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# Towards quantification of covalent modification on semiconducting $MoS_2$

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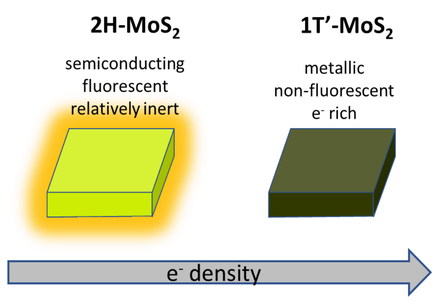
## Introduction

One of the challenges in integrating 2D materials into technological applications is a lack of scalable means of controlling and quantifying properties of these materials. Weak covalent molecular functionalization methods have been reported to allow modifications of these materials without compromising their valued physical and mechanical properties.[1]

$MoS_2$ has caught the attention of researchers for its phase-dependent optoelectronics among other interesting properties. In its stable 2H-phase, $MoS_2$ is a fluorescent semiconductor with a direct bandgap. Upon charge injection, it turns into the 1T-phase which is reactive and metallic in nature.

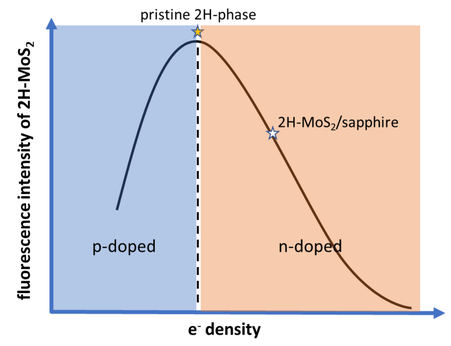



## Electronic properties and photoluminescence of 2H-$MoS_2$

Single layer 2H-$MoS_2$ is highly photoluminescent due to a direct bandgap in its monolayer state. Functionalization and its corresponding doping introduce additional charges into the basal plane of $MoS_2$. In a photoexcited material, these charges will interact with excitons to form trions.

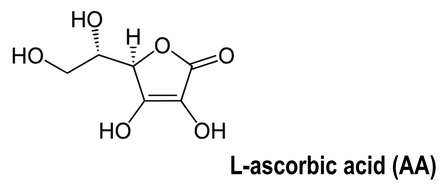
Formation of trions opens new non-radiative recombination pathways that lead to a decrease in the yield of radiative recombination. This allows us to probe and quantify the changes in electronic state of the material by studying variations in its photoluminescence (PL).

The monolayer of $MoS_2$ used in our experiments is prepared by chemical vapor deposition (CVD) on a sapphire substrate.

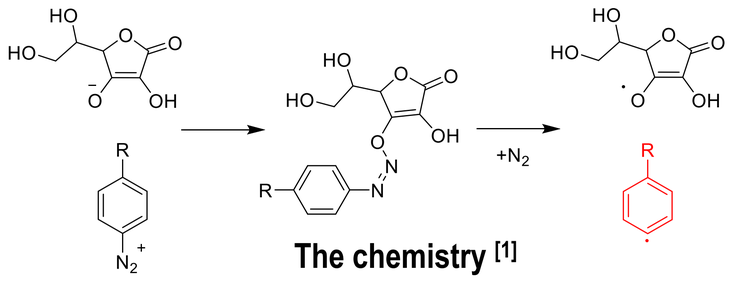



## Covalent functionalization using diazonium chemistry

Efficient bond formation and its tunable nature makes diazonium chemistry suitable for functionalizing 2D surfaces.[2,3] 2D materials are very sensitive to surface phenomena. Hence it is also crucial to have a method of functionalization that does not dope or introduce defects to the material.

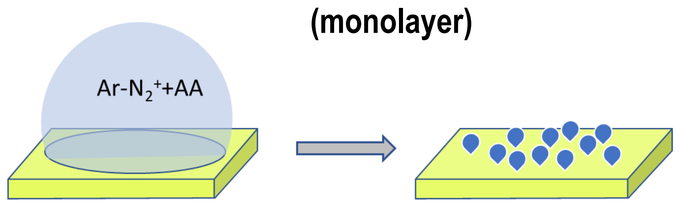


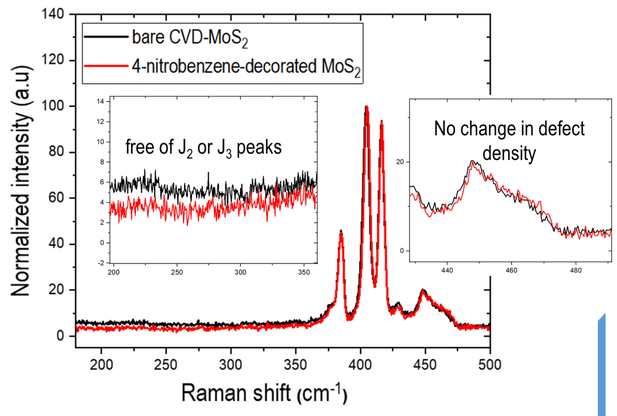

**Weak reducing agent, Can be removed by washing**




**The chemistry [1]**

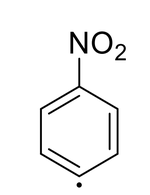
**self-limiting, molecular functionalization (monolayer)**

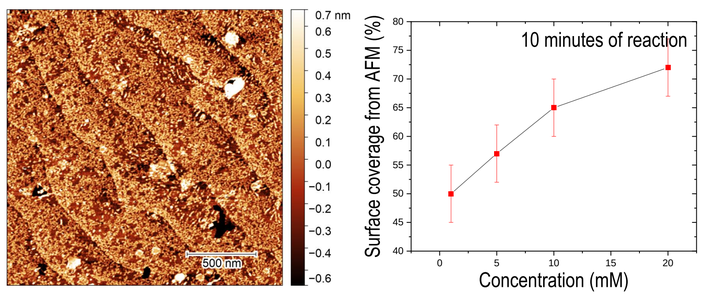



**Conserves semiconducting phase, no additional defects.**

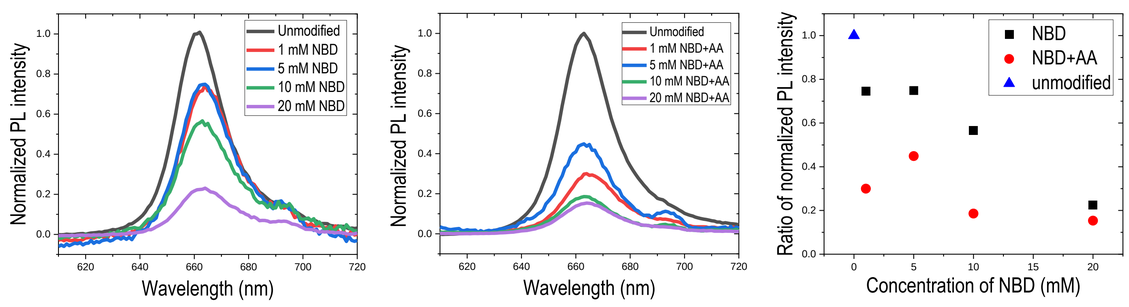
## Demonstrating concentration dependence of functionalization




**AFM and PL studies independently confirm the concentration dependence**

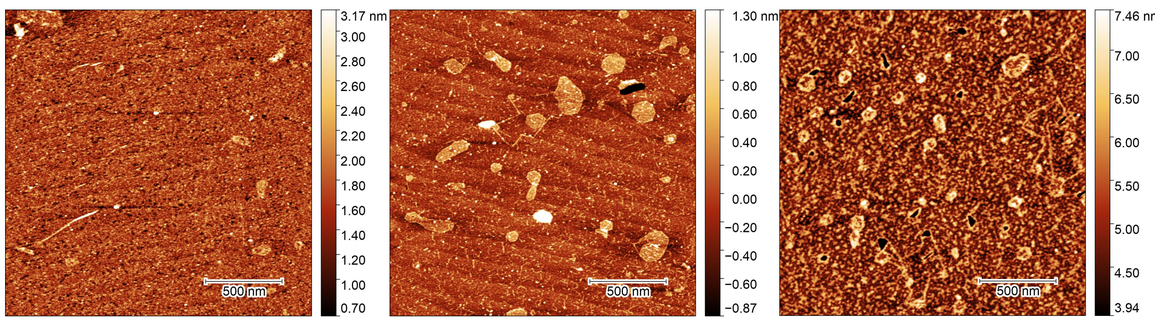
## Reaction dynamics: influence of the reducing agent




**Visualizing the promotion of functionalization by reducing agent**

## Visualizing evolution of surface structures

**Nucleation-growth of grafted structures**

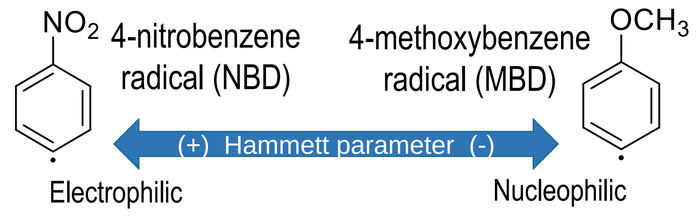


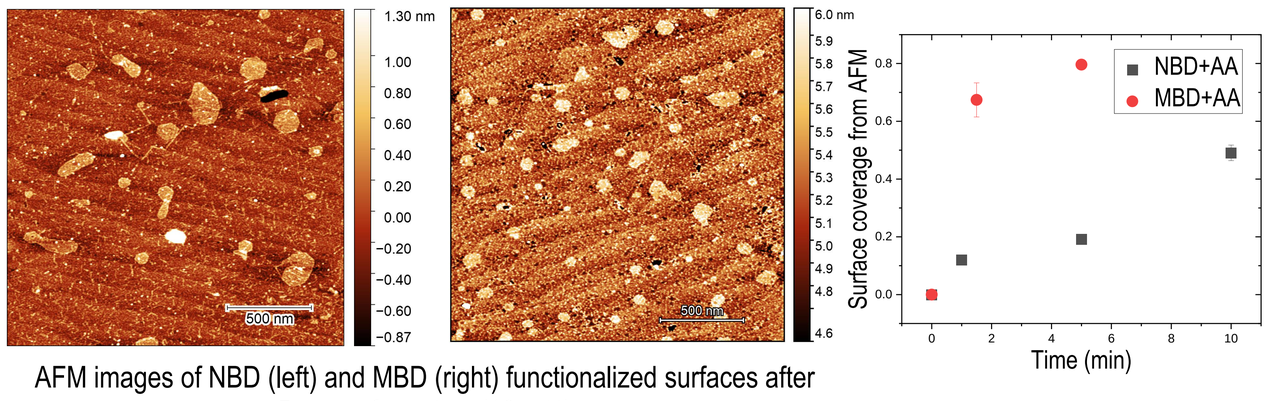

AFM images at different stages of NBD functionalization

Thickness of the film (0.6 nm-0.8 nm) corresponds to monolayer coverage at all stages.

## Kinetics and substituent group effect on functionalization

**Displaying differences in functionalization between radicals of different nature.**




AFM images of NBD (left) and MBD (right) functionalized surfaces after 5 mins of reaction (10 mM)

## Conclusions

We present a tool for quantifying surface and electronic effects of chemical functionalization on sl-$MoS_2$ by combining AFM and photoluminescence means of characterizations.

We demonstrate the versatility of this approach by studying various facets of chemical functionalization on the surface of single layer, 1H-$MoS_2$.

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## REFERENCES

[1] González, Miriam C. Rodríguez, Rahul Sasikumar, and Steven De Feyter, Surface Review and Letters (2021): 2140002.
[2] González, M. C. R., Brown, A., Eyley, S., Thielemans, W., Mali, K. S., & De Feyter, S. Nanoscale 12.36 (2020): 18782-18789
[3] Li, Duo O., Ximo S. Chu, and Qing Hua Wang, Langmuir 2019, 35, 17, 5693–5701

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