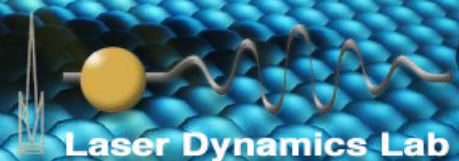


# Mechanistic Understanding of Electrochemical Nitrogen Reduction Reaction using *Operando* Surface-enhanced Raman Spectroscopy

Mohammadreza Nazemi, Mostafa A. El-Sayed  
School of Chemistry and Biochemistry, Georgia Tech

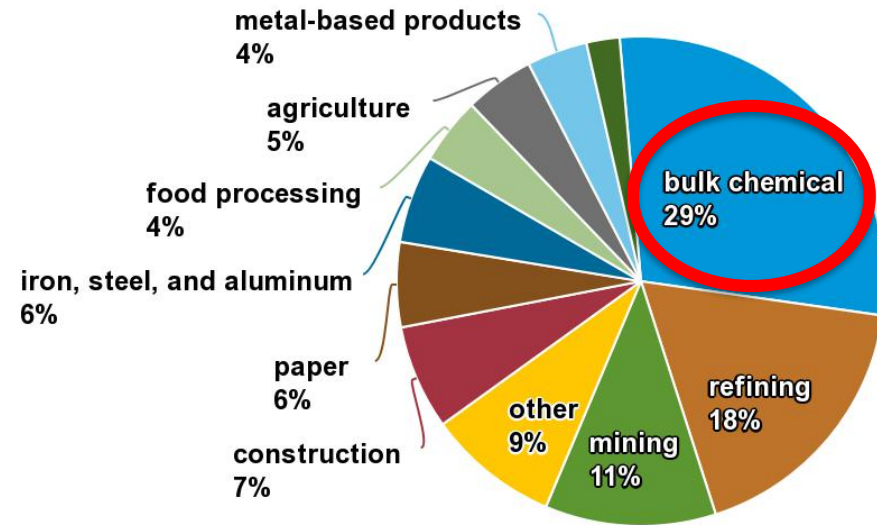
April 6, 2021  
ACS Meeting

Georgia  
Tech

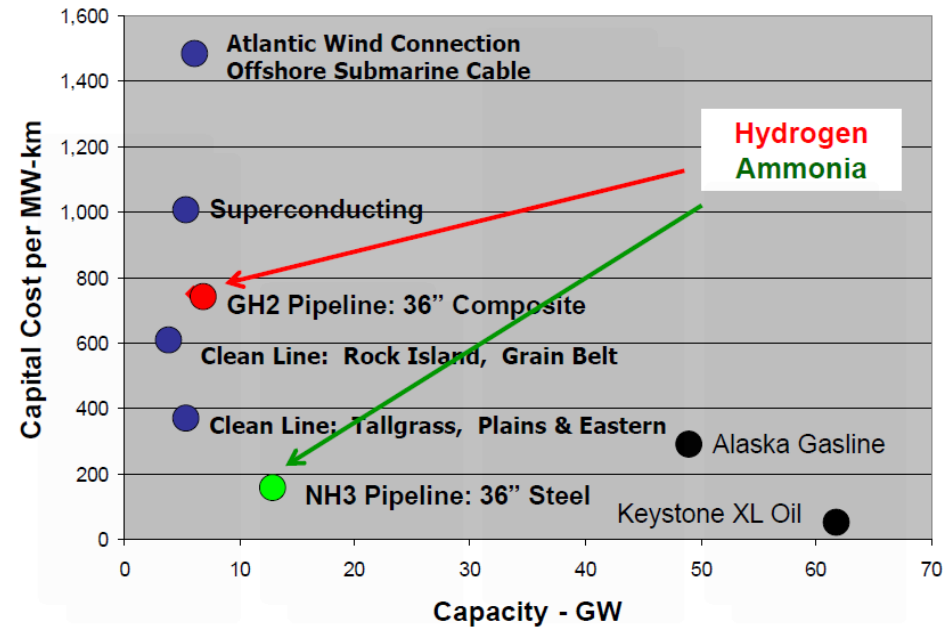


# Renewables Intermittency-Chemical Energy Storage

U.S. industrial sector energy consumption by type of industry, 2019



Transmission CAPEX



**Chemical Energy Storage** could be a transformative opportunity for **reliable** and **resilient** electricity system! It also results in the **decarbonization**, **electrification**, and **sustainability** of the modern chemical industry!

**Liquid Ammonia**  
-33°C, 11.5 GJ m<sup>-3</sup>



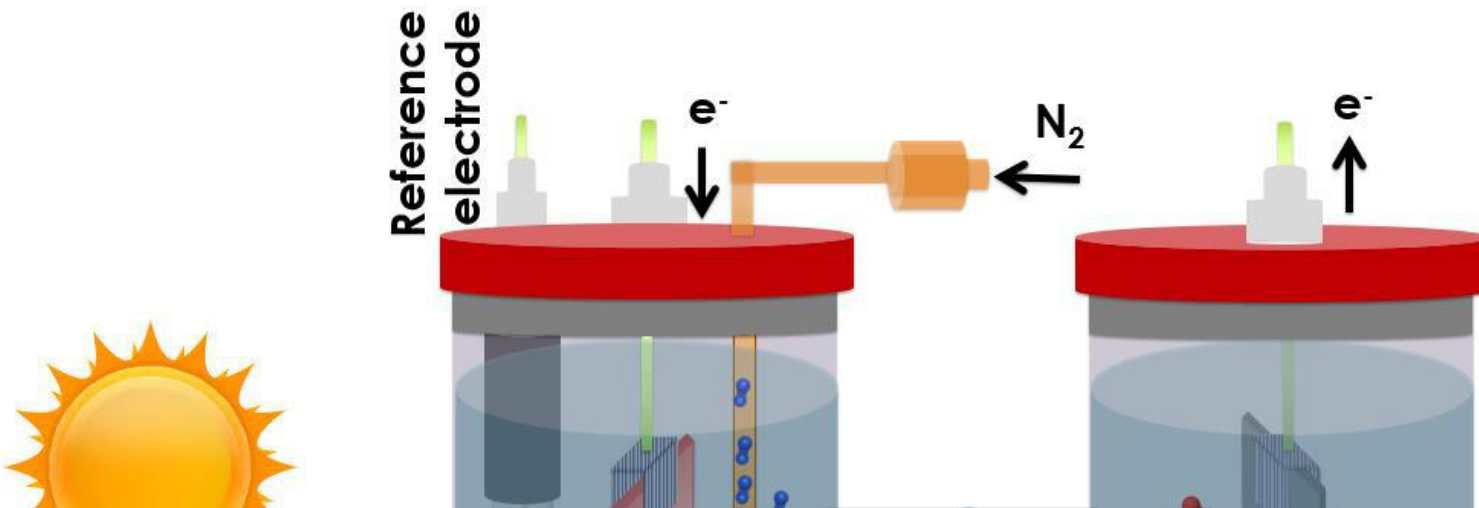
**Liquid Hydrogen**  
-253°C, 4.5 GJ m<sup>-3</sup>



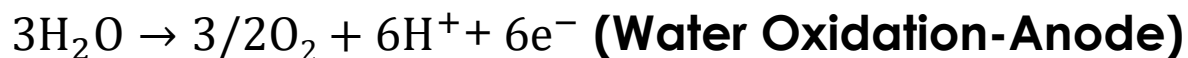
**Liquid Natural Gas**  
-161°C, 22.2 GJ m<sup>-3</sup>



# Photo-Electrochemical Ammonia Synthesis



**Major Challenge:** The rational design of electrode-electrolyte that produces ammonia with high **yield** and **efficiency**!



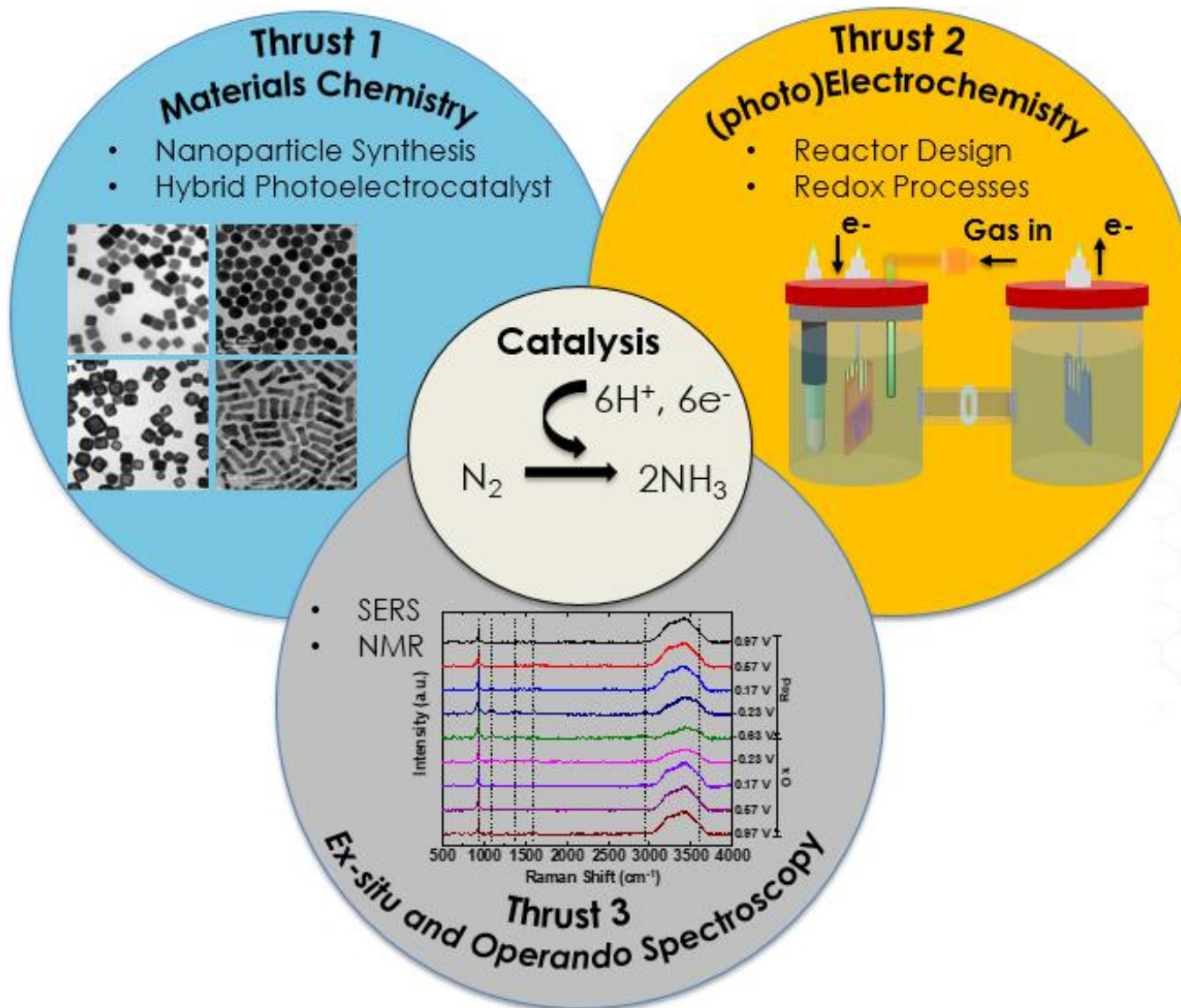
M. Nazemi, M. A. El-Sayed, et. al. *Nano Energy*, vol. 49, pp. 316-323, **2018**.

M. Nazemi, M. A. El-Sayed, *The Journal of Physical Chemistry Letters*, vol. 9, pp. 5160-5166, **2018**.

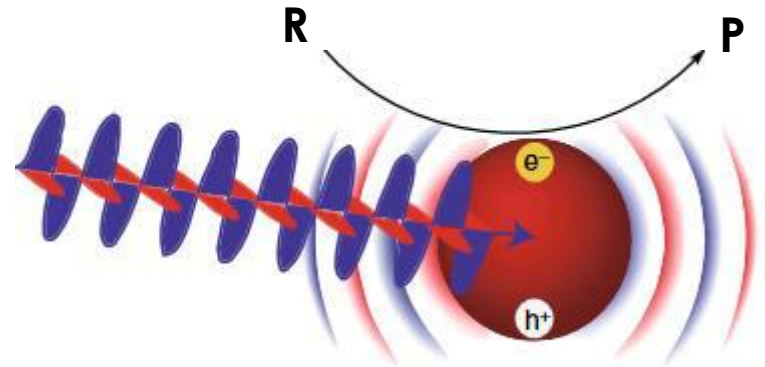
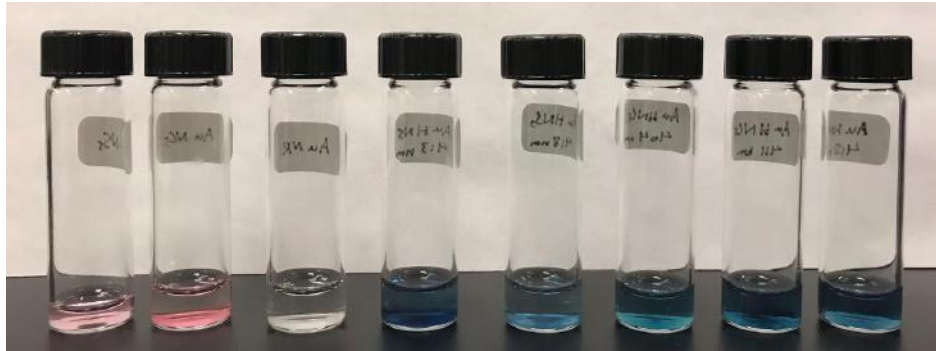
M. Nazemi, M. A. El-Sayed, *The Journal of Physical Chemistry C*, 123, 18, 11422-11427, **2019**.

M. Nazemi, M. A. El-Sayed, *Nano Energy*, vol. 63, 103886, **2019**.

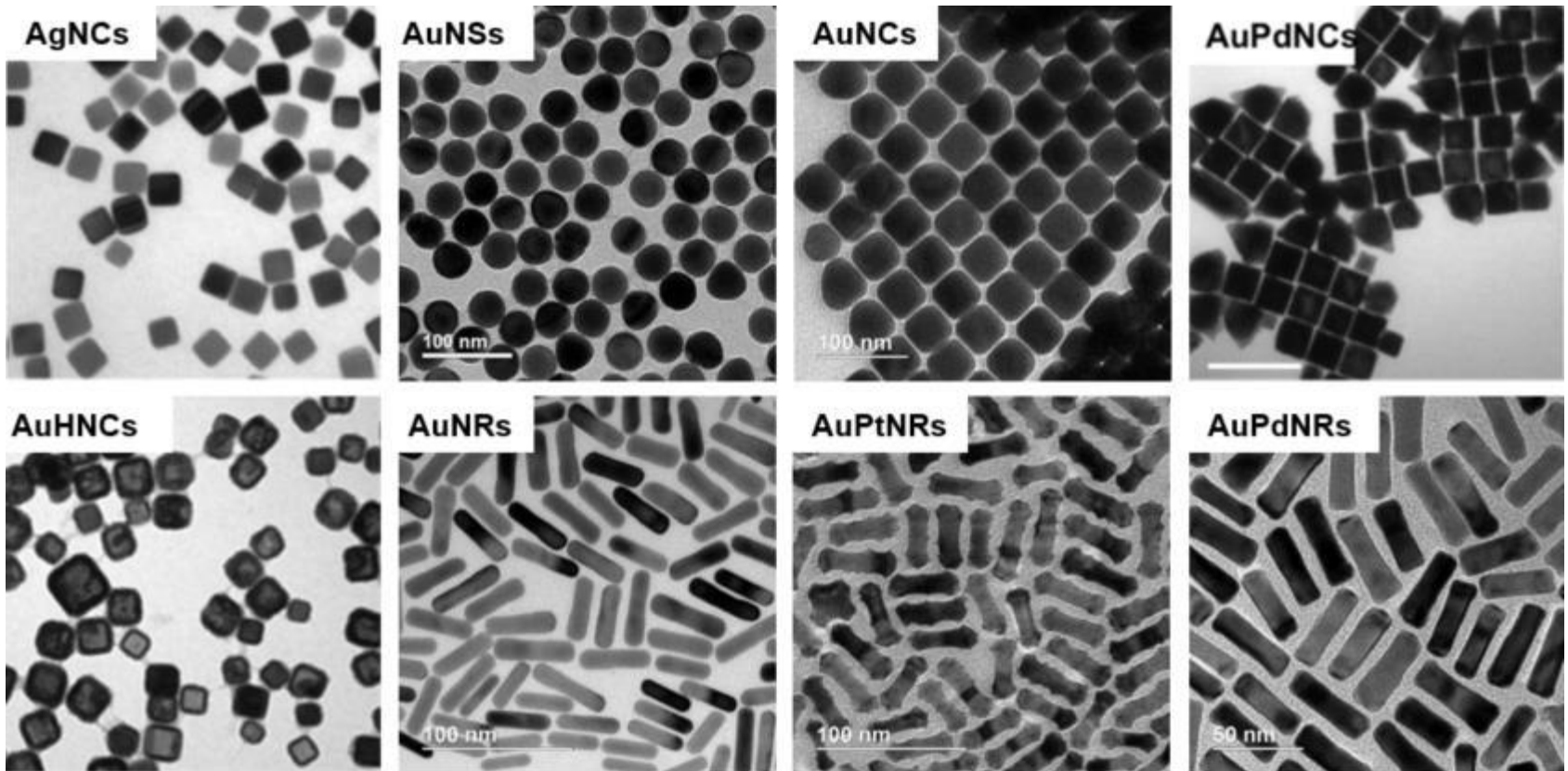
# Scientific Thrusts of Our Research



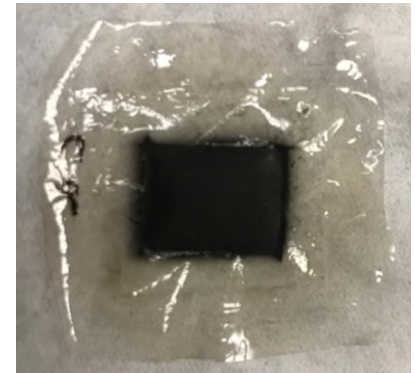
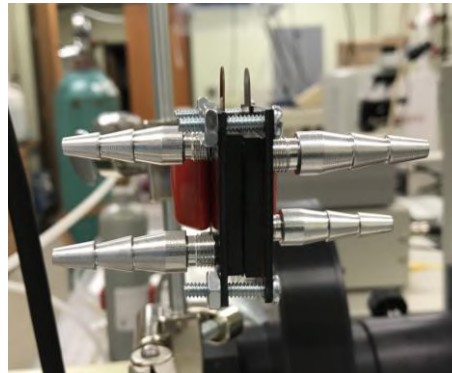
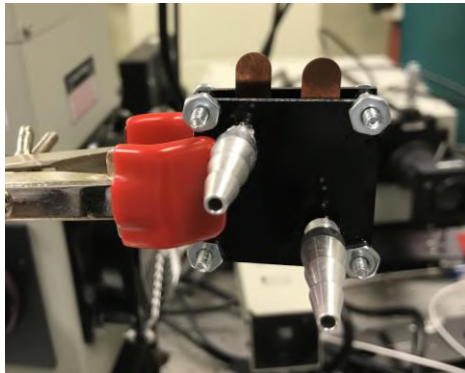
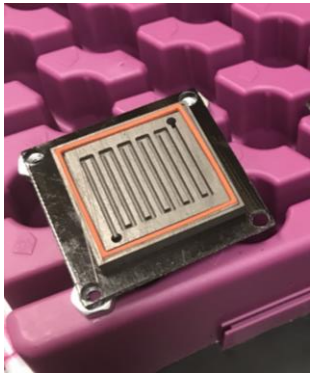
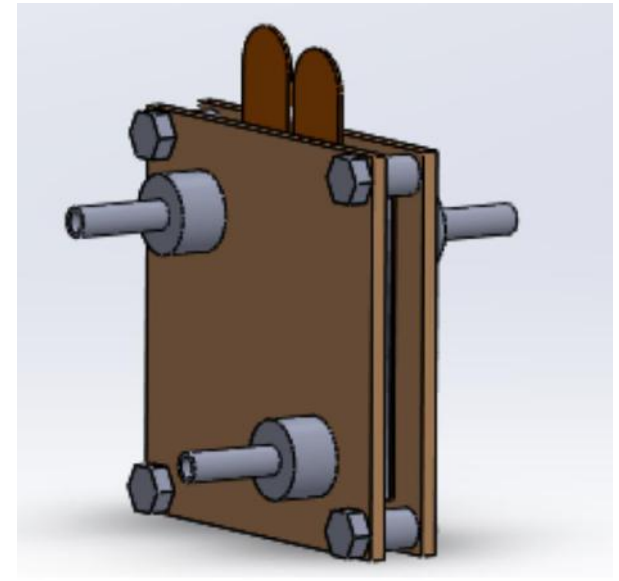
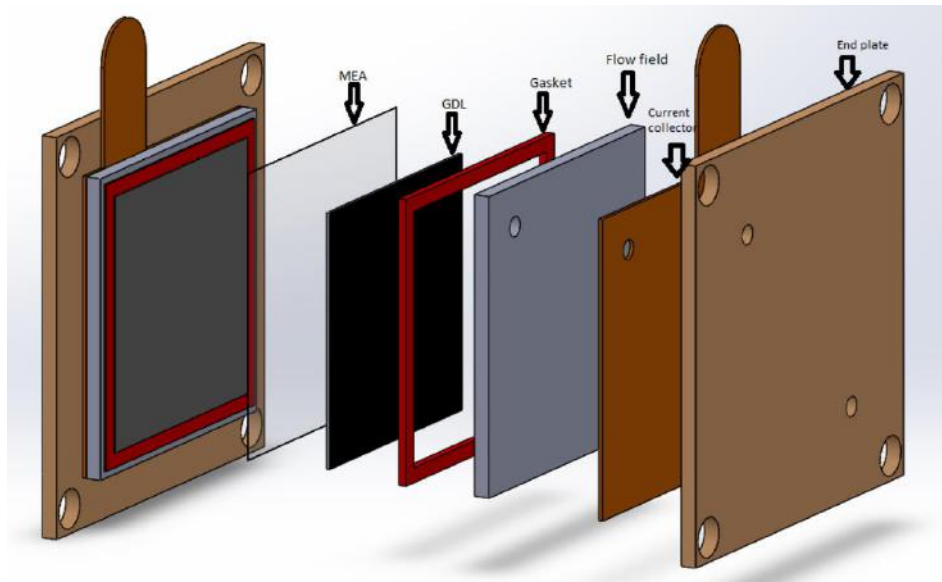
# Plasmonic Nanostructures



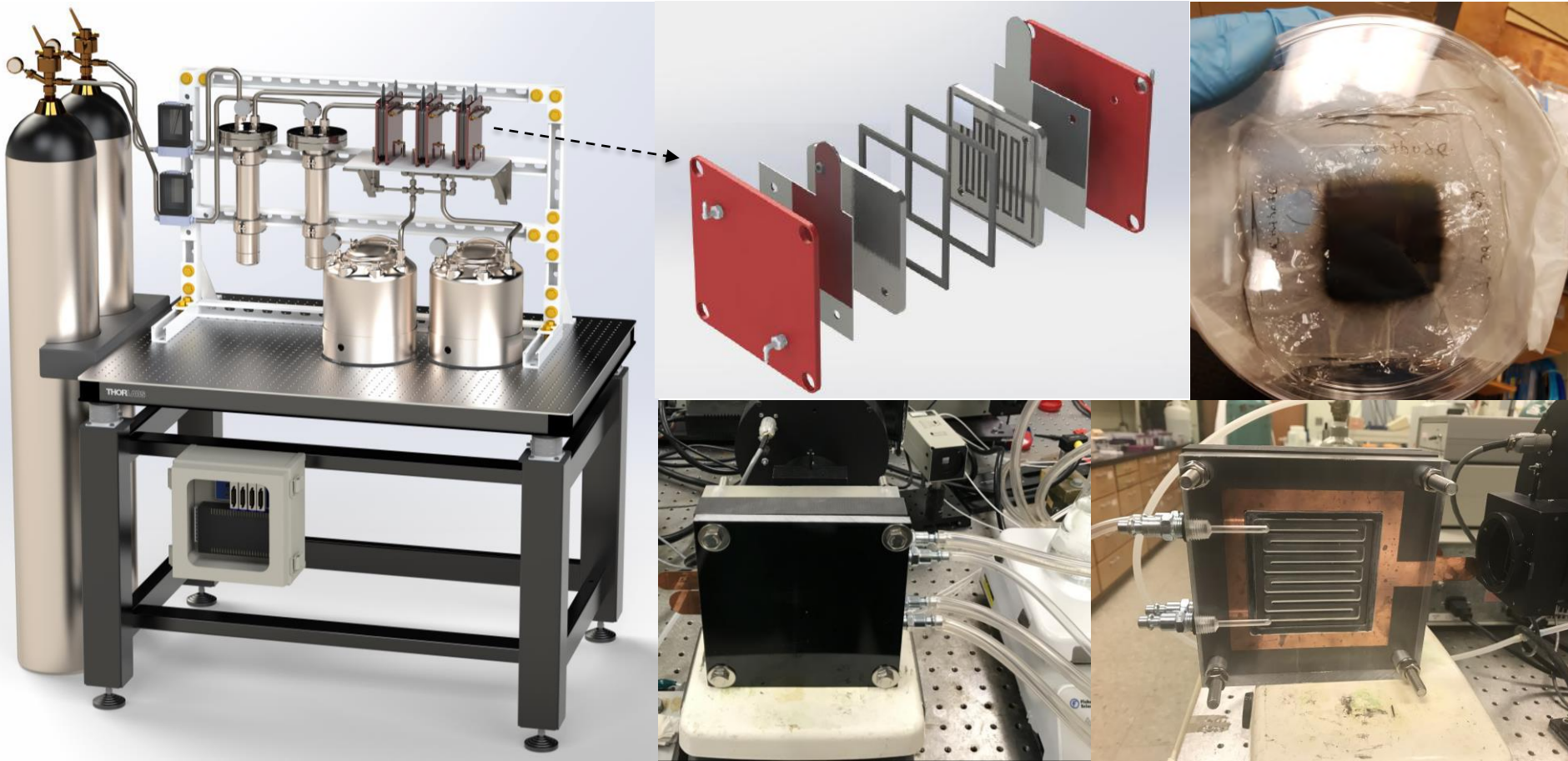
P.K. Jain, El-Sayed, M.A., et. al, *JPC B*, 110(14), 2006.



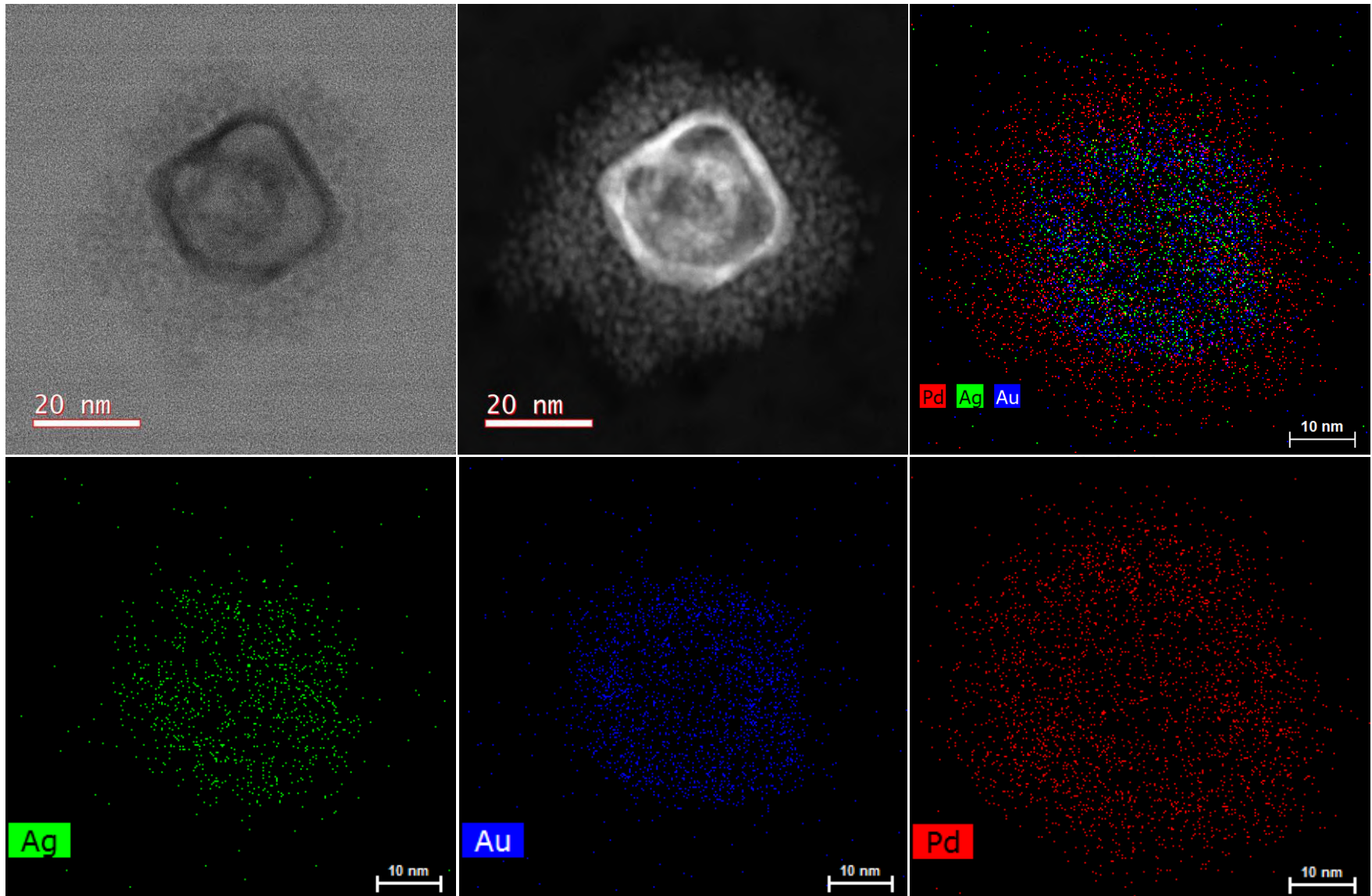
# Gas-phase Electrochemical Cell



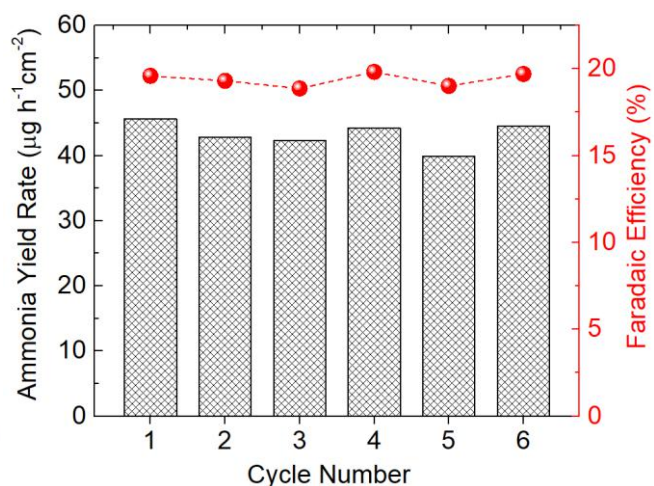
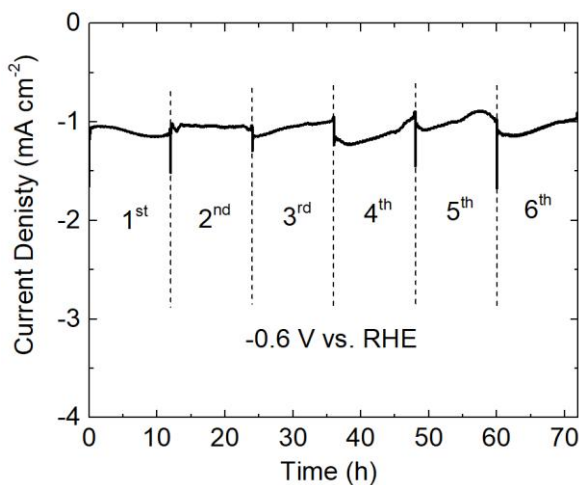
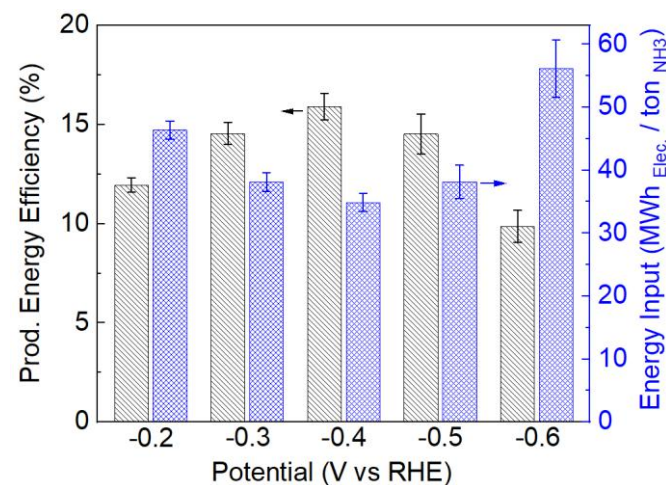
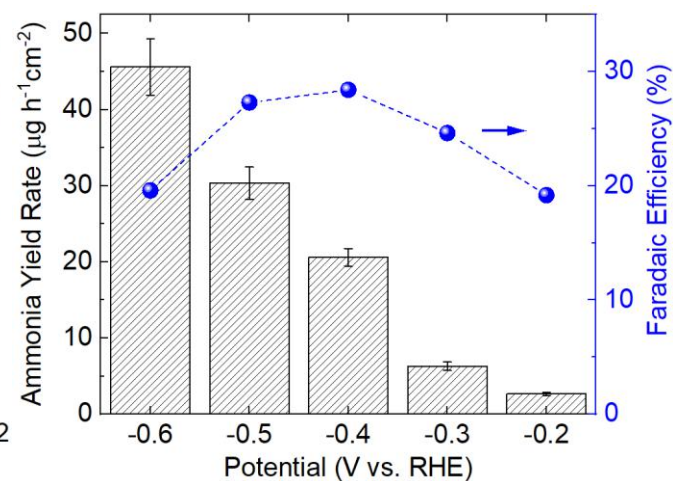
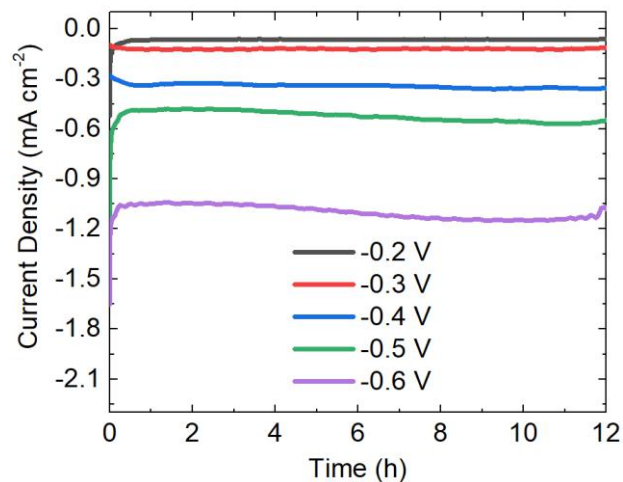
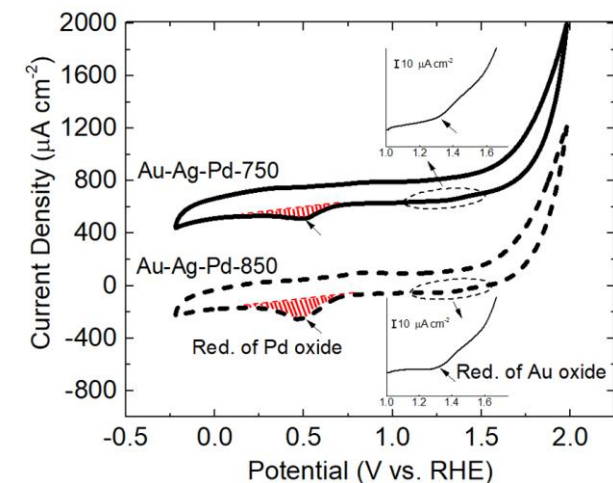
# Modular (Photo)Electrochemical System for Ammonia Synthesis



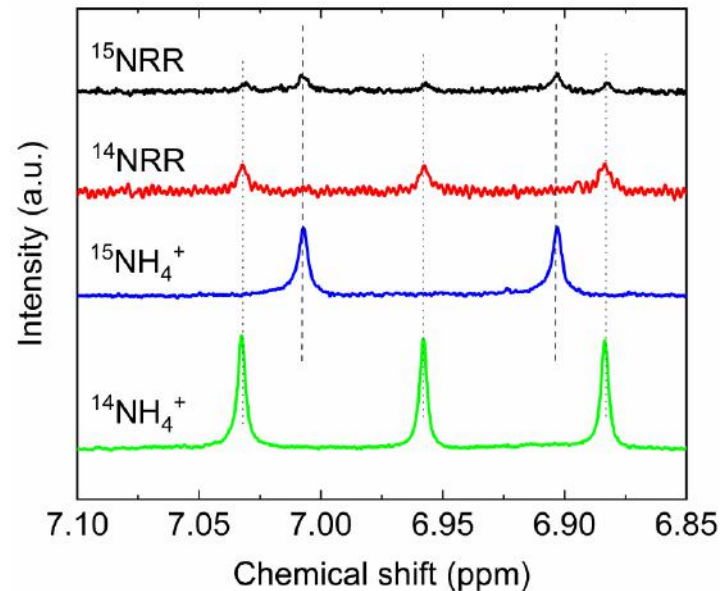
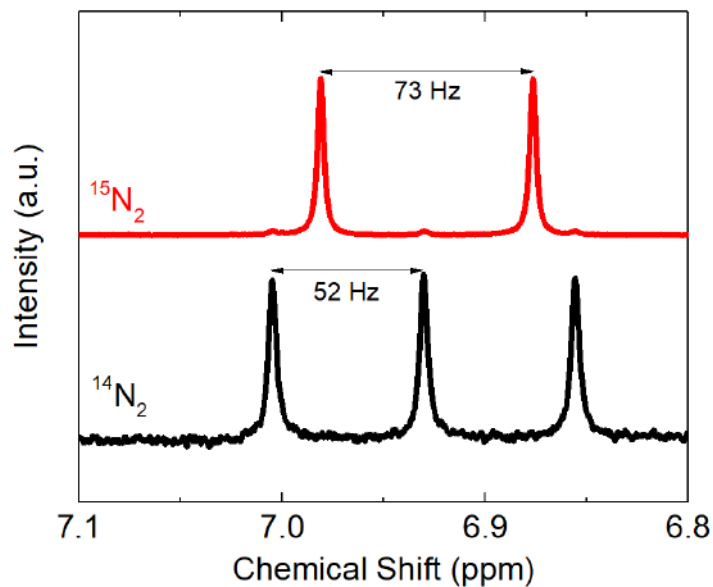
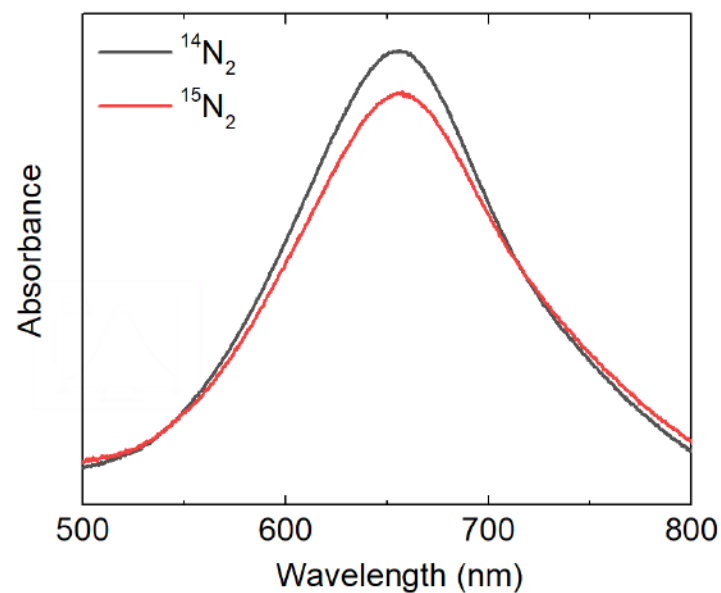
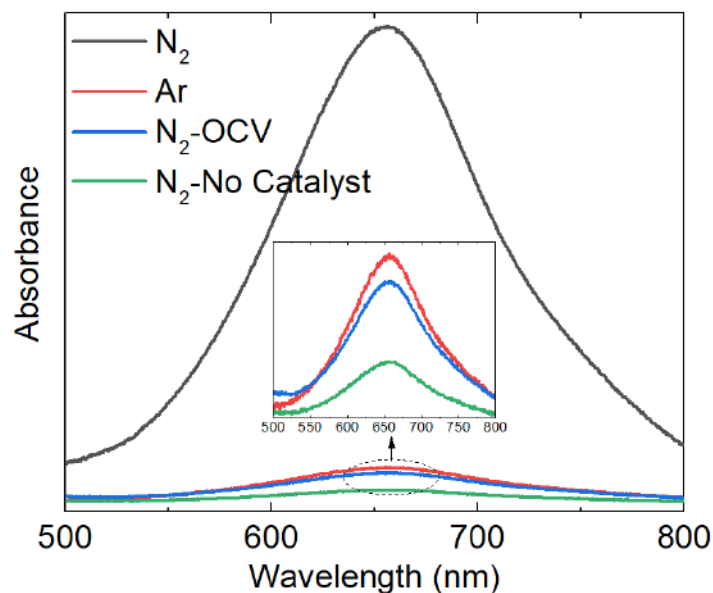
# Energy Dispersive X-ray Elemental Mapping of Trimetallic Nanoparticles



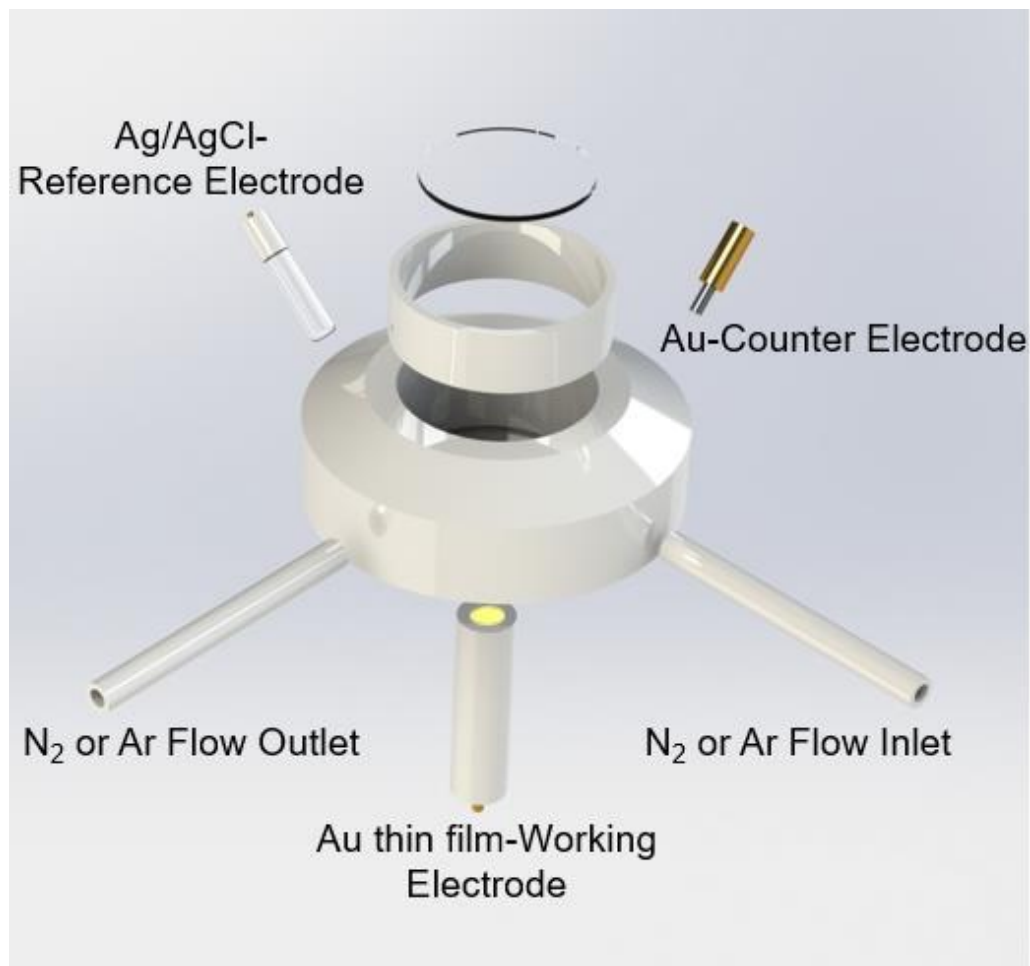
# Electrochemical Characterization and Catalytic Performance



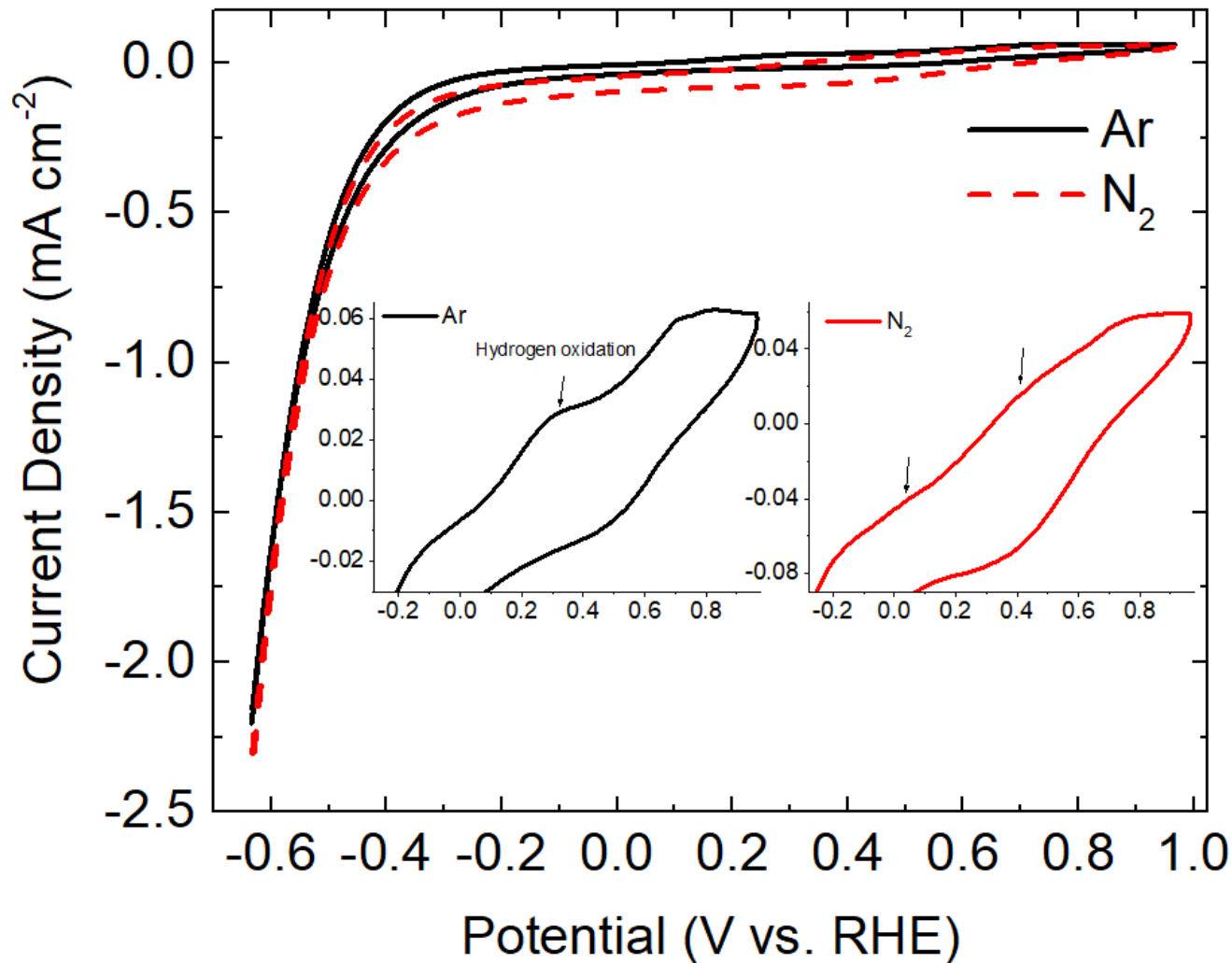
# Source of N in Electrochemical Nitrogen Reduction Reaction



# Operando Surface Enhanced Raman Spectroscopy (SERS) in Electrochemical Nitrogen Reduction Reaction



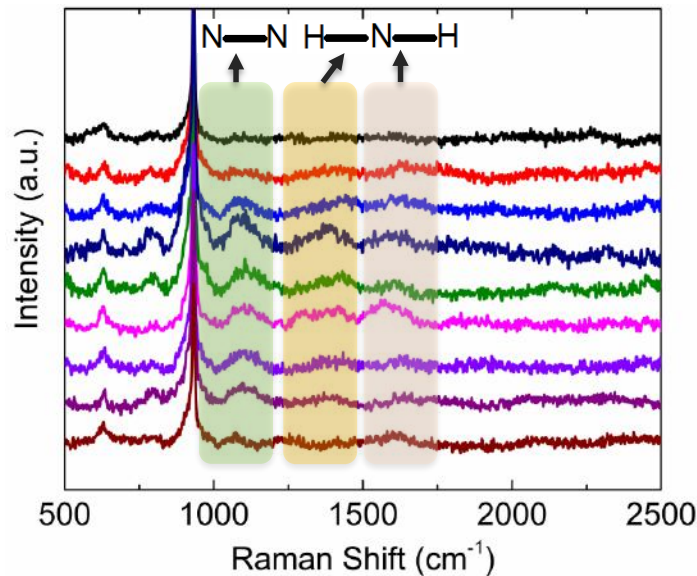
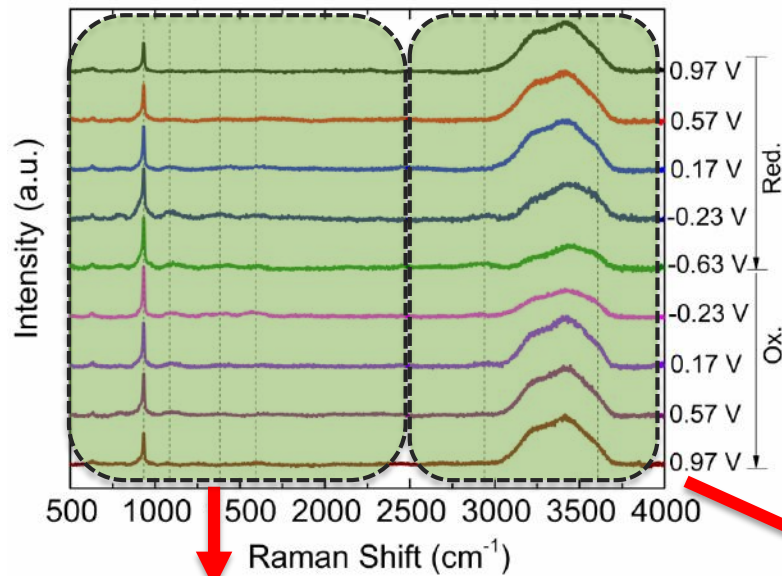
# Cyclic Voltammograms during Operando SERS



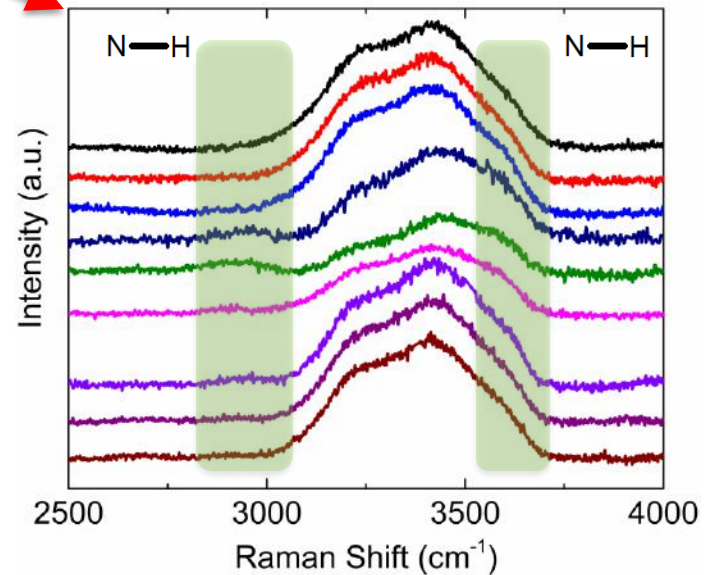
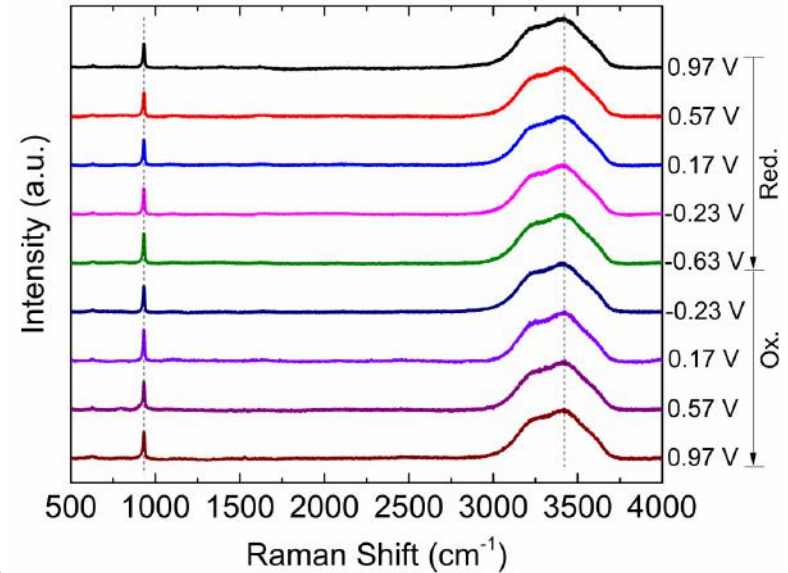
M. Nazemi, M. A. El-Sayed, et. al, *Journal of The Electrochemical Society*, 167(5), p. 054511, 2020.

# SERS Spectra of Trimetallic Nanoparticles

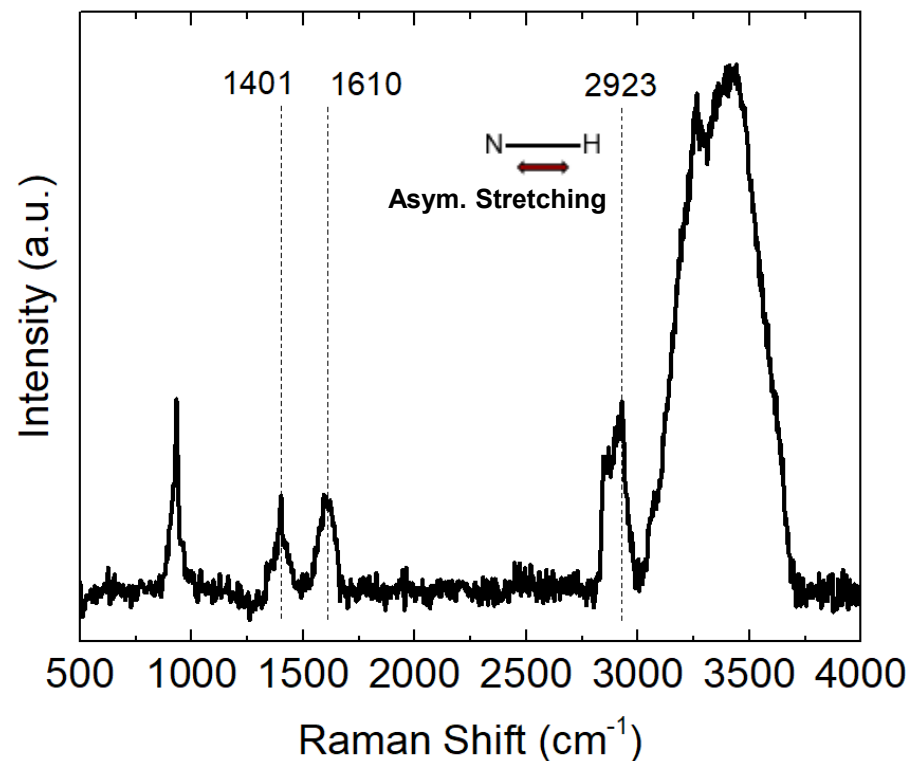
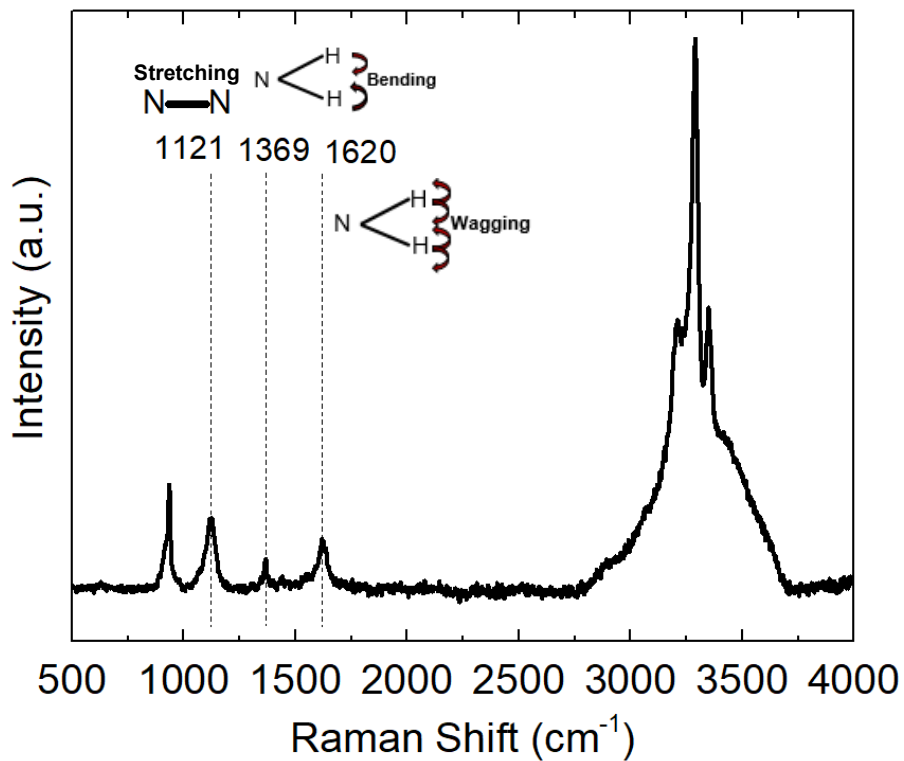
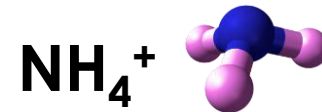
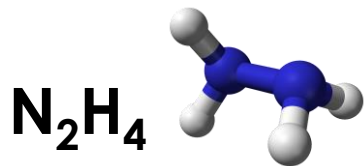
$N_2$ -Saturated electrolyte



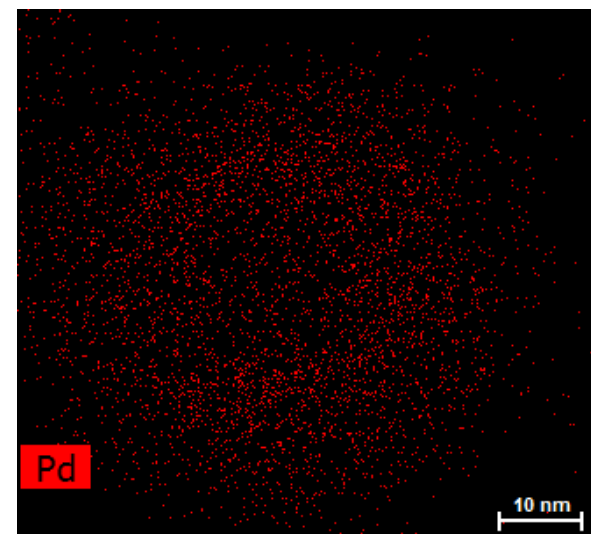
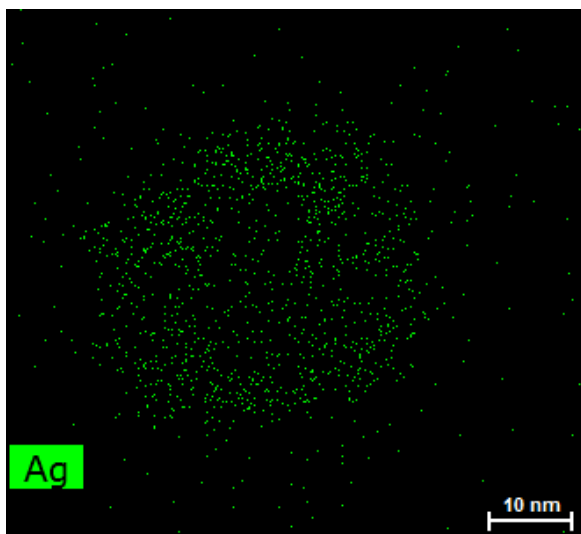
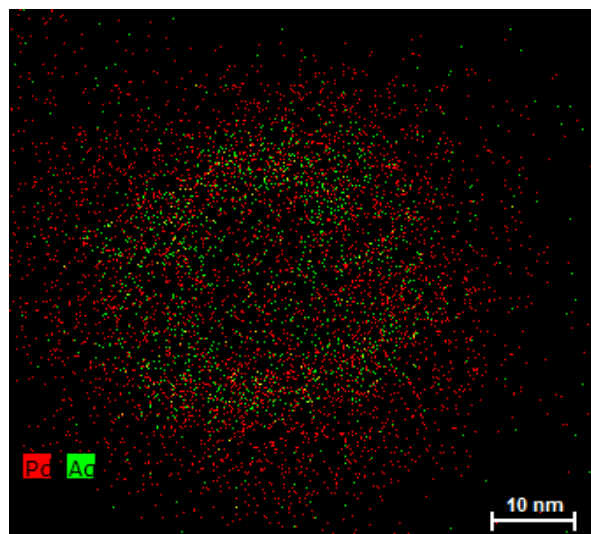
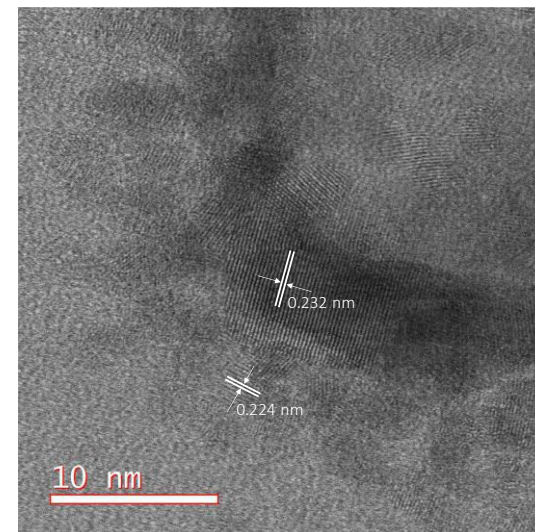
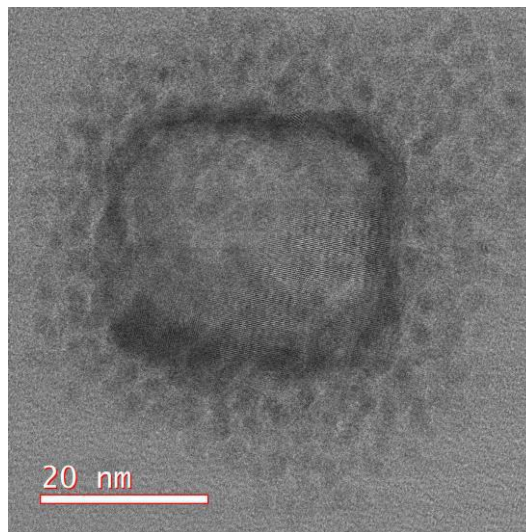
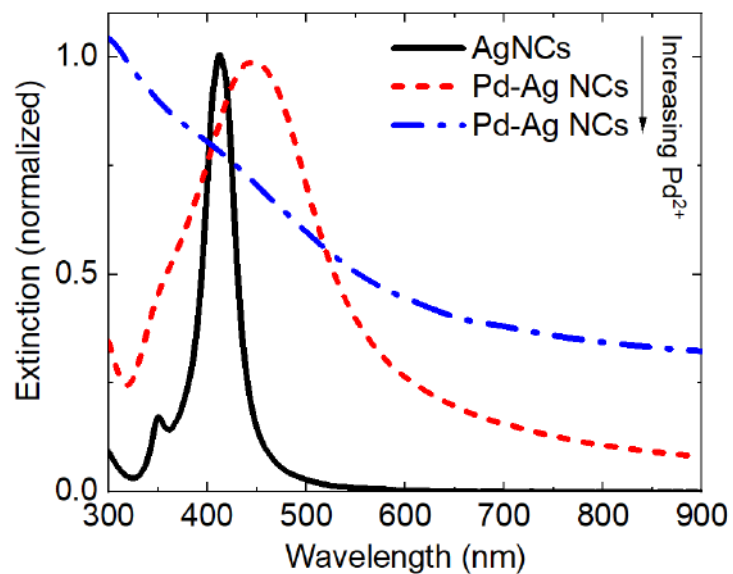
Ar-Saturated electrolyte



# SERS Spectra of Standard Ammonia and Hydrazine

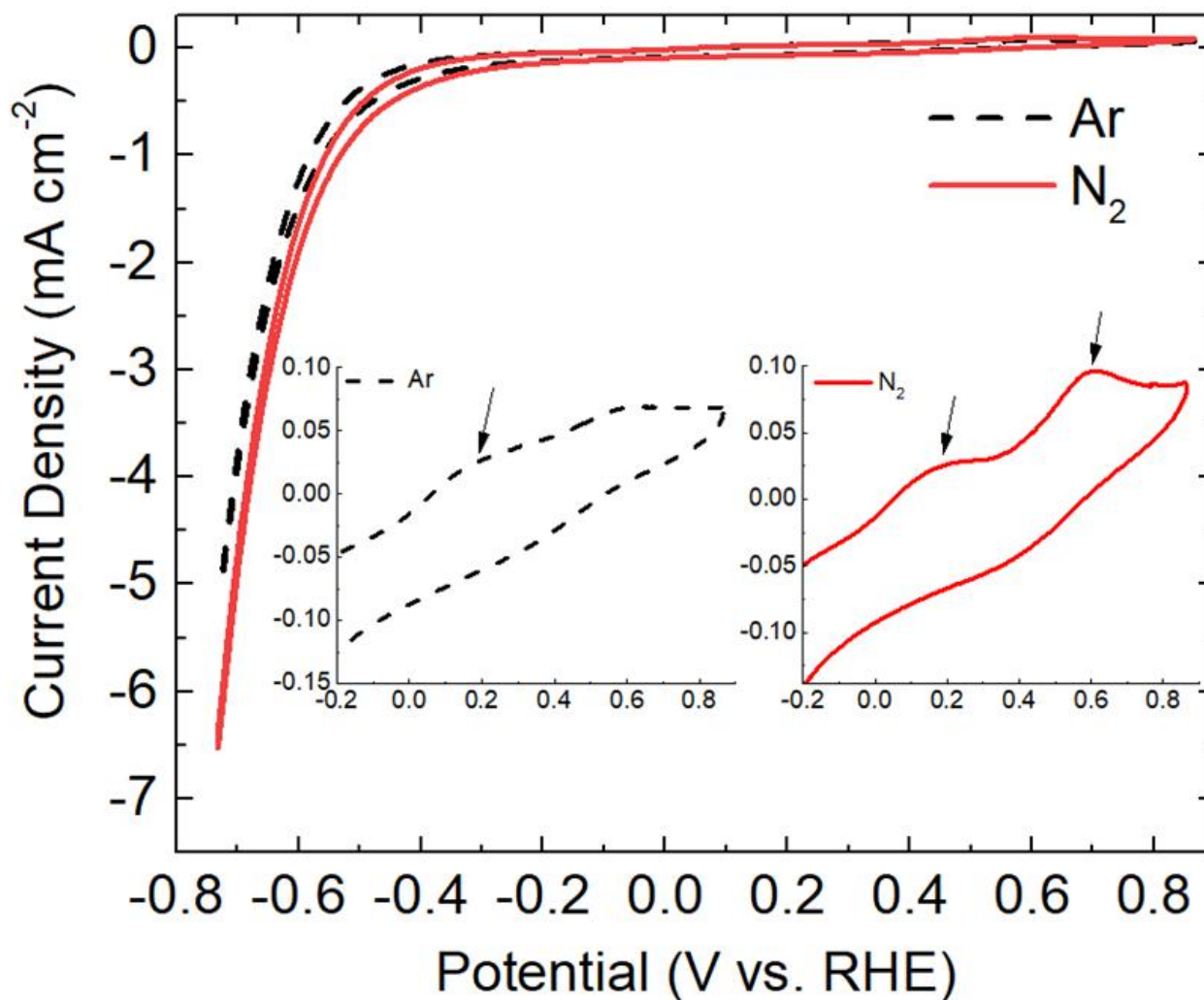


# Pd-Ag Nanoparticles



M. Nazemi, M. A. El-Sayed, et. al., ACS Catalysis, 10, 10197–10206, 2020.

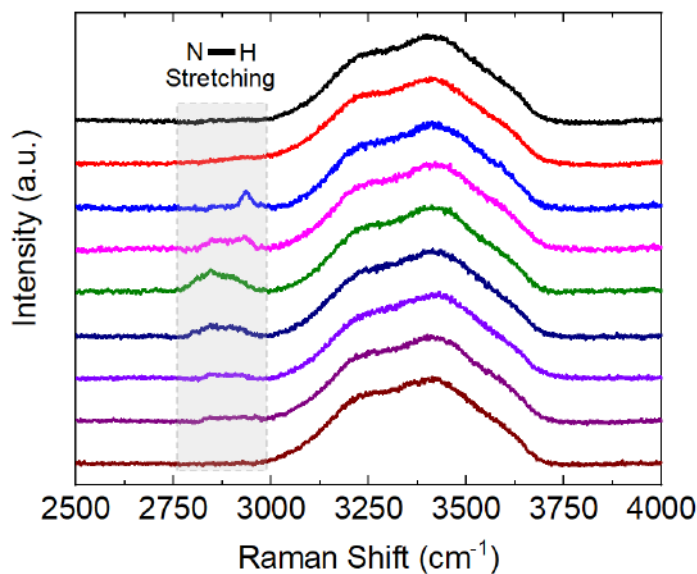
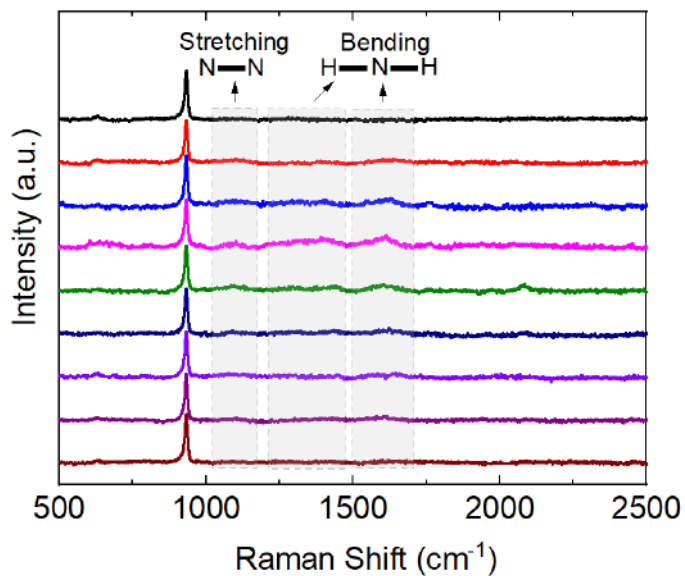
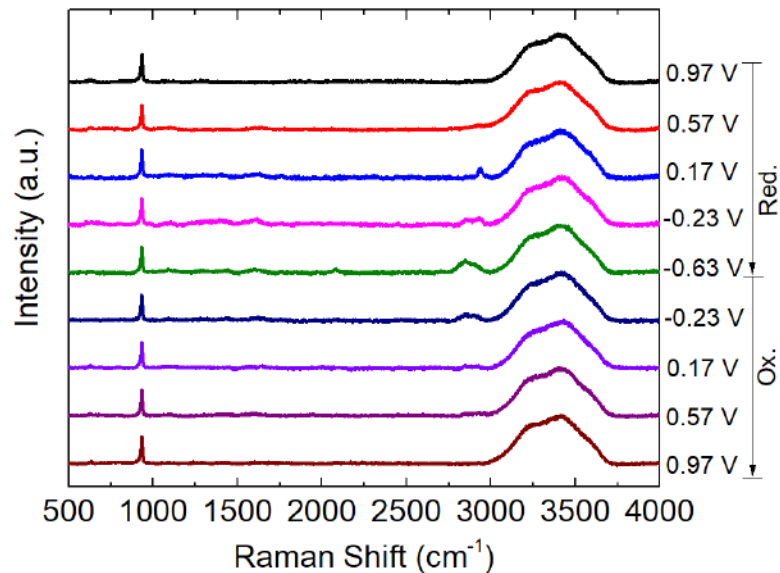
# Cyclic Voltammograms during Operando SERS



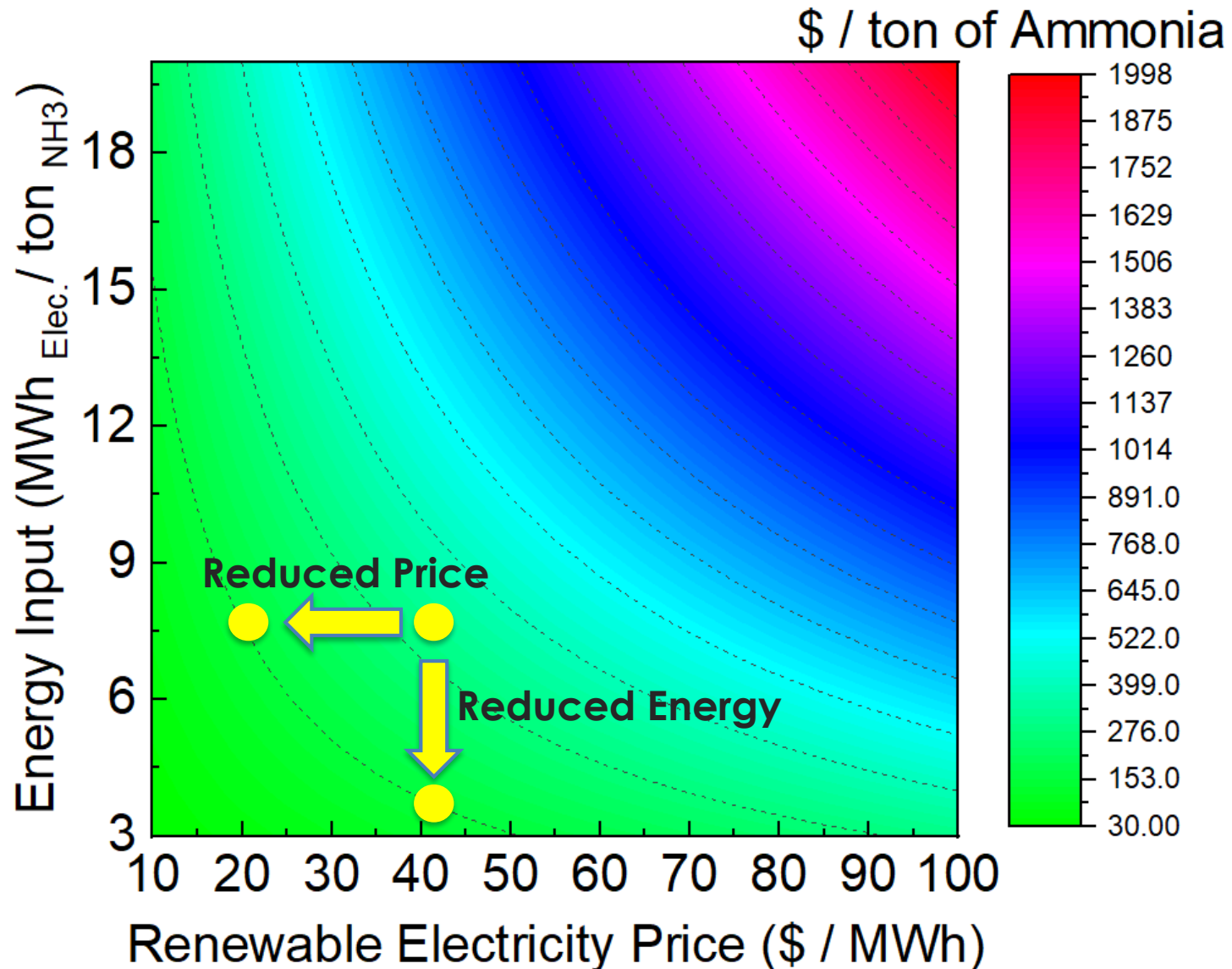
M. Nazemi, M. A. El-Sayed, et. al., *ACS Catalysis*, 10, 10197–10206, 2020.

# SERS SPECTRA OF Pd-Ag NANOPARTICLES

$N_2$ -Saturated electrolyte



# Feasibility of Electrochemical Ammonia Synthesis



# Summary

- There is an opportunity to utilize **ammonia** as a medium for renewable energy storage (Electrons to fuels) and transport.

## Catalyst Discovery

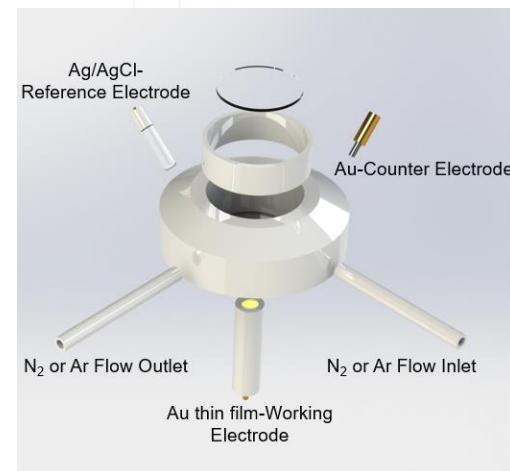
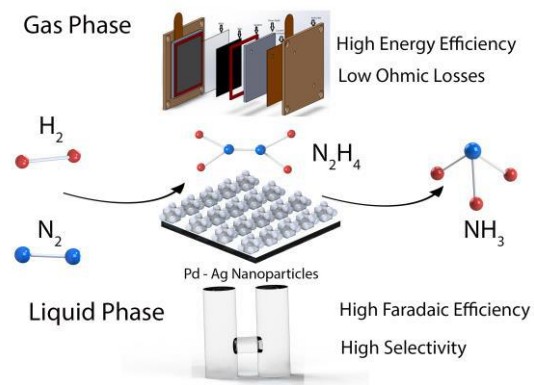
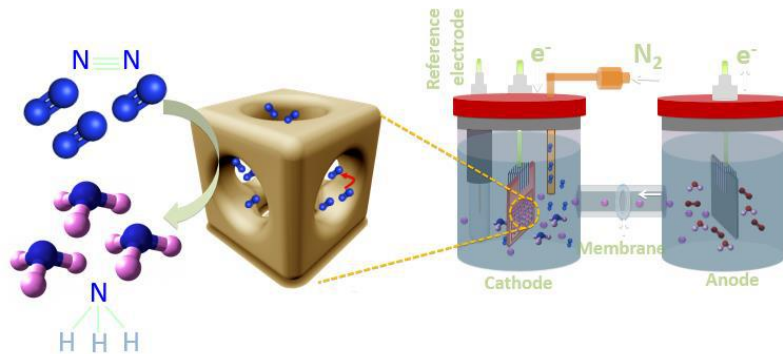
- The optimization of the **structure**, **morphology**, and **composition** is critical to enhancing the rate of electro-reduction of  $N_2$  to  $NH_3$ .

## Photo-electrochemistry

- Cell design that integrate membrane-electrode assembly (MEA) is an effective route to reduce ohmic losses and achieve high **energy efficiency**!

## Operando Spectroscopy

- Operando* SERS revealed that electrochemical NRR takes place on the Pd-based catalyst surface through an associative mechanism with  $N_2H_4$  as an **intermediate species**.



# Acknowledgement

## Advisors and Collaborators

- Prof. Mostafa El-Sayed (Ph.D. advisor, CHE-GT)
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- Prof. Paul Kohl (ChBE-GT)
- Prof. Jun Song, Dr. Pengfei Ou (MSE-McGill)
- Prof. Vladimir Tsukruk, Jing Zhou, Shuaidi Zhang, Saewon Kang (MSE-GT)
- Prof. Todd Sulchek, Alan Liu (ME-GT)
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Team: Amanda Guarisco, Pete Nicolay, Ian Schubert, Aaron Savit, Michael Liu



U.S. DEPARTMENT OF  
**ENERGY**



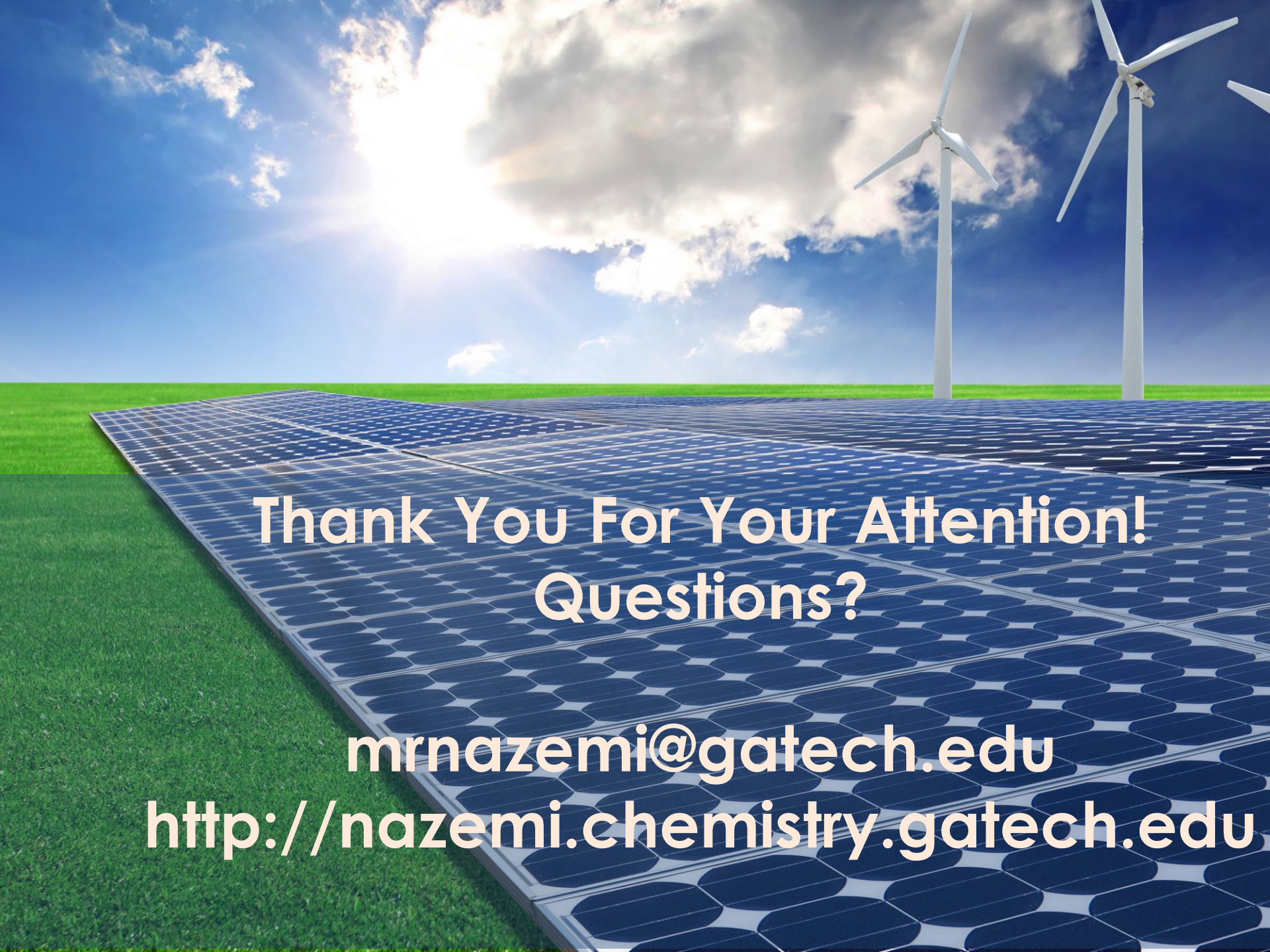
Georgia Research Alliance

**amazon** catalyst

**Georgia  
Tech**

**ti:ger**  
Technological Innovation:  
Generating Economic Results

**OAK RIDGE**  
National Laboratory



**Thank You For Your Attention!  
Questions?**

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**<http://nazemi.chemistry.gatech.edu>**