GRAPHENE AND 2DM VIRTUAL CONFERENCE & EXPO

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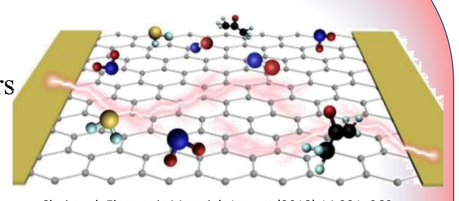
Theoretical investigation of gas molecule adsorption on WS monochalcogenide

Dhanshree Pandey, Aparna Chakrabarti

Motivation

Why need **Gas Sensors**:

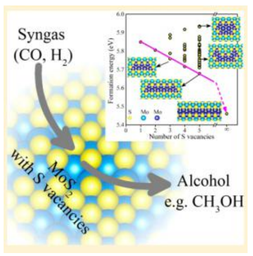
- ✓ Quickly identify toxic gases and organic vapours
- ✓ For environmental and human safety
- ✓ For the emission control
- ✓ In industry sector, etc.



Choi et al. Electronic Materials Letters (2018) 14:221–260

Why **2 Dimensional nanomaterials**

- 2D layered nanomaterials possess **large surface area** and **high surface-to-volume ratio**
- The interaction between adsorbates and pristine graphene is generally quite weak : **pristine graphene is chemically stable at ambient environments**.
- For the transition metal dichalcogenides (TMDs), **the layers are stable against the interaction between environmental species with the absence of dangling bonds**

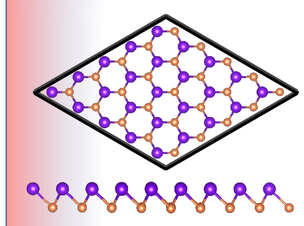


Single-Layer MoS_2 with Sulfur Vacancies: Structure and Catalytic Application, Le *et al*, J. Phys. Chem. C, 118, 5346 (2014)

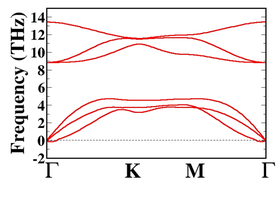
3.3. MoS_2 with Sulfur Vacancies for Catalytic Application. The existence of the sulfur-vacancy rows and the possibility to control their directions[38] suggest a possibility of using them for catalytic applications since, as discussed in the Introduction section, sulfur vacancies will provide great conditions for catalytic activity: Mo atoms and their d-electrons are exposed to adsorbates. It is important to note that the variation of formation

Kim *et al*. Chemosensors 5, 15 (2017)

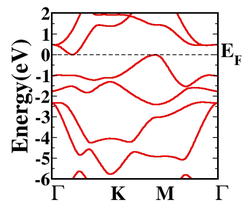
Prediction of WS monochalcogenide



Optimized geometry



Phonon dispersion



Band structure

Systems	E_B/atom (eV/atom)	a(Å)	Buckling height, Δ (Å)	Charge Transfer, ΔQ (e)
WS-buckled	-5.84	2.98	1.62	0.55

- ***Variable coordination number (due to presence of d-orbitals) of TMs allows their reactivity.***
- ***WS monochalcogenide has the W atoms on the surface and hence has active site for gas adsorption.***

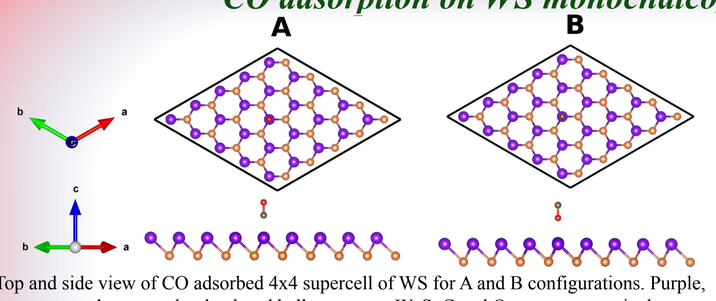
Methodology

- ❑ Density Functional Theory (DFT) based electronic structure calculations have been performed using Veinna Ab-initio Simulation Package (VASP).
- ❑ Exchange correlation functional: Generalized gradient approximation (GGA) given by Perdew, Burke, and Ernzerhof (PBE)
- ❑ Plane wave cutoff- 500 eV
- ❑ k points- 7x7x1
- ❑ Vacuum length- 16Å
- ❑ Energy convergence criterion: 10^{-6} eV
- ❑ van der Waals correction through DFT-D3
- ❑ Adsorption energy has been calculated to find the stable configuration

Adsoprtion Energy, $E_{ads} = E_{2D+gas} - E_{2D} - E_{gas}$

Results and Discussion

CO adsorption on WS monochalcogenide



Top and side view of CO adsorbed 4x4 supercell of WS for A and B configurations. Purple, orange, brown and red colored balls represent W, S, C and O atoms, respectively.

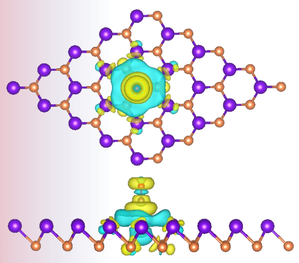
(a) HOMO and (b) LUMO of CO molecule (the C atom is black and the O atom is red) *

[a]Leenaerts *et al.* Phys. Rev. B **77**, 125416 (2008)

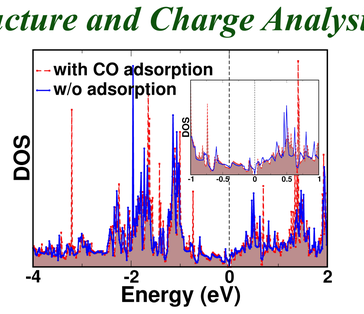
- **Configuration A is preferred for the CO adsorption.**
- **LUMO of CO molecule is primarily located on the less electronegative C atom.**
- **Large charge transfer takes place when C atom is facing the sheet.**

Configuration	E_{ads} (eV)	Δq (e)	C-O (Å)	D(W-C or W-O) (Å)
A	**-2.44**	**-0.40**	**1.17**	**2.03**
B	-0.32	-0.14	1.16	2.27

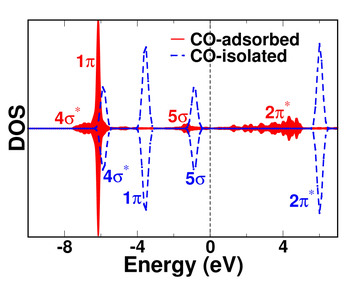
Electronic structure and Charge Analysis



Difference charge density (DCD, $\Delta\rho = \rho_{2D+gas} - \rho_{2D} - \rho_{gas}$). Yellow and blue region show the charge accumulated and depleted regions, respectively.



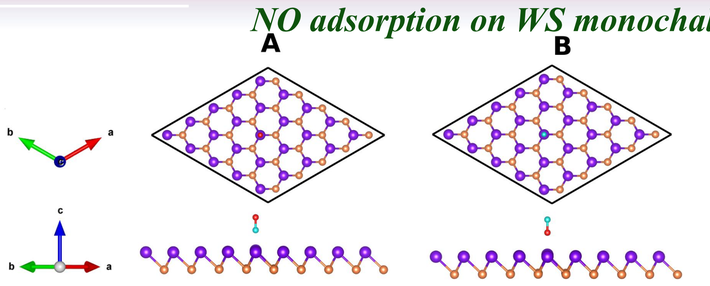
Total density of states (DOS). Inset shows the DOS plot in the energy range of -1 to 1 eV.



Partial DOS corresponding to the CO molecule in the isolated (blue dashed line) and adsorbed (red colored) phase.

- ✓ **Electron accumulation around the CO molecule with the depletion around the WS sheet.**
- ✓ **WS shows a transition to a semiconducting character upon CO adsorption.**

NO adsorption on WS monochalcogenide



Top and side view of NO adsorbed 4x4 supercell of WS for A and B configurations. Purple, orange, cyan and red colored balls represent W, S, N and O atoms, respectively.

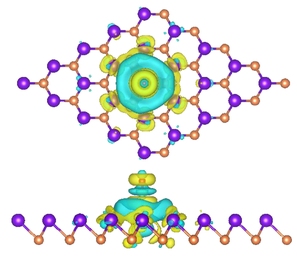
(a) 5σ orbital and (b) HOMO/LUMO of NO (the N atom is blue and the O atom is red).*

[a]Leenaerts *et al.* Phys. Rev. B **77**, 125416 (2008)

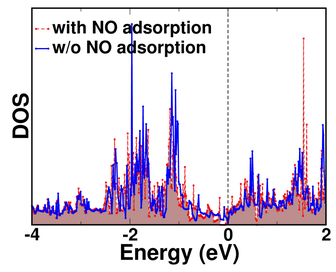
- **Configuration A is preferred for the NO adsorption, similar to CO adsorption.**
- **HOMO/LUMO of NO molecule is primarily located on N atom.**

Configuration	E_{ads} (eV)	Δq (e)	N-O (Å)	D(W-N or W-O) (Å)
A	**-2.80**	**-0.49**	**1.19**	**1.89**
B	-0.97	-0.34	1.19	2.02

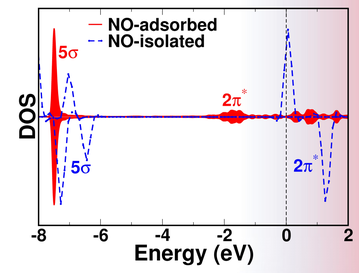
Electronic structure and Charge Analysis



Difference charge density ($\Delta\rho = \rho_{2D+gas} - \rho_{2D} - \rho_{gas}$). Yellow and blue region show the charge accumulated and depleted regions, respectively.



Total density of states (DOS)

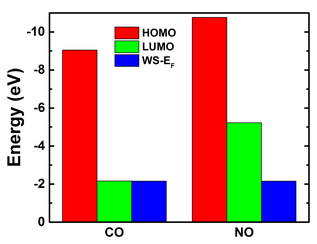


Partial DOS corresponding to the NO molecule in the isolated (blue dashed line) and adsorbed (red colored) phase.

- ✓ **Electron accumulation around the NO molecule with the depletion around the WS sheet.**
- ✓ **Consistent with the direction of the charge transfer from 2D sheet to the NO molecule.**
- ✓ **Upon NO adsorption, appreciable change in the electronic structure is observed.**

Charge Transfer Theory

- ***A charge transfer depend on the relative positions of the highest occupied molecular orbital (HOMO) and the lowest un-occupied molecular orbital (LUMO) of the gas molecules.***
- ***LUMO of CO molecule is located at -2.162 eV and E_F of WS at -2.157 eV, hence charge transfer from WS to CO molecule***
- ***Similar argument holds good for the charge transfer from WS to NO molecule.***
- ***This analysis is consistent with the Bader charge analysis and DCD.***



Molecular LUMO and HOMO levels and Fermi-level (E_F) of the pristine WS monolayer.

Comparison of E_{ads} (in eV) for CO and NO gas adsorption on different 2D nanostructures from literature

System	CO	NO
Graphene[1,2]	-0.01 (-0.12)	-0.03 (-0.30)
Silicene[3]	-0.18	-0.35
Phosphorene[4]	-0.31	-0.31
Borophene[5]	-1.38	-1.79
MoS_2[6]	-0.44	-0.55
WS_2[7]	-0.13	-0.22
WS	**-2.44**	**-2.80**

Summary and Conclusion

1) Adsorption of CO and NO gases on 2D surfaces of pristine buckled WS monochalcogenide has been studied.

2) E_{ads}, Bader charge analysis and the difference charge density analysis reveal that, both, CO and NO molecule prefer the adsorption on the 2D sheet with C or N, respectively, pointing towards the sheet.

3) Charge transfer theory has been discussed to study the direction of charge transfer from the sheet to molecule

4) Significant changes in the electronic states have been observed for both the cases with semimetallic to semiconductor transition in case of adsorption of CO gas molecule on the WS monolayer

5) CO and NO molecule adsorbed systems have high value of E_{ads} which suggest their applicability as a potential candidate for gas sensor.

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