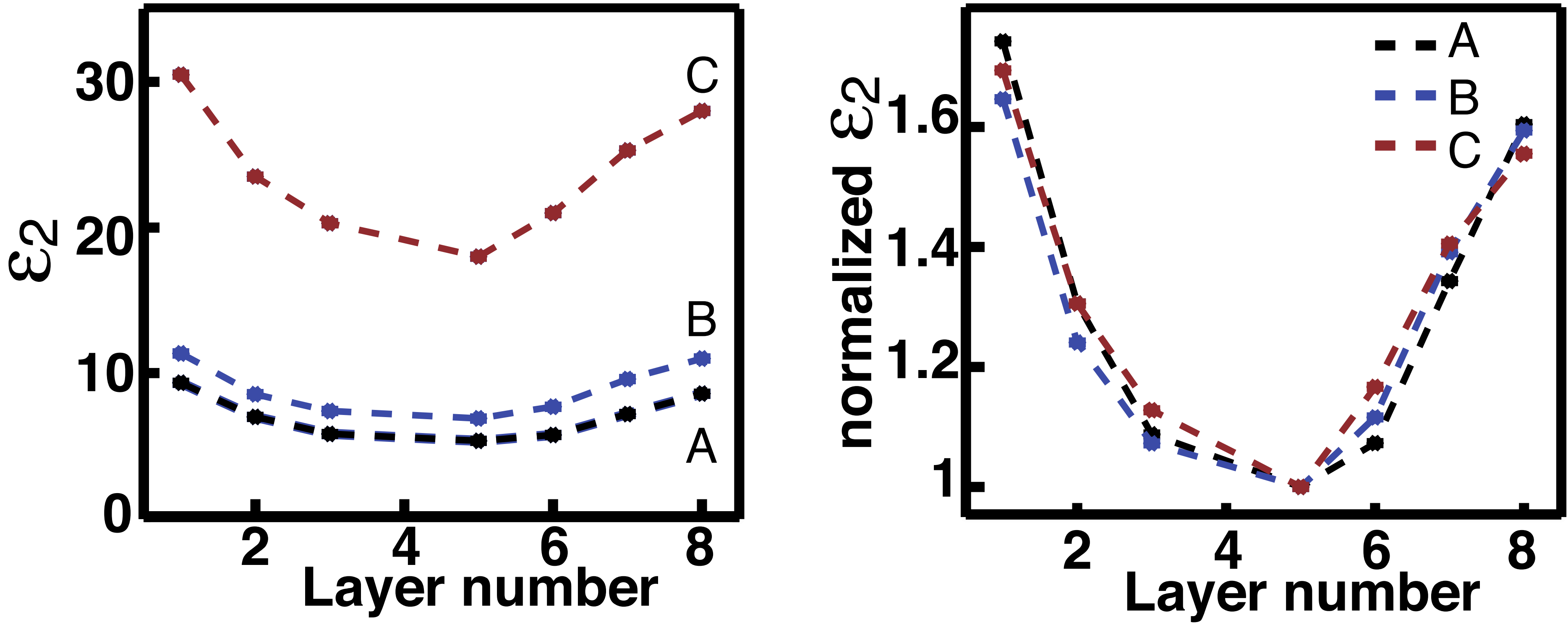




2D MoS2 exhibit an abnormal dependence on the layer number!

Yiling Yu et al, **Sci. Rep.** 5, 16996 (2015)

Layer-dependent Optical Constants

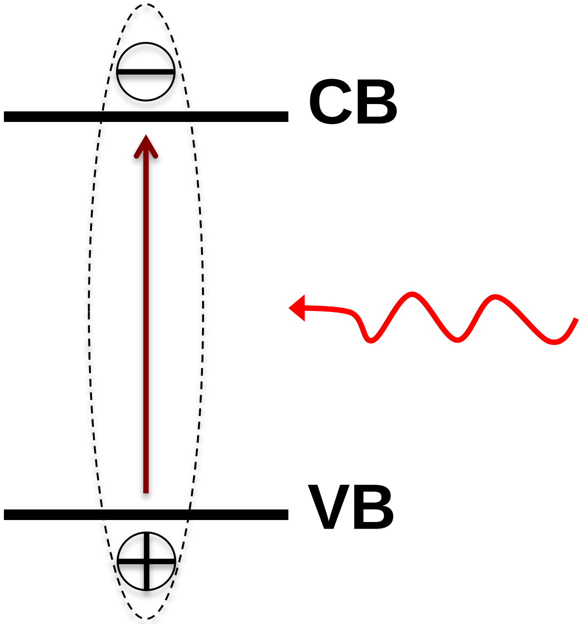


The layer-dependence of dielectric constant remains similar for the entire visible range.

Yiling Yu et al, **Sci. Rep.** 5, 16996 (2015)

Physics of Dielectric Constant

$$\varepsilon_{2,L}(\omega) = A_0 J_{cv,L} \left|U_L(0)\right|^2$$



A_0 a constant related with optical matrix element and transition bandwidth, which is layer-independent.

$J_{cv,L}$ joint density of the initial and final states involved in the transition

$U_L(0)$ the effect of excitons

Yiling Yu et al, **Sci. Rep.** 5, 16996 (2015)

Excitonic Effects

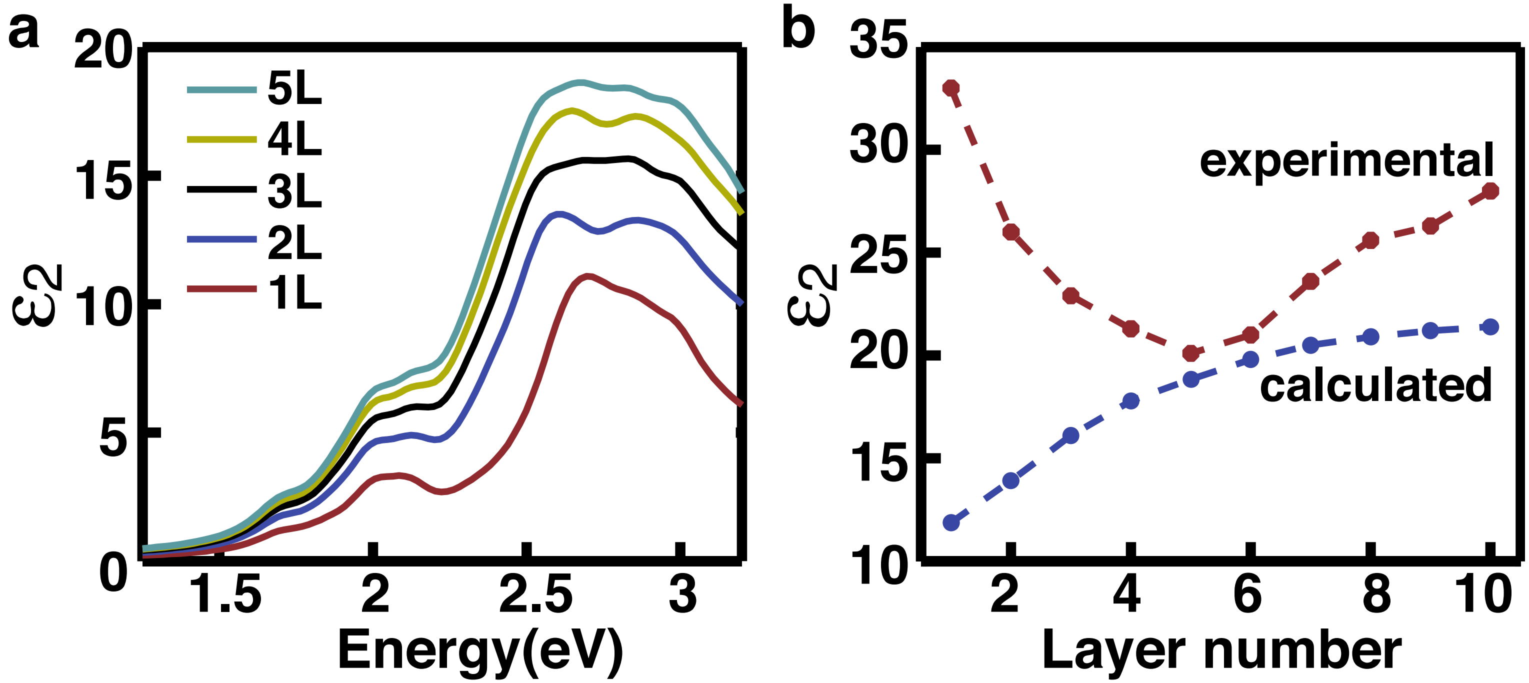
Conventional semiconductor:

$$\varepsilon_{2,L}(\omega)=A_0J_{cv,L}$$

Atomic thin MoS$_2$:

$$\varepsilon_{2,L}(\omega)=A_0J_{cv,L}\left|U_L(0)\right|^2$$

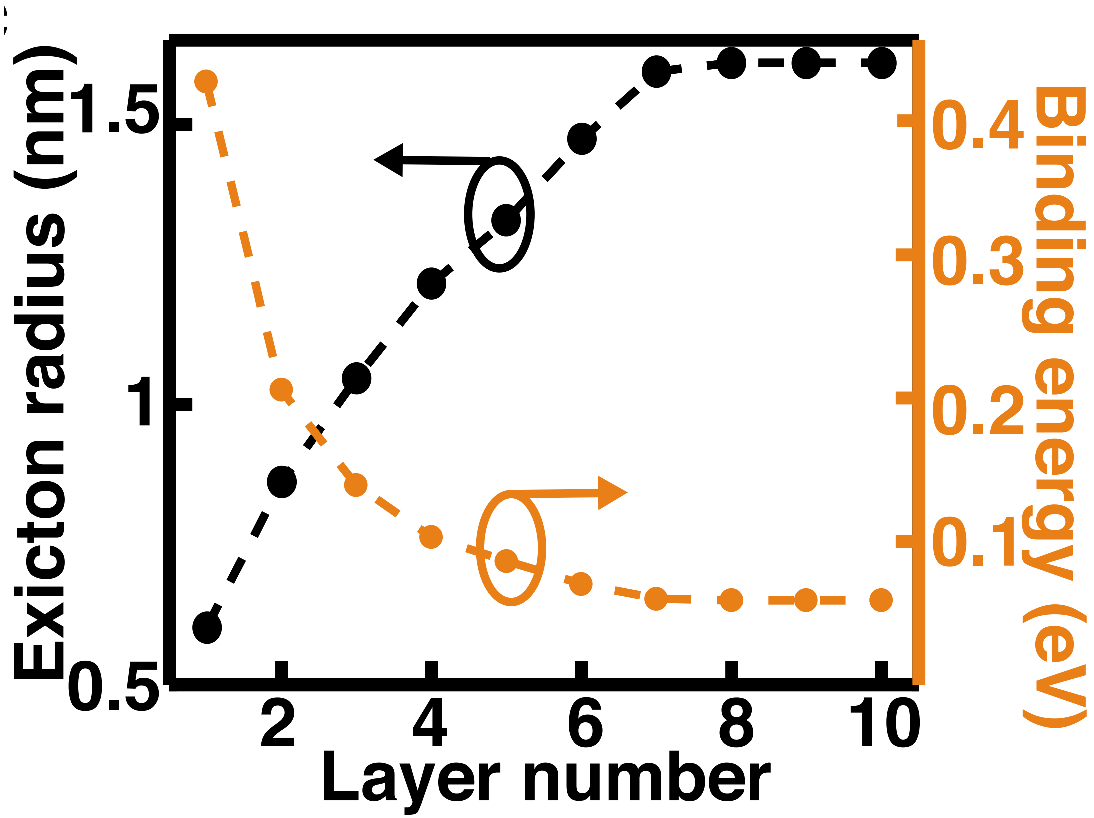
Excitonic effect



The excitonic effects dominates over the effect of the band structure.

Yiling Yu et al, **Sci. Rep.** 5, 16996 (2015)

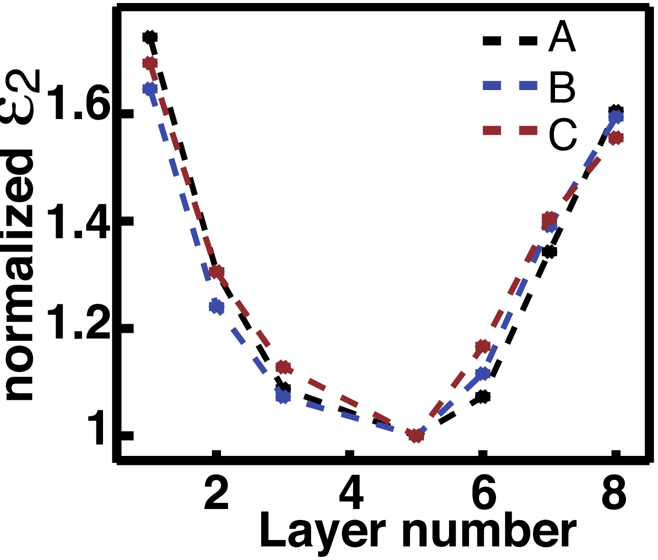
Exciton Binding Energy and Exciton Radius

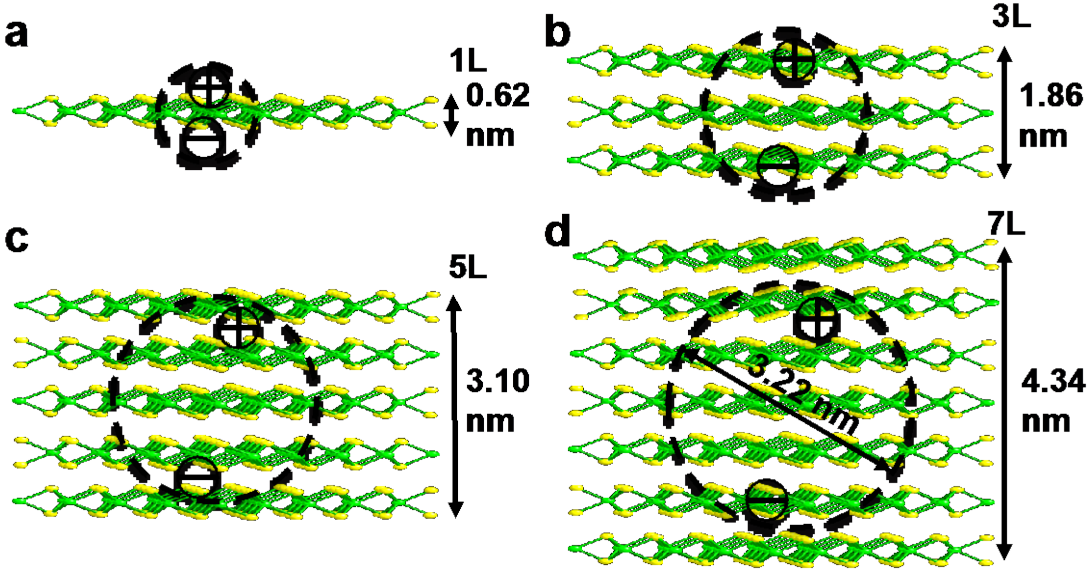


The experimental results are consistent with the theoretical calculations in references.

Yiling Yu et al, **Sci. Rep.** 5, 16996 (2015)

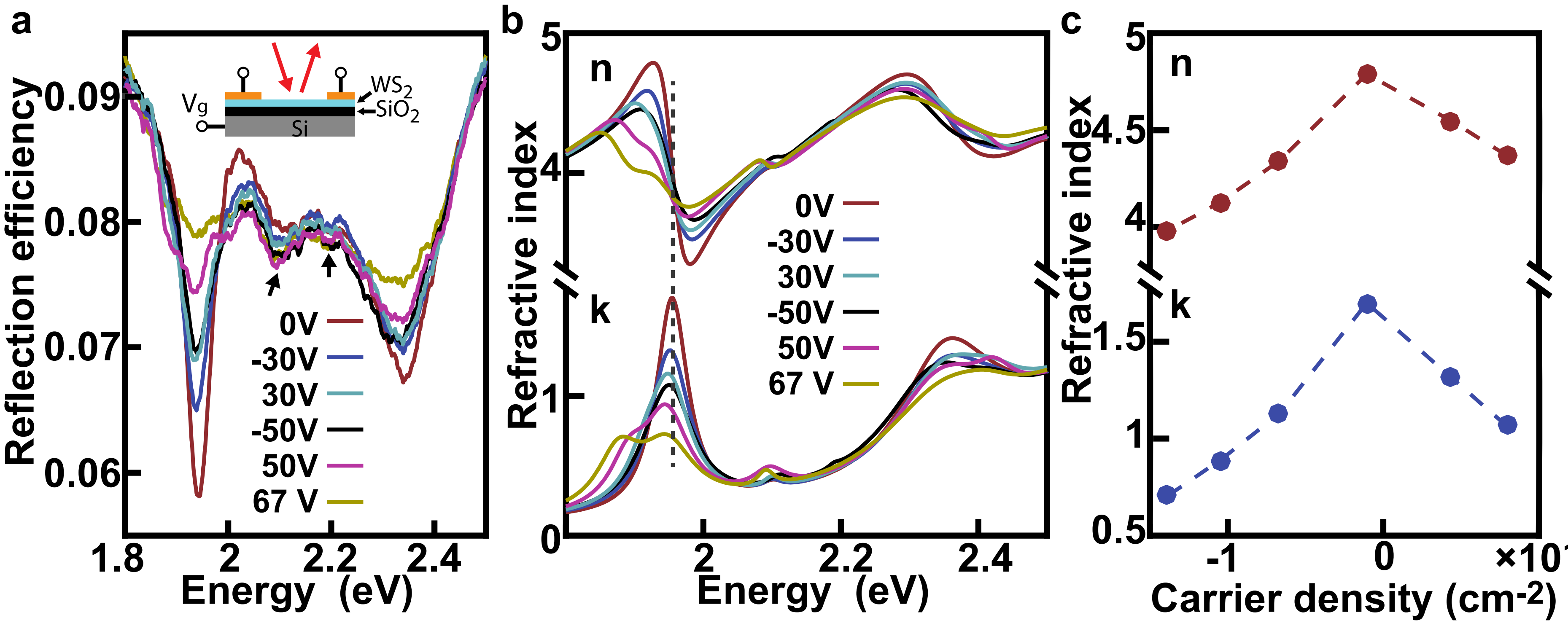
Geometric Confinement





The excition radius in bulk MoS2 is 3.22 nm, close to the thickness of 5L films

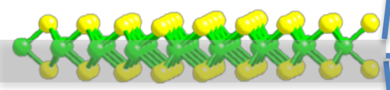
Electrically Tunable Light-Matter Interactions: Field-Effect Photonics



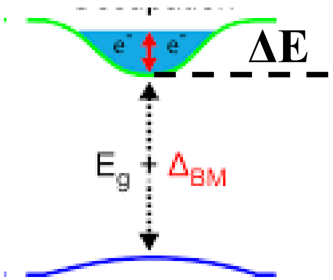
The refractive index can be tuned by > 60% with electrical gating!

Yiling Yu et al, **Submitted**

Doping Effect



Phase Space Filling (Pauli principle)



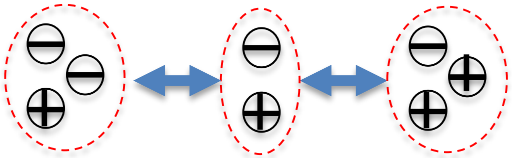
$\Delta E = \pi\hbar^2 n/2m$

m: effective mass

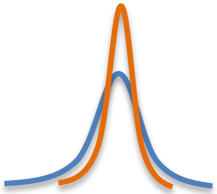
n: density of charge

Coulomb scattering

Interchange of charged and neutral excitons

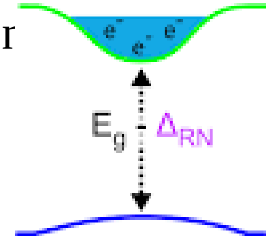


Dephasing: spectral broadening



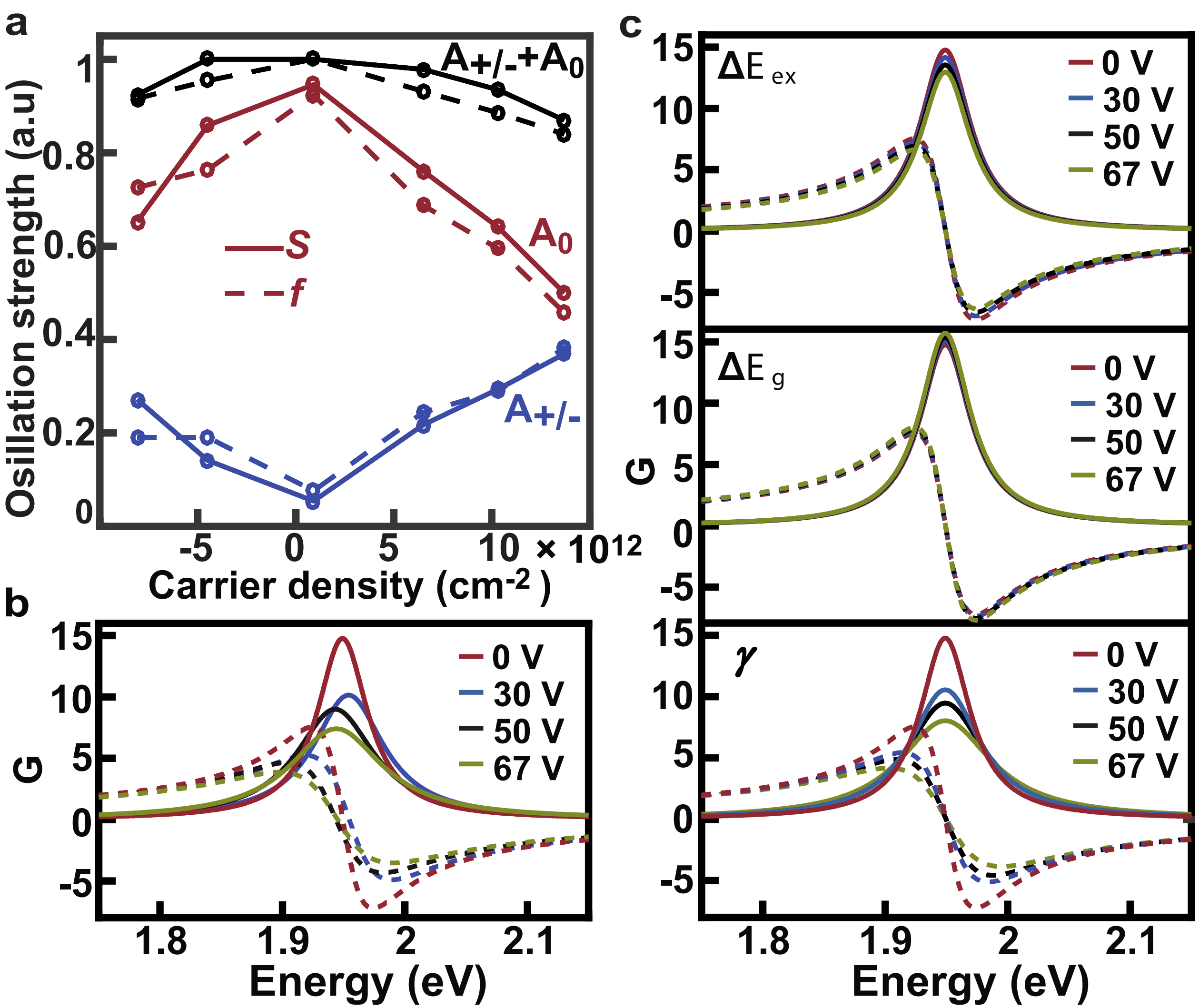
Dielectric screening scattering

Bandgap renormalization



Change in exciton binding energy

Electrically Tunable Light-Matter Interactions

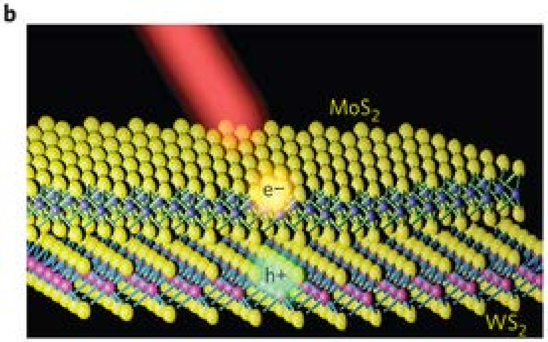


The dominant mechanism: interchange of trions and excitons and spectral broadening (Coulomb Scattering)

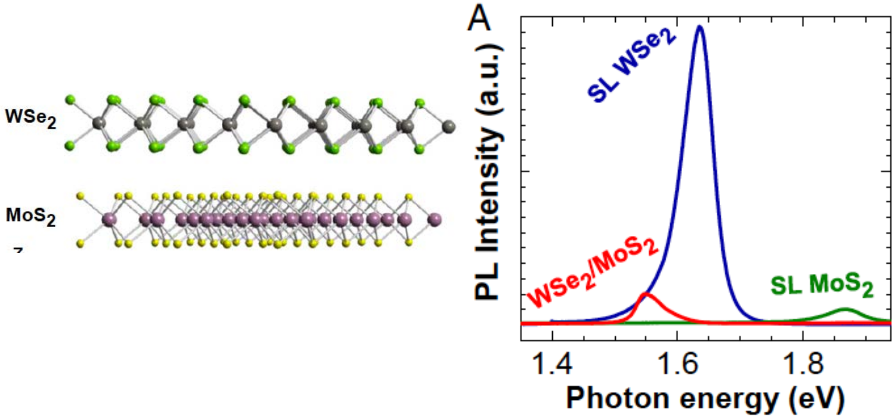
Yiling Yu et al, **Submitted**

Exciton Engineering in Heterostructures

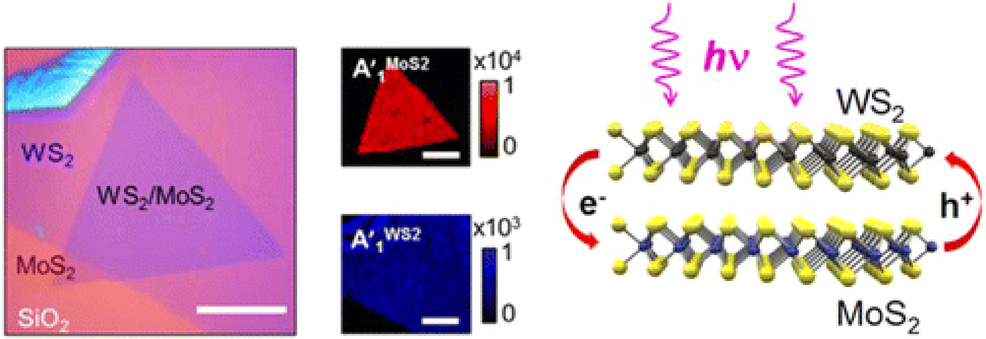
Exicton Dynamics in Heterostructures



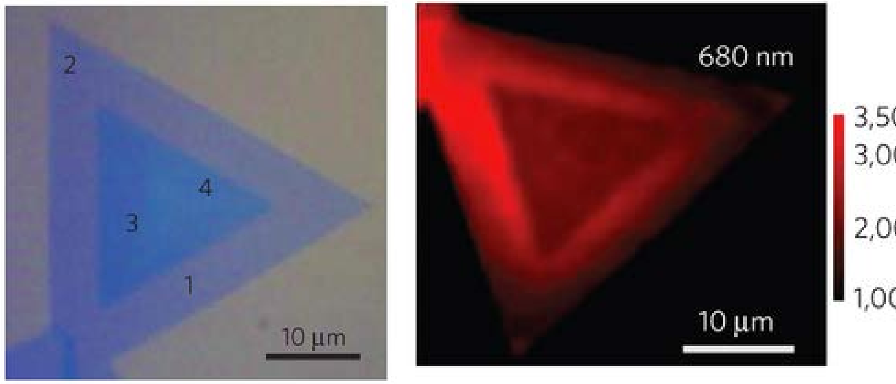
Nature Nanotechnology 9, 682–686 (2014)



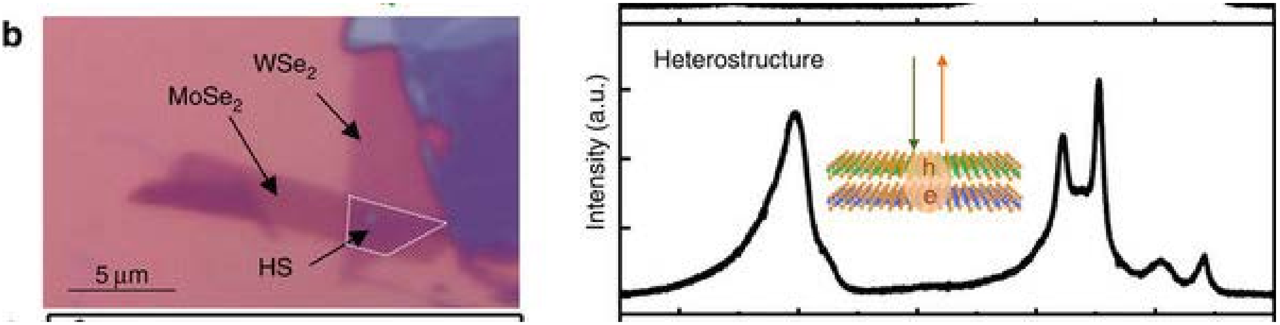
| PNAS | | vol. 111 | 6198–6202 , 2014



Nano Lett., 2014, 14 (6), pp 3185–3190

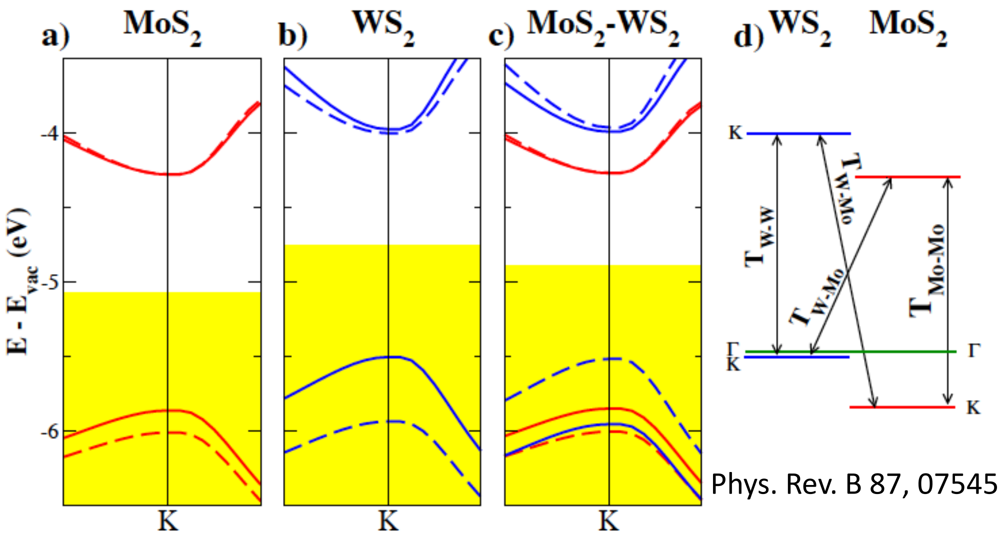


Nature Materials 13, 1135–1142 (2014)

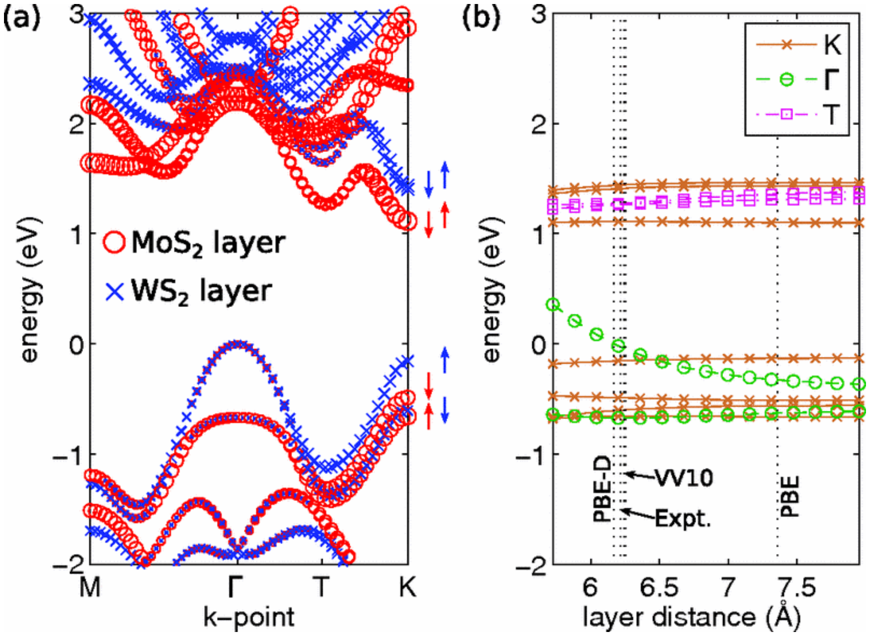


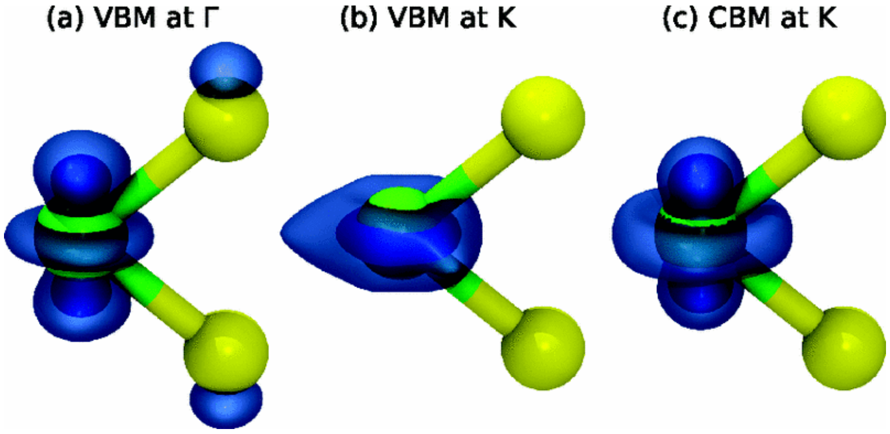
Nature Communications 6, Article number: 6242

Band Structures in MoS2/WS2 Heterostructures



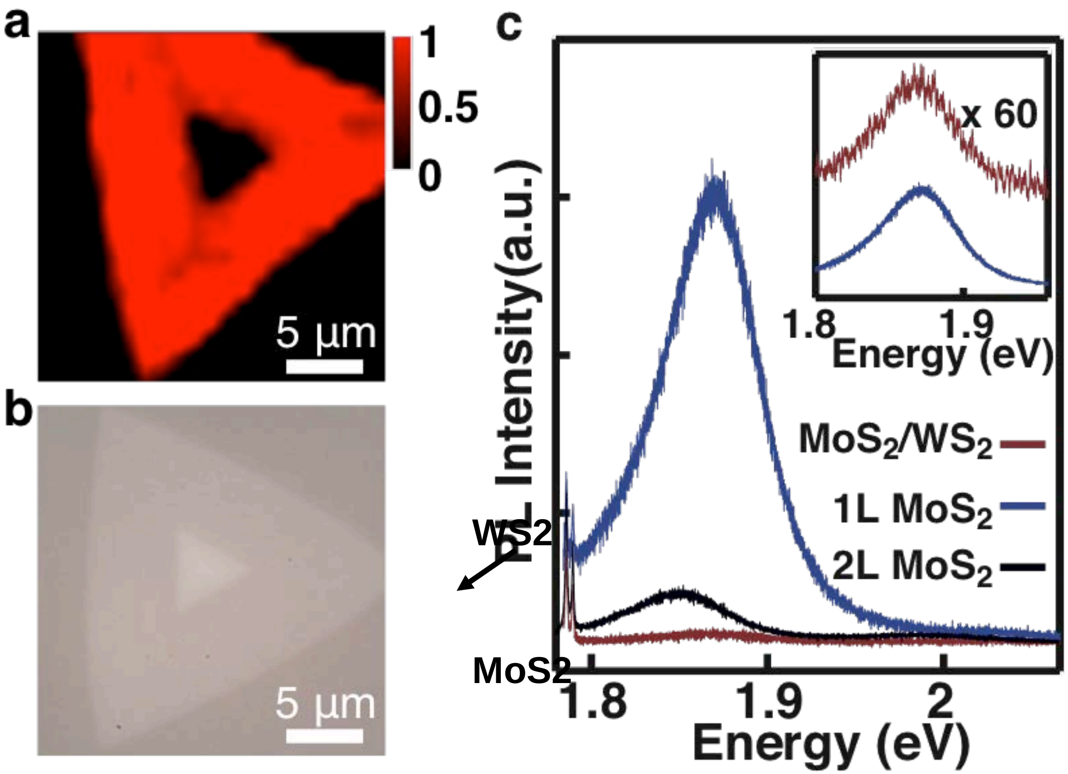
Phys. Rev. B 87, 075451 (2013)

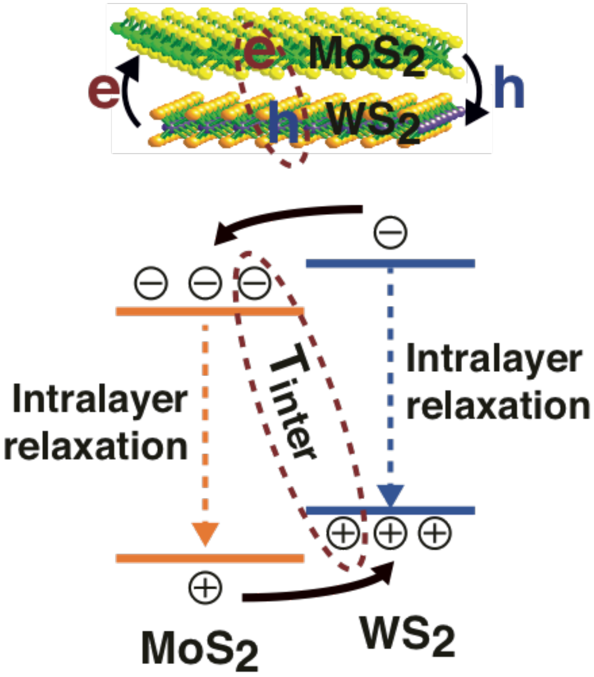




Phys. Rev. B 88, 085318

Equally Efficient Interlayer Charge Transfer in Epitaxial and Non-epitaxial MoS2/WS2 Heterostructures

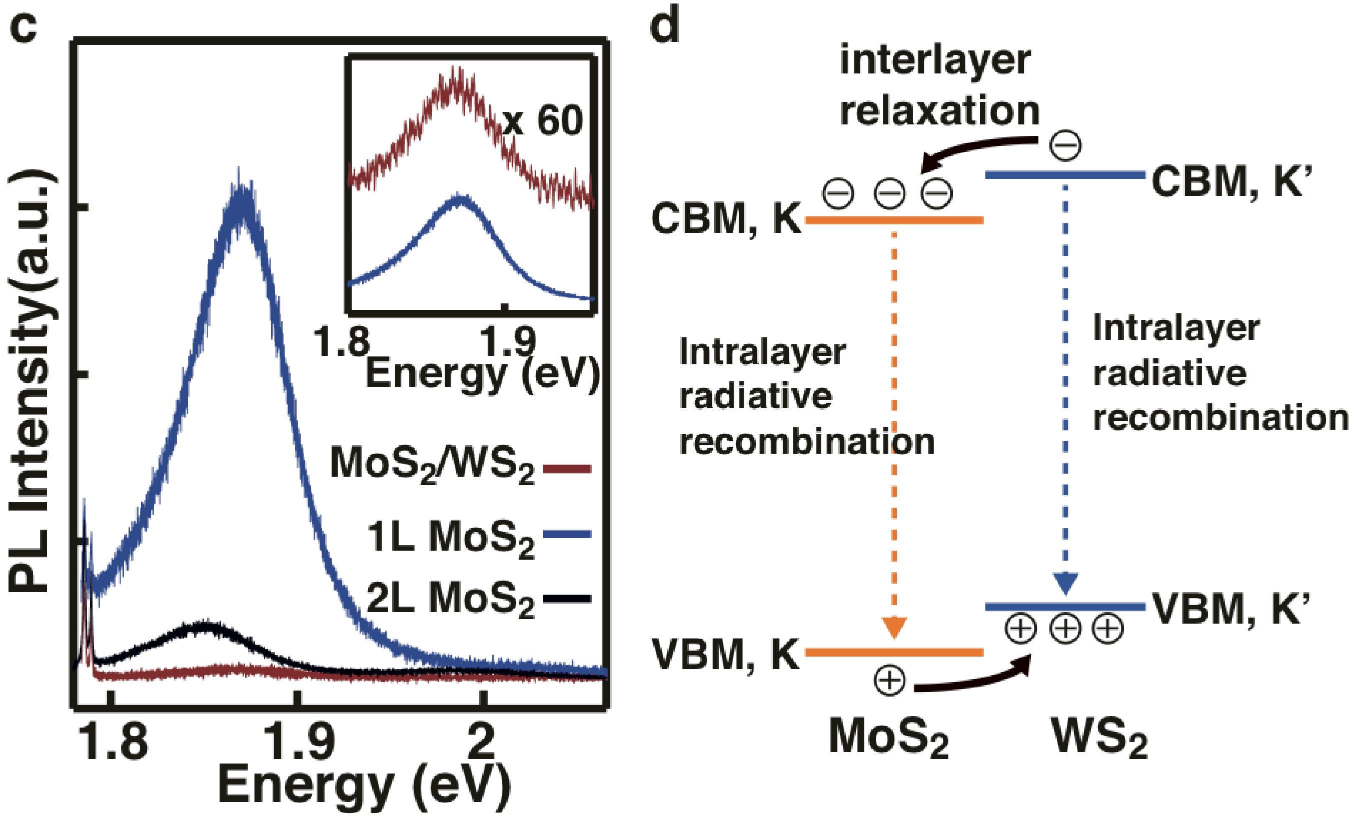




The PL in MoS2/WS2 is two orders of magnitude less!

Yifei Yu et al. *Nano Lett*, DOI: 10.1021/nl5038177, **2014**

Efficient Interlayer Exciton Relaxation

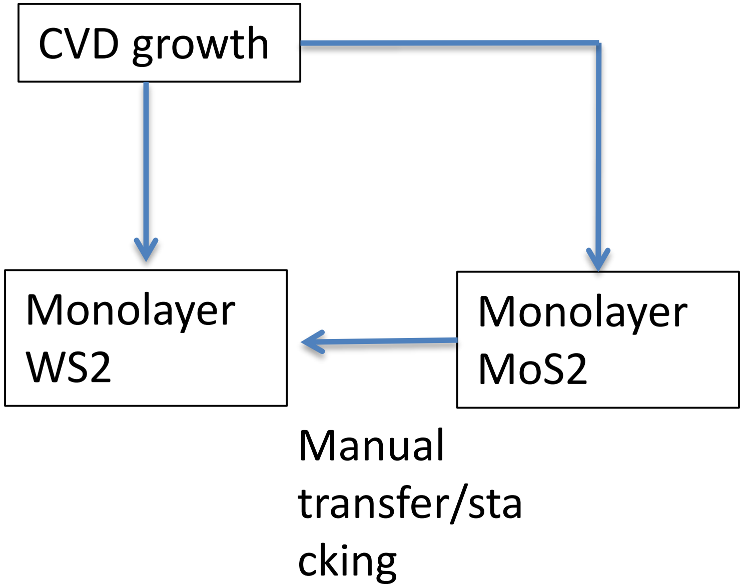


- The radiative lifetime of excitons in MoS2 is around 1-5 ps.
- The PL is supressed by 50 -100 times after the heterostructuring.

The interfacial charge transfer is in scale of 10-100 fs!

Yifei Yu et al. *Nano Lett*, DOI: 10.1021/nl5038177, **2014**

Equally Efficient Interlayer Charge Transfer in Epitaxial and Non-epitaxial MoS2/WS2 Heterostructures

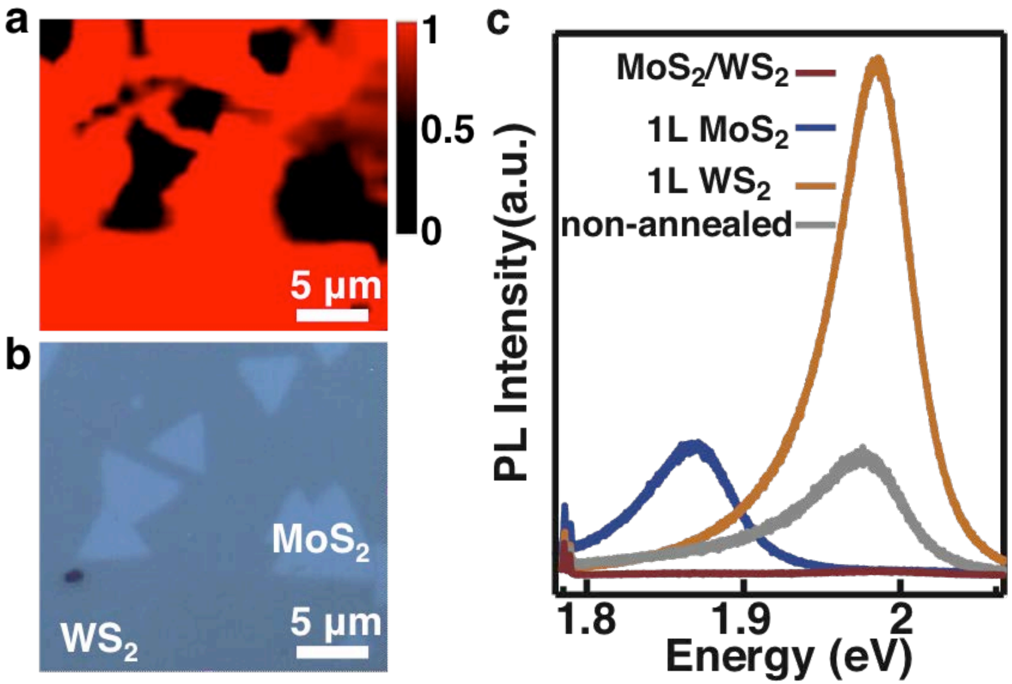


CVD growth

Monolayer WS2

Monolayer MoS2

Manual transfer/stacking

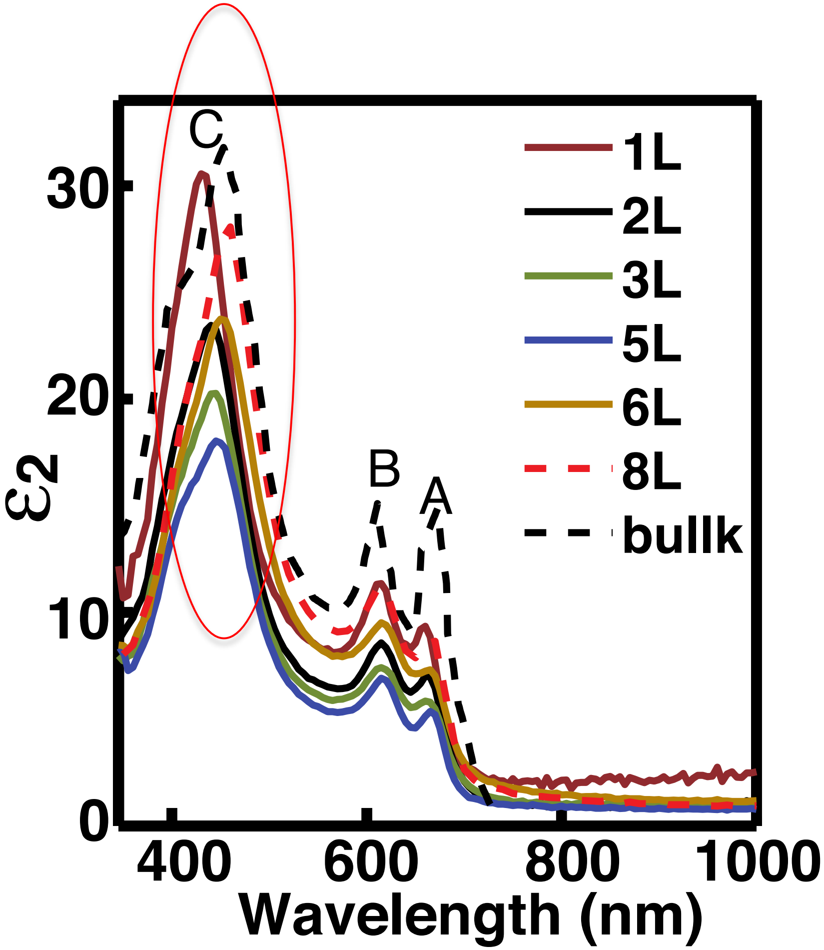


Efficient interlayer relaxation in non-epitaxial heterostructures!

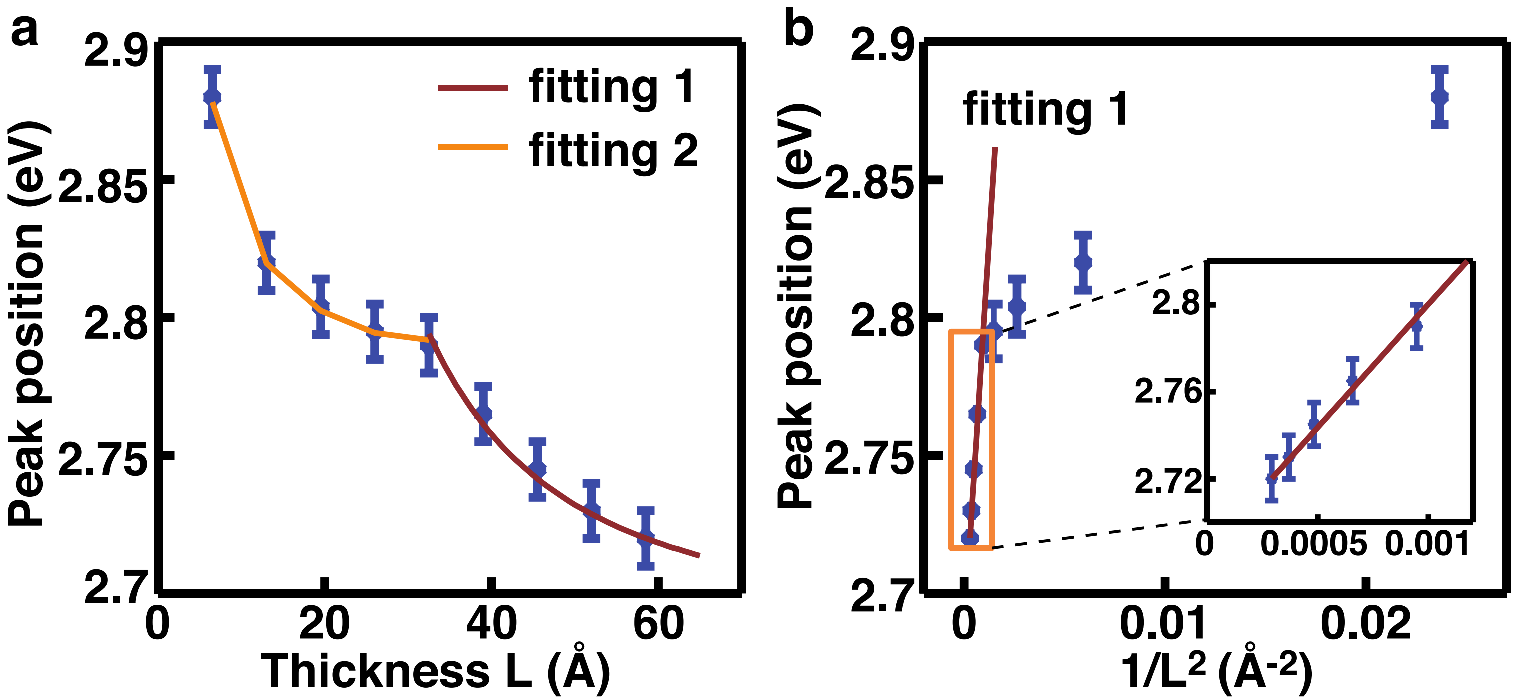
Yifei Yu et al. *Nano Lett*, DOI: 10.1021/nl5038177, **2014**

Thank You!

Layer-dependent Peak Positions: Excitonic Effects



Layer-dependent Exciton Binding Energy



Model 1.conventional quantum confinement, which assumes a constant excitonic binding energy

$$E = E_g + \pi^2\hbar^2/(2m_{eff}L^2)$$

Model 2 based on quantum confinement in fractional space. It assumes the excitonic binding energy varies.