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

Integrating Circuits

Photodetectors

Lasers

Chemical/bio Sensors

Catalysts
Light Reflection/scattering

Light absorption

Light Emission

Light Emission

Exciton Dynamics

Light Reflection/scattering

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
A and B from interband transition of K/K’ points, and C from transition in the Brillouin zone between Γ and Λ.
Extraordinarily Strong Binding Energy

The exciton binding energy in 1L MoS2 is reported ~ 0.4-1.1 eV (0.4-0.6 eV more reasonable)
The exciton binding energy in WS2 monolayer is $0.71 \pm 0.01$ eV around K valley.
The exciton radius is estimated to be 0.5-2 nm
Anisotropy: Fractional Dimensional Space

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

**Fractional dimensional space model**

\[ \alpha = \left( \frac{E_{\text{bulk}}}{E_{2D}} \right)^{1/2} + 1 \]

Many-body Interactions

- Exciton-charge
- Exciton-exciton
Trions have a binding energy estimated to be $\sim 20\text{meV}$ and much lower efficiency than neutral excitons.
The PL intensity and position can be substantially affected by the doping level.
Doping Effect: More than Coulomb Scattering

Phase Space Filling (Pauli principle)

Coulomb scattering

Dielectric screening scattering

\[ \Delta E = \frac{\pi \hbar^2 n}{2m} \]

- \( m \): effective mass
- \( n \): density of charge

Interchange of charged and neutral excitons

Dephasing: spectral broadening

Bandgap renormalization

Change in exciton binding energy
The electronic bandgap can be renormalized due to the dielectric screening effect of doping.
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

**Phase space filling**

\[ \text{change in binding energy } \Delta E_{\text{ex}} = \Delta E_g - \Delta E_{\text{opt}} \]

\( \Delta E_g \): bandgap renormalization, \( \Delta E_{\text{opt}} \): change in optical bandgap

**Change in exciton binding energy:** 5-25 meV
Exciton-Excitons Annihilation

High exciton-exciton annihilation rate!

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

Slope: $k_{ee}N_0$

$N_0 \propto$ Incident power fluence

\[ \frac{dN}{dt} = -k_{ee}N^2 \]

\[ \frac{N_0}{N(t)} - 1 = k_{ee}N_0t \]

Dependence of exciton-exciton annihilation rate on substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_{ee}$ (cm$^2$/s)</th>
<th>$\tau_r$ (ns)</th>
<th>$\tau_{nr}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended WS$_2$</td>
<td>0.3</td>
<td>1</td>
<td>0.76</td>
</tr>
<tr>
<td>As-grown WS$_2$</td>
<td>0.1</td>
<td>4.5</td>
<td>0.13</td>
</tr>
<tr>
<td>Suspended MoS$_2$</td>
<td>0.1</td>
<td>28</td>
<td>1</td>
</tr>
<tr>
<td>As-grown MoS$_2$</td>
<td>0.05</td>
<td>80</td>
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Yiling Yu$^\dagger$, Yifei Yu$^\dagger$, Chao Xu$^\dagger$ et al, Phys. Rev. B 93, 201111(R)
The pumping threshold is solely dictated by the exciton-exciton annihilation rate.

\[
\frac{dN}{dt} = -\left(\frac{1}{\tau_r} + \frac{1}{\tau_{nr}}\right)N - k_{ee}N^2 + \alpha I_0
\]
Exicton Dynamics: Defect-assisted Electron–Hole Recombination


Defect-Assisted Electron–Hole Recombination

ACS Nano, 2014, 8 (11), pp 11147–11153
Exciton lifetime in many reports: 1-30ps.
Exciton Lifetime

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

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

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Our result

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Substrate Effects
Effects of Substrate

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

As-grown MoS2: 0.1%
As-grown WS2: 1.5%
Suspended MoS2: 3%
Suspended WS2: 35%

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

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

mica and Teflon best for WS2 and MoS2

Polystyrene and h-BN best for WSe2.

Substrate may facilitate non-radiative lifetime of excitons by providing defects to serve as recombination centers.
Exciton Dynamics: Defect-assisted

Defect-Assisted Electron–Hole Recombination


ACS Nano, 2014, 8 (11), pp 11147–11153
The interference effect of monolayers may affect the PL efficiency depending on the refractive index of the substrates.
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.

Exciton-Dominated Light-Matter Interactions
Layer-dependent Optical Constants

Ellipsometry measurement

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

Layer-dependent Optical Constants

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

Physics of Dielectric Constant

\[ \varepsilon_{2,L}(\omega) = A_0 J_{cv,L} |U_L(0)|^2 \]

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

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

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

The excitation radius in bulk MoS2 is 3.22 nm, close to the thickness of 5L films.
The refractive index can be tuned by > 60% with electrical gating!
Doping Effect

- Phase Space Filling (Pauli principle)

\[ \Delta E = \frac{\pi \hbar^2 n}{2m} \]

- 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
The dominant mechanism: interchange of trions and excitons and spectral broadening (Coulomb Scattering)
Exciton Engineering in Heterostructures
Exciton Dynamics in Heterostructures


Nature Communications 6, Article number: 6242

PNAS | vol. 111 | 6198–6202, 2014
Band Structures in MoS2/WS2 Heterostructures

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
The radiative lifetime of excitons in MoS2 is around 1-5 ps.

The PL is suppressed by 50-100 times after the heterostructuring.

The interfacial charge transfer is in scale of 10-100 fs!
Equally Efficient Interlayer Charge Transfer in Epitaxial and Non-epitaxial MoS2/WS2 Heterostructures

CVD growth

Monolayer WS2

Manual transfer/stacking

Monolayer MoS2

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

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

Efficient interlayer relaxation in non-epitaxial heterostructures!
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

\[ E = E_g + \frac{\pi^2 \hbar^2}{(2m_{\text{eff}} L^2)} \]

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