Emerging 2D/0D Heterostructures: Spectroscopic Studies and Device Applications

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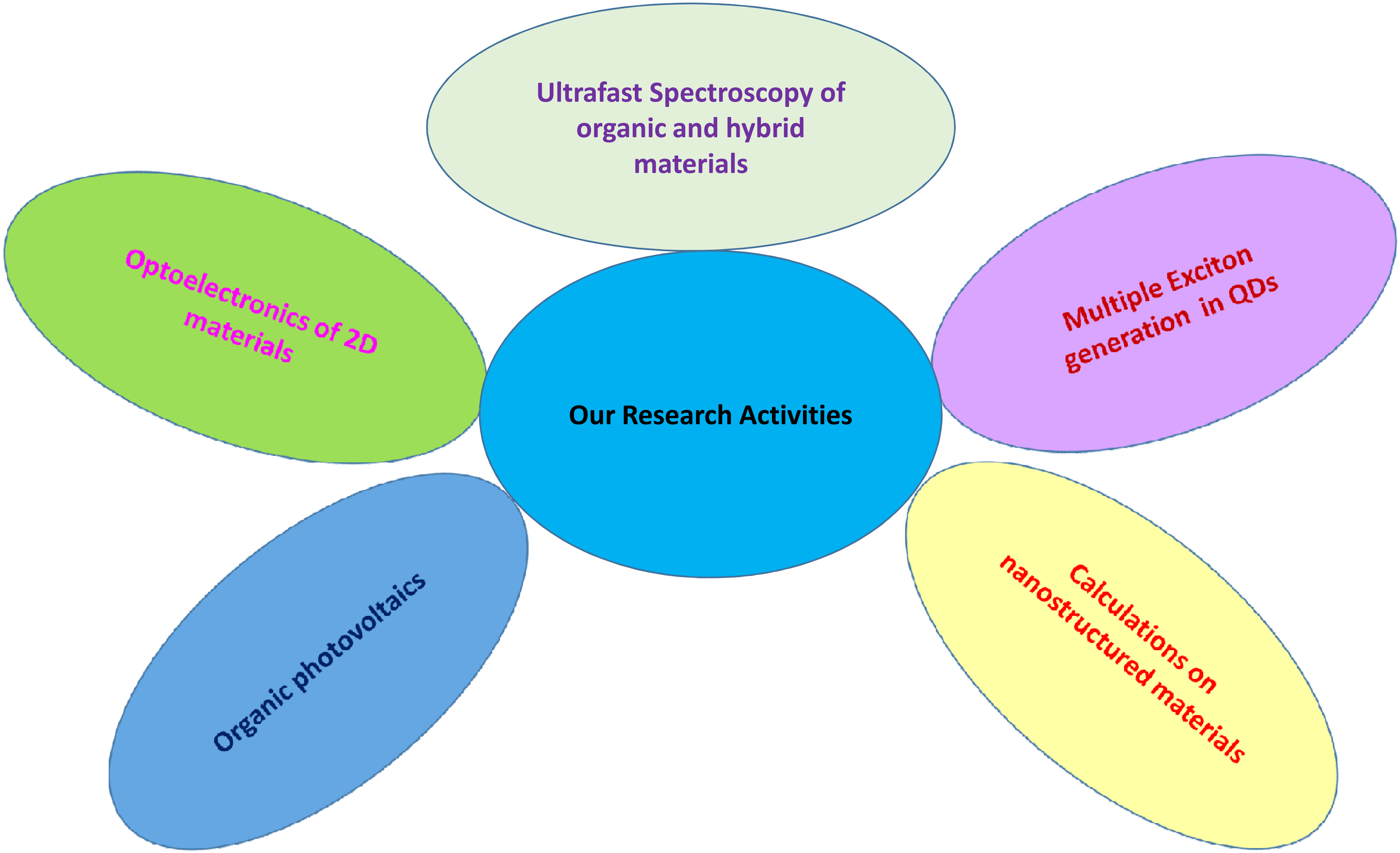


Our Research Activities

Ultrafast Spectroscopy of organic and hybrid materials

Optoelectronics of 2D materials

Multiple Exciton generation in QDs

Organic photovoltaics

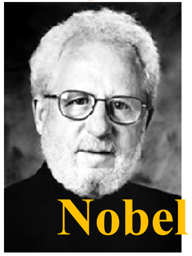
Calculations on nanostructured materials

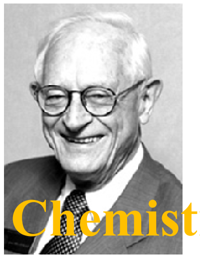
Outline

- Introduction
- Motivation
- Experimental results
- Conclusions

Introduction

Organic electronics


A. J. Heeger


A. G. MacDiarmid


H. Shirakawa

Nobel in Chemistry 2000

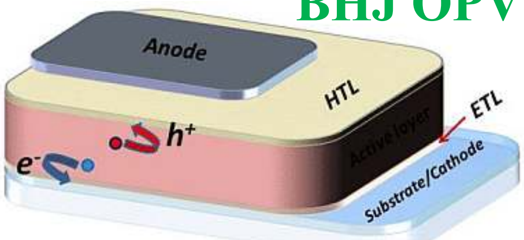
Electronics with carbon-based materials

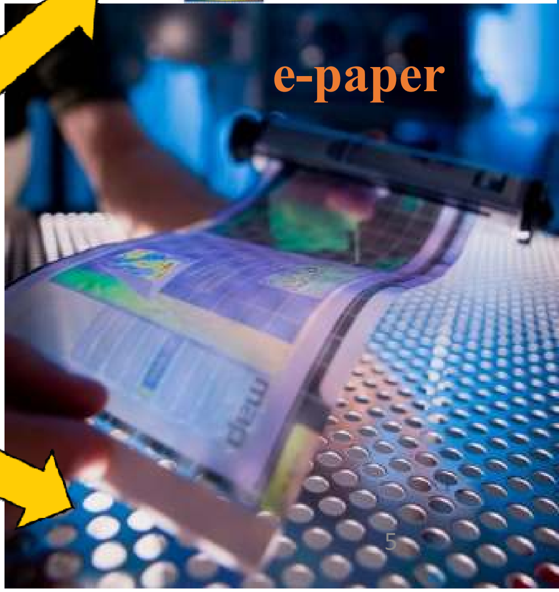
Organic electronics is electronic devices in which semiconductor is an organic material


Organic semiconductors

Carbon-based materials

BHJ OPV



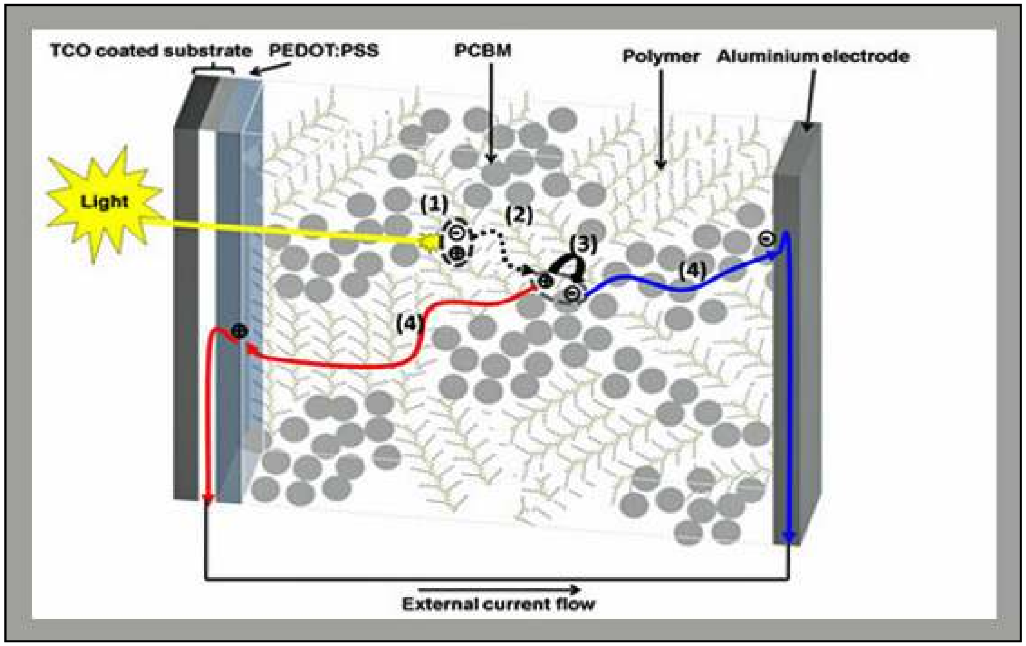


Introduction

Organic solar cells

The general mechanistic picture:

- Light absorption and exciton formation
- Exciton migration
- Exciton dissociation
- Charge transport
- Charge collection



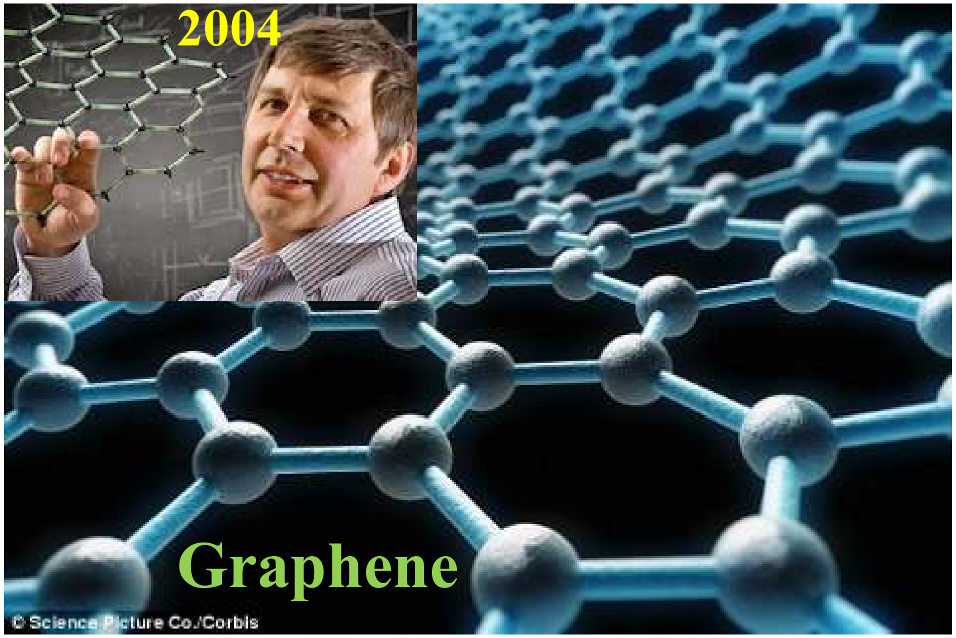
Benefits

- Light weight and flexible
- Vacuum free coating process
- Cheap

Drawback

- Poor charge transport
- Less solar light absorption

Introduction



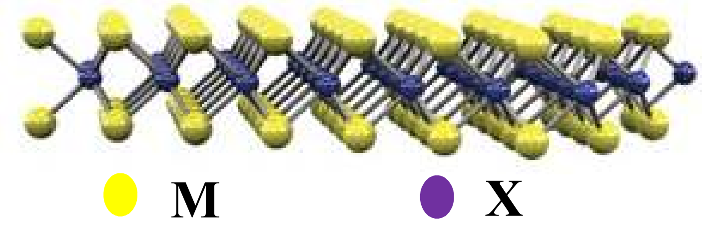
2D materials

"A material in which the atomic organization and bond strength along two-dimensions are similar and much stronger than along a third dimension".

Butler et al. ACS Nano, 2013, 7, 2898–2926

Transition metal dichalcogenides (TMDCs): 2D semiconductors

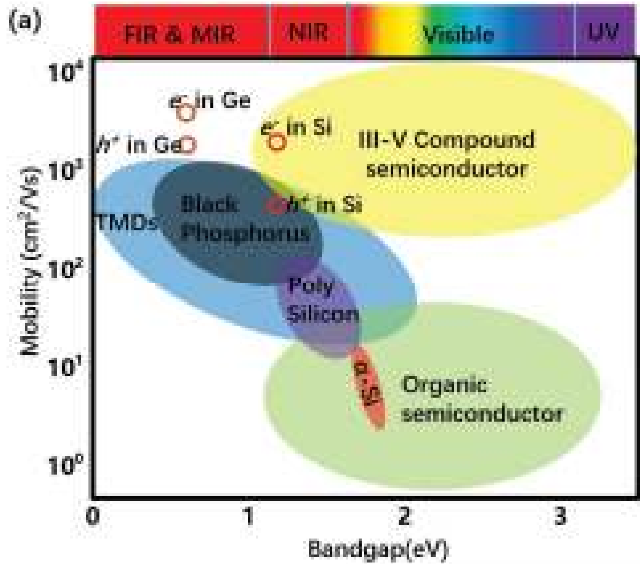
Chemical formula MX_2 (X-M-X)
M transition metal (M = Mo, W, Nb, Ta, Ti, Re)
X chalcogen like S, Se or Te

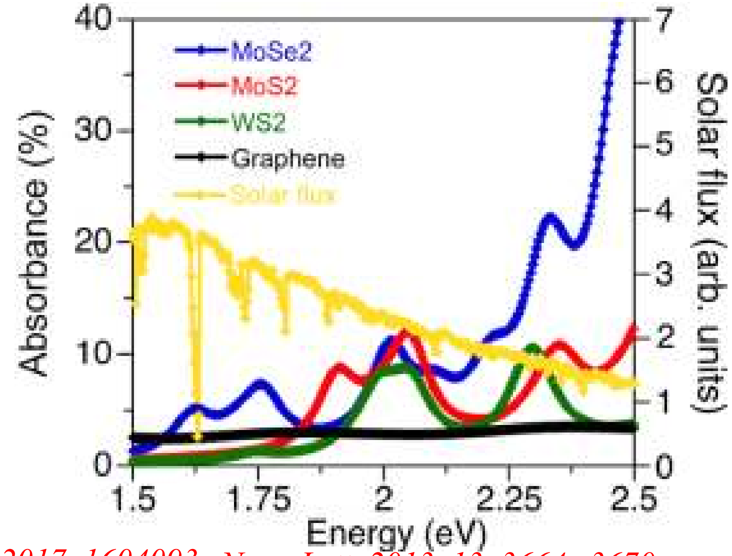


Promising features for next generation electronic devices

Why TMDCs ?

- High charge carrier mobility (>500 cm^2 V^{-1} s^{-1})
- Tunable band gap
- Large light capture cross section
- Layer dependent optoelectronic property





Adv. Funct. Mater. 2017, 1604093; Nano Lett. 2013, 13, 3664−3670

Challenges

- Exfoliation in non-polar solvents
- Preservation of semiconductive nature (phase integrity)
- Integration in organic semiconductor (conjugated polymer) devices

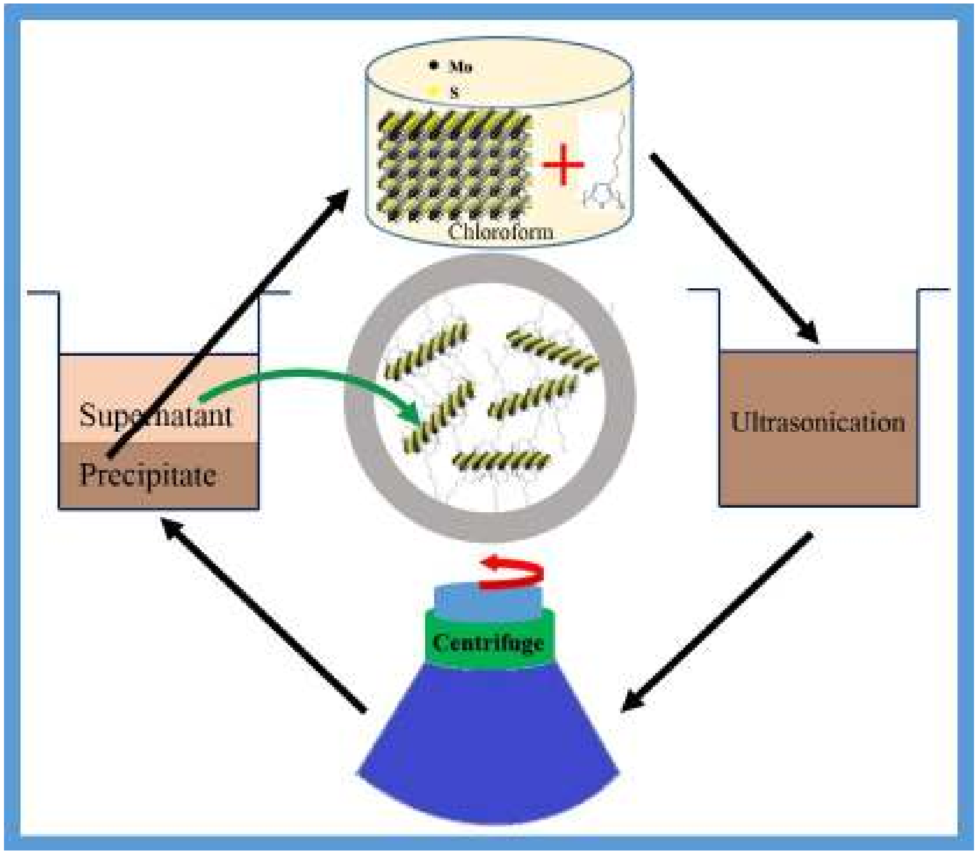
Motivations

- **Preparing semiconducting TMDCs in non-polar solvent for organic electronic applications**
- **Preparation of 2D heterostructures**
- **Study of their optical and electrical properties**

✓ **Synthesis of TMDCs nanostructures modified by organic semiconductors is a fascinating idea**

Experimental

Materials preparation

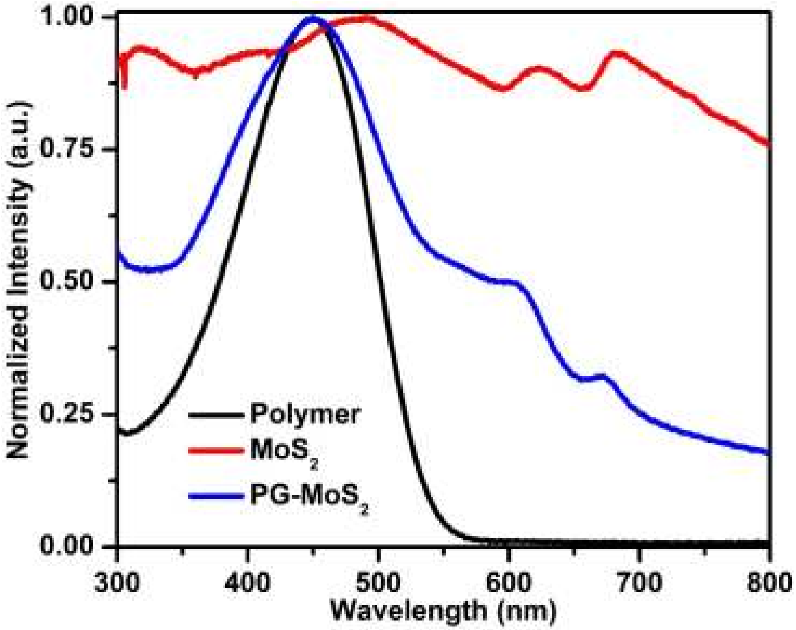


“Semiconductive Polymer Assisted Chemical Exfoliation (SPACE)”

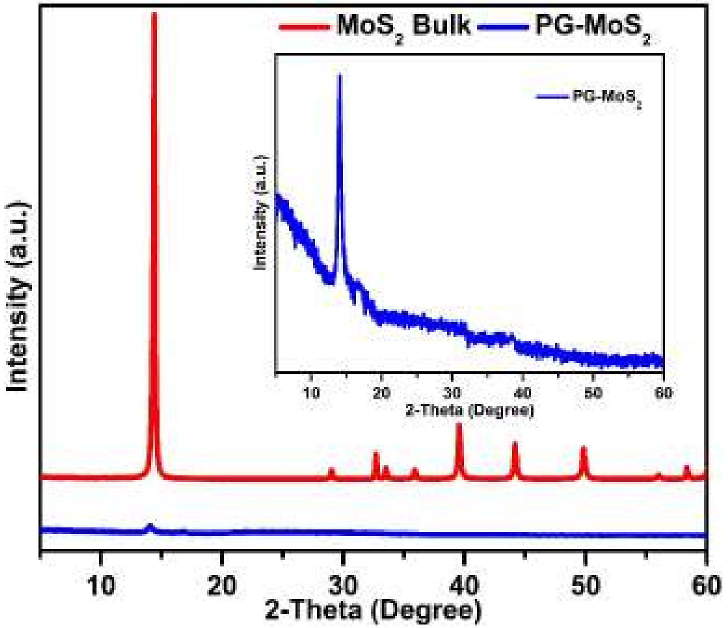
Pal and coworkers ACS Omega 2017, 2, 4333−4340; J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

Absorption spectra



X-ray diffraction



- Absorption peaks of MoS_2 : 614 nm and 673 nm
- MoS_2 has been modified by P3HT.

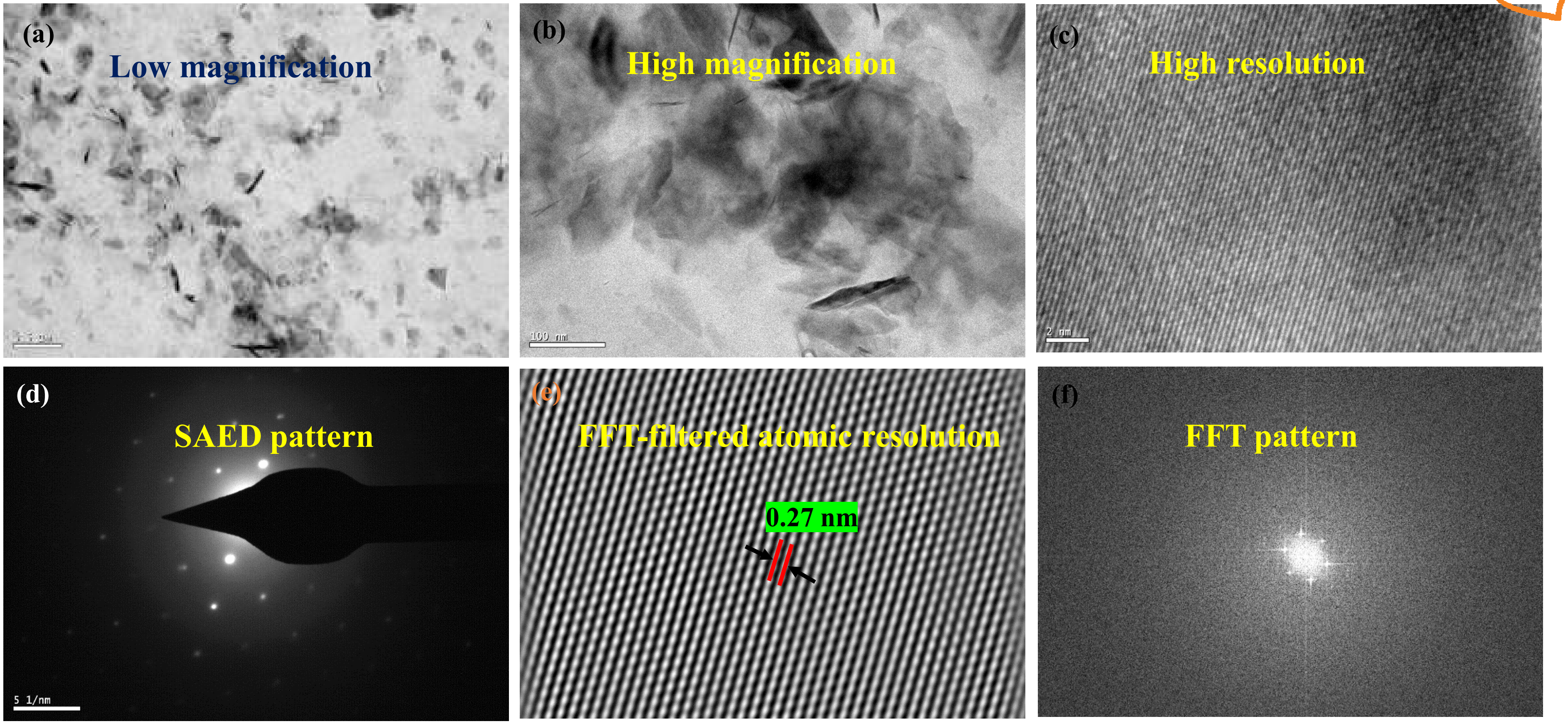
- ❑ Diffraction peaks located at $2\theta = 14^{\circ}, 33^{\circ}, 40^{\circ}, 50^{\circ}$, and 59° corresponding to the planes of (002), (100), (103), (105) and (110) of hexagonal MoS_2
- ❑ $2\theta = 14^{\circ}$:production of a few layers did not change the structure of MoS_2

Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

TEM images

Morphology of prepared polymer assisted 2D MoS_2 nanosheets and their atomic structure



☐ Average flakes size of MoS_2 : 150 nm

☐ Blur image: presence of polymer coat

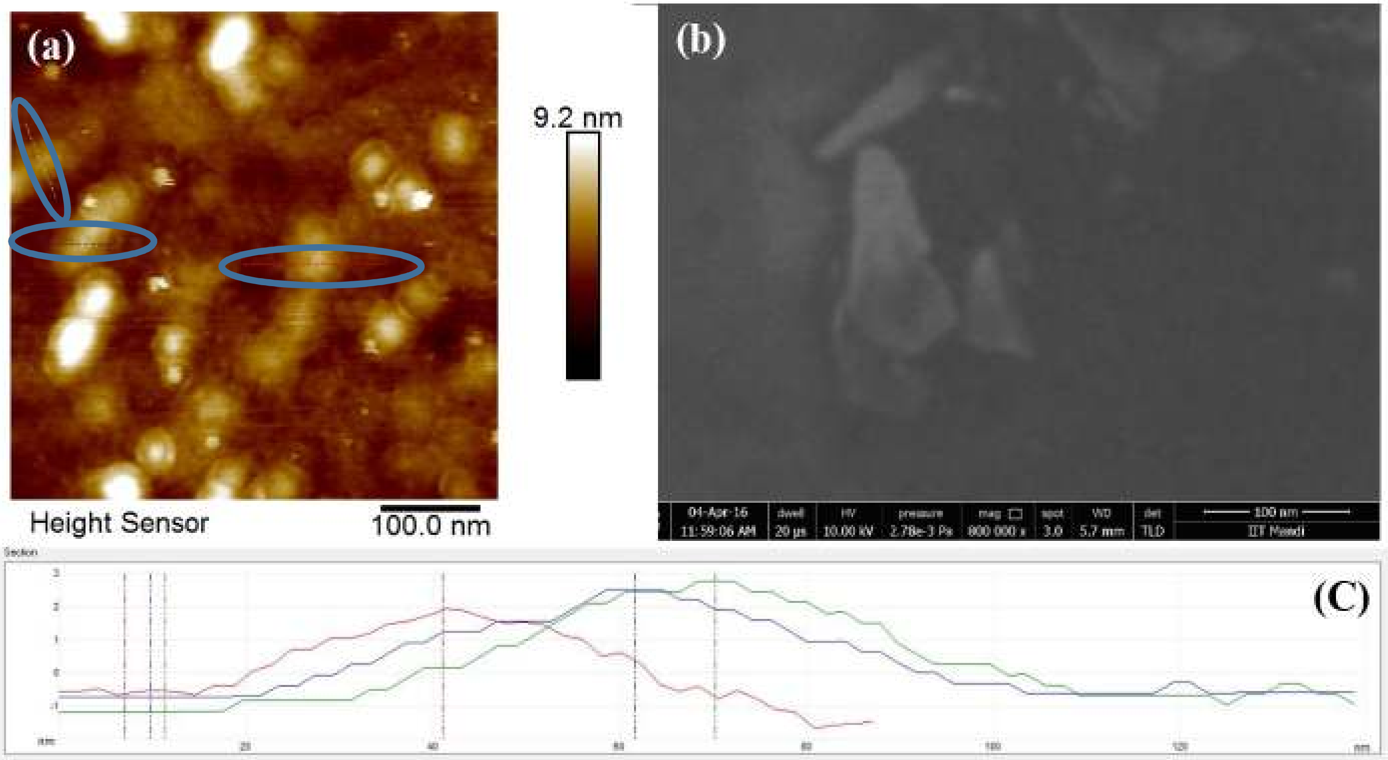
☐ Six fold symmetry : highly crystalline

☐ Hexagonal pattern with lattice spacing 2.7 Å

Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

AFM image **SEM image**

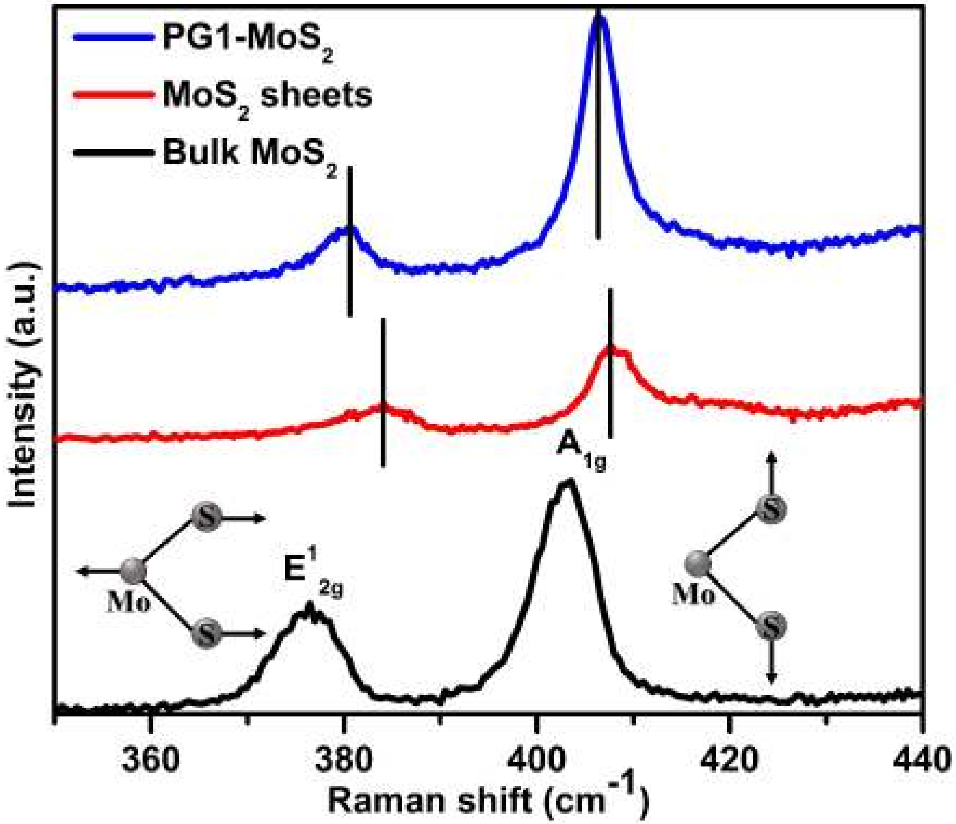


- ❑ Blur image, MoS_2 sheets are soft polymer coated
- ❑ MoS_2 flakes distribution lateral dimensions between few nm to few hundred nm
- ❑ Average thickness ~3 nm

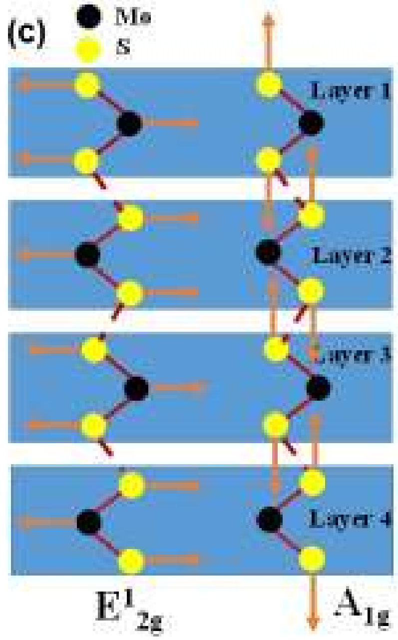
Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

Raman spectra



Motion of atoms in different Raman active modes

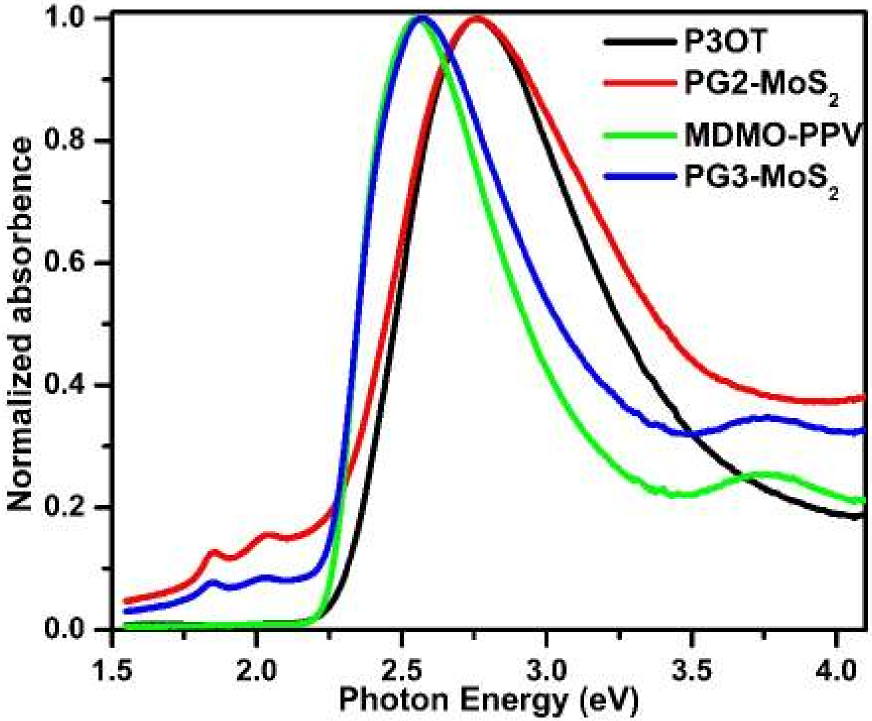


- Δω=25 cm^{-1} for PG1-MoS$_2$ (4 layers)

Kim et.al, Nano Lett. 2015, 15, 229−234. Liu et. al, ACS Nano., 2013, 7, 4202−4209.

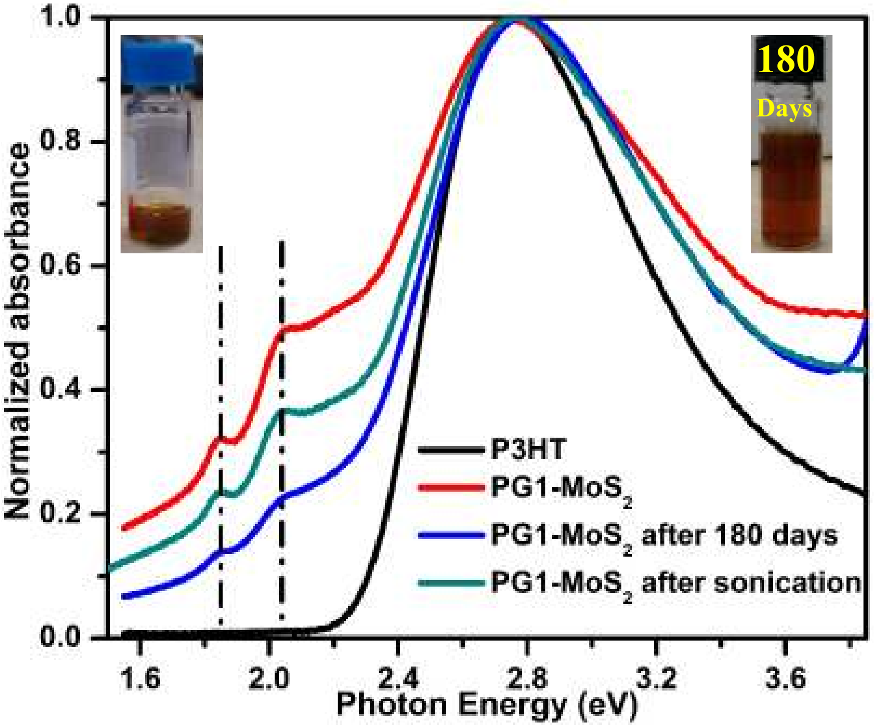
Results

Absorption spectra



Negligible restacking

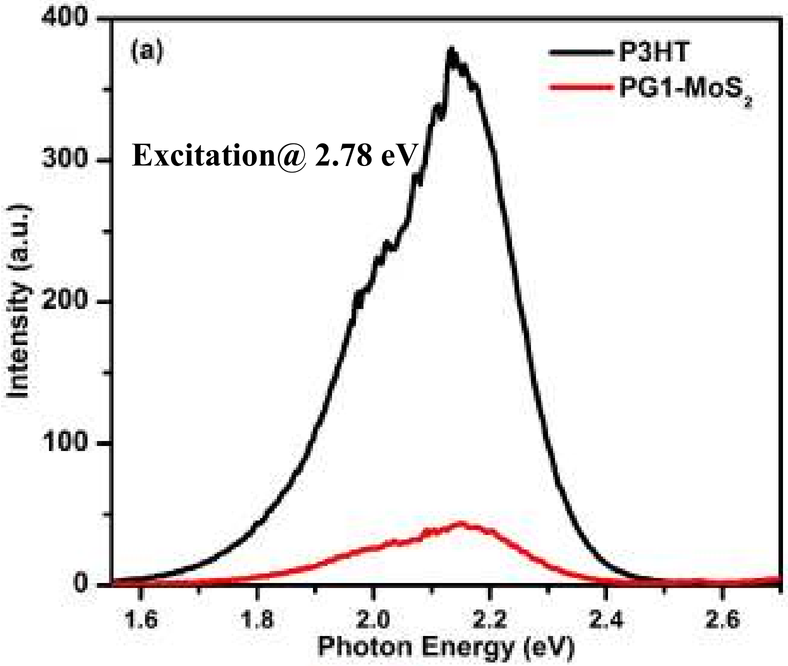
Absorption spectra



❖ Chemical stability in chloroform

Results

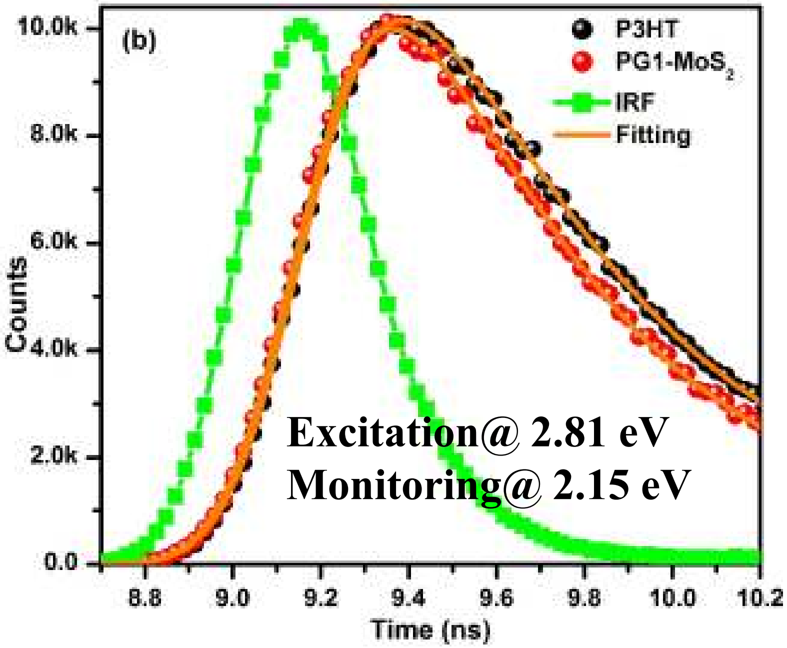
Photoluminescence spectra



- ❖ Photoluminescence of P3HT is quenched (90 %)

Electron transfer rate~1.2×10^{8} s^{-1}

Time resolved Photoluminescence



Sample	f_1	τ_1 (ns)	f_2	τ_2 (ns)	τ_{av} (ns)
Polymer	0.82	0.56	0.18	0.34	0.52±0.02
PG-MoS$_2$	0.69	0.58	0.31	0.29	0.49±0.01

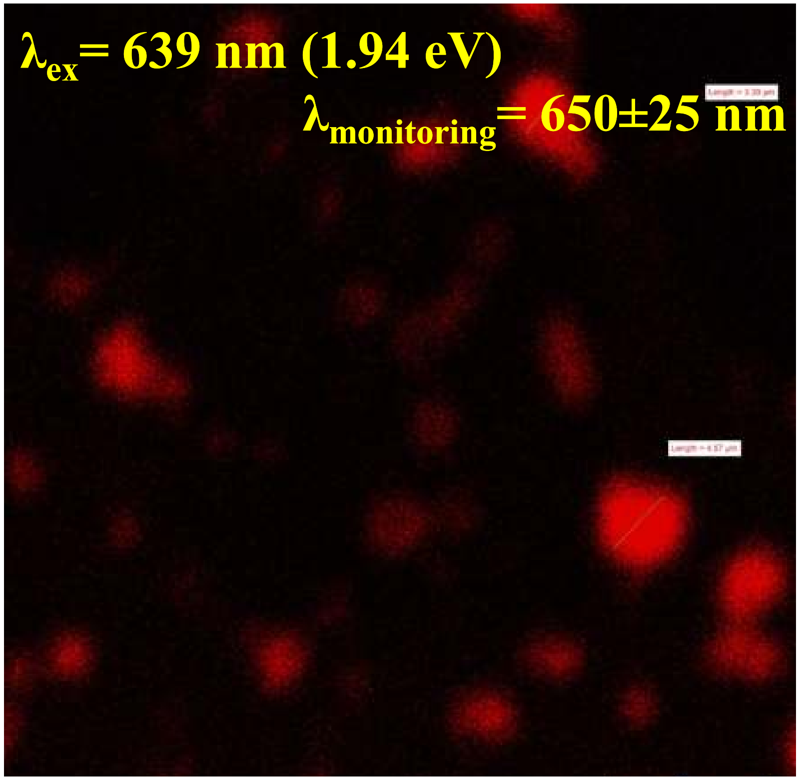
- ➢ Possibility of charge or energy transfer from polymer to MoS$_2$

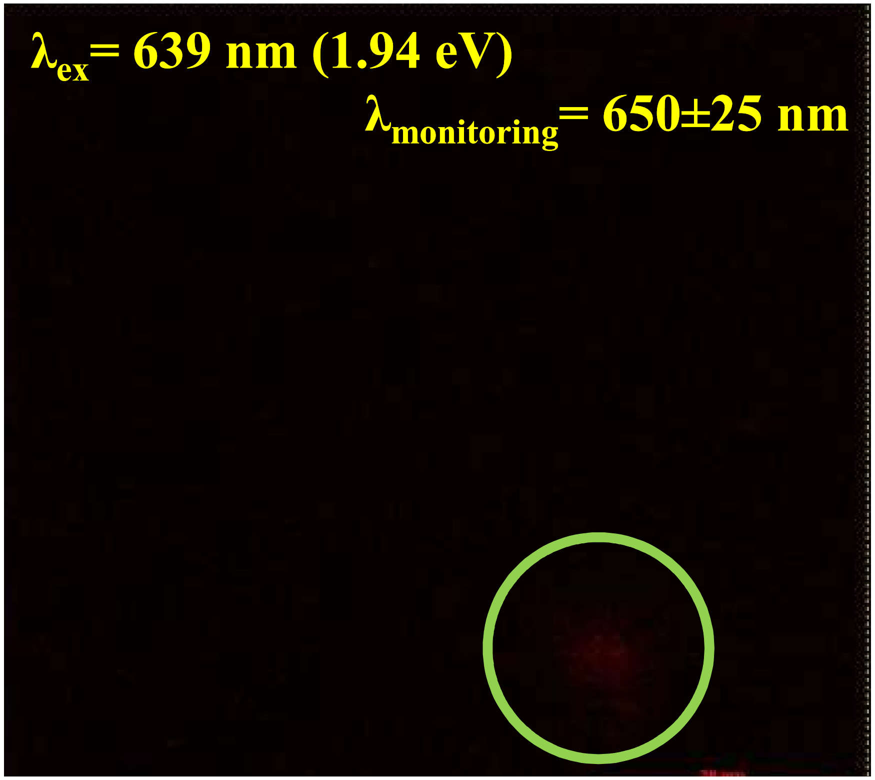
Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

Confocal image of MoS_2

Confocal image of PG1-MoS_2





- ☐ Single flake Photoluminescence
- ☐ Photoluminescence is quenched

Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

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Photoluminescence decay of a single flake of MoS_2 and PG1-MoS_2

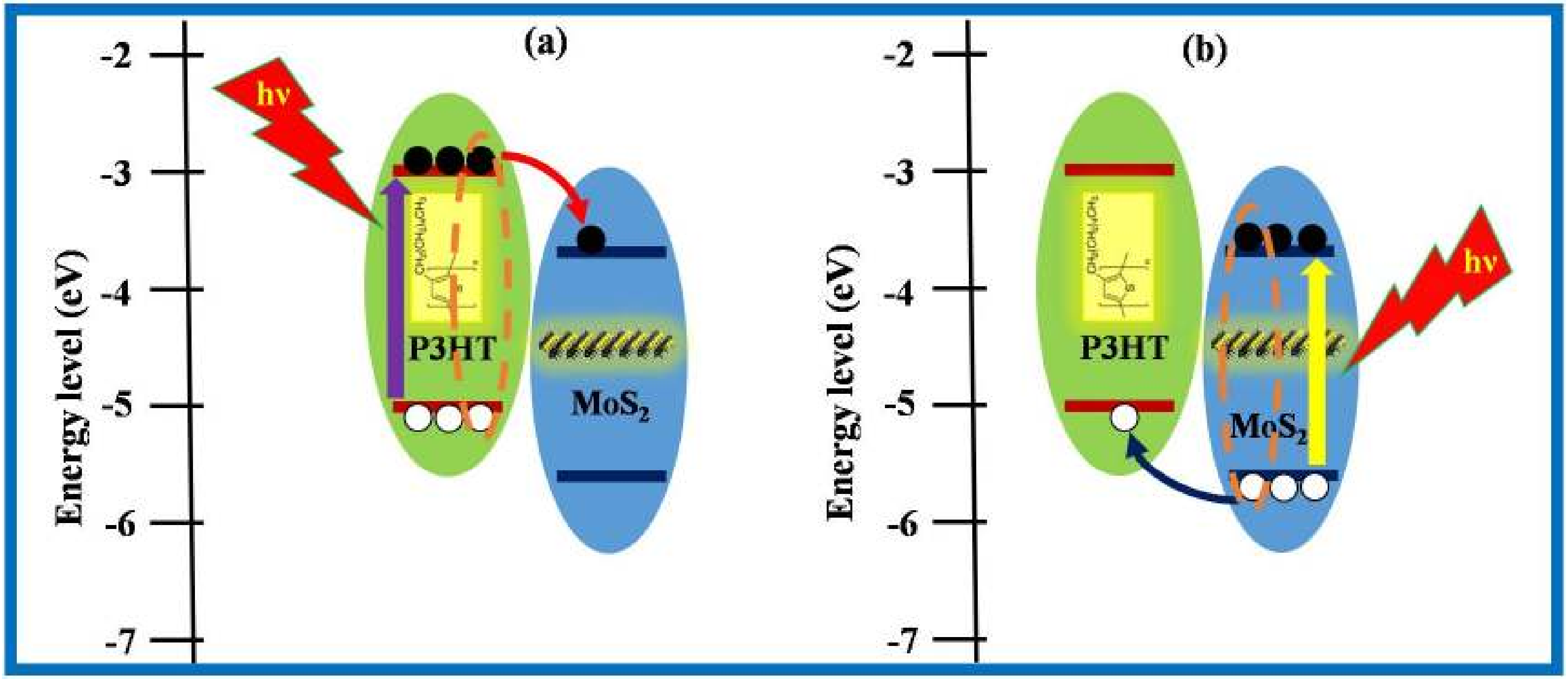
	τ_1 (ns)	A_1(%)	τ_2 (ns)	A_2(%)	τ (ns)	χ^2	τ_{av} (ns)
MoS_2	1.33	43	0.31	57	1.09	1.0	1.14±0.04
MoS_2	1.65	34	0.39	66	1.24	1.0	
MoS_2	1.28	49	0.28	51	1.09	1.0	
PG1-MoS_2	0.91	14	0.09	86	0.60	1.0	0.62±0.04
PG1-MoS_2	1.1	12	0.12	88	0.64	1.1	
PG1-MoS_2	1.2	6	0.09	94	0.62	1.2	

- Photoluminescence quenching infers the interaction between the photoexcited MoS_2 and P3HT

Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

Mechanism of electron and hole transfers



- Excitation of P3HT: Electron transfer
- Excitation of MoS_2: Hole transfer

Electron transfer rate~1.2×10^8 s^{-1}

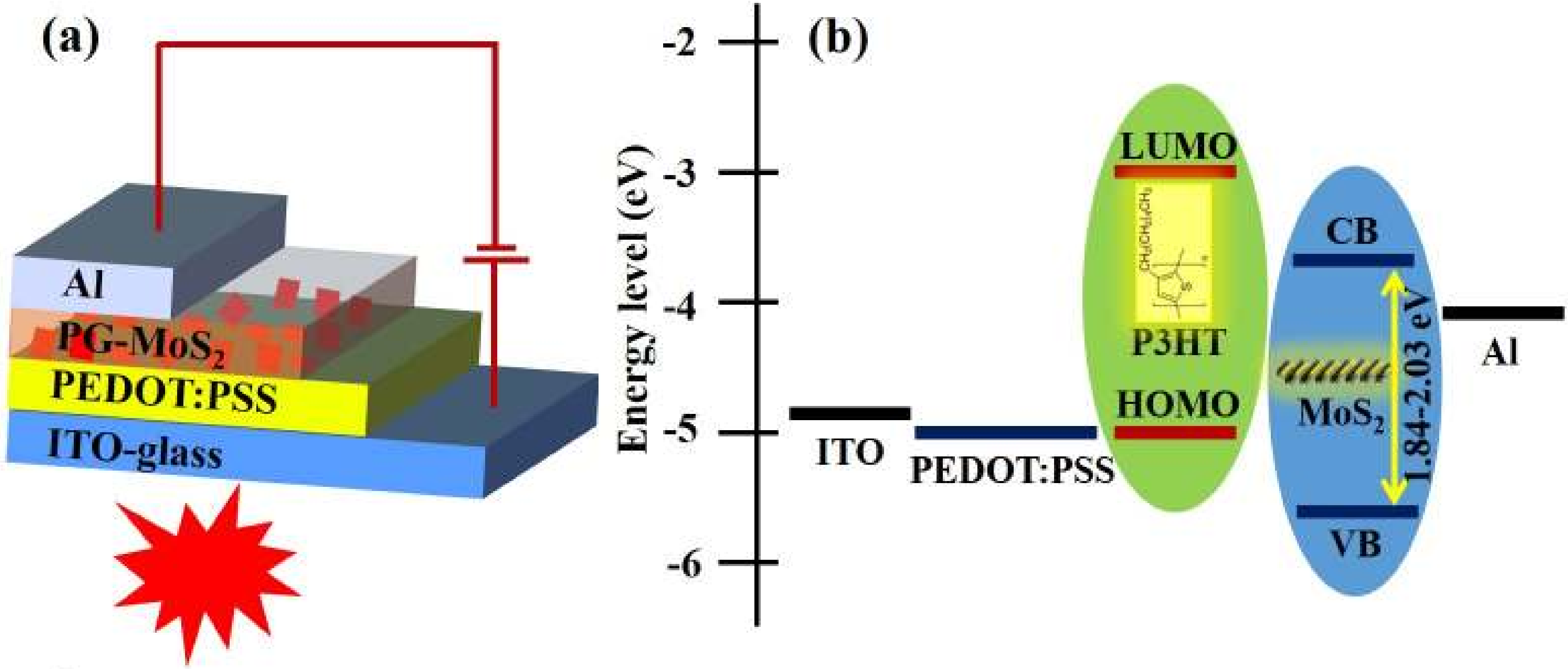
Hole transfer rate~7.2×10^8 s^{-1}

Efficient breaking of excitons: the formation of P3HT/MoS_2 nanoheterojunction (type-II)

Simultaneous light harvesting followed by charge separation: Photovoltaic performance

Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

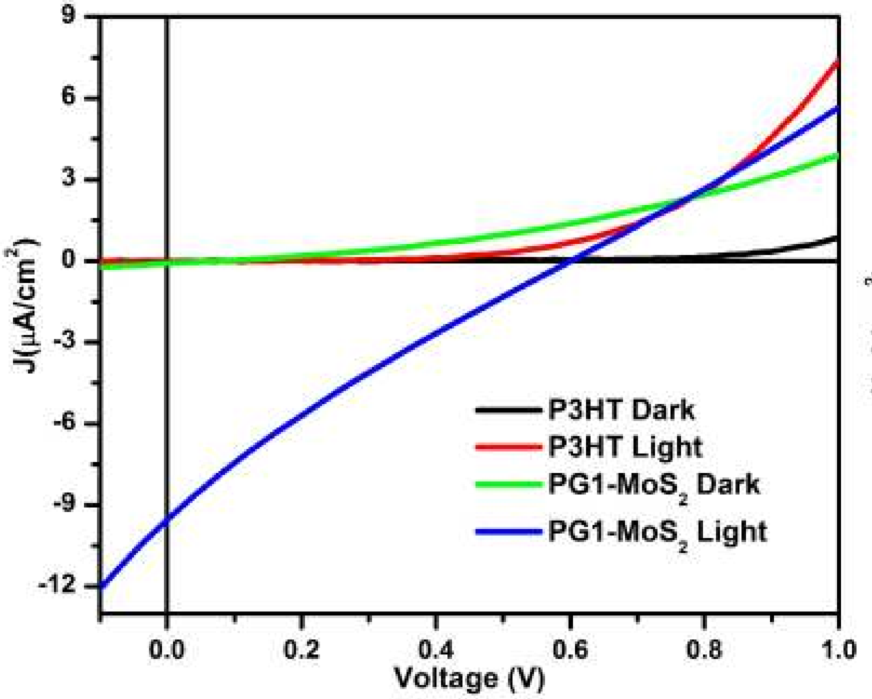
Results

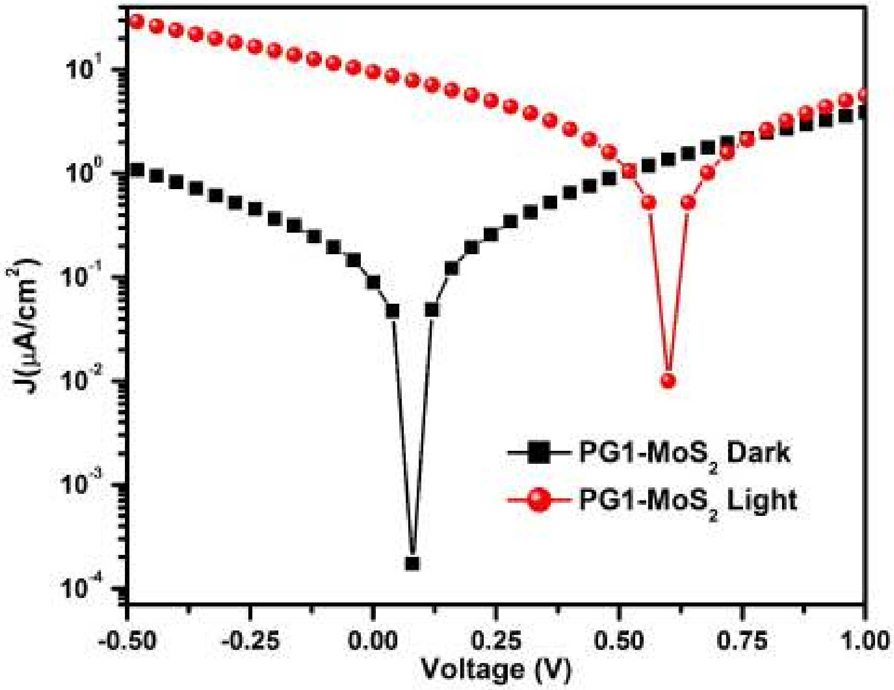


Photovoltaic device structure with energy level diagram

Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results



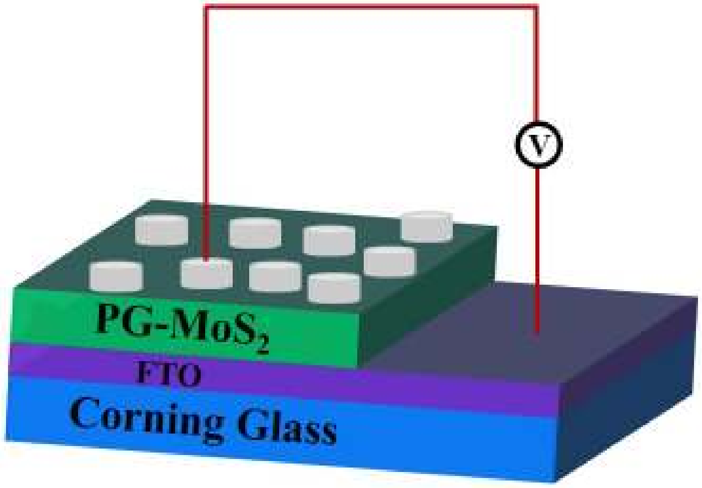


Active layer	V_{oc} (V)	J_{sc} (μA/cm^2)	FF (%)
P3HT:MoS_2	0.60	10.50	22

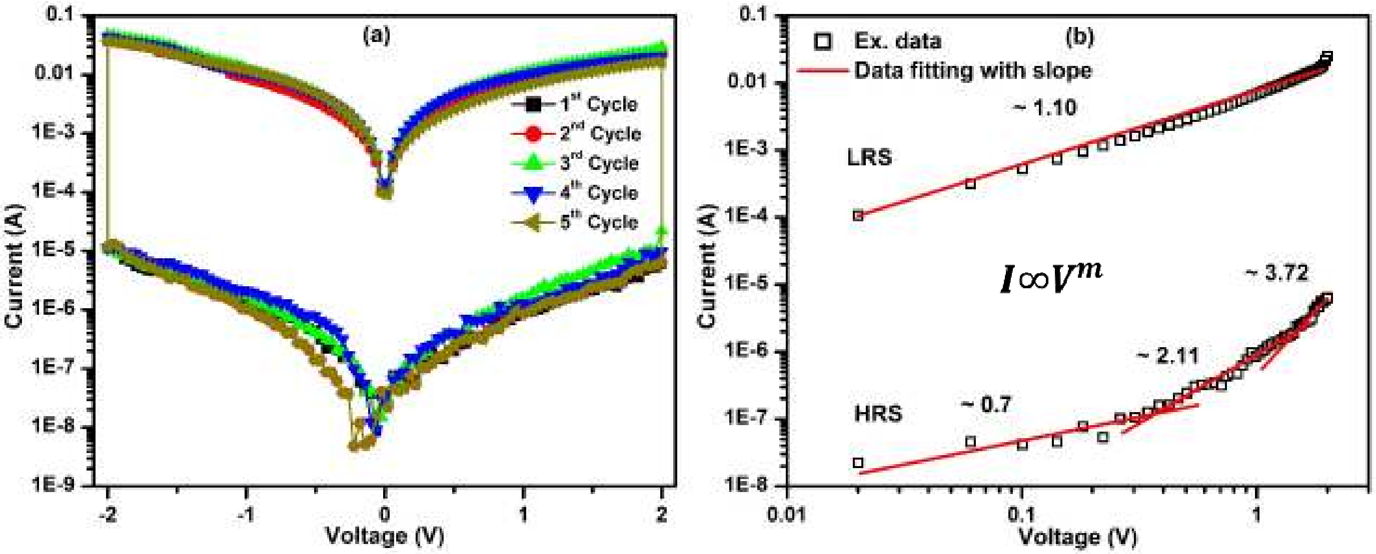
Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

Schematic of Device



I-V characteristics



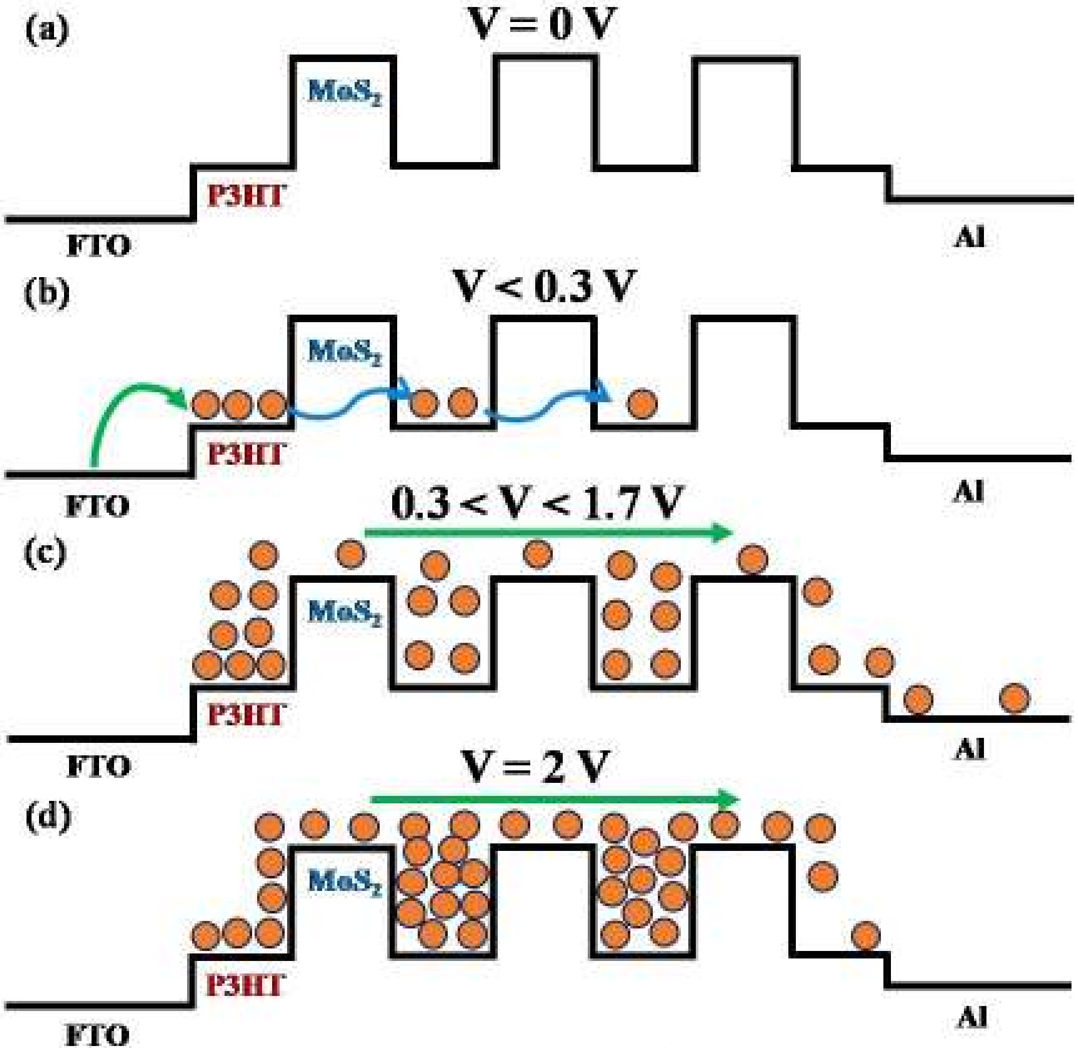
- Indication of resistive switching
- High ON/OFF ratio (~10^4)
- Memory effect: due to formation of Van der Waal heterojunctions (type-II)

- High-resistance state (HRS) (0 to -2 V), V_{set} ~1.99 V V_{RESET} ~ -1.99 V
- Indication resistive switching process

Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

Charge transport mechanism



HRS

TE

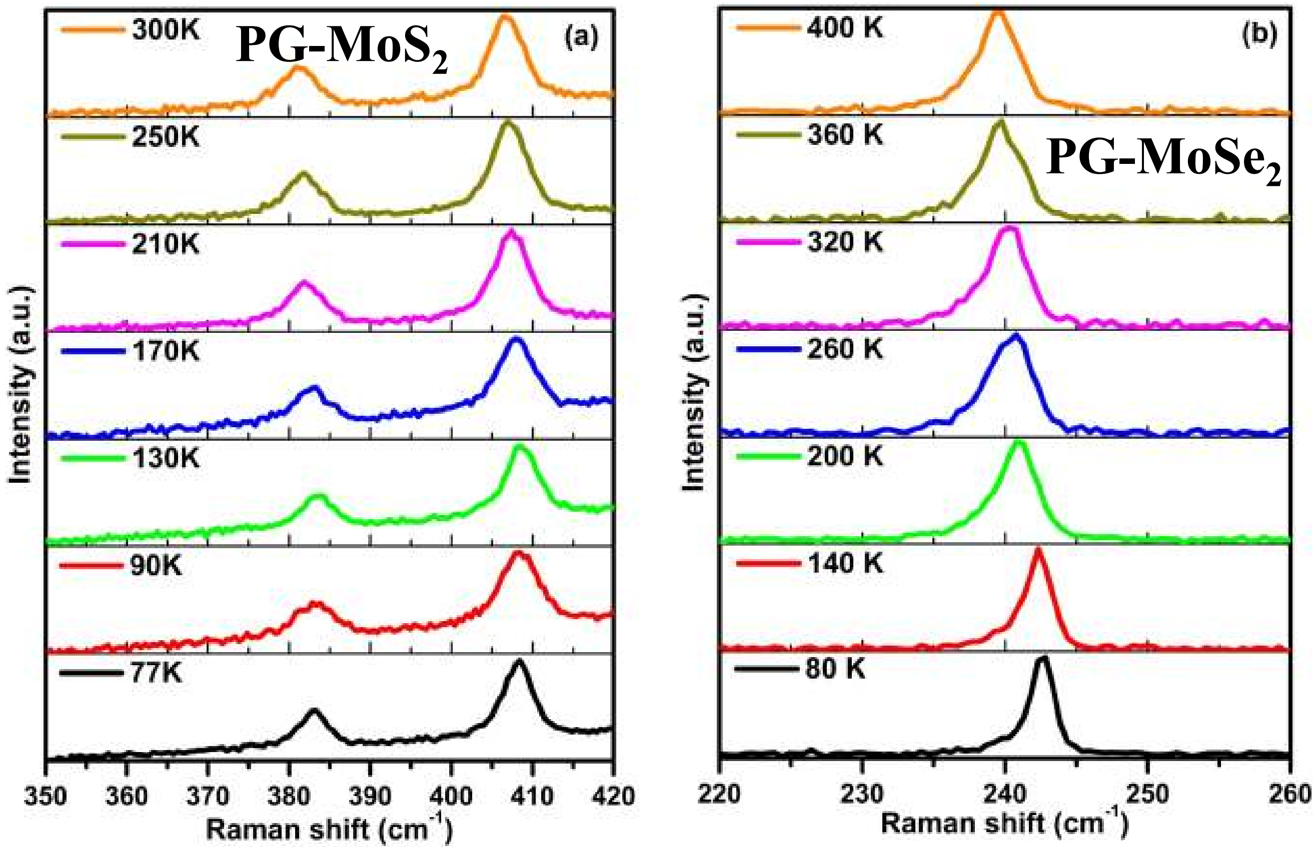
SCLC

Ohmic/LRS

Pal and coworkers J. Phys. Chem. C 2017, DOI: 10.1021/acs.jpcc.7b07132

Results

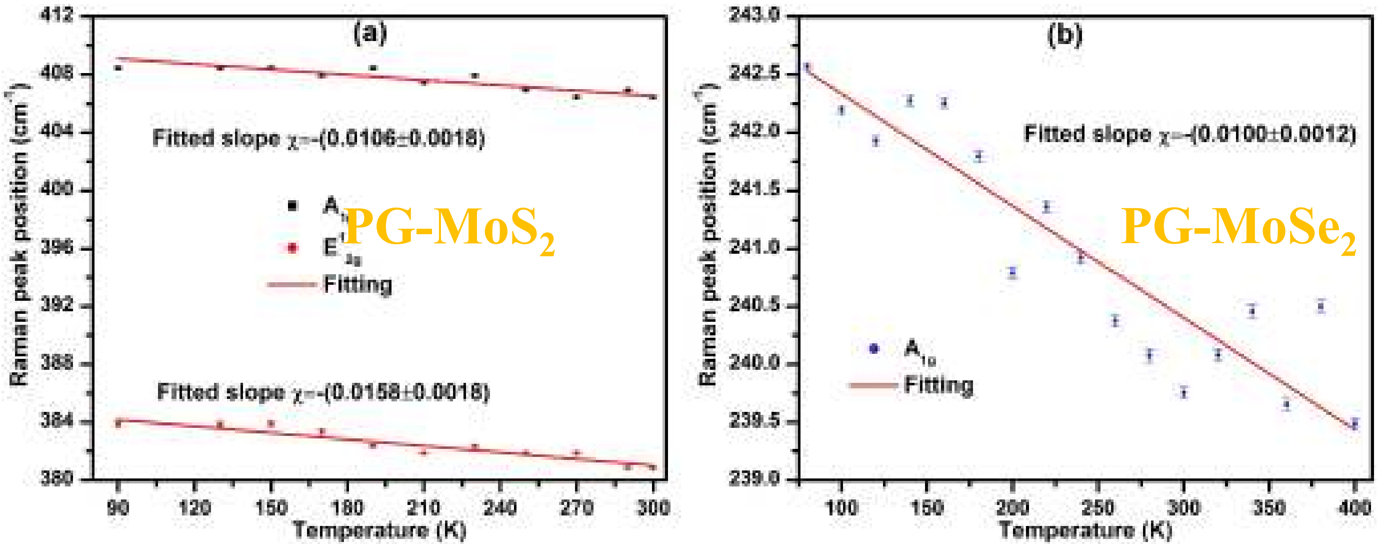
Variable temperature Raman spectra of PG -MoS$_2$ and -MoSe$_2$



- ☐ Peak position shift towards lower wave number
- ☐ Both modes vary linearly with temperatures

Pal and coworkers ACS Omega 2017, 2, 4333−4340

Results



Grùneisen model

$$\omega(T) = \omega_0 + \chi T$$

ω_0 is the frequency of the vibration of E^1_{2g} or A_{1g} modes at absolute zero of temperature

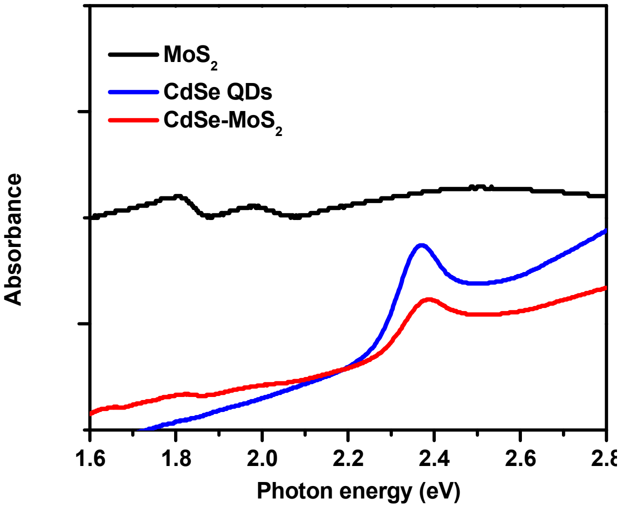
χ is the first order temperature coefficient of the E^1_{2g} or A_{1g} modes

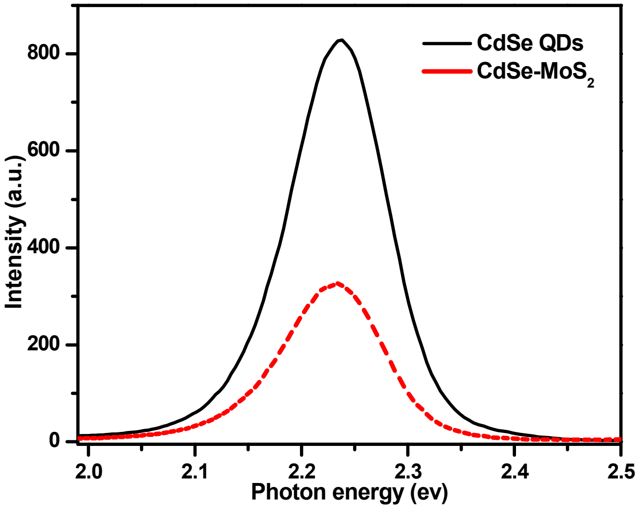
Pal and coworkers ACS Omega 2017, 2, 4333−4340

Chalcogenide nanosheets	Raman modes	χ Value	Reference
PG-MoS$_2$	E^1_{2g}	-0.0158	Present work
PG-MoS$_2$	A_{1g}	-0.0106	Present work
PG-MoSe$_2$	A_{1g}	-0.0100	Present work
MoS$_2$	E^1_{2g}	-0.016	*Appl. Phys. Lett. 2014, 104, 081911*
MoS$_2$	A_{1g}	-0.011	
MoSe$_2$	A_{1g}	-0.0096	*Nanoscale, 2014, 6, 8949-8955*

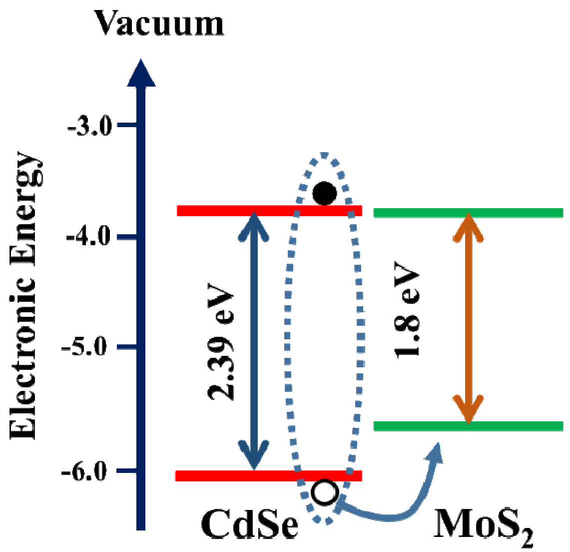
Results

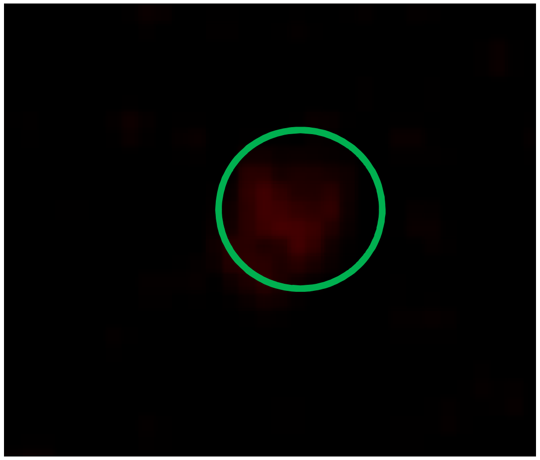
MoS_2 Nanosheet/CdSe QD: 2D/0D heterostructure





- ❖ Photoluminescence of P3HT is quenched (90 %)
- ❖ Possibility of charge or energy transfer from CdSe to MoS_2

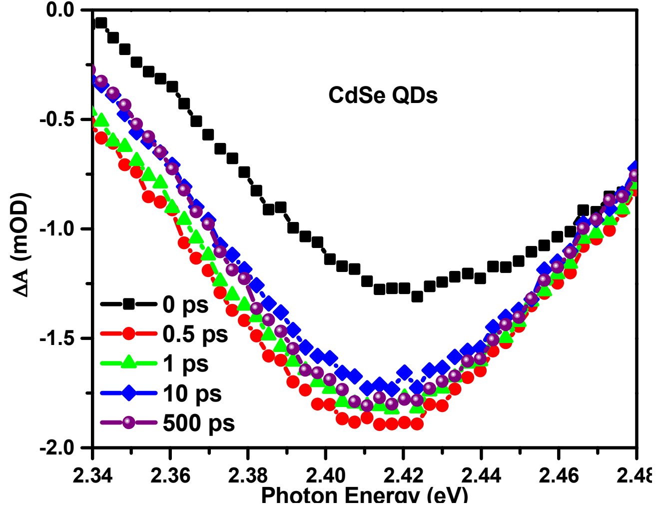


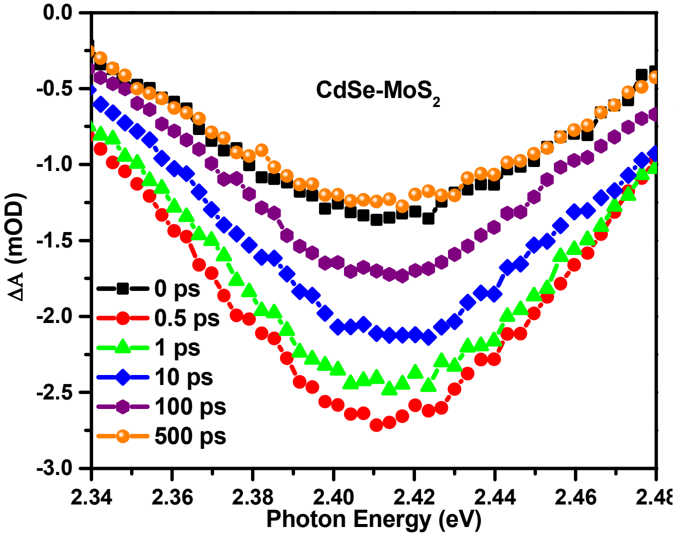


- ❖ No energy transfer, only hole transfer

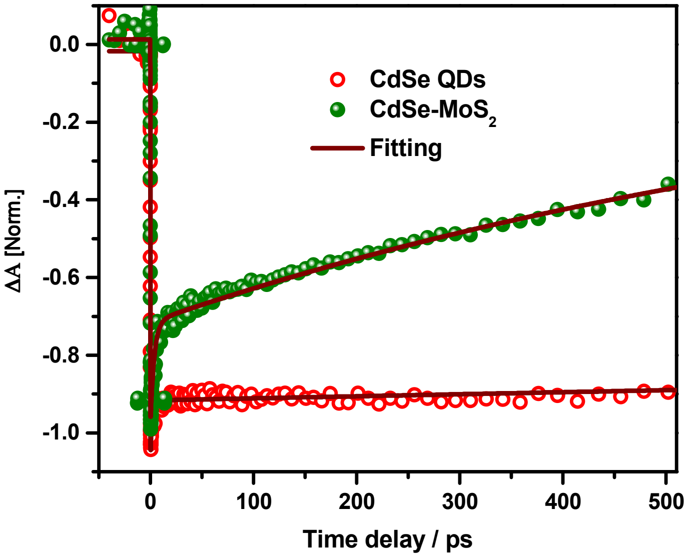
Pal and coworkers ACS Energy Lett. 2017, 2, 1879−1885

Results





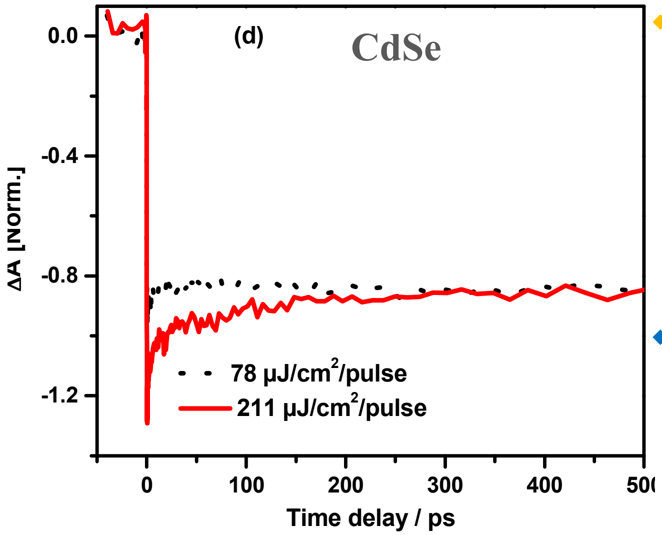
- ❖ Transient absorption (TA) spectra of CdSe in the absence and presence of MoS_2 showing ground state bleach signal



- ❖ TA kinetics are biexponential
  average time constants: 14.7 ns for only CdSe
  0.58 ns for CdSe/ MoS_2
- ❖ Hole injection rate of 1.65 × 10^9 s^{-1} (injection time, ~600 ps)

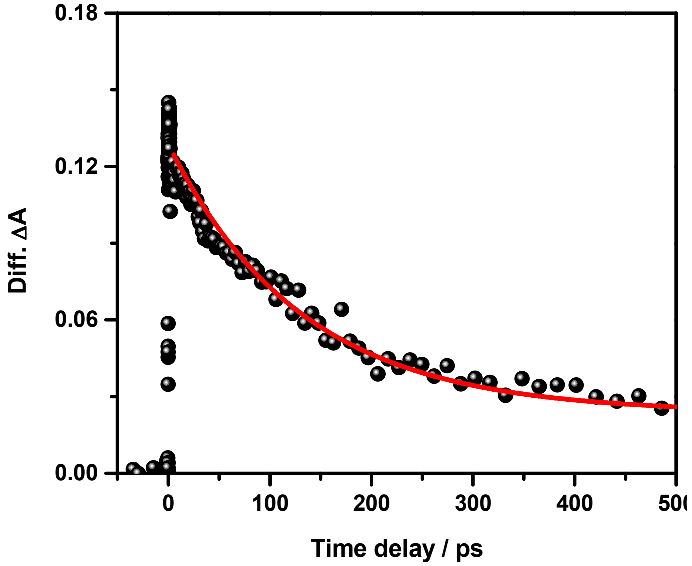
Pal and coworkers ACS Energy Lett. 2017, 2, 1879−1885

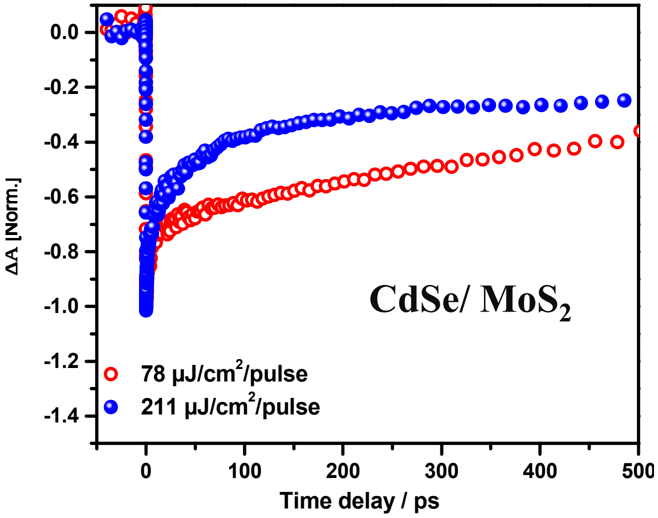
Results



- Signal height at early time is much higher for high power excitation due to multiple exciton generation

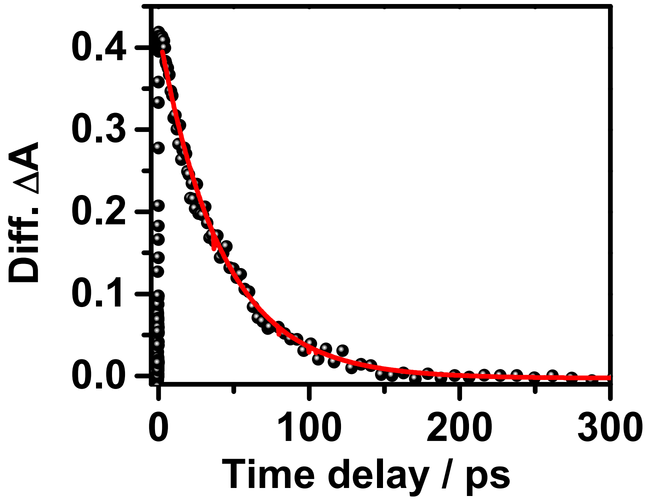
- Biexcitonic Auger recombination time is 120 ps





- High power signal also decays faster in case of CdSe/ MoS$_2$

- But the time constant of the differential signal is low (42 ps)

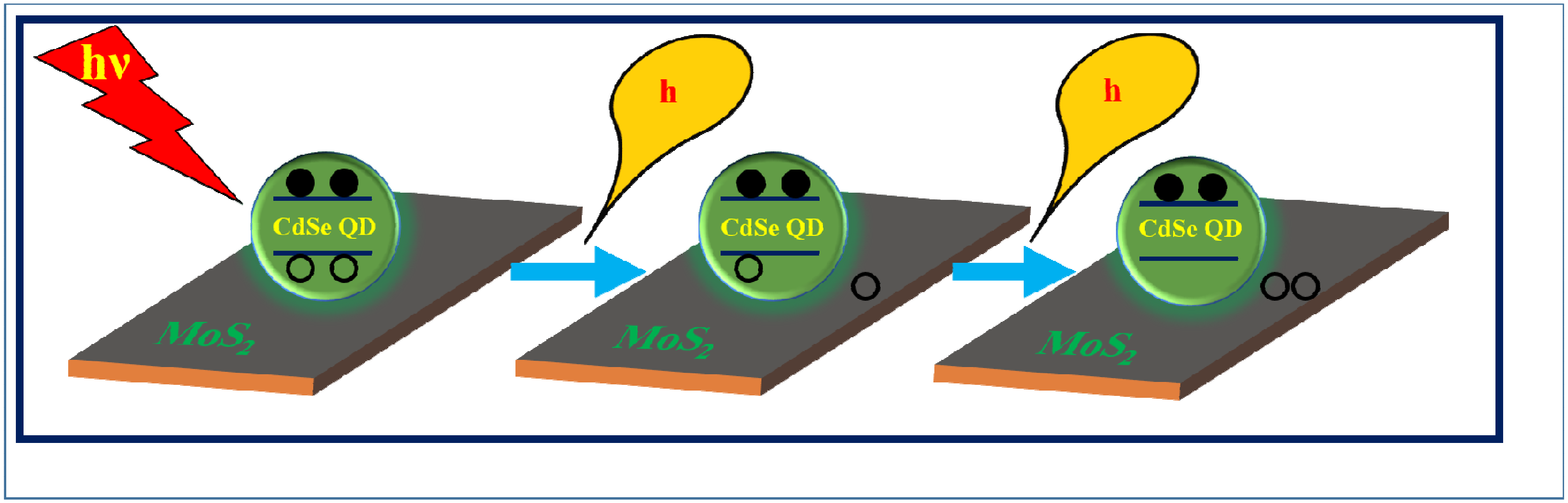


Pal and coworkers ACS Energy Lett. 2017, 2, 1879−1885

Take away from this study

- ❖ MoS_2 nanosheets/CdSe QDs form 2D/0D p-n heterostructures where excitons break via hole transfer

- ❖Biexcitons dissociate at the heterostructures in steps: the hole first injects within 42 ps, followed by slow injection (in 600 ps) of the second one



Pal and coworkers ACS Energy Lett. 2017, 2, 1879−1885

Conclusions

- ✓ MoS_2 nanosheets have been prepared successful via *“polymer assisted”* method, where MoS_2 2H-phase is preserved.
- ✓ *Polymer grafting* does not affect the electron phonon interaction in MoS_2.
- ✓ Polymer grafted .MoS_2 forms a p-n (van der Walls) heterostructure where charge carriers are formed following excitation breaking.
- ✓ PG- MoS_2 nanosheets could be used for photovoltaic as well as memory devices.
- ✓ Collection of multiple charges via dissociation of biexcitons at the 2D/0D interface is a feasible scenario.

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Article

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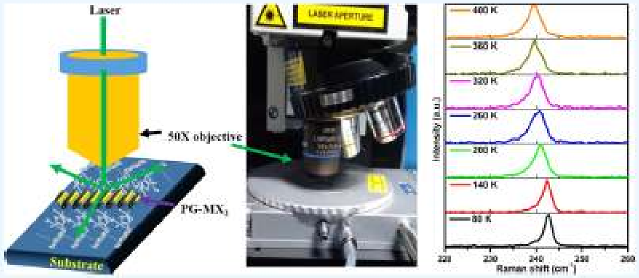
Electron−Phonon Interaction in Organic/2D-Transition Metal Dichalcogenide Heterojunctions: A Temperature-Dependent Raman Spectroscopic Study

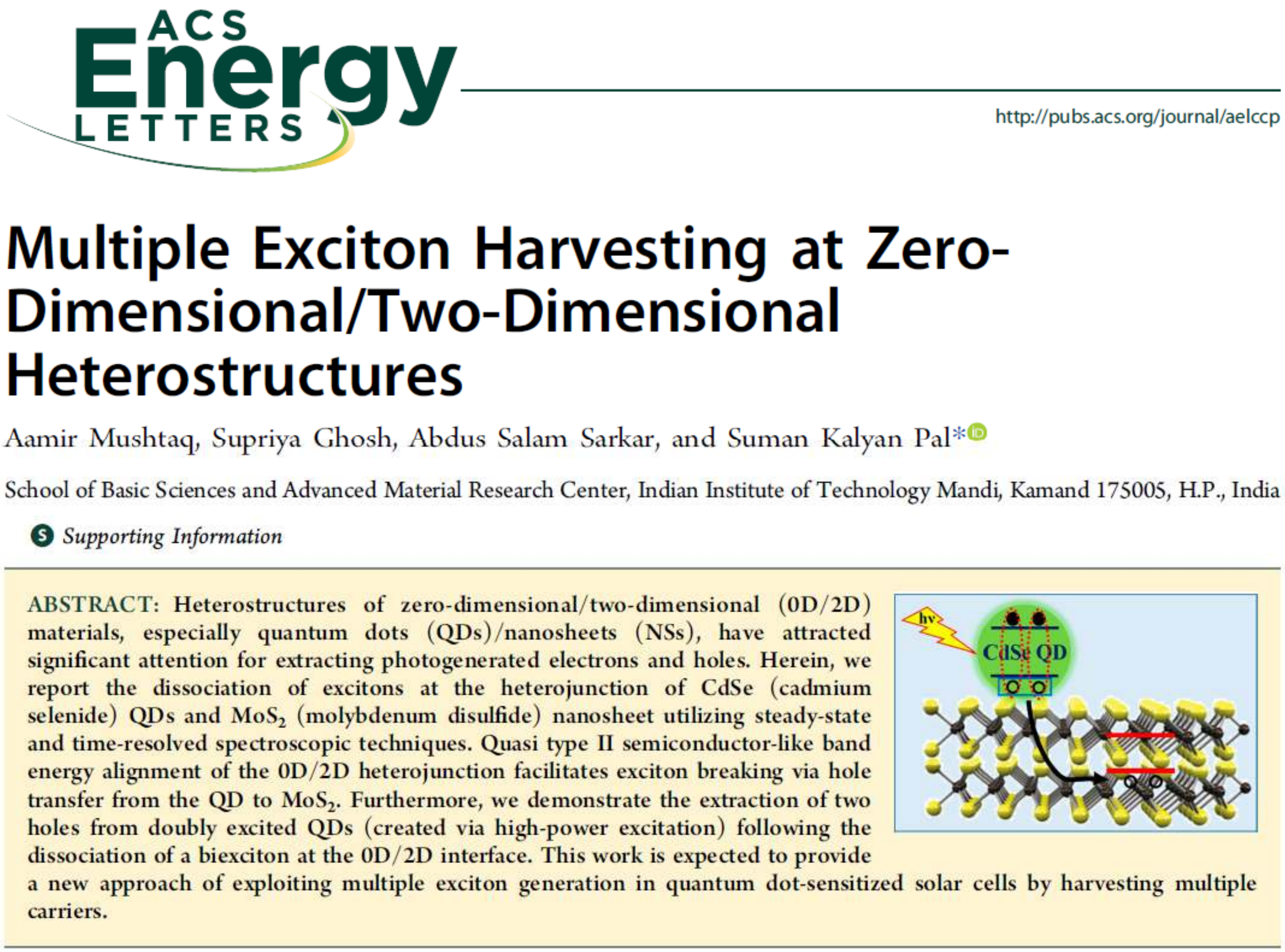
Abdus Salam Sarkar and Suman Kalyan Pal*

School of Basic Sciences & Advanced Materials Research Centre, Indian Institute of Technology Mandi, Kamand, 175005 Mandi, Himachal Pradesh, India

Supporting Information



ABSTRACT: The heterojunctions of organic/two-dimensional transition metal dichalcogenides (TMDs) have the potential to be used in the next-generation optoelectronic and photonic devices. Herein, we have systemically investigated the temperature-dependent Raman spectroscopy to elucidate the phonon shift and thermal properties of the semiconducting TMD nanosheets grafted by a conjugated polymer (PG-MoS_2 and PG-$MoSe_2$) forming heterojunctions. Our results reveal that softening of Raman modes of PG-TMDs as temperature increases from 77 to 300 K is due to the negative temperature coefficient (TC) and anharmonicity. The TCs of E^1_{2g} and A_{1g} modes of PG-MoS_2 nanosheets and A_{1g} mode of PG-$MoSe_2$ were found to be −0.015, −0.010, and −0.010 cm^{-1} K^{-1}, respectively. The origin of negative TCs is explained on the basis of a double resonance process, which is more active in single- and few-layer MoS_2 and $MoSe_2$. Interestingly, the temperature-dependent behavior of the phonon modes of PG-MoS_2 and PG-$MoSe_2$ is similar to that of pristine nanosheets. Grafting by conjugated polymer does not affect the electron−phonon (e−p) interaction in the semiconducting (2H-phase) TMDs, hinting the application potential of such materials in field-effect electronic devices.



ACS Energy LETTERS
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Multiple Exciton Harvesting at Zero-Dimensional/Two-Dimensional Heterostructures

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Supporting Information

ABSTRACT: Heterostructures of zero-dimensional/two-dimensional (0D/2D) materials, especially quantum dots (QDs)/nanosheets (NSs), have attracted significant attention for extracting photogenerated electrons and holes. Herein, we report the dissociation of excitons at the heterojunction of CdSe (cadmium selenide) QDs and MoS_2 (molybdenum disulfide) nanosheet utilizing steady-state and time-resolved spectroscopic techniques. Quasi type II semiconductor-like band energy alignment of the 0D/2D heterojunction facilitates exciton breaking via hole transfer from the QD to MoS_2. Furthermore, we demonstrate the extraction of two holes from doubly excited QDs (created via high-power excitation) following the dissociation of a biexciton at the 0D/2D interface. This work is expected to provide a new approach of exploiting multiple exciton generation in quantum dot-sensitized solar cells by harvesting multiple carriers.

Group

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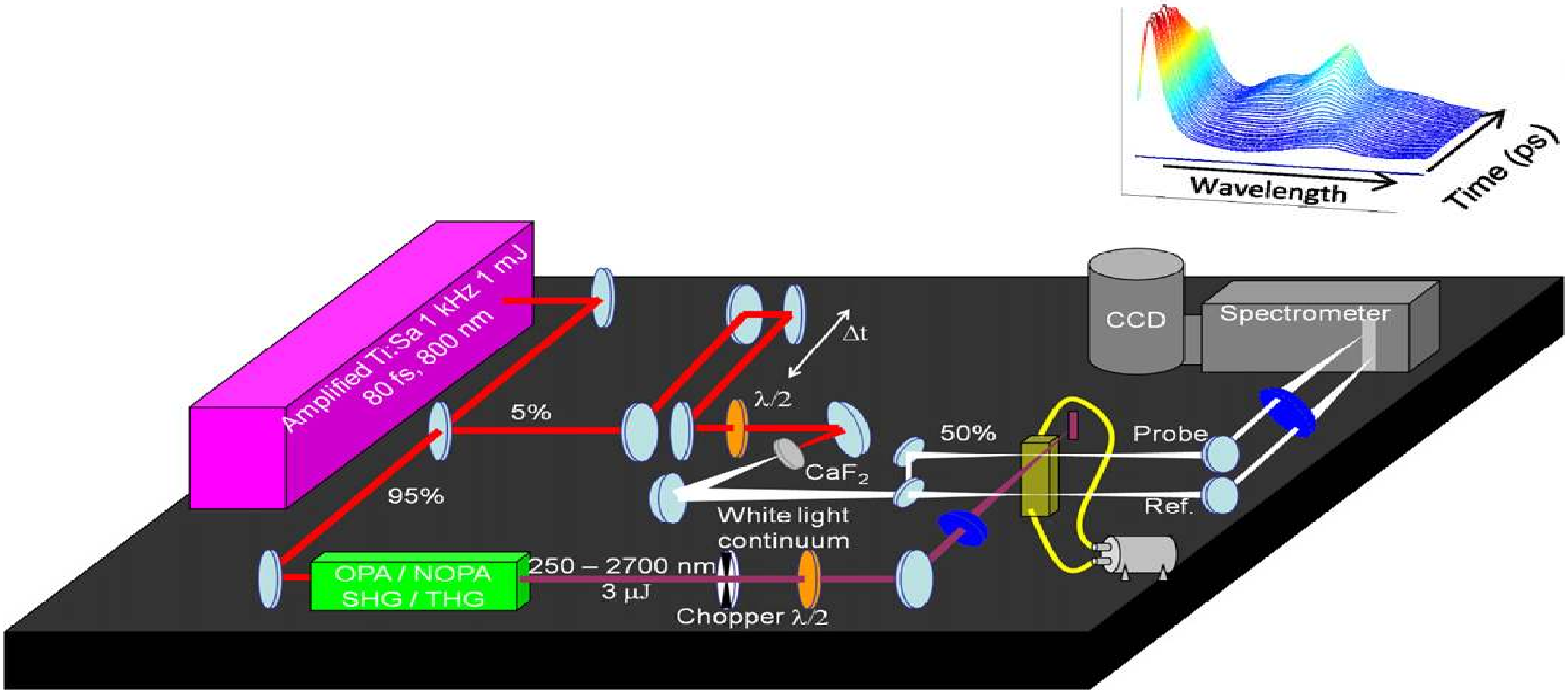
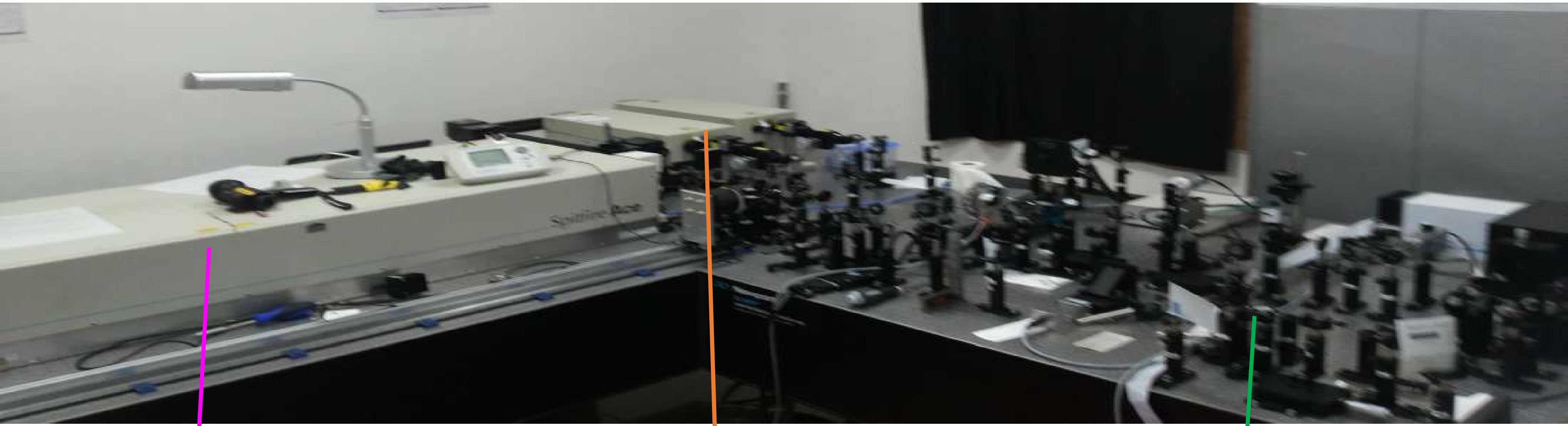
THANK YOU

TA measuring setup



Experimental setup



Amplifier: 800 nm, 35 fs

TOPAS

Detection Optics

Femtosecond Transient absorption measuring system