Understanding the Fundamentals of Hydrogen Evolution in Earth Abundant Catalysts

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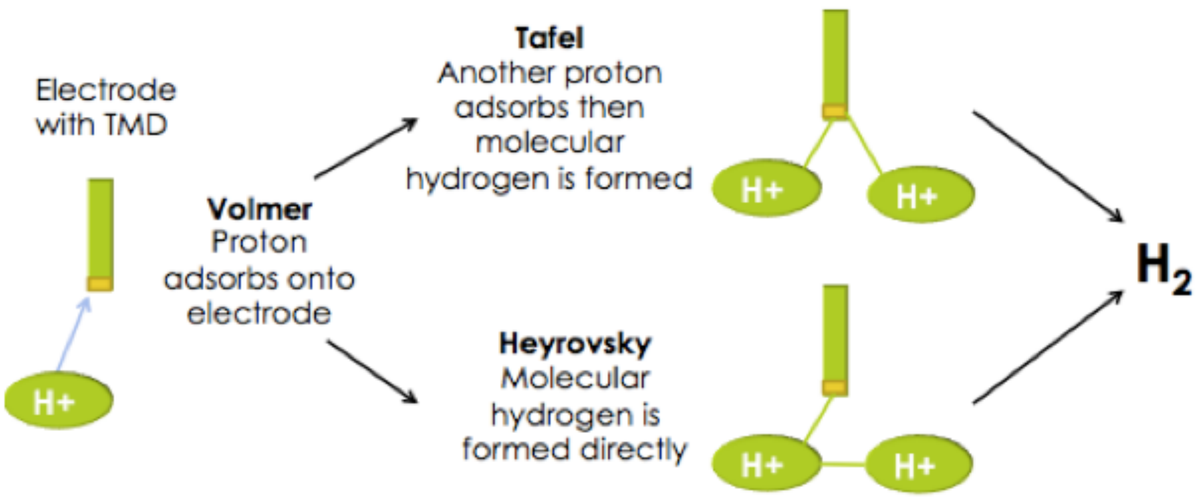
IMPACT Research Experience for Undergraduates

Award ID 1542164

What is the Hydrogen Evolution Reaction (HER)?

- Process than involves three mechanistic steps in an acidic medium:
  - Volmer: proton adsorption
    - Tafel: Second proton adsorbs
    - Heyrovsky: molecular hydrogen is formed directly
      - Ideally Volmer-Heyrovsky mechanism forms more H_2 efficiently



Why Hydrogen?

- Most of our energy comes from fossil fuels
  - Nonrenewable, finite resource
  - Environmentally unfriendly, carbon oxide pollutants

https://www.carbonbrief.org/two-charts-show-how-fossil-fuels-could-peak-2020

- Small portion of energy comes from hydrogen gas
  - Environmentally friendly, water splitting process
    - Currently used for ammonia production for fertilizers and hydrocracking for fuels

http://www.agmrc.org/renewable-energy/ethanol/using-the-wind-to-fertilize-corn/

Current HER material

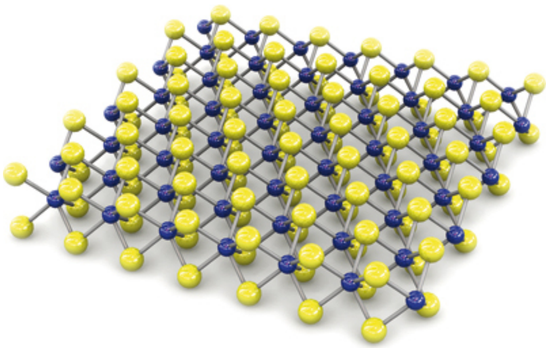
- Platinum metal is currently the state of the art for hydrogen production by HER
  - Catalyzes the reaction efficiently
  - Platinum is an expensive, rare earth metal
  - Cannot create sizeable reaction, unfeasible for industrial application

https://seekingalpha.com/article/4056144-platinum-historical-enigma

Alternative to Platinum

- There is a need for cheaper and more earth abundant hydrogen evolution catalysts
- One promising class of materials: transition metal dichalcogenides TMD, i.e. MoS_2
  - Good electrochemical properties for HER
  - More abundant, inexpensive
  - However does not yet perform as well as platinum

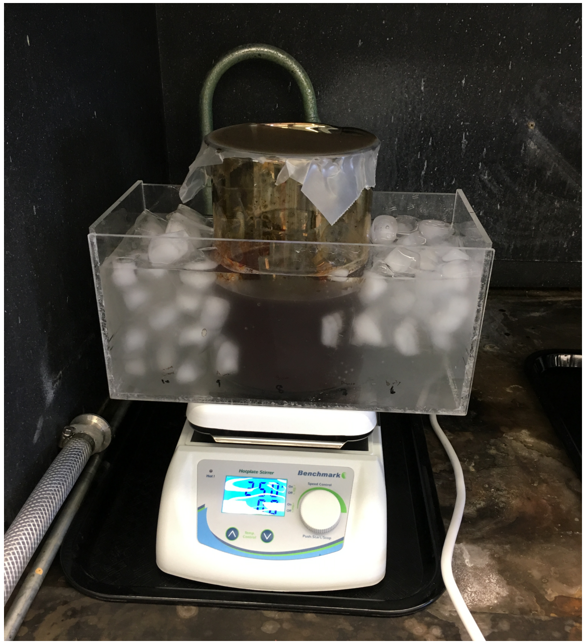
Crystalline MoS_2



https://www.researchgate.net/post/

Project Goals

- Here we attempt to improve the catalytic activity and shorten the synthesis of TMD based catalysts
  - Coupling ammonium tetrathiomolybdate(ATM), MoS_2 precursor, with support of graphene oxide (GO)
    - Crystalline MoS_2 vs. amorphous ATM
  - Use Intense pulsating light (IPL) for catalyst preparation to reduce synthesis time from hours to just minutes



Synthesizing Graphene Oxide

Materials and Methods

Synthesis and Evaluation of ATM-GO catalyst

Synthesis of Graphene Oxide

Creating an ink with catalyst bound to GO for Characterization

Made ink with H_2O and Ethanol and drop casted onto electrode.

Intense Pulse Light on dried material

20 pulses of $17.7\ J/cm^2$ of light onto material

Characterize Catalyst in an electrochemical cell

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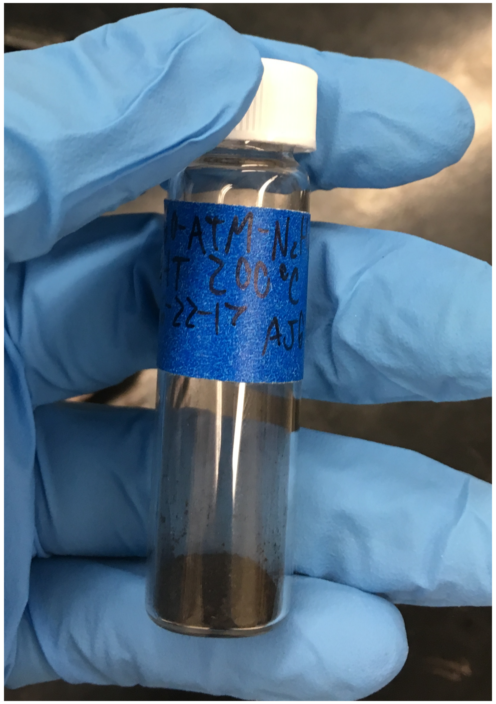
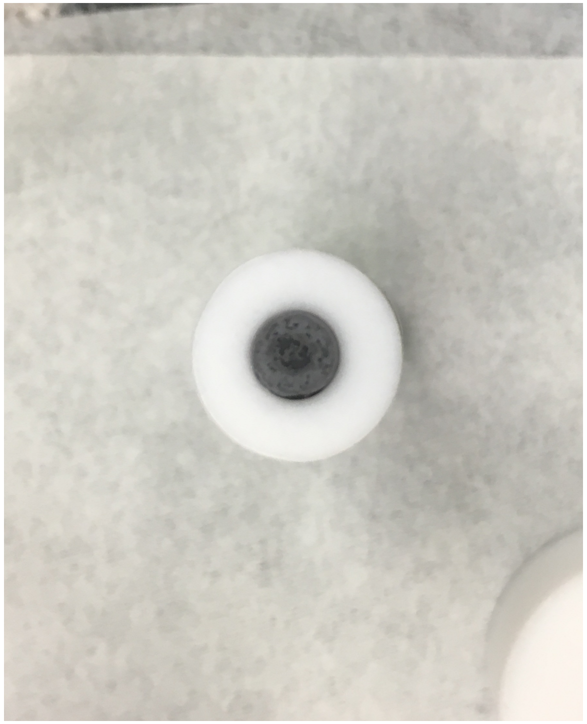
Creating an ink



Dry material

Ink



Material Ready for IPL

Materials and Methods

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Characterize Catalyst in an electrochemical cell

Electrochemical Characterization

Counter Electrode

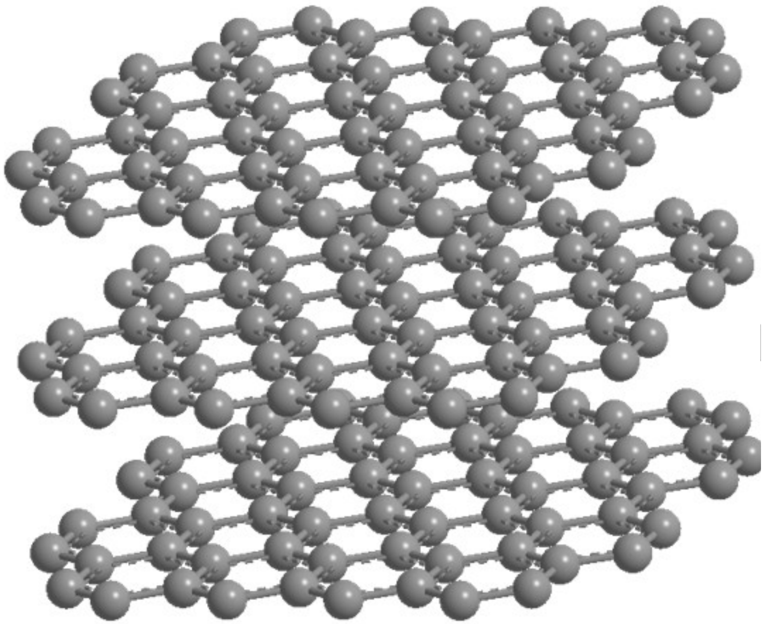
Working Electrode

Nitrogen Gas

Reference Electrode

Graphene Oxide, a supporting nanostructure

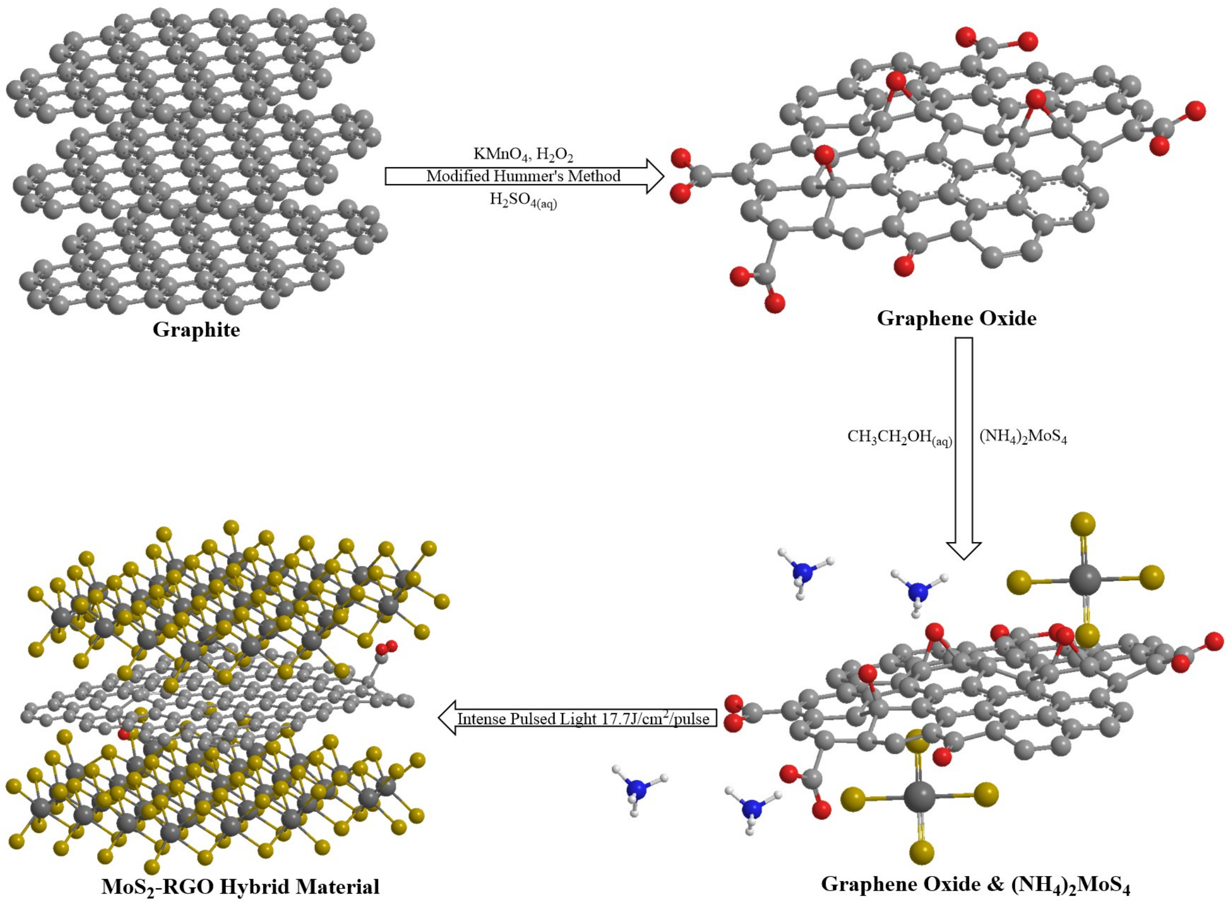
- Graphite: layers of graphene
- Sheets contribute to more exposed surface area of catalyst
- More area for activity, more Hydrogen formation



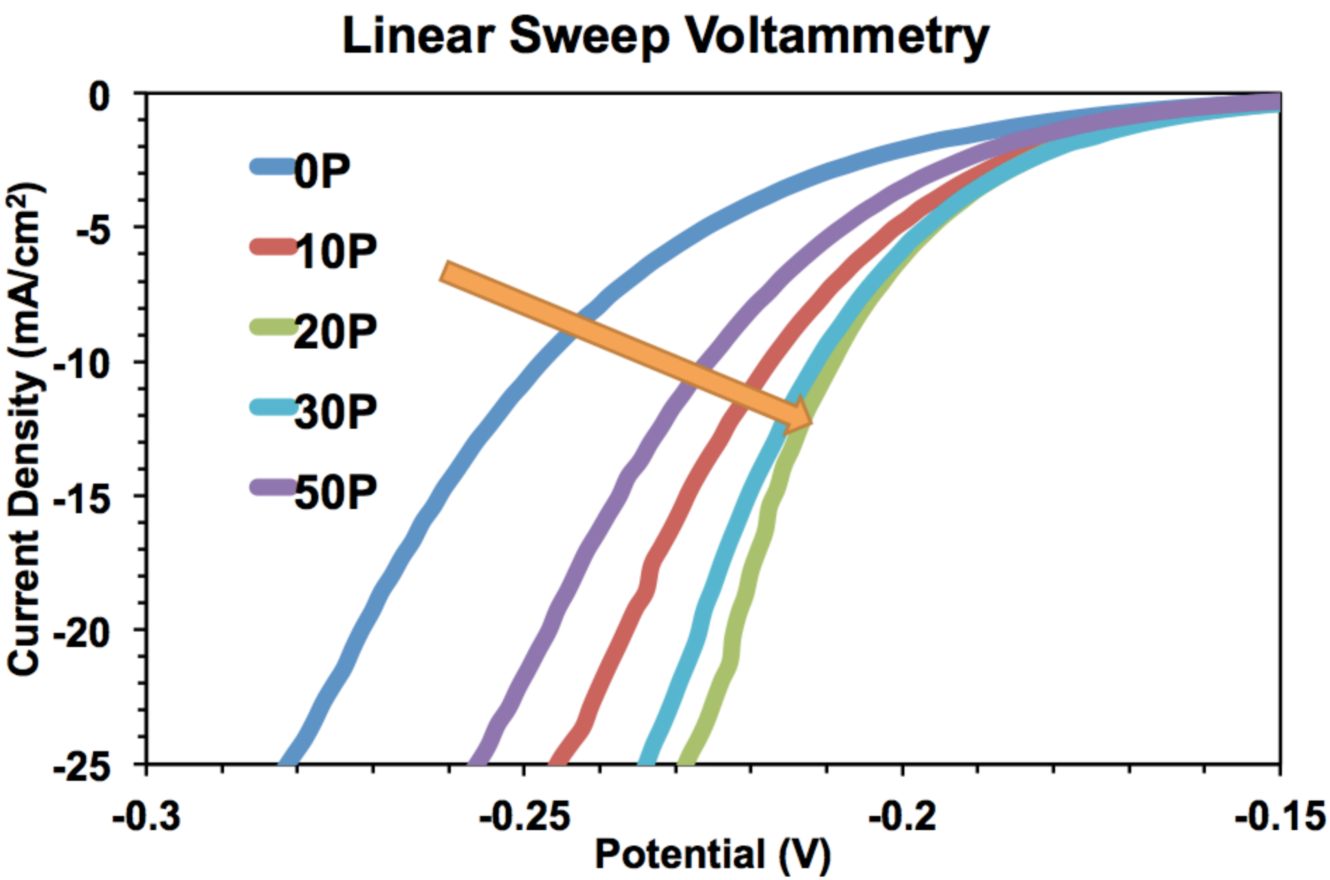
Graphite

How does IPL contribute to better efficiency?

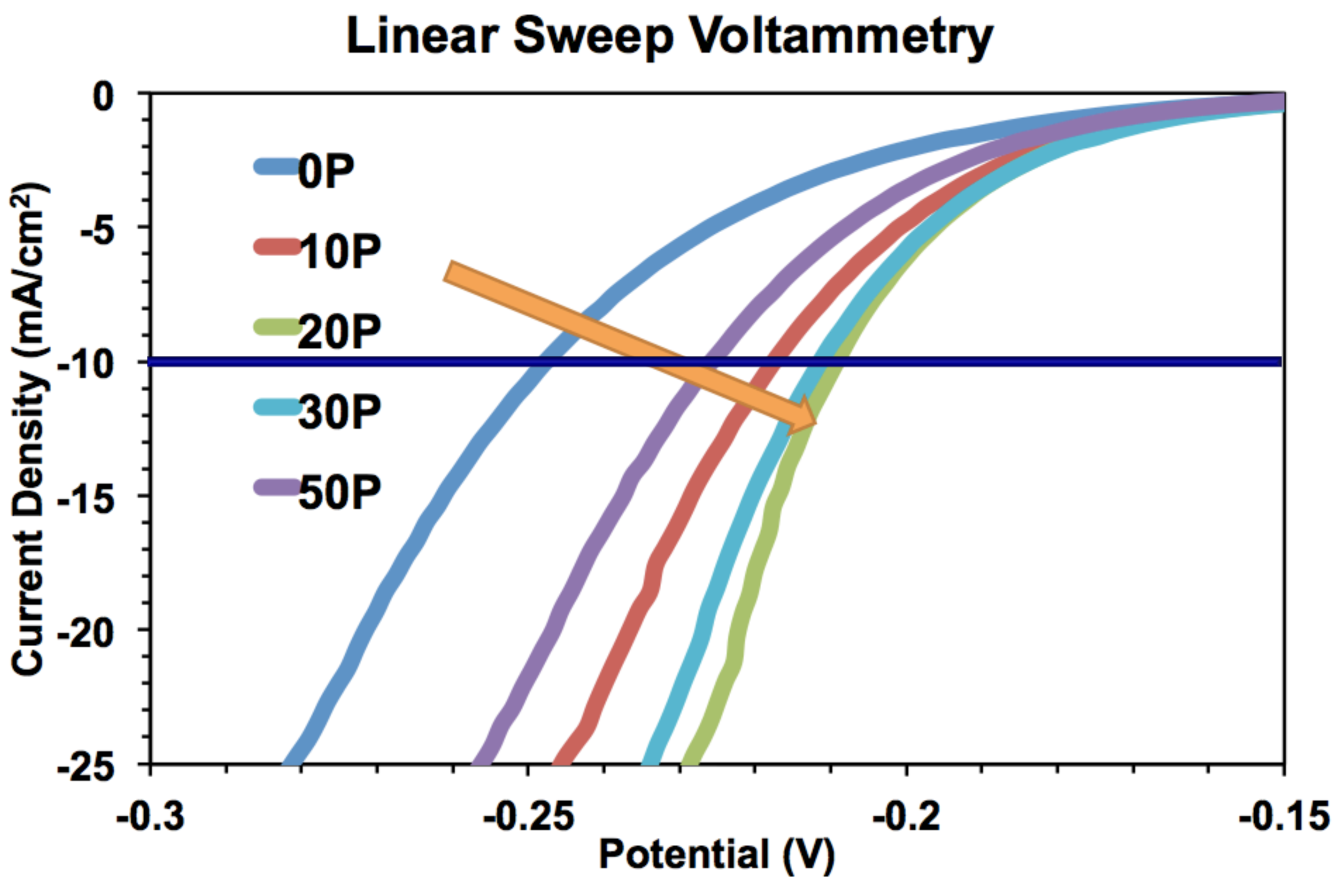
- Graphene oxide transforms to reduced graphene oxide
  - Better conductivity for HER
  - Reduced normal synthesis time from hours to minutes



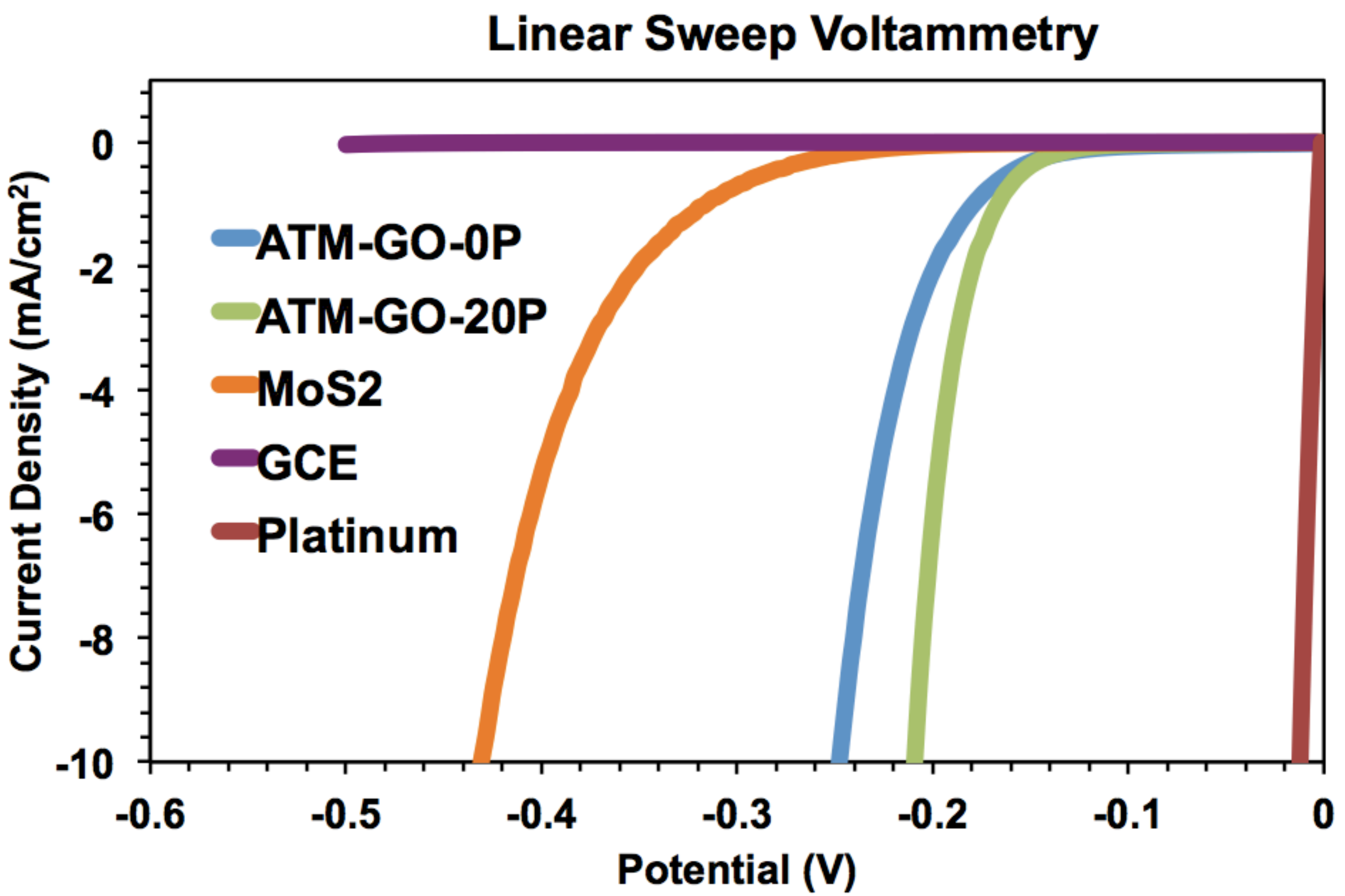
Characterizing the best IPL catalyst



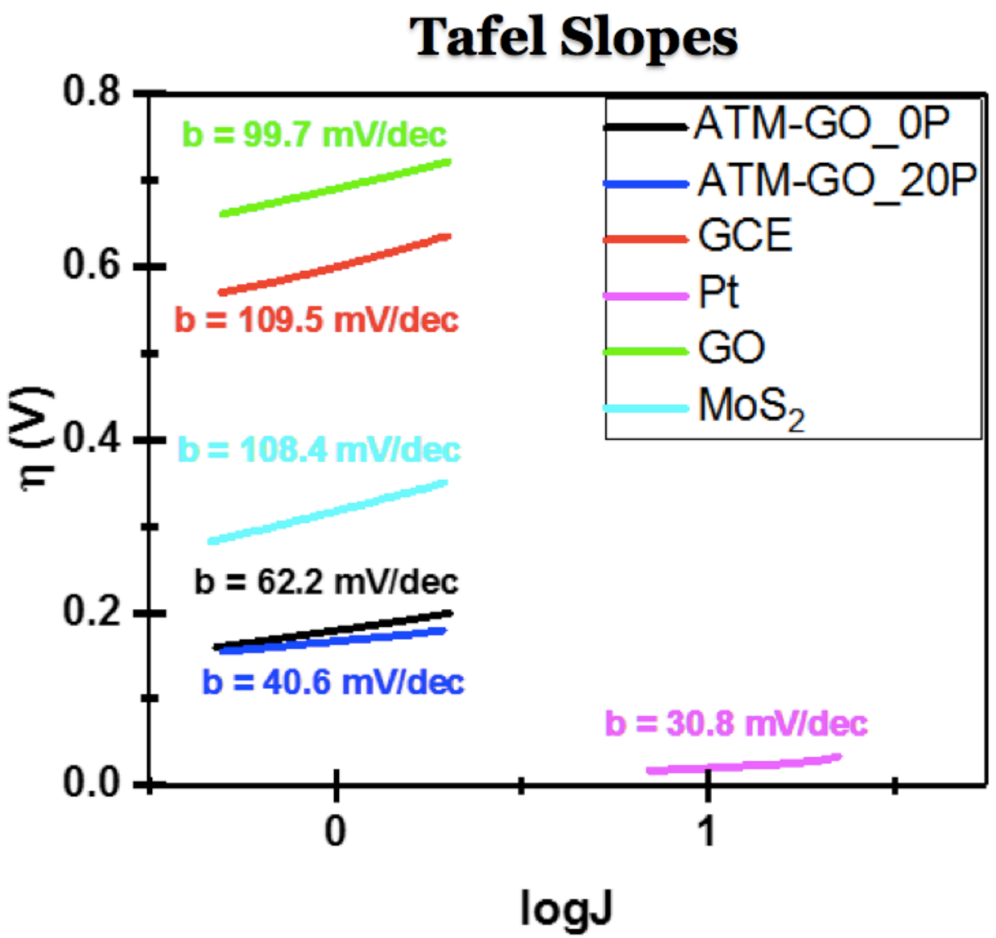
Characterizing the best IPL catalyst



Characterization of Materials

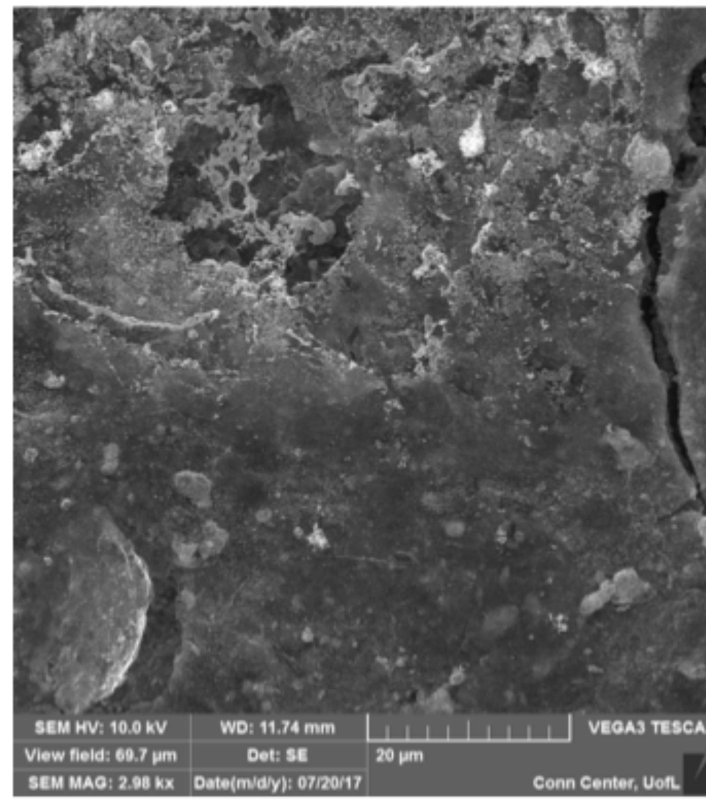


Characterization of Materials



In conclusion…

- The support of graphene oxide materials substantially increased the catalytic activity of HER
- IPL successfully shortened the synthesis time of the material and also showed a slight increase in catalytic activity



SEM imaging of ATM-GO with IPL

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- NSF for funding our REU program

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The NSF NNCI Multi-Scale Manufacturing & Nano Integration Node

References

Zou, Xiaoxin, and Yu Zhang. "Noble Metal-free Hydrogen Evolution Catalysts for Water Splitting." *Chem. Soc. Rev.* 44.15 (2015): 5148-180. Web.

Li, Yanguang, Hailiang Wang, Liming Xie, Yongye Liang, Guosong Hong, and Hongjie Dai. "MoS2Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction." *Journal of the American Chemical Society* 133.19 (2011): 7296-299. Web.