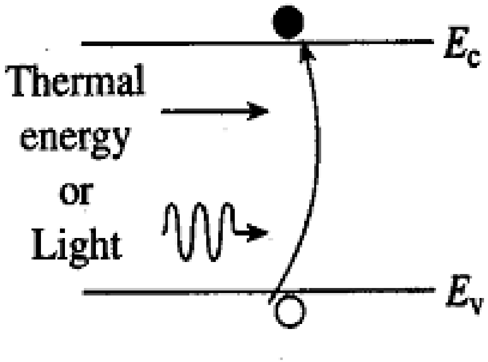
Harvard John A. Paulson
School of Engineering
and Applied Sciences

Recombination in Conventional and Unconventional Semiconductors

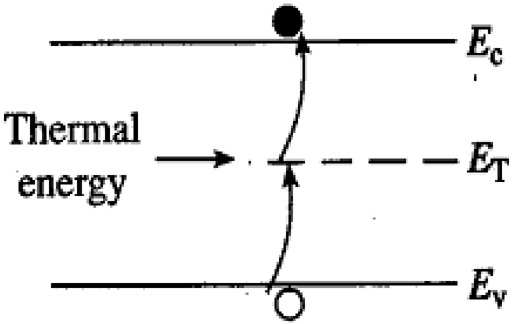
Tuesday, November 22nd, 2021

Free-Carrier Generation

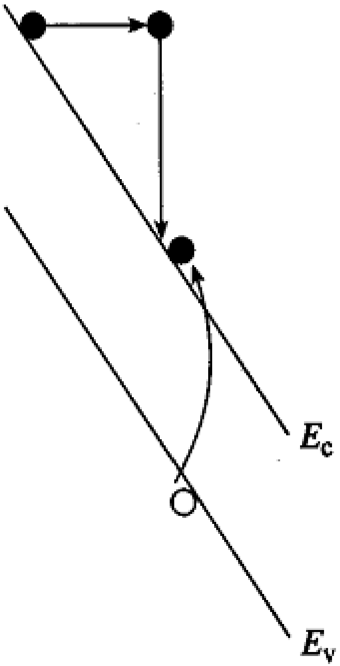
Band-to-Band



R-G Center



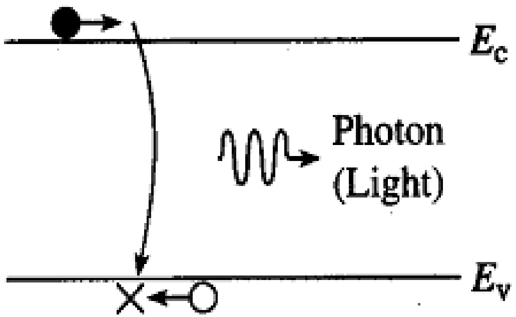
Impact Ionization



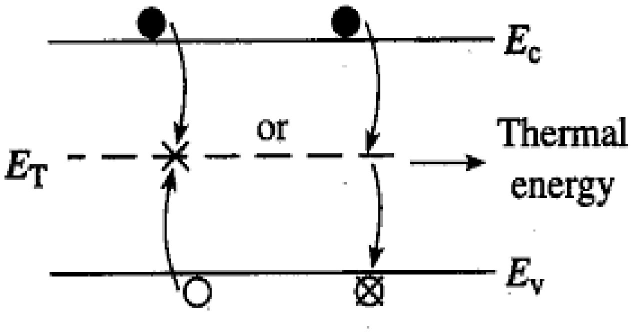
R.F. Pierret, *Semiconductor Device Fundamentals*

Free-Carrier Recombination

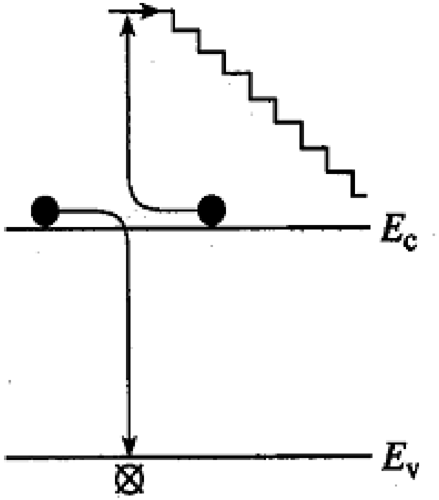
Direct



R-G Center



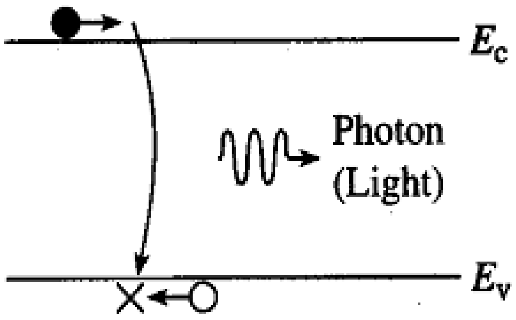
Auger



What do you expect the proportionality factors to be?
i.e. $R \propto n^x p^y$?

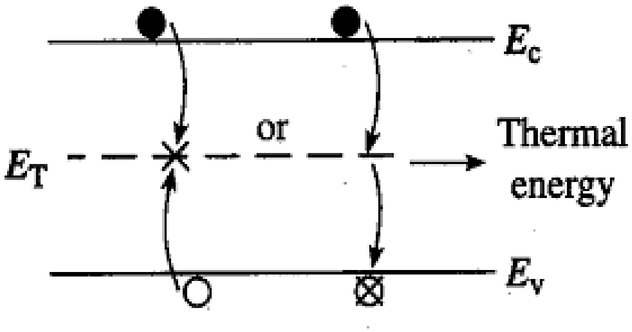
Free-Carrier Recombination

Direct



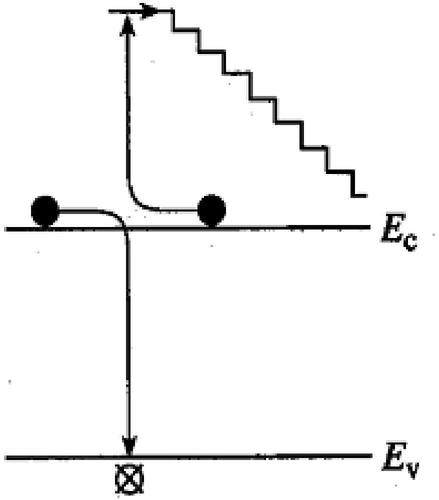
$\propto np$

R-G Center



$\propto n$ (p-type)
$\propto p$ (n-type)

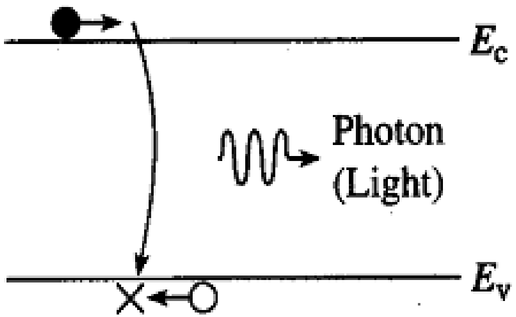
Auger



$\propto n^2 p$ (n-type)
$\propto np^2$ (p-type)

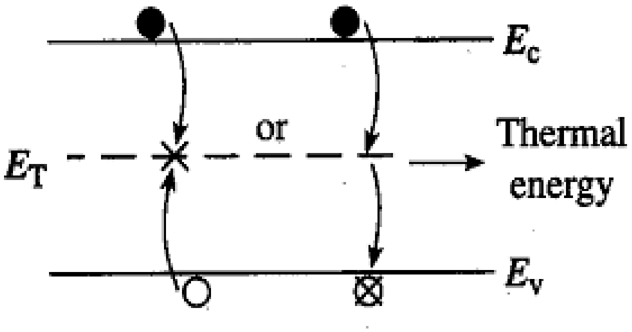
Aside: detailed expressions

Direct



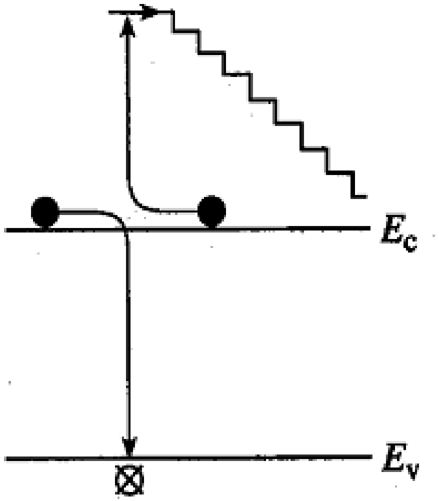
$$R_{b-b} = B(np - n_i^2)$$

R-G Center



$$R_{SRH} = \frac{np - n_i^2}{p + n + 2n_i \cosh(\frac{E_i - E_T}{kT})} N_T v_{th} \sigma$$

Auger



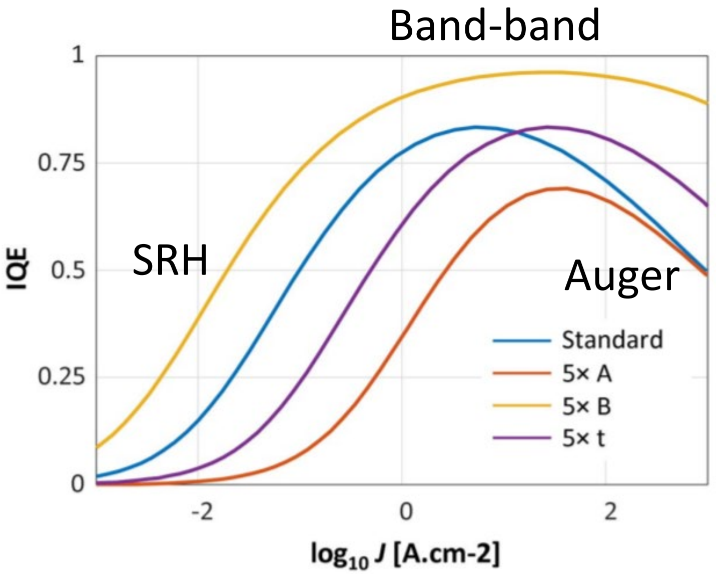
$$R_{Auger} = \Gamma_n n\left(np - n_i^2\right) + \Gamma_p p(np - n_i^2)$$

https://ece.colorado.edu/~bart/book/book/chapter2/ch2_8.htm

ABC Model

Key metric: Photoluminescence Quantum Yield (PL QY) = Photons Out/Photons In

$$QY = \frac{R_{rad}}{R_{rad} + R_{nonrad}} = \frac{Bn^2}{An + Bn^2 + Cn^3}$$



A. David, et al., *ECS J. Solid State Sci*. Technol. **9,** 016021, 2020.

NANOMATERIALS

Near-unity photoluminescence quantum yield in MoS_2

M. Amani, D.-H. Lien, D. Kiriya, et al., *Science*, 2015

DEVICE TECHNOLOGY

Electrical suppression of all nonradiative recombination pathways in monolayer semiconductors

D.-H. Lien, S.Z. Uddin, et al., *Science*, 2019

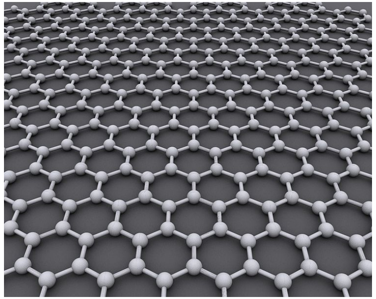
PHOTOPHYSICS

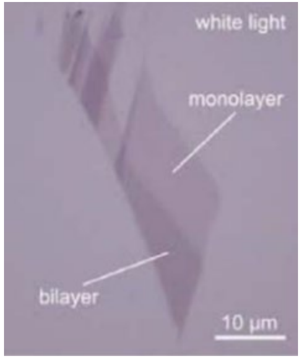
Inhibited nonradiative decay at all exciton densities in monolayer semiconductors

H. Kim, S.Z. Uddin, et al., *Science*, 2021

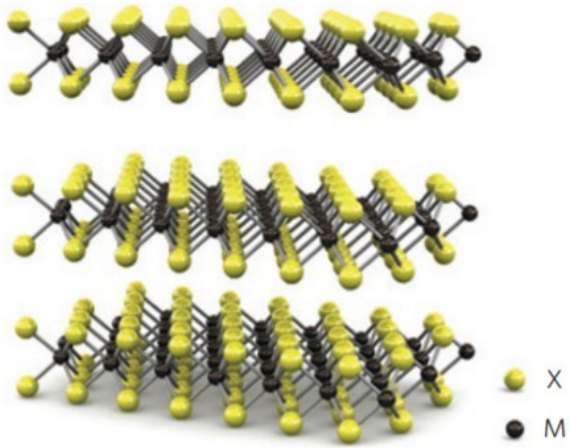
2D Materials

Graphene: great transport properties (high mobility), but no bandgap!



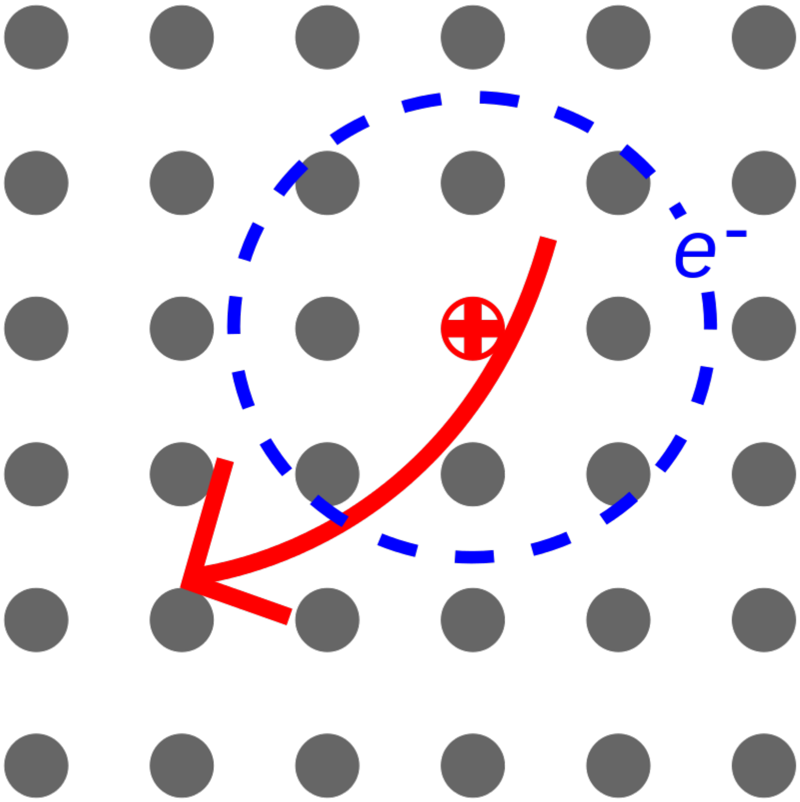


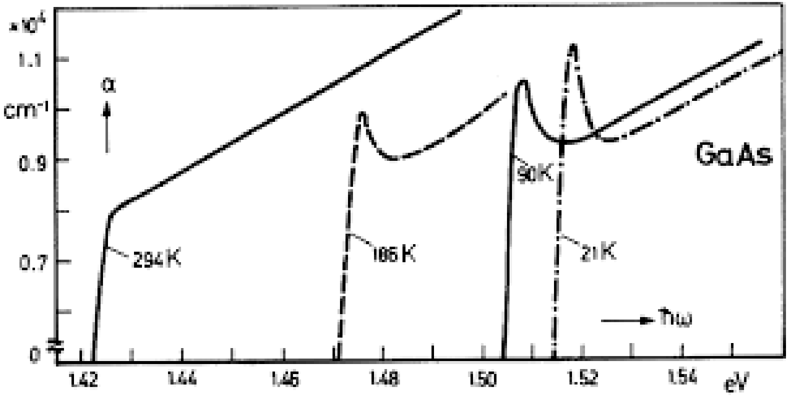
Transition Metal Dichalcogenides (TMDCs)



Semiconductors, metals, insulators, superconductors, ferroelectrics…

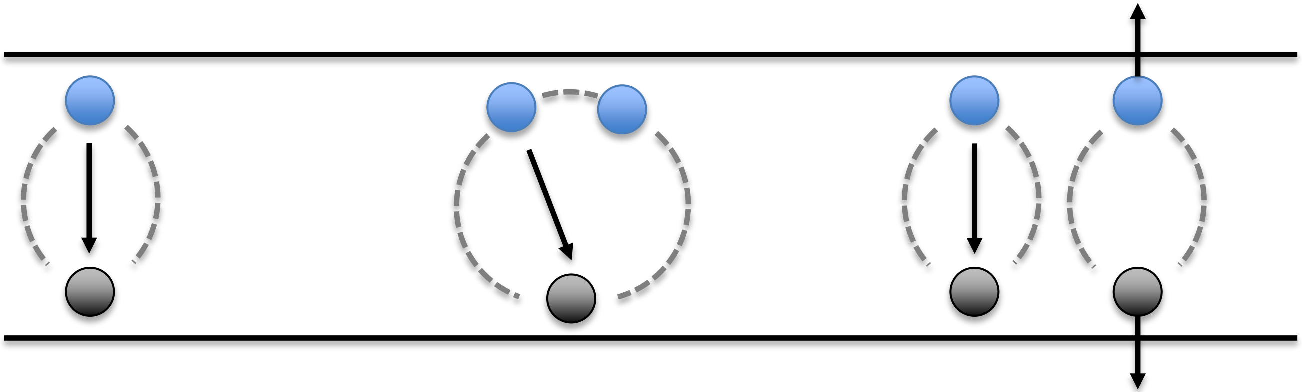
Excitons





- Small binding energies → normally need cryogenic temperatures
- Quantum confinement in 2D materials leads to large exciton binding energies → room temperature excitons!

Exciton Recombination Pathways



Neutral Excitons

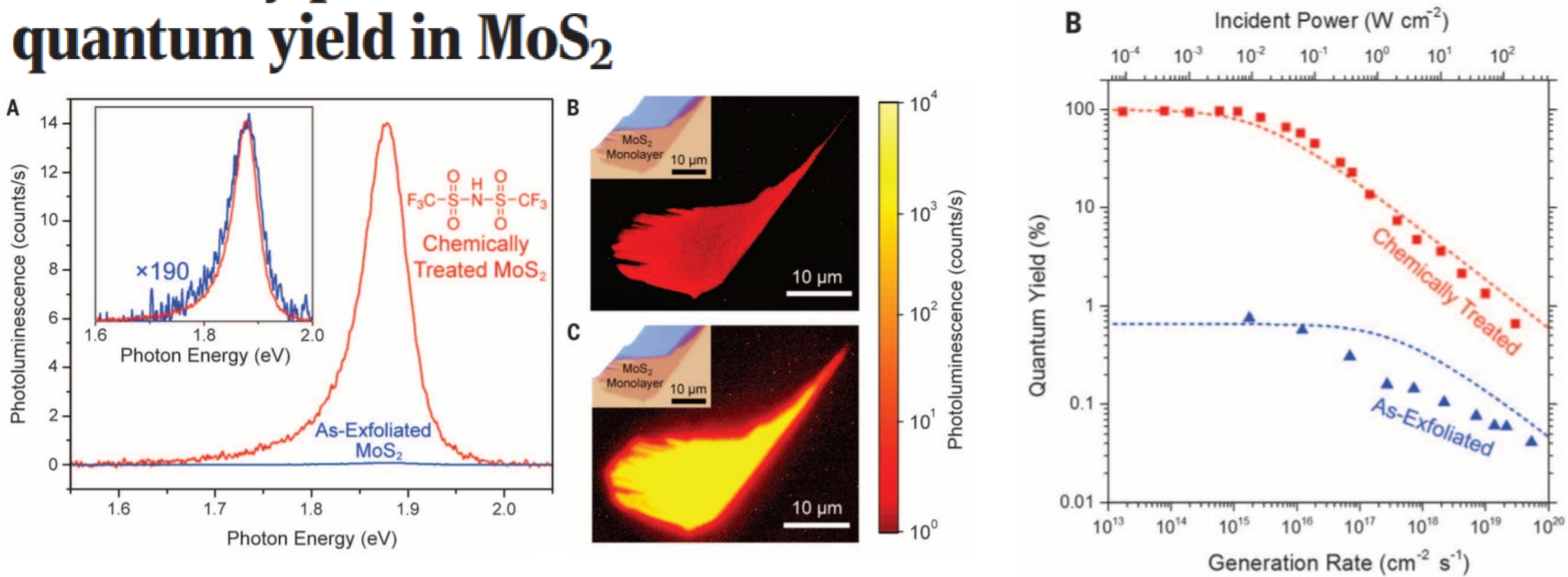
Charged Excitons / Trions

Exciton-Exciton Annihilation

Which are radiative? Which are nonradiative?

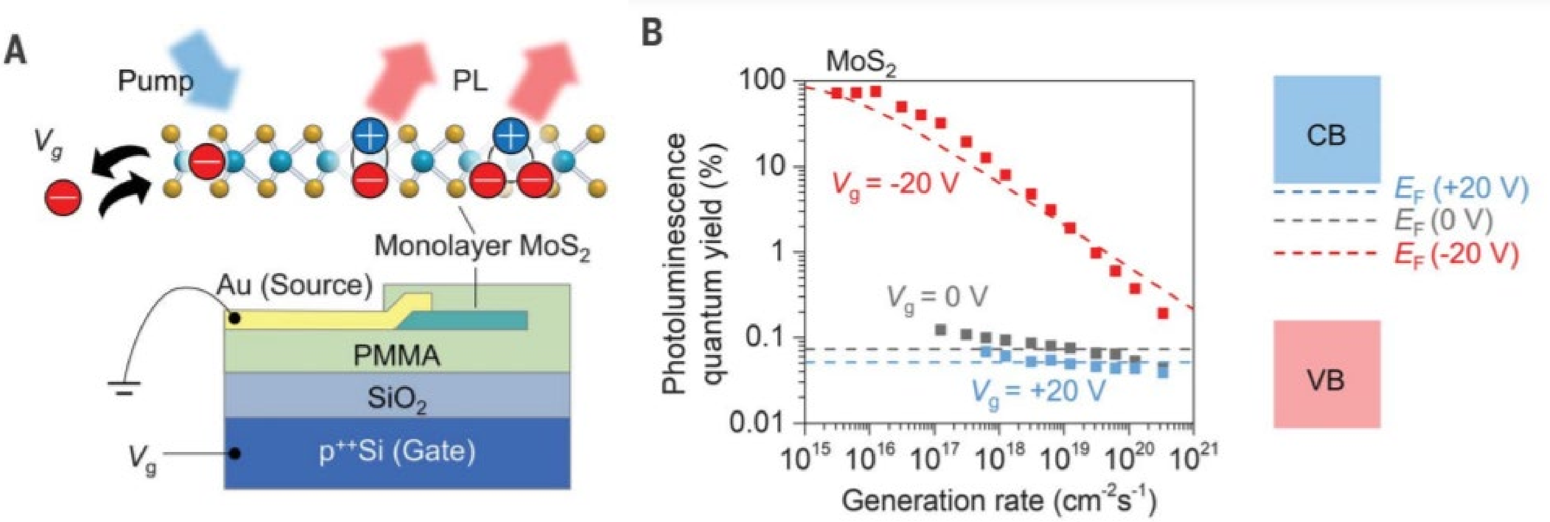
NANOMATERIALS

Near-unity photoluminescence quantum yield in MoS_2



- Treatment with an organic superacid (TFSI) leads to near-unity PL QY…but what is the underlying mechanism?
- Clue toward next steps: PL QY clearly does not follow a free-carrier trend

Electrical suppression of all nonradiative recombination pathways in monolayer semiconductors

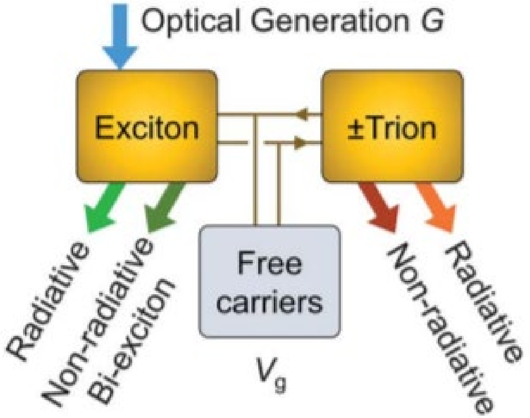


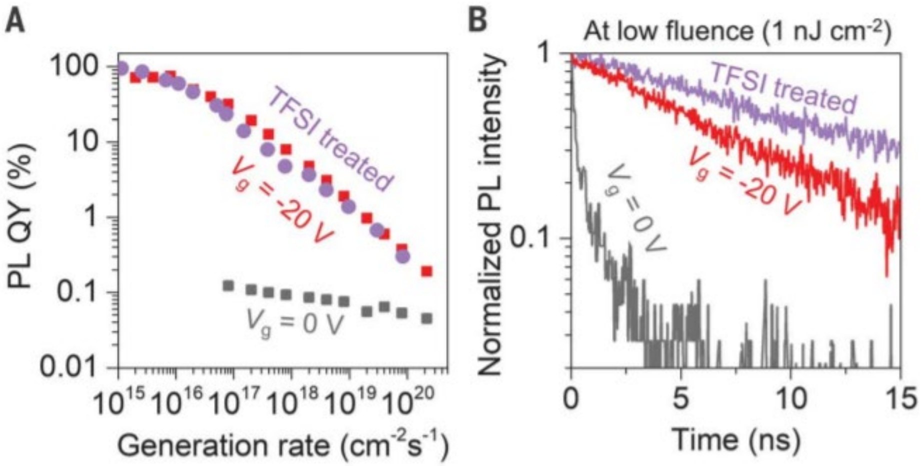
- Suspect that presence of charge would lead to Auger-like effects – verify by **electrically doping** the monolayer
- Reproduces previous paper's results, and verifies background doping degrades QY

Electrical suppression of all nonradiative recombination pathways in monolayer semiconductors

$$QY = \frac{1}{G}\left(\frac{n_X}{\tau_X} + \frac{n_T}{\tau_T}\right)$$

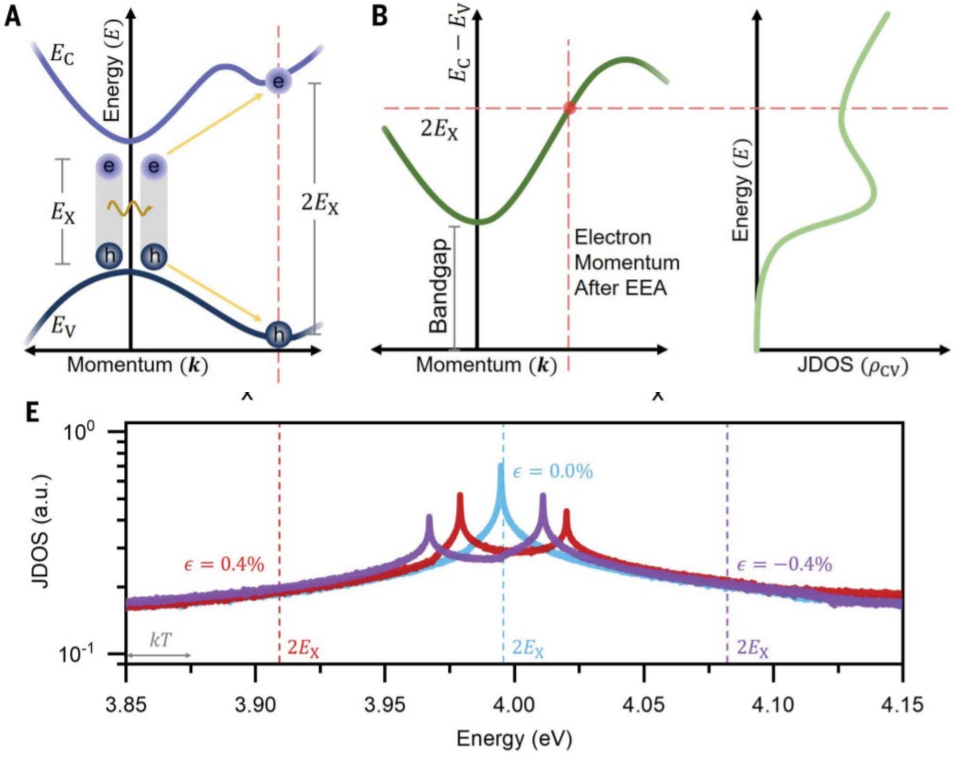
$$G = \frac{n_X}{\tau_X} + \frac{n_T}{\tau_T} + C_{bx} n_X^2$$





- Lifetime measurements and analytical modeling indicate that neutral excitons are almost entirely radiative, while trions are almost entirely nonradiative (very short nonradiative lifetime ~50ps).
- Exciton-exciton annihilation is also dark and causes an efficiency droop at high densities where most applications operate → problem!

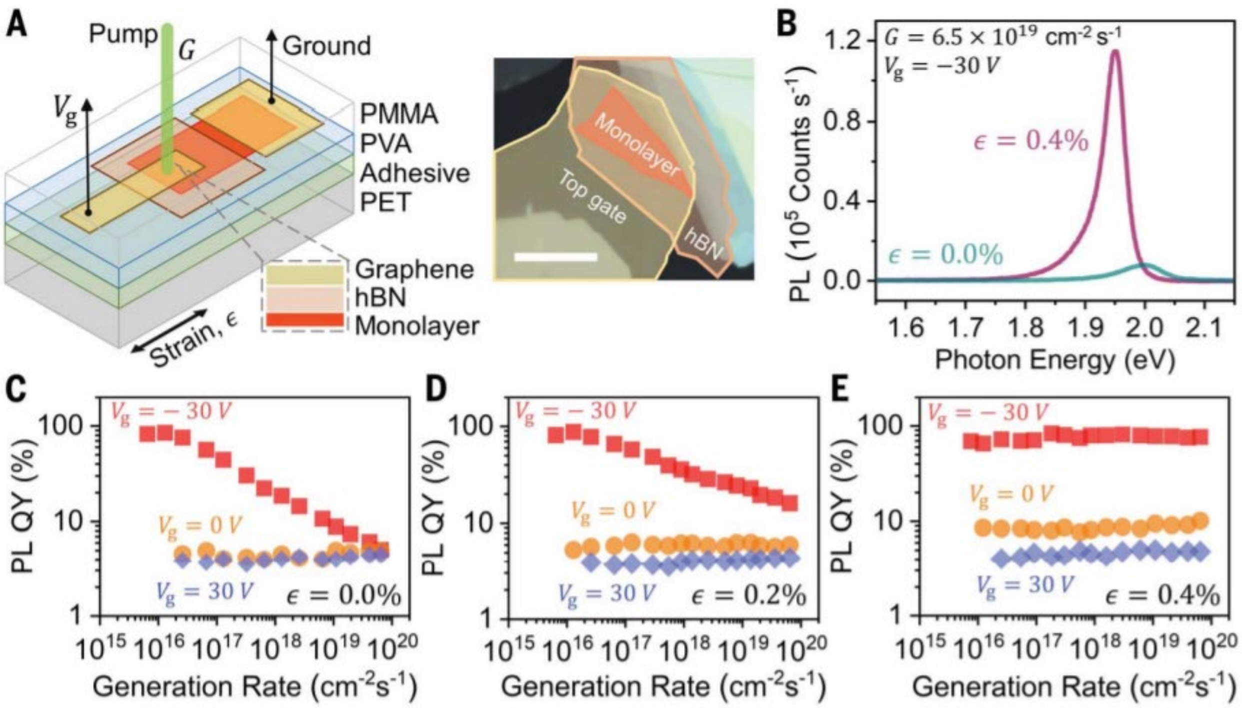
Inhibited nonradiative decay at all exciton densities in monolayer semiconductors



- Energy + Momentum Conservation
  $E_e + E_h = E_C(k_e) - E_v(k_e) \approx 2E_X$
- Fermi's Golden Rule: Transition rate $\propto$ joint density of states (JDOS)
- Turns out that $2E_X$ coincides with peak of JDOS resonance (van Hove singulairty) → **Strain** the material to split the resonance and shift the transition energy away

PHOTOPHYSICS

Inhibited nonradiative decay at all exciton densities in monolayer semiconductors



Conclusions

- Room-temperature excitonic behavior of 2D materials leads to unexpected behavior in the recombination photophysics.
- Multiple **material tuning knobs:**
  - Doping to tune dominant species from trions to neutral excitons
  - Strain to engineer bandstructure and suppress exciton-exciton annihilation
- What's next?
  - Scalability – exfoliation is not sustainable, but currently leads the highest quality material
  - How to make an electroluminescent device without doping for efficient carrier injection/contacts?