Hydrogen fuel production on MoS_2 nanotubes

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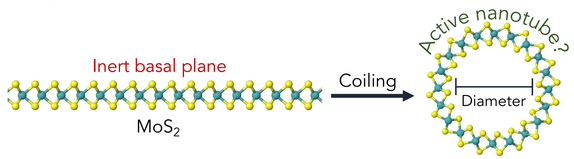
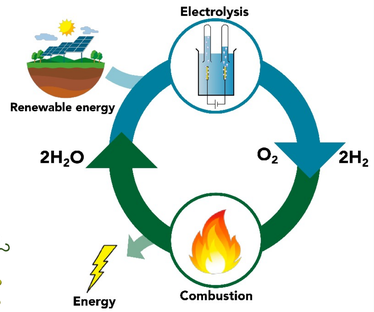
1 Motivation

H_2 is a promising carbon-zero fuel, which can be produced cleanly by the electrolysis of water, using a catalyst.[1]

MoS_2 nanosheets are a promising hydrogen evolution catalyst. However, the flat basal plane – which makes up most of the material – is inactive.

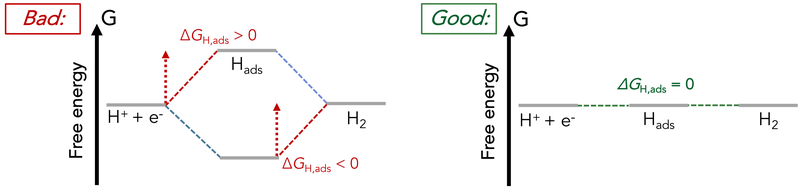
In this density functional theory study, we examine how coiling MoS_2 into nanotubes can enhance catalysis.





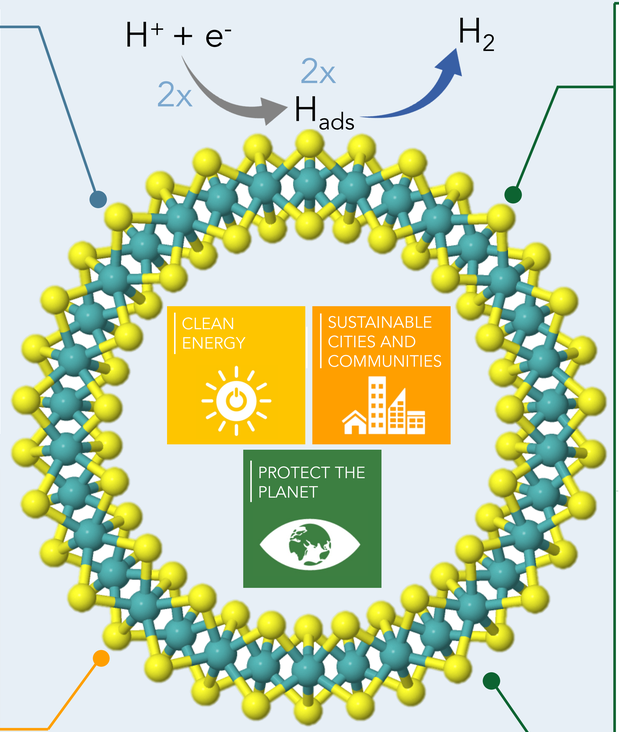
2 What makes a good catalyst?

H^+ must (1) adsorb to the catalyst, (2) combine with another H, then (3) desorb as H_2.[2] Density functional theory (BEEF-vdW, VASP) is used to calculate the energetics:



If a catalyst adsorbs H too strongly ($\Delta G_{H,ads} < 0$) or weakly ($\Delta G_{H,ads} > 0$), an energy cost must be paid to either get H onto the surface or remove it again after reaction.

A ideal catalyst both adsorbs and desorbs H without an energy penalty ($\Delta G_{H,ads} = 0$).[3] The closer $\Delta G_{H,ads}$ is to zero, the better the catalyst.



Want to know more?

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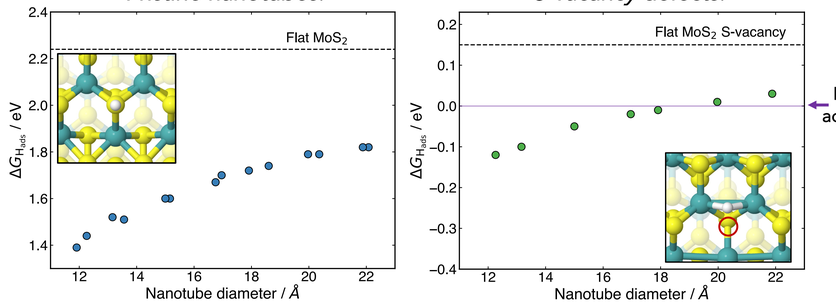
3 MoS_2 nanotubes

Pristine nanotubes: *S-vacancy defects:*

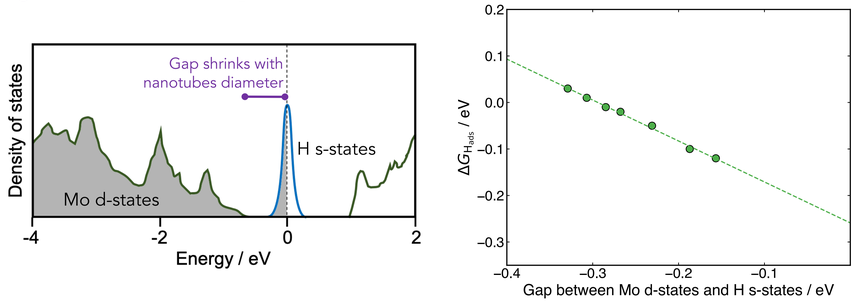


$\Delta G_{H,ads}$ on nanotubes is lowered relative to flat MoS_2, especially at small diameters.

At S-vacancy defect sites, $\Delta G_{H,ads}$ is close to thermoneutral (0 eV) when the nanotubes are 18–20 Å in diameter. These materials may make very good hydrogen evolution catalysts!

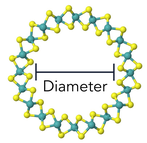
What causes size-dependent tuning of H adsorption?

As the nanotubes get smaller, the Mo d-states get closer in energy to the H s-states. This leads to a stronger bond between MoS_2 and H.[4]



For the S-vacancy defect site, we find a reliable linear relationship between $\Delta G_{H,ads}$ and the Mo d-state to H s-state energy gap.

Controlling the size of MoS_2 nanotubes offers a clear way to fine-tune and improve their hydrogen evolution activity.



References

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[2] Ruffman, C.; Gordon, C. K.; Skúlasson E.; Garden, A. L. *J. Phys. Chem. C.* **2020**, *124*, 17015-17026.
[3] Tsai, C.; Chan, K.; Nørskov, J. K.; Abild-Pedersen, F. *Surf. Sci.* **2015**, *640*, 133-140.
[4] B. Hammer B.; Nørskov, J. *Surf. Sci.* **1995**, *343*, 211–220.

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