Correlation between Electronic Structure and Electron Conductivity in MoX_2 (X = S, Se, Te)

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Supercapacitor

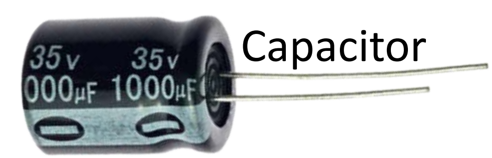
SUPERCAPACITOR

Capacity = High Energy Density
Speed = High Power Density

Application in Electric Bike:

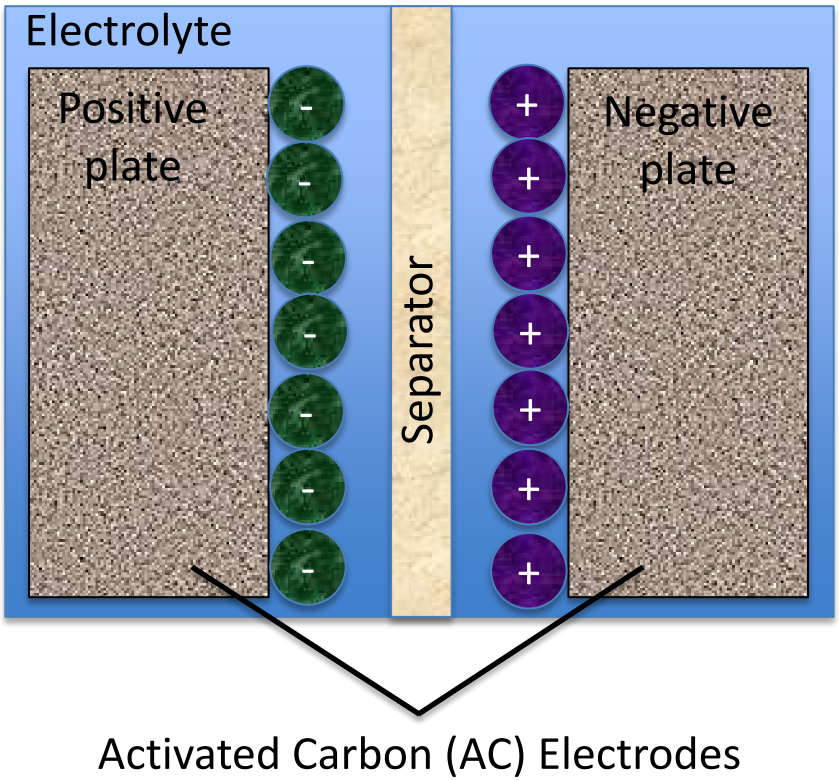
1. Battery: Main source
2. Supercapacitor: Acceleration

High Energy Density
Low Power Density



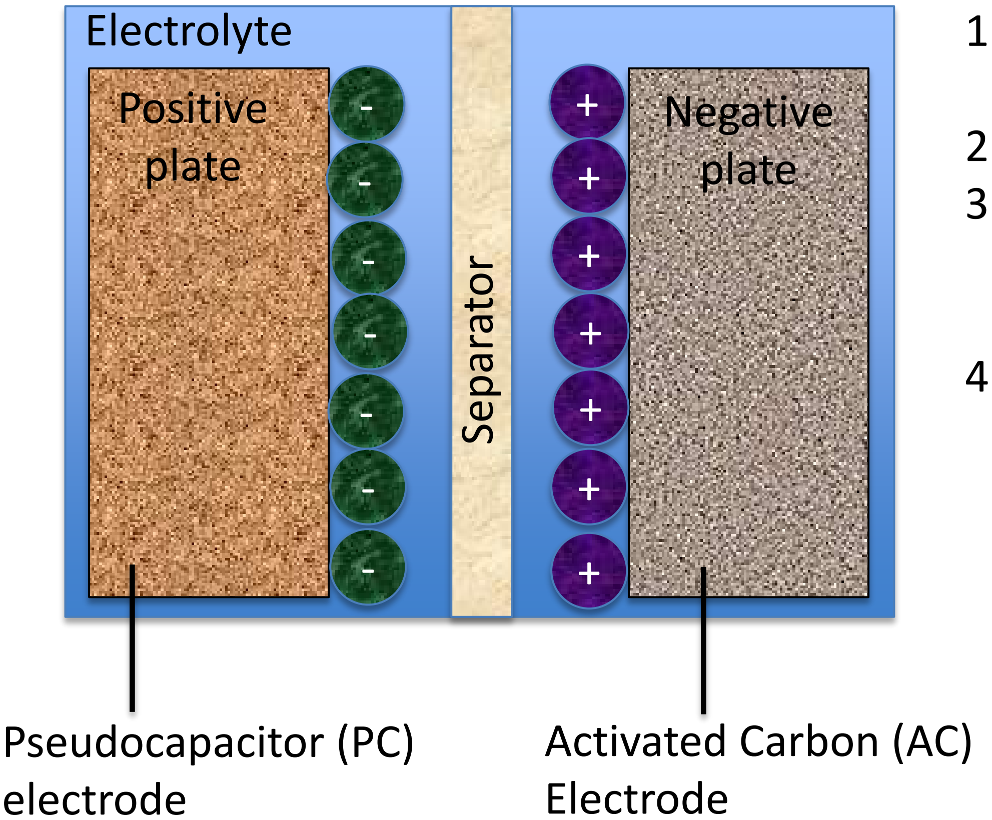
Low Energy Density
High Power Density

Symmetric Supercapacitor (SSC)

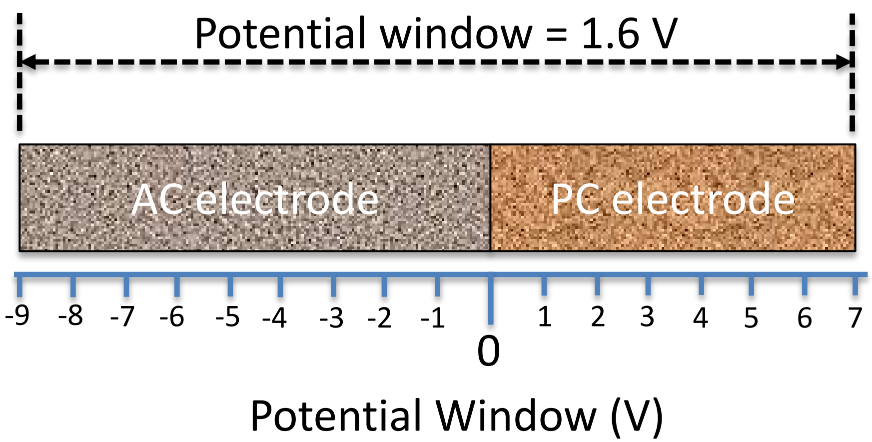


1. Working potential of each AC electrodes are ca. 0 to -0.9 V (Zhang et al., 2015).
2. A combination of two similar electrodes produces maximum working potential of an SSC device ca. 0.9 V.

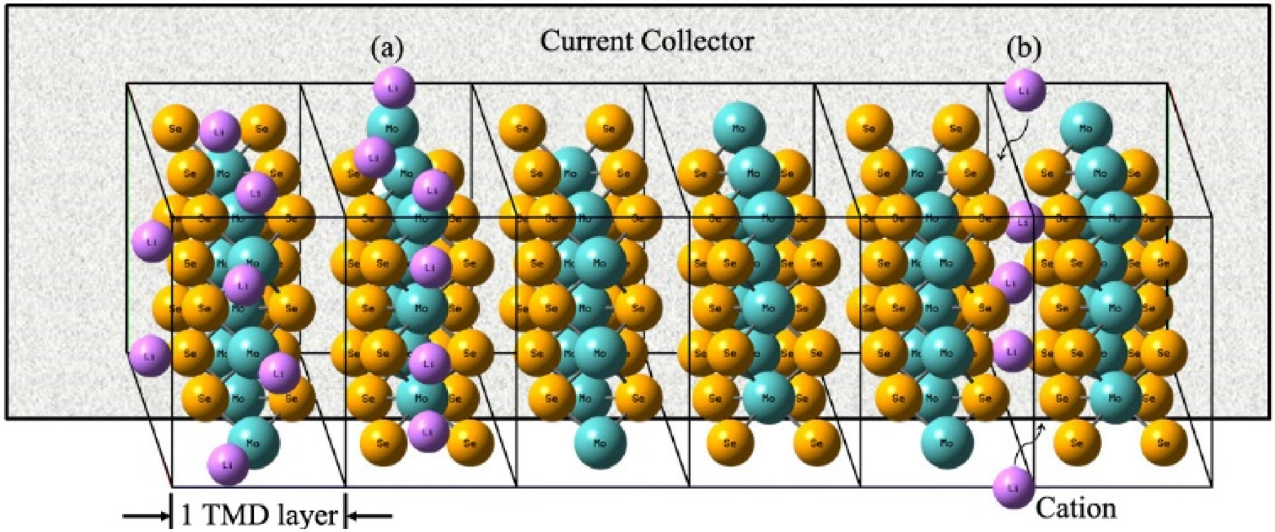
Asymmetric Supercapacitor (ASC)



1. Potential window of a SC could be widen using an ASC device structure.
2. Example of a PC-type material is $MoSe_2$.
3. The working potential of an $MoSe_2$-electrode is ca. 0 to 0.7 V (Aziz et al., 2016)
4. The potential window widens:



Pseudocapacitive TMD-ASC



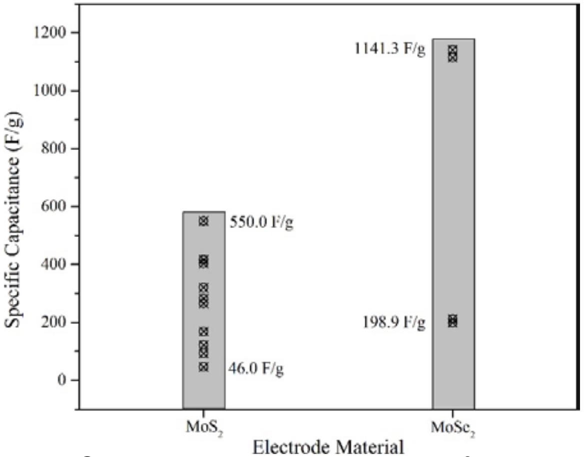
(a) Electrochemical-charge storage:
Chemisorption of electrolyte cations at the surface of TMD e.g., $MoSe_2$ with Mo oxidation states of +4, +5, and +6 (Stark et al, 1969).

$$\left(Mo^{+6}Se_2\right) + Li^{+} + 1e^{-} \underset{discharge}{\overset{charge}{\rightleftharpoons}} \left(Mo^{+5}Se_2Li\right)_{surface/bulk}$$

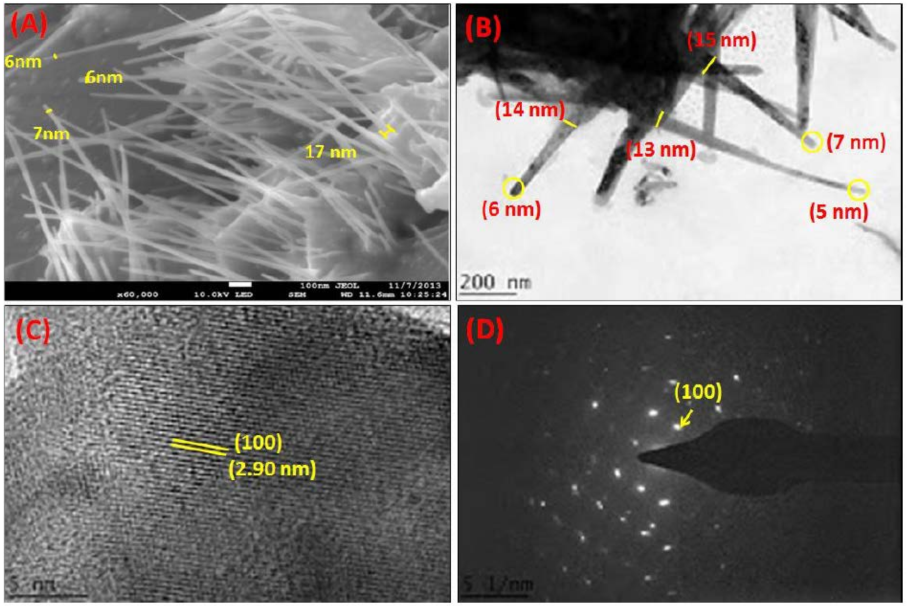
$$\left(Mo^{+5}Se_2Li\right) + Li^{+} + 1e^{-} \underset{discharge}{\overset{charge}{\rightleftharpoons}} \left(Mo^{+4}Se_2Li_2\right)_{surface/bulk}$$

(b) Electrostatic-charge storage:
Intercalation pseudocapacitance charge storage mechanism at surface and bulk of TMD.

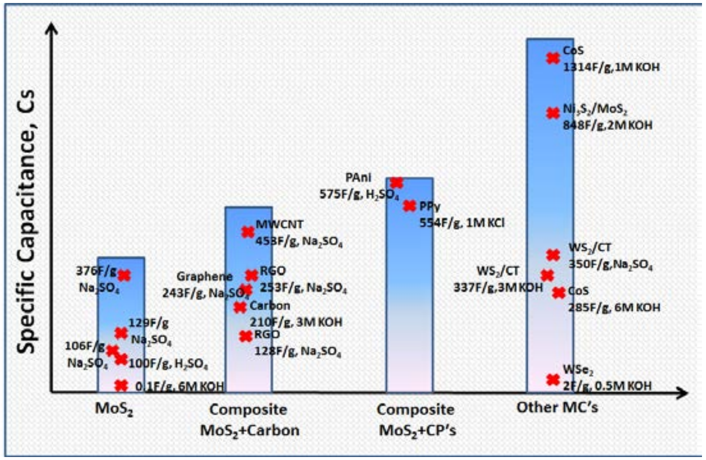
Performance of TMD-ASCs



Specific capacitance, C_S obtained by MoS_2 and $MoSe_2$-based electrodes with various device structures.



Single crystal molybdenum selenide nanoneedles produced C_s ca. 601 F/g (Aziz et al, 2016)



Specific capacitance, C_s obtained by TMDs-based electrode with various type of optimization.

Increasing Power Density of TMD-ASCs

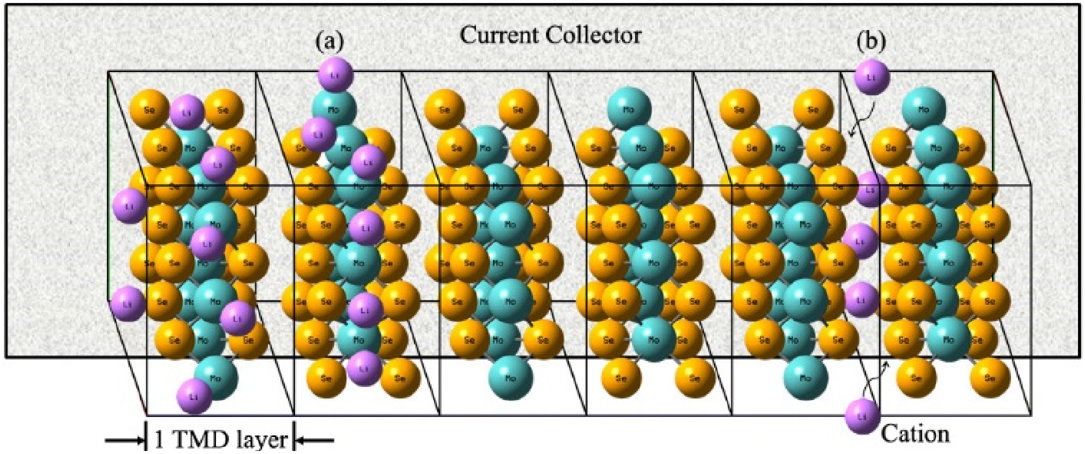
$v_d = \mu \times E$ (Eq. 1)

$\sigma = \eta \times e \times \mu$ (Eq. 2)

$\mu = (e \times \tau)/m_e^*$ (Eq. 3)

$m_e^* = (2\hbar^2/9t_o^2\, r_o^2)E_G$ (Eq. 4)

$$\sigma \propto 1/E_G$$



v_d = drift velocity of electron in TMD

μ = electron mobility in TMD

E = applied electric field

σ = electron conductivity in TMD

η = concentration of electron

e = charge of electron

τ = relaxation time between electron scatterings

m_e^* = effective mass of electron in TMD

$\hbar$ = reduced Plank's constant

t_o = electron hopping parameter

r_o = equilibrium bond length

E_G = bandgap

Electronic properties of TMDs

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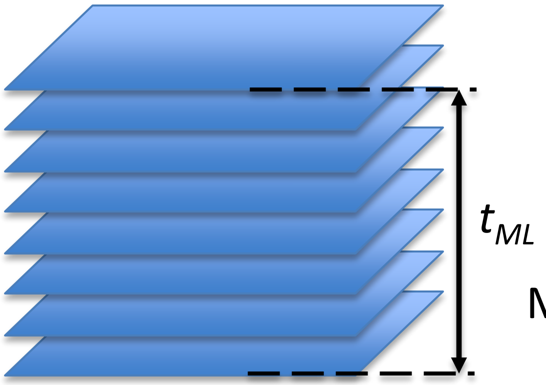
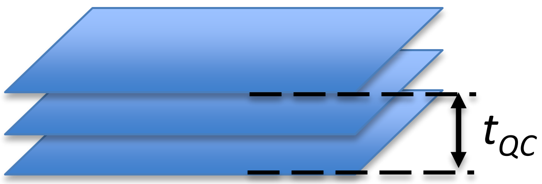
t_{ML} > exciton bohr radius



Bulk multi-Layered TMD

Mechanical exfoliation

t_{QC} < exciton bohr radius



Quantum confined multi-layered TMD

- Indirect bandgap
- Low conductivity

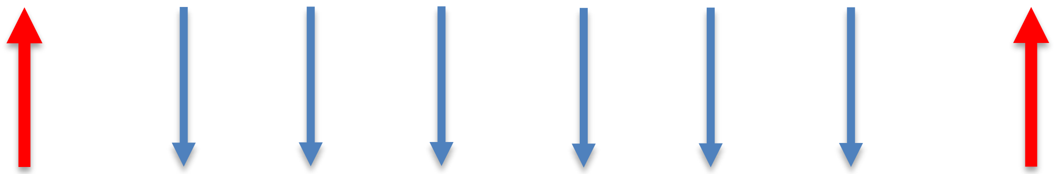
- Direct bandgap
- High conductivity

Zhang et al. (2014), Shaw et al, (2014), and Hosseini et al. (2015)

Problem: What is the correlation between thickness of a monolayer and conductivity?

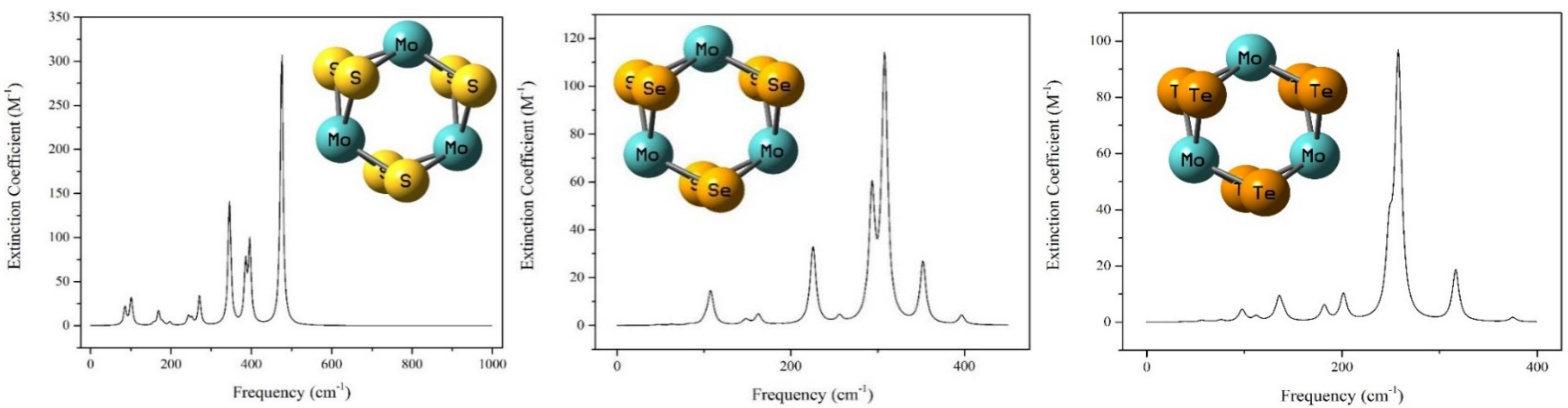
Properties of basic crystal of TMDs

Material	MW (g/mol)	a_0 (nm)	t_{-1L} (nm)	$t_{-Offset}$ (nm)	E_{g-1L} (eV)	E_{g}-Bulk (eV)	$E_{g-Offset}$ (eV)	σ (S/m)
MoS_2	160.07	2.00	1.00	1.00	1.89	1.54	0.35	0.30
$MoSe_2$	253.89	1.20	0.80	0.40	1.55	1.33	0.22	10.00
$MoTe_2$	351.15	1.00	0.70	0.30	1.02	0.88	0.14	22.00



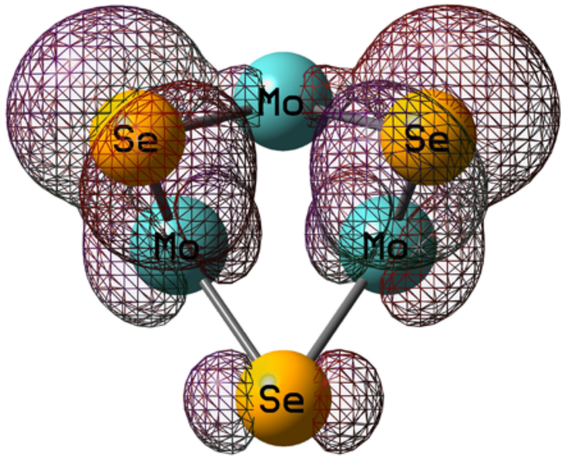
Correlation: Thickness of monolayer decreases, conductivity increases.

Problem: What is the optimum thickness of a monolayer?

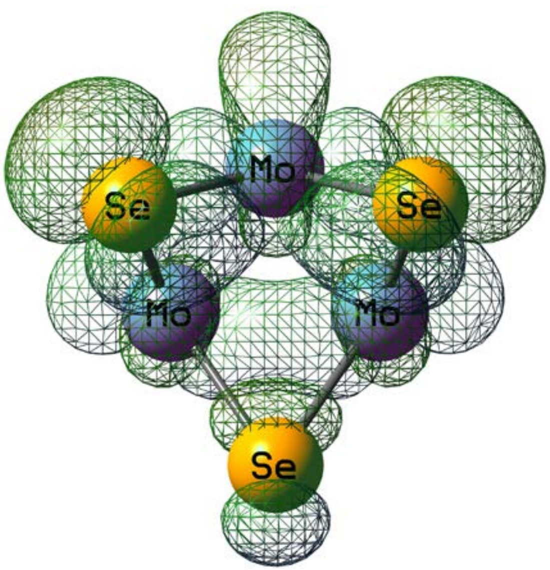


Optimized structure of basic crystal of TMDs; calculated at B3LYP/lanl2dz level of theory

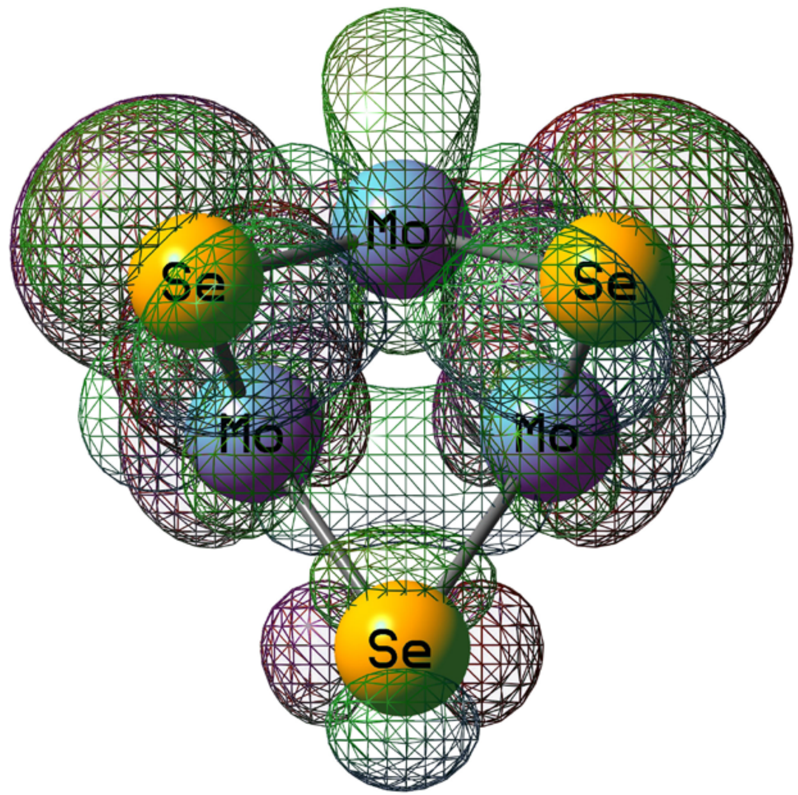
Electronic properties of $MoSe_2$



Ground state electron density



Excited state electron density



Ground & excited state electron density

RED: Ground state electron density

GREEN: Excited state electron density

Comparison of overlapped orbitals

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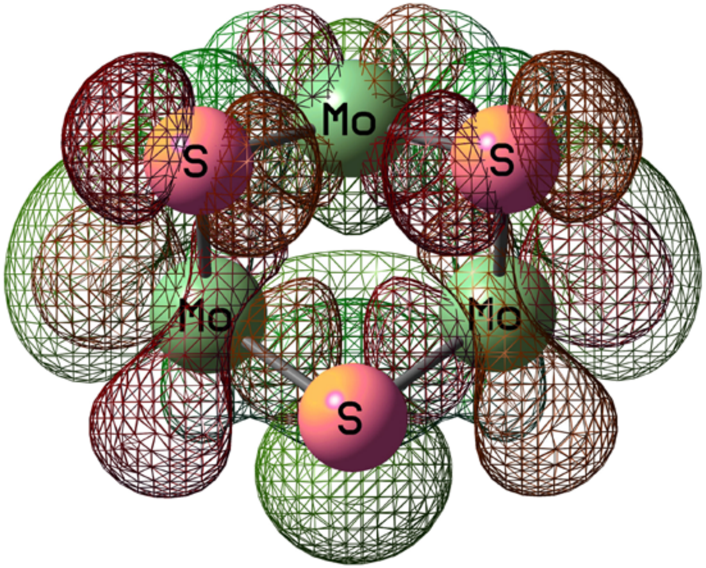
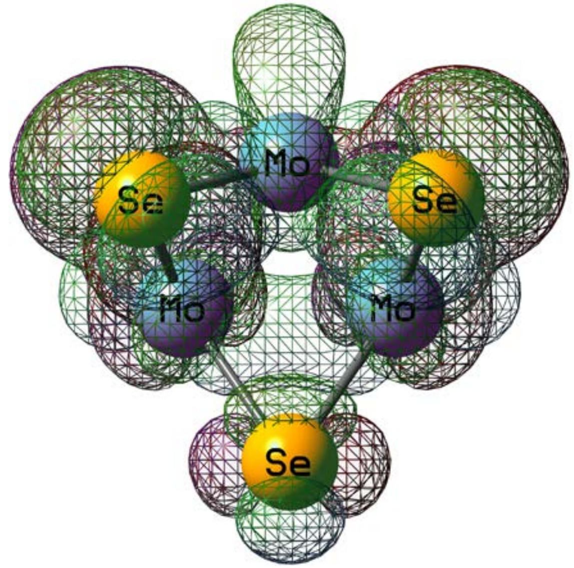
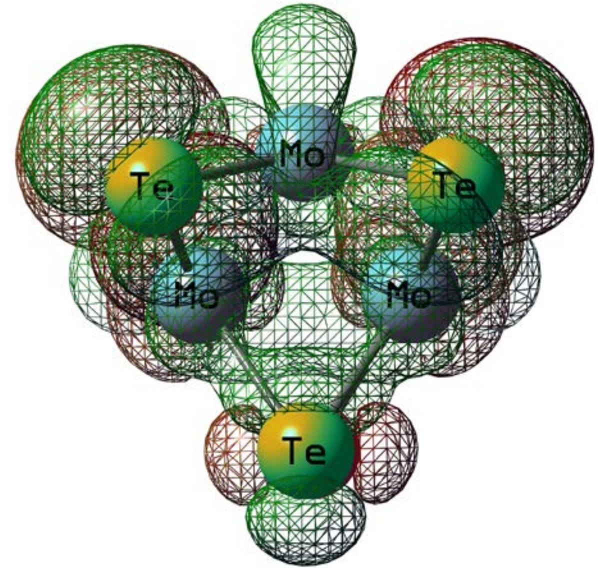
σ = 0.3 S/m



σ = 10 S/m



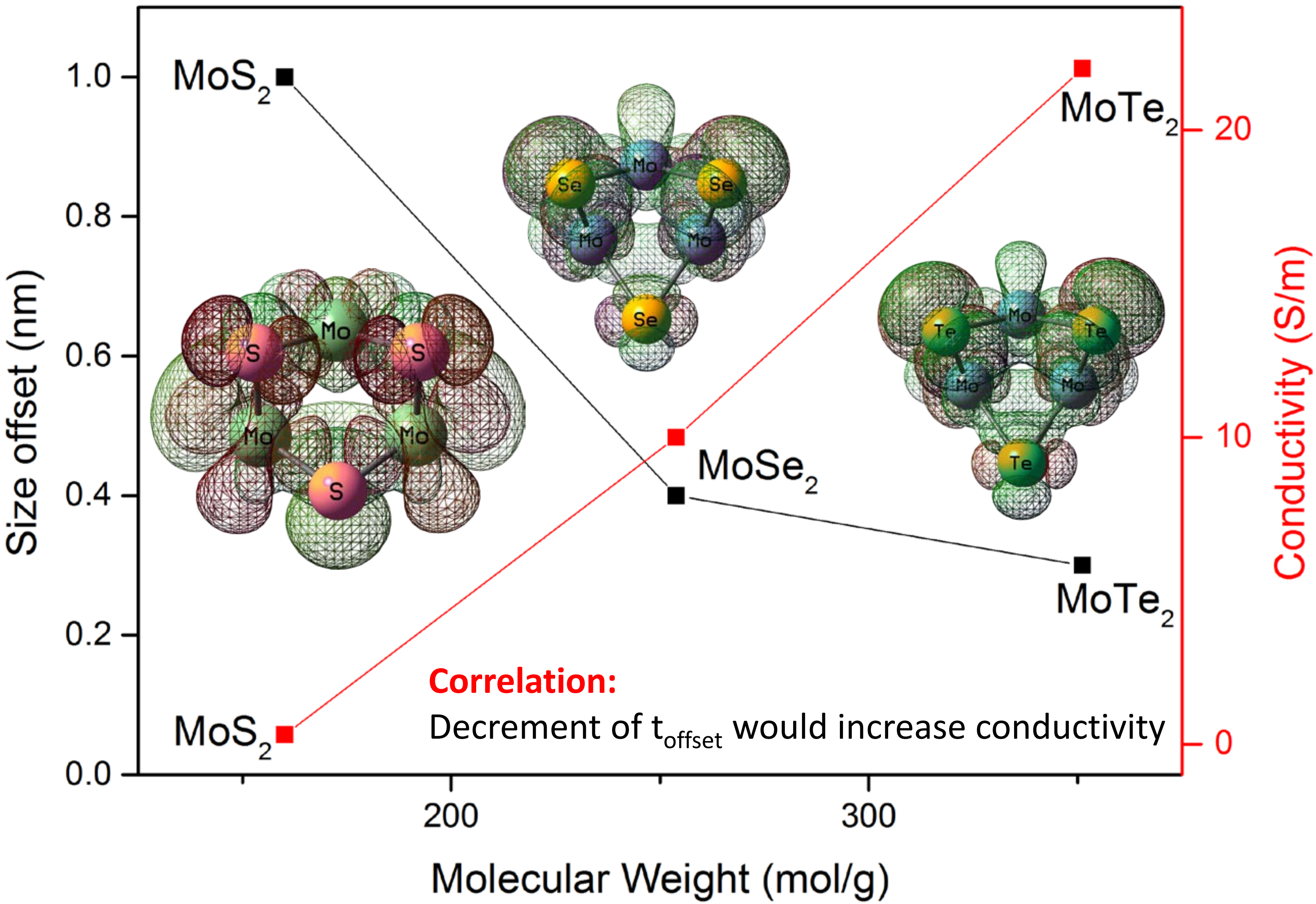
σ = 22 S/m



Overlapped area: $(MoSe_2)_3$ < $(MoTe_2)_3$

$(MoS_2)_3$		**$(MoSe_2)_3$**		**$(MoTe_2)_3$**	
Atom	**Site**	**Atom**	**Site**	**Atom**	**Site**
Mo	3 partial overlap	Mo	3 partial overlap	Mo	3 partial overlap
S	2 non overlap + 4 partial overlap	Se	6 partial overlap	Te	6 partial overlap

Size offset *vs.* electronic structure *vs.* conductivity



Conclusions

1. MoS_2 ($t_{-Offset}$ = 1.0 nm), $MoSe_2$ ($t_{-Offset}$ = 0.4 nm), and $MoTe_2$ ($t_{-Offset}$ = 0.3 nm) showed a trend of increasing conductivity i.e., MoS_2 (0.3 S/m) < $MoSe_2$ (10.0 S/m) < $MoTe_2$ (22.0 S/m).
2. The increment of electron conductivity of the MoX_2 is due to increment of possibility of wave functions overlap between the ground state and excited state electrons.
3. A monolayer thickness which is similar to its exciton Bohr radius ($t_{-Offset}$ = 0) is hypothesized would show maximum area of overlapping orbitals of excited state and ground state electron; therefore optimum conductivity could be achieved.