Exciton dynamics and valley-contrasting properties in heterostructures based on atomically-thin semiconductors

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Workshop on Chiral Optical Modes, Aussois, Nov. 27, 2018
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Entering “Flatland”

2H-TMD (semiconductors)  
M= Mo, W  X= S, Se, Te

Graphene (semimetal)

Direct bandgap emission

Entering “Flatland”

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Graphene (semimetal)

Helicity-dependent valley addressability

Photolum. (u.a.)

Energy (eV)

MoTe$_2$

PRB 2016

Ajayan, Kim, Banerjee - Physics Today (2016)
2D Materials: a unique toolkit for fundamental and applied physics

- Room T excitonic effects
  - Spin-valley locked properties
  - Electron-phonon coupling

- Interlayer charge and exciton transport

- Nanophotonics, single photon emission
  - Materials engineering (phase, anisotropy, strain)

- Optoelectronics
- Valleytronics
- Nanomechanics

Massicotte et al., Nat Nano 2016
Mak et al., Science 2014
De Alba et al., Nat. Nano 2016
Spin-valley locking in monolayer TMDs

Broken inversion symmetry + strong spin orbit coupling

MoX$_2$

$\sigma^+$

$\sigma^-$

WX$_2$

$\sigma^+$

$\sigma^-$

Valley-polarized excitons...and their coherent superpositions

exciton $|+1\rangle$

exciton $|-1\rangle$

Coulomb Exchange

$\sigma^+$

$\sigma^-$

$|K\rangle$

$|K\rangle + i|K'\rangle \over \sqrt{2}$

G. Wang et al.
RMP 2018

**Fragile Valley Contrasts**

MoS$_2$

$T=14$K

Exc: $\sigma^-$

\[\rho = \frac{\rho_0}{1 + 2\tau_X/\tau_S}\]

$\rho$ ($\gamma$) degrees of circular (linear) polarization

- $\rho$ up to $\sim$100% at low T (MoS$_2$)
- $\gamma$ up to 60% at low T (MoS$_2$)

Valley contrasts are lost at room T

How to protect/tailor valley contrasts?

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K.F. Mak et al., Nat. Nano 2012

C. R. Zhu et al., PRB 2014
Room temperature Chiral coupling of valley excitons with spin-momentum locked surface plasmons

Graphene/TMD heterostructures as a 2D optoelectronic building block

Room temperature valley polarization and coherence in TMD/Graphene heterostructures
2D Matter meets 2D Light

Semiconducting 2H-TMDs

Surface plasmons (SPs)

Helicity-dependent valley addressability

Helicity-dependent directional SP launching
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Semiconducting 2H-TMDs

Surface plasmons (SPs)

Helicity-dependent valley addressability

Helicity-dependent directional SP launching

Tailored control of the valley pseudospin using TMD-SP architectures
2D Matter meets 2D Light

Room temperature chiral coupling between valley excitons and helicity-momentum locked surface plasmons

T. Chervy*, S. Azzini*, et al., ACS Photonics 5, 1281 2018 (Arxiv 1701.07972)
See also K. Kuipers’ “intermezzo”

Y. Gorodetzki (Ariel, IL), S. Wang (Eindhoven, NL)
Chiral coupling: 1L-TMD exciton with spin-orbit SP mode

- Resonant condition TMD excitons / \( n = \pm 1, \sigma = \mp 1 \) SP modes

Grating period \( \Lambda = 480 \text{ nm} \)

\[ \omega_{\text{SP}} \sim \omega_{\text{Aex}} \sim 2.010 \text{ eV} \]

- Angle-resolved WL absorption (1-R \( \sim \) A) – CPL analysis

Anticrossing \( \hbar (\omega_+ - \omega_-) = 40 \text{ meV} \)

Strong-coupling FOM

\[
C = \frac{2\Omega_R}{\gamma_{\text{exc}} + \Gamma_{\text{SO}}} \approx 0.9
\]
Room temperature chiralitons

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Chiralitons

- Plasmon sorter efficiency: 15%
- Net chiraliton flow: 6% → 40%

Recent related results: Spin-momentum locking: TU Delft (Science 2018), UT Austin (arXiv:1801.06543)
```
Coherent superposition of counterpropagating chiralitons

- **PL polarization tomography on a linear basis**
  Measured as the $m_{11}$ Mueller matrix element

- **Chiralitonic valley coherence**
  \[ \frac{(S_1|^{TM} - S_1|^{TE})}{2} = m_{11} \sim 5 - 8\% \]

\[ |\Psi\rangle = |P_{K,\sigma_+, -k_{SP}}^\pm\rangle + |P_{-K,\sigma_-, +k_{SP}}^\pm\rangle \]

Outlook: No valley contrasts in bare TMD $\rightarrow$ Cavity protection mechanism? Designing new 2D building blocks for chiral optics.
Room temperature Chiral coupling of valley excitons with spin-momentum locked surface plasmons

Graphene/TMD heterostructures as a 2D optoelectronic building block

Room temperature valley polarization and coherence in TMD/Graphene heterostructures
**Graphene: 2D semi-metallic channel**
- Quasi-transparent (~2% absorption per layer)
- High carrier mobility and large carrier density
- Gate-tunable properties

**TMD: 2D semiconducting channel**
- Strong light-matter interaction
- Broadband absorption and tunable emission

**Gr-TMD heterostructures:**
- Strong interlayer coupling
  (J. He *et al.*, Nat Comm. 2014)
- Photogating/photodetection
- ps-range photoresponse
  (M. Massicotte *et al.*, Nat Nano 2016)
Gr/TMD heterostructures: why the interest?

- Strong interlayer coupling
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- Photogating/photodetection

- ps-range photoresponse
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Low efficiency with monolayer TMD
- Energy transfer?
Charge and energy transfer mechanisms

(a) Interlayer Electron Transfer

(b) Interlayer Hole Transfer

(c) Dexter-type Interlayer Energy Transfer

(d) Förster-type Interlayer Energy Transfer

- Probed in the steady state (Raman)
- Balanced electron and hole transfer

- Determine exciton dynamics
  → Relative efficiencies?
Our Experimental Approach

- Understanding near-field interactions (IET vs ICT)
- Implications for optoelectronic devices

Tunable excitation

Photolum. Raman

< 1 nm

Gr

TMD

Understanding near-field interactions (IET vs ICT)

Implications for optoelectronic devices
Atomic Force Microscopy

Smooth Gr/MoSe$_2$ domains

MoSe$_2$

Gr/MoSe$_2$

Gr

Height (nm)

Distance (µm)

0.0 0.5 1.0 1.5

0
1
2
3

0.6

0

10 nm

5 µm
Photoluminescence mapping

Bare MoSe$_2$

Coupled Gr/MoSe$_2$

Decoupled Gr/MoSe$_2$

Strong PL Quenching $\sim$ 300
Exciton: dynamics: PL vs $\Phi_{\text{photons}}$

- PL saturation on bare and decoupled MoSe$_2$
Exciton dynamics: PL vs $\Phi_{\text{photons}}$

- PL saturation on bare and decoupled MoSe$_2$:
  $\rightarrow$ *Exciton-Exciton Annihilation (EEA)*

Exciton dynamics: PL vs $\Phi_{\text{photons}}$

- PL saturation on bare and decoupled MoSe$_2$
  $\rightarrow$ Exciton-Exciton Annihilation (EEA)

- No PL saturation on Gr/MoSe$_2$ and $I_{\text{PL}}(B) \sim I_{\text{PL}}(A)$
• PL saturation on bare and decoupled MoSe$_2$

• No PL saturation on Gr/MoSe$_2$ and $I_{PL}(B) \sim I_{PL}(A)$
  → Drastic reduction of the excitonic lifetime ($< 1$ ps)
  → Fast interlayer Energy Transfer?

Exciton dynamics: PL vs $\Phi_{\text{photons}}$

- PL saturation on bare and decoupled MoSe$_2$
- No PL saturation on Gr/MoSe$_2$ and $I_{\text{PL}}(B) \sim I_{\text{PL}}(A)$
  $\rightarrow$ Drastic reduction of the excitonic lifetime ($< 1$ ps)
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Outline

Room temperature Chiral coupling of valley excitons with spin-momentum locked surface plasmons

Graphene/TMD heterostructures as a 2D optoelectronic building block

Room temperature valley polarization and coherence in TMD/Graphene heterostructures
Back to valley contrasts

Photonic state | Excitonic state
--- | ---
|σ±⟩ | |±1⟩

\[
\frac{1}{\sqrt{2}} (|\sigma^+⟩ \pm |\sigma^-⟩) \quad \frac{1}{\sqrt{2}} (|1⟩ \pm |-1⟩)
\]

⇒ \( \Gamma_{\text{TMD}} \ll \Gamma_S \Rightarrow 0\% \) valley polarization
Back to valley contrasts

<table>
<thead>
<tr>
<th>Photonic state</th>
<th>Excitonic state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>\sigma^{\pm}\rangle$</td>
</tr>
</tbody>
</table>

\[
\frac{1}{\sqrt{2}}\left(|\sigma^{+}\rangle \pm |\sigma^{-}\rangle\right) = \frac{1}{\sqrt{2}}\left(|+1\rangle \pm |-1\rangle\right)
\]

- $\Gamma_{\text{TMD}} \ll \Gamma_{S} \Rightarrow 0\%$ valley polarization
- $\Gamma_{\text{TMD}/Gr} \ll \Gamma_{S} \Rightarrow$ finite valley polarization
Our experimental approach

**BN-encapsulated WS₂-Gr heterostructure**

**Mueller polarimetry setup**

![Diagram of the experimental setup including components such as BPF, V-LP, QWP, 20X OBJ, Na 0.45, Sample, 100X OBJ, Na 0.8, QWP, H-LP, BPF, TL, AS, Grating, and Si CCD.]
Mueller Polarimetry

\[ \mathbf{S}_{\text{out}} = \begin{pmatrix} I \\ I_V - I_H \\ I_{45} - I_{-45} \\ I_{\sigma^+} - I_{\sigma^-} \end{pmatrix}_{\text{out}} = \mathbf{M} \cdot \mathbf{S}_{\text{in}} = \mathbf{M} \begin{pmatrix} I_0 \\ I_V - I_H \\ I_{45} - I_{-45} \\ I_{\sigma^+} - I_{\sigma^-} \end{pmatrix}_{\text{in}} \]

\[ \mathbf{M} = \begin{pmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{pmatrix} \]

- \( m_{11,22} \): valley coherence
- \( m_{33} \): valley polarization

Degrees of linear and circular polarization

\[ \gamma_{VH} = \frac{m_{10} + m_{11}}{m_{00} + m_{01}}, \quad \gamma_{45^\circ, -45^\circ} = \frac{m_{20} + m_{22}}{m_{00} + m_{02}}, \quad \rho_\pm = \frac{m_{30} \pm m_{33}}{m_{00} \pm m_{03}} \]
Mueller Polarimetry in WS$_2$/Gr

Experimental “sanity check”: $m_{11} = m_{22}$ and $m_{ij, i \neq j} = 0$
Mapping valley contrasts

- 45% valley polarization, 30% valley coherence @ Room Temperature

2.07 2.06 2.05 2.04
(b)
*
 s+s+
 s+s-
PL Intensity (arb. units)
598 601 604 607
0.0
0.5
1.0 ... XX
 XY
PL Intensity (arb. units)
(a)
598 601 604 607
0.0
0.5
1.0 (c)
m11
Wavelength (nm)
Energy (eV)
Energy (eV)
2.07 2.06 2.05 2.04
(b)
*
 s+s+
 s+s-
PL Intensity (arb. units)
598 601 604 607
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PL Intensity (arb. units)
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598 601 604 607
0.0
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1.0 (c)
m11
Wavelength (nm)
Energy (eV)
Energy (eV)

Large valley contrasts in WS$_2$/Gr (20 K)

*Raman features

Record valley coherence up to 60% (10%) in BN-capped WS$_2$/Gr (BN capped WS$_2$)


F. Cadiz et al. PRX 2017 (valley coherence of 50% in BN-capped MoS2)
Conclusion and outlook

✔ 2D matter meets 2D light:

*many games to play at the interface between (chiral) nanophotonics, condensed matter physics and materials science*

- Interfacing 2D materials with chiral plasmonic resonators
- Probing dark excitonic states using surface plasmons
- Electrical and electromechanical control of chiral coupling

- Charge and energy transfer mechanism(s)
- Intervalley scattering mechanisms in TMD/Gr vs bare TMD
Acknowledgements

Stefano Azzini
Thibault Chervy
Yuri Gorodetzki (Ariel, IL)
Shaojun Wang (Eindhoven, NL)
James Hutchinson
Thomas Ebbesen
Cyriaque Genet

Etienne Lorchat
Guillaume Froehlicher
Luis Parra-Lopez
Florentin Fabre
StNano Clean room

Cédric Robert,
Delphine Lagarde,
Xavier Marie

Takashi Taniguchi
Kenji Watanabe

Funding:
Supplementary Slides
Net charge transfer in TMD-Gr heterostructures
General slides on heterostructures and on energy transfer
How about *photoinduced* charge transfer?

...study of net (and slow) electron transfer from TMD to graphene (cf PRX 2018). This effect is likely extrinsic (not observable if we replace SiO2 by hBN) but is of interest for photodetection/photogating (see next slide).
Gr/TMD heterostructures: why the interest?

✔ **Strong interlayer coupling**  
  (J. He et al., Nat Comm. 2014)

✔ **Photogating/photodetection**  

✔ **ps-range photoresponse**  
  (M. Massicotte et al., Nat Nano 2016)
Raman spectroscopy: a quantitative probe of doping

Counts (arb. units) vs. Raman Shift (cm$^{-1}$)

- 2L sus
- 1L sus
(no) D mode

G mode

Counts (arb. units) vs. Raman Shift (cm$^{-1}$)

- electrons
- holes

Sample 1
Sample 2
Sample 3
Sample 4
Sample 5

S. Pisana et al., Nat Mater 2007, J. Yan et al., PRL 2007,...
Raman response vs photon flux (1)

Bare MoSe₂

Decoupled Gr/MoSe₂

Coupled Gr/MoSe₂

Reference on SiO₂

Eₜ = 2.33 eV

$\Phi_{ph}$ increases

5 µm
Clear signatures of a net photoinduced charge transfer
Clear signatures of a net photoinduced charge transfer
Evidence for TMD→Gr electron transfer

Correlation between the 2D- and G-mode frequencies

\[
\begin{align*}
\omega_{2D} (\text{cm}^{-1}) & \quad \omega_{G} (\text{cm}^{-1}) \\
2692 & \quad 1584 - 1592 \\
2676 & \quad 1584 - 1592 \\
2674 & \quad 1584 - 1592 \\
\end{align*}
\]

\[ e^{-} \text{ transfer} \]
Quantifying photoinduced doping

- Evidence for net photoinduced electron transfer
- Extrinsic effect – slow dynamics

Reproducibility and environmental effects

Several Gr/MoSe$_2$/SiO$_2$ samples
Ambient AIR

Gr/MoSe$_2$/SiO$_2$ vs MoSe$_2$/Gr/SiO$_2$
Air (full) vs vacuum (open)

- Electron trapping by molecular adsorbates in air
- Direct saturation under vacuum
Microscopic mechanism (in vacuum)

Light on, $t=0$

$\text{MoSe}_2$ \hspace{1cm} van der Waals gap \hspace{1cm} graphene

$e^-$ \hspace{1cm} $h^+$

$E_{Fi}^M \hspace{1cm} E_{Fi}^M \hspace{1cm} E_{Fi}^M$

$E_{Fi}^G$ \hspace{1cm} $E_{Fi}^G$

Light on, $t \rightarrow \infty$

$\text{MoSe}_2$ \hspace{1cm} van der Waals gap \hspace{1cm} graphene

$e^-$ \hspace{1cm} $h^+$

$E_{Fi}^M \hspace{1cm} E_{Fi}^M \hspace{1cm} E_{Fi}^M$

$E_{Fi}^G$ \hspace{1cm} $E_{Fi}^G$

✓ Balanced electron and hole currents at saturation

➢ Intrinsic mechanism?

➢ Optical determination of band offsets?
Recap: Fermi level and PL intensity

- Exciton dynamics in MoSe$_2$ is largely independent of the electron and hole transfer efficiencies
  - Strong hint for dominant energy transfer
Recap: Fermi level and PL intensity

- Exciton dynamics in MoSe$_2$ is largely independent of the electron and hole transfer efficiencies
  - Strong hint for dominant energy transfer
Partial conclusion

✓ Strong interlayer coupling in Gr/TMD heterostructures
✓ Saturation of the net electron transfer
✓ Highly efficient (sub)-picosecond energy transfer

➢ Förster vs Dexter energy transfer?
➢ Electrical control of charge and energy transfer
➢ Implications for optoelectronics and optospintronics

van der Waals Heterostructures

✓ No dangling bounds
✓ No lattice mismatch issues
✓ Rotational degree of freedom

• 2010 : Graphene on hBN
• 2017 : wet or dry transfer, pick up and lift,…
• Numerous possibilities!

Atomically thin p-n junctions

C-H Lee et al.
Nat. Nano (2014)
(Columbia)

Haigh, Gorbachev et al., Nature Materials 2012
Manchester Group
Band offsets in 2D materials

TMD/TMD: Type II band alignment
TMD/Graphene: Photoinduced TMD $\rightarrow$ Graphene and hole transfer

Microscopic Mechanism

In the dark

Before contact:
- n-doped MoSe$_2$
- Weakly doped graphene

After contact (in the dark):
- Neutral MoSe$_2$
- n-doped graphene
Outlook: low-temperature photoluminescence

PL Intensity (arb. units) vs. Energy (eV) for Defect states, Trion, and Exciton in MoSe$_2$ and MoSe$_2$/Gr.

No trion emission!
Förster energy transfer: near field dipole-dipole interaction

\[ \mathbf{E}_D = \frac{1}{4\pi\varepsilon_0} \left[ k^2 \left( \mathbf{r} \times \mathbf{\mu}_D \right) \times \mathbf{\mu}_D \frac{e^{ikr}}{r^2} + \left( \frac{3\mathbf{r} \cdot \mathbf{\mu}_D}{r^2} - \mathbf{\mu}_D \right) \left( \frac{1}{r^3} - \mathbf{\nabla} \frac{1}{r} \right) e^{ikr} \right] \]

\[ P_{D\rightarrow A} = -\frac{1}{2} \int_{V_A} \text{Re}\{\mathbf{j}_A^* \cdot \mathbf{E}_D\} \, dV \approx \frac{\omega_0}{2} \text{Im}\{\alpha_A\} \left| \mathbf{n}_A \cdot \mathbf{E}_D(\mathbf{r}_A) \right|^2 \]

\[ \frac{\gamma_{D\rightarrow A}}{\gamma_0} = \left[ \frac{R_0}{R} \right]^6 \quad R_0^6 = \frac{9 \kappa^2}{8\pi} \int_0^\infty f_D(\omega) \frac{\sigma_A(\omega)}{n^4(\omega) \omega^4} \, d\omega \]

Th. Förster Annalen der Physik 437, 55 (1948)
Novotny, Hecht Principles of Nano Optics, Ch 8

\( R_0 \): Förster radius
Förster and Dexter energy transfer

\[(D^*, A) \rightarrow (D, A^*)\]

\[U = \langle \Psi_{D^*}(1)\Psi_{A}(2) | \hat{V} | \Psi_{D}(1)\Psi_{A^*}(2) \rangle - \langle \Psi_{D^*}(1)\Psi_{A}(2) | \hat{V} | \Psi_{D}(2)\Psi_{A^*}(1) \rangle\]

Coulomb (FRET) term
- ‘Long’ range (power law)
- Implies spectral overlap

Exchange (Dexter) term
- Short range (exponential, idem CT)
- Implies overlap of molecular orbitals

A Govorov, PL Hernandez Martinez, HV Demir
Understanding and Modeling Förster-type Resonance Energy Transfer (FRET), Springer 2016
Energy transfer in low-dimensional heterostructures

Nanoscale emitter/graphene

Z. Chen et al., ACS Nano 4, 2964 (2010) (QD-Gr)

Molecules/nanotubes

© F. Vialla

C. Roquelet et al., APL 97, 141918 (2010)

TMD/TMD

D. Kozawa et al., Nano Lett. 16, 4087 (2016)

Interlayer energy transfer has been largely overlooked in TMD/Gr
2D Materials at IPCMS

- Optical spectroscopy
- Phonons, excitons and their coupling(s)

 ✓ Interlayer interactions: Davydov splitting and unified description of the phonon modes


1T' TMD - Lorchat et al. ACS Nano 2016 (ReS$_2$ and ReSe$_2$)

See also Froehlicher et al., J. Raman Spec. 2018 (special issue on 2D materials)