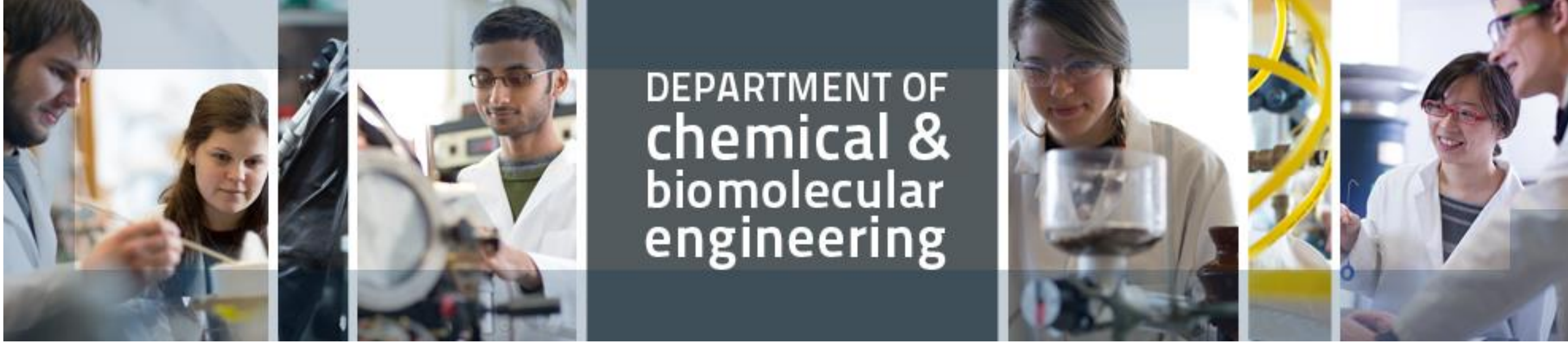


# Exploring Peptide-Bound Catalysts for Electrochemical Ammonia Generation

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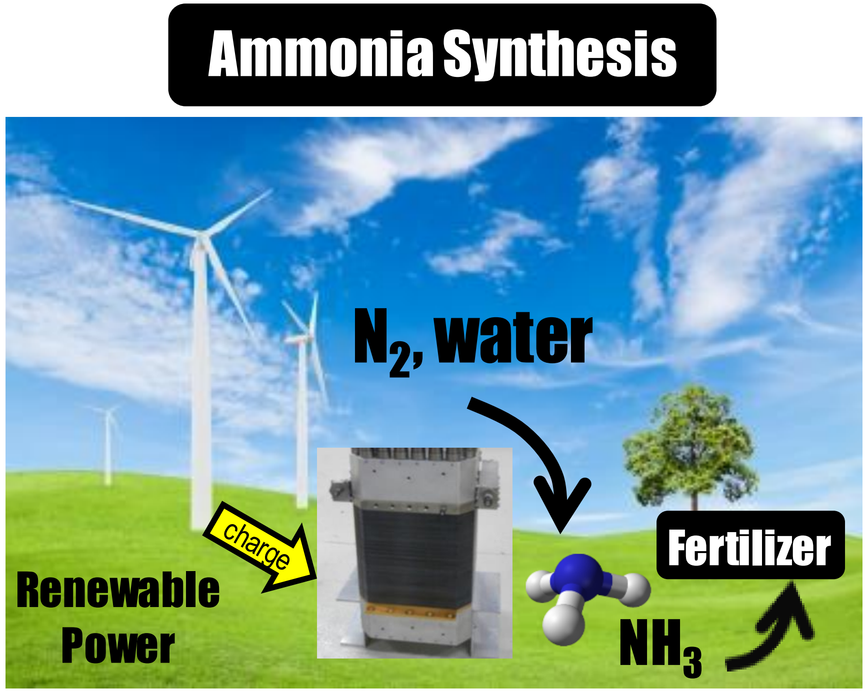
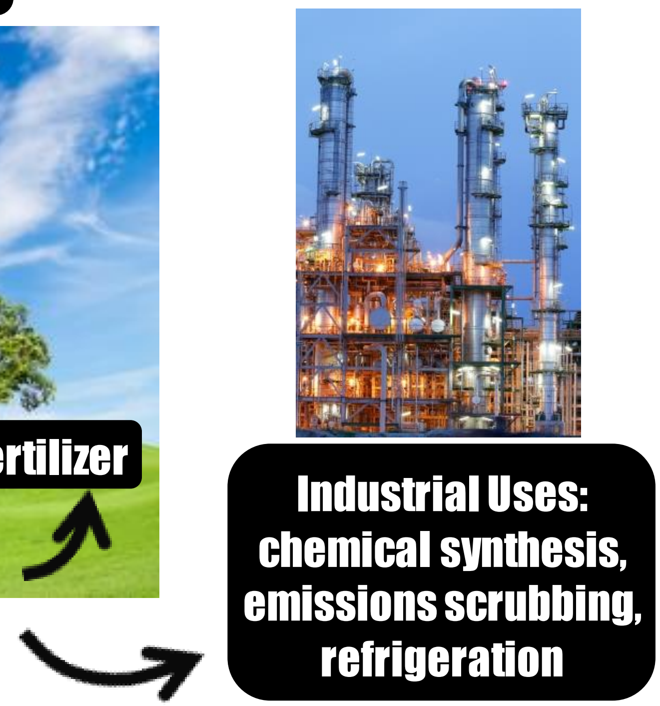
2017 Annual AIChE Meeting
Minneapolis, MN

CASE WESTERN RESERVE UNIVERSITY EST. 1826

# Vision for Electrochemical Ammonia Production




J.N. Renner, L.F. Greenlee, A.M. Herring, K.E. Ayers, The Electrochemical Society Interface, Summer 2015.

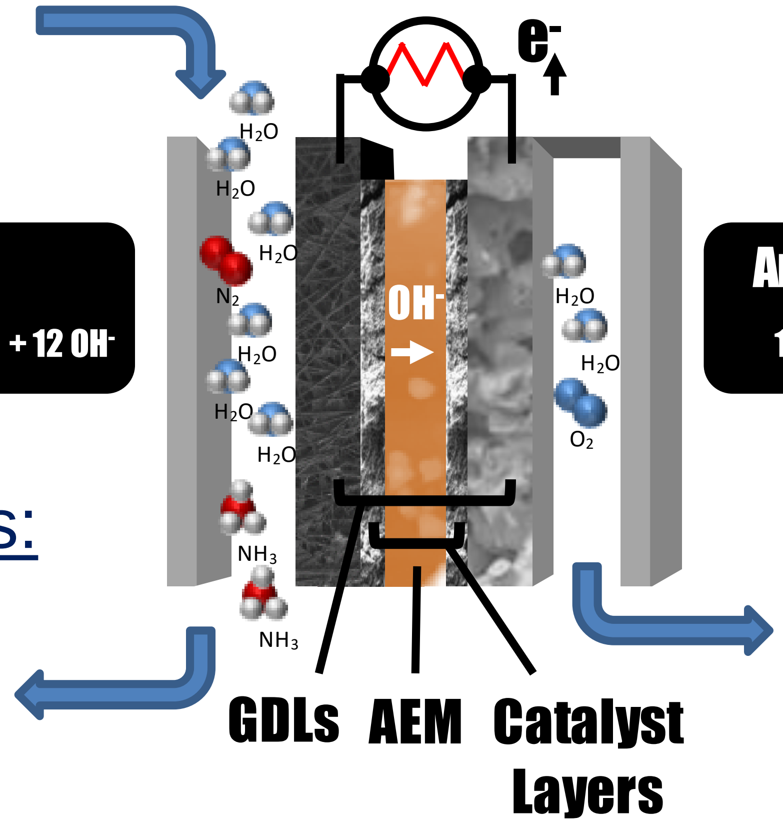



- Electrically driven process for low temp/pressure/emissions
- Compatible with intermittent operation
- High regional demand for fertilizer co-located with renewables

# AEM-based Approach

**Cathode:**

$12\,H_2O + 2\,N_2 + 12\,e^- \rightarrow 4\,NH_3 + 12\,OH^-$




**Anode:**

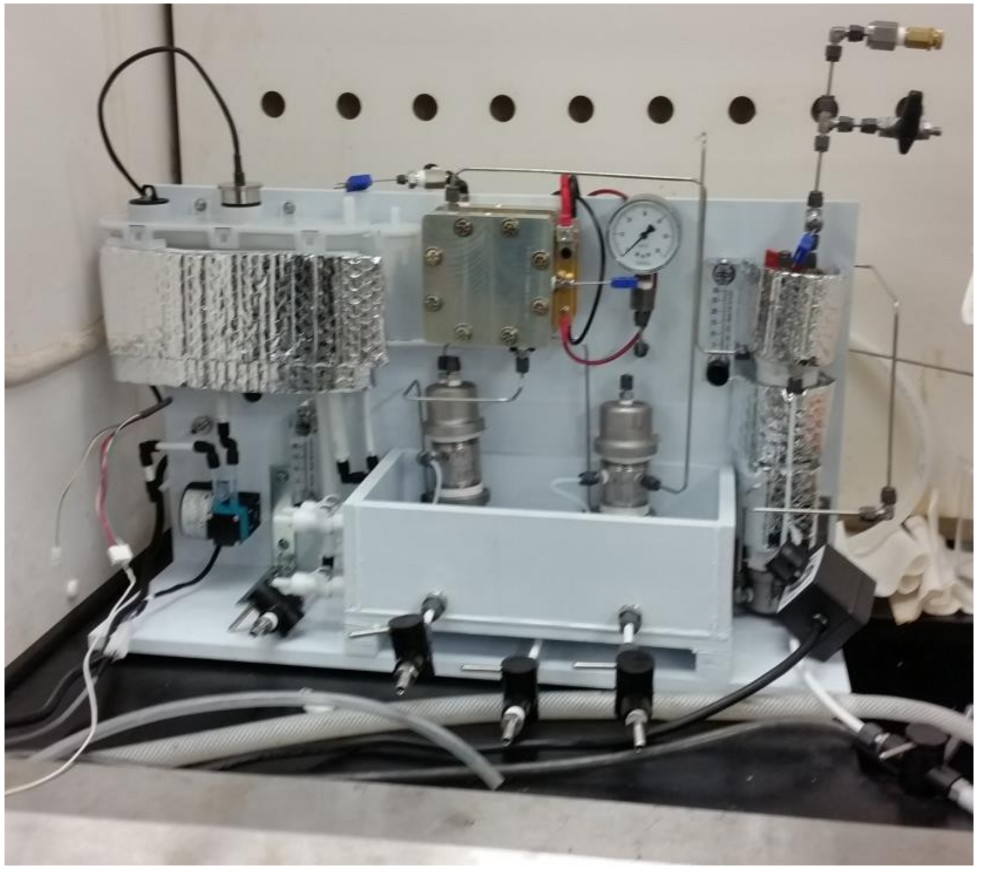
$12\,OH^- \rightarrow 3\,O_2 + 6\,H_2O + 12\,e^-$

<u>More Catalyst Options:</u>

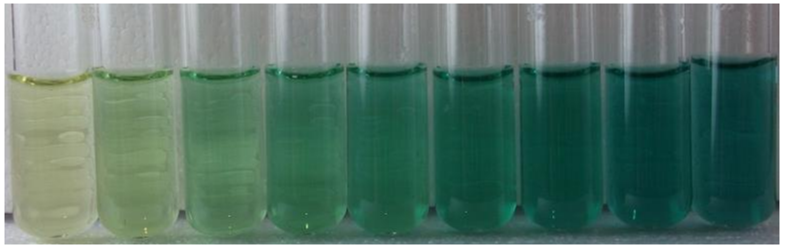
- Non-noble
- Blended metals
- Core-shell
- Ligands

- AEM enables wider range of efficient catalysts vs. PEM
- Lower cost materials of construction in alkaline environment

# Ammonia Generation Testbed



- Design reviewed by senior engineers
- Acid trap to collect ammonia



Increasing ammonia concentration

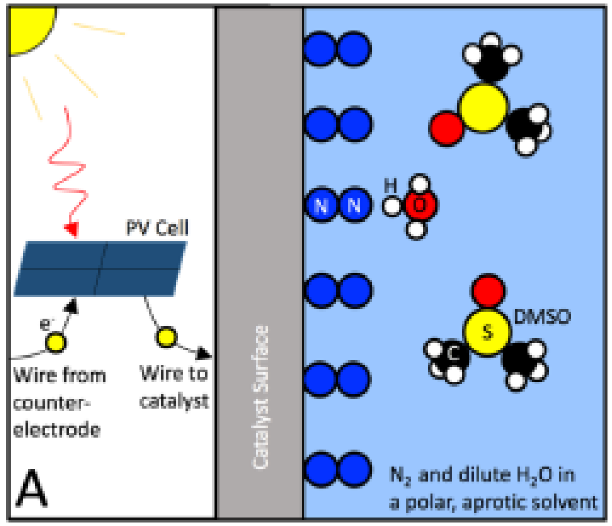
<u>Key Issues Solved</u>:

- Sources of non-electrochemically generated $NH_3$ can and have clouded results
- Added robust controls (argon gas), careful sample prep

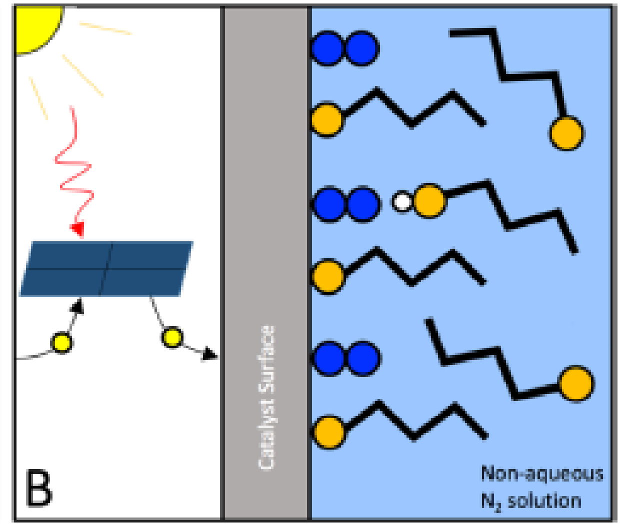
Sustainable Ammonia Synthesis. Roundtable discussion sponsored by DOE BES held on 2-18-16.
http://science.energy.gov/~/media/bes/csgb/pdf/docs/2016/NH3_Report.

# Strategies for Increasing Efficiency

Limit the proton transfer rate

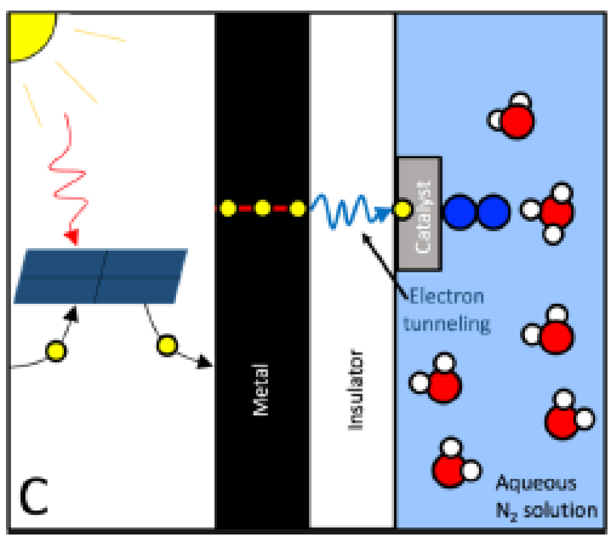



Reduce protons in bulk solution

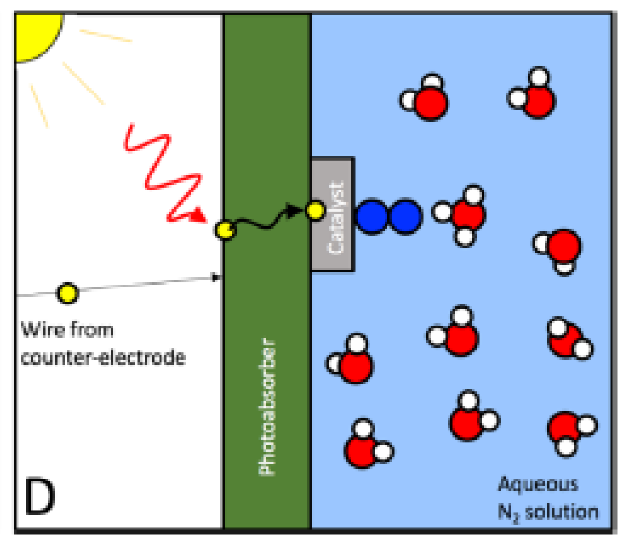



Limit proton transfer rate

Limit the electron transfer rate




Thin insulators




Photoadsorbers

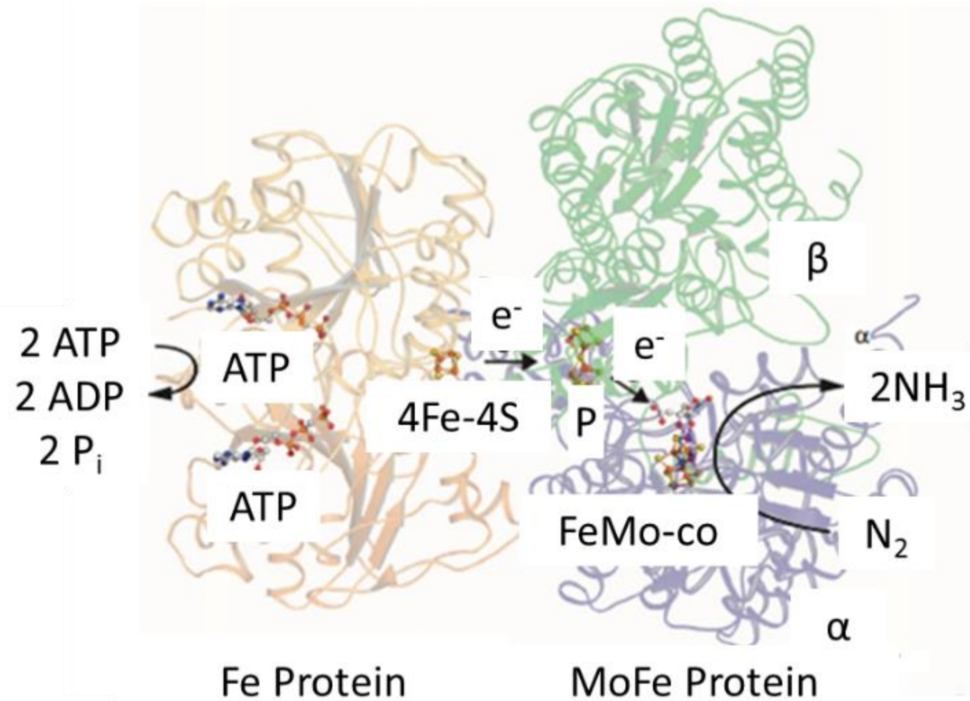
- Qualitative model suggests limiting active sites being taken up by recombination of H+ and e−

A. R. Singh, *et al.*, Acs Catalysis, 7, (2017).

# Biological Strategies

$$8H^+ + 8e^- + N_2 + 16\,ATP \rightleftharpoons 2NH_3 + H_2 + 16\,ADP + 16\,P_i$$

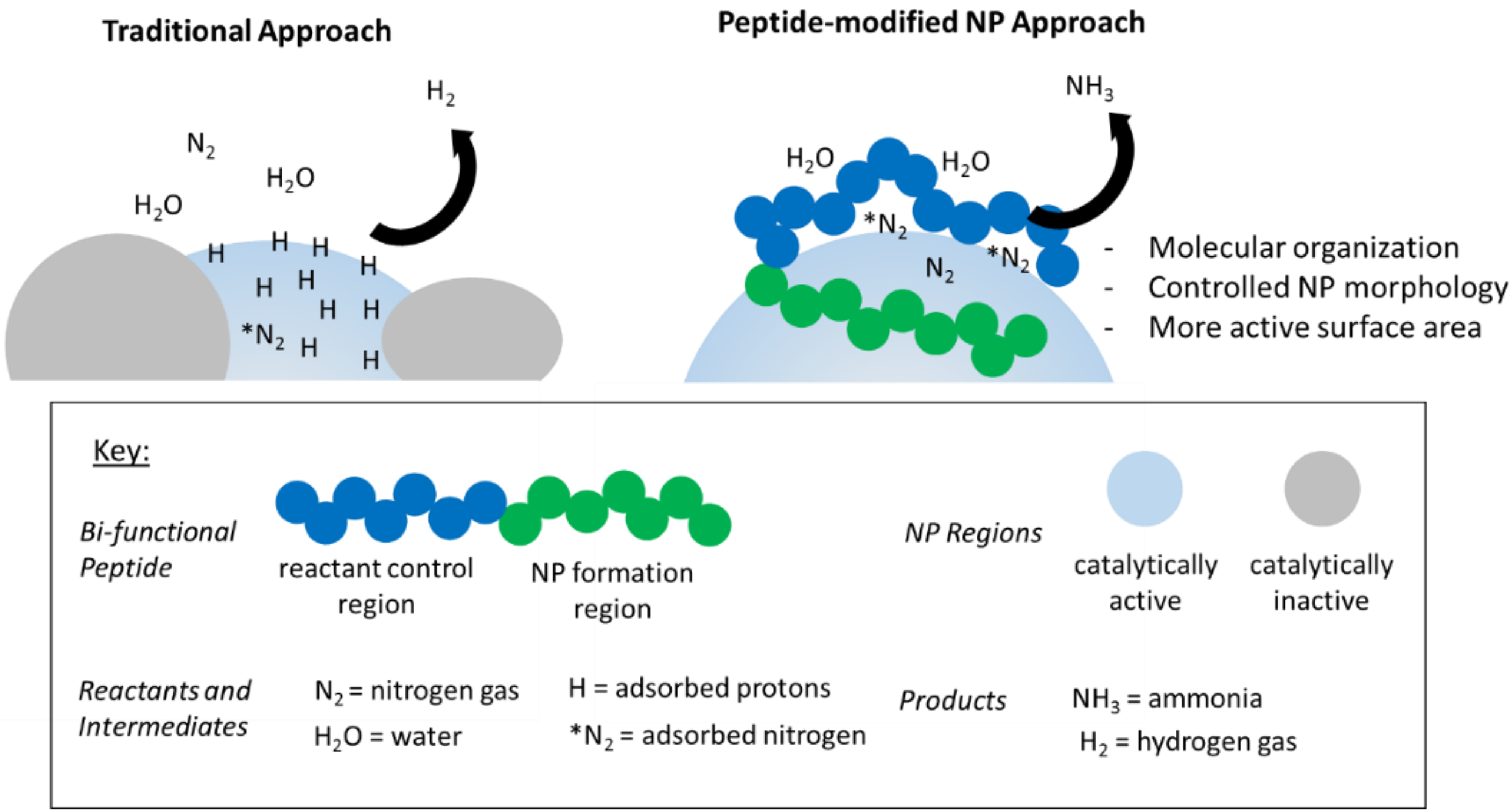
| Enzyme Part | Function |
|---|---|
| FeMo-cofactor | Catalyzes reduction of nitrogen to ammonia |
| $Fe_4S_4$, F-cluster | Facilitates hydrolysis of ATP and electron transfer |
| $Fe_8S_7$, P-clusters | Transfer the electrons from the Fe-protein to the FeMo-cofactor |
| Water chain | Limits water interacting with FeMo-co |




L. C. Seefeldt, *et al.* Curr Opin Chem Biol, 16 (2012).

- Operates at mild conditions
- 75% of electrons are utilized for $NH_3$ production
- Controls electron and proton transfer
- TOF ~ 2 $NH_3$/s, 10 mA/cm$^2$ requires ~3 mg/cm$^2$ (reasonable)

# Hybrid Approach




- Peptides designed for:
  - Nanoparticle formation – more active catalyst
  - Reaction control – nitrogenase mimics for efficiency

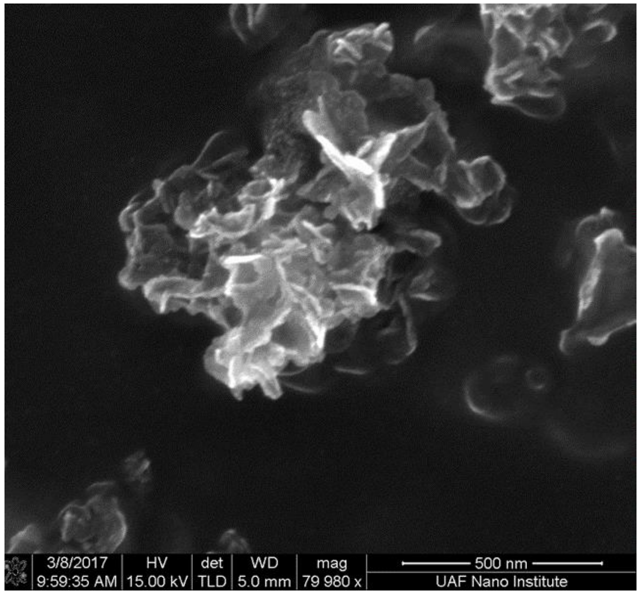
# Peptide Control of Nanoparticle Formation

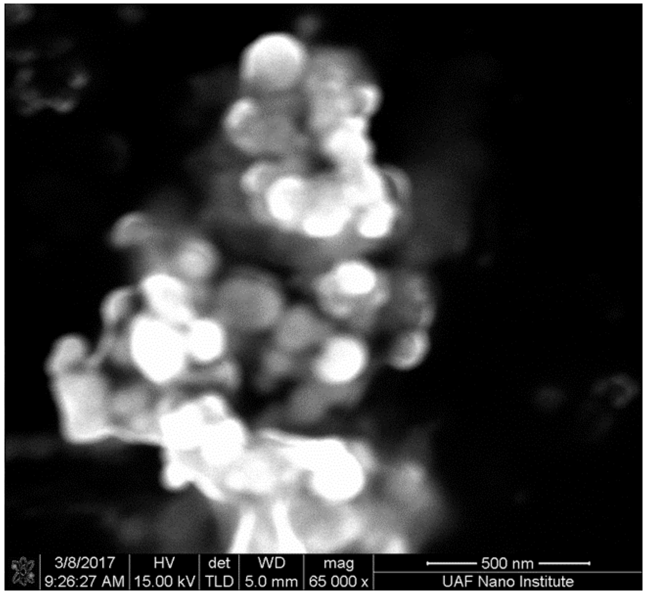
## Composition

| | Weight % | |
|---|---|---|
| | Fe | O |
| Peptide A | 86% | 14% |
| Peptide B | 86% | 14% |
| Peptide C | 83% | 17% |
| Peptide D | 44% | 56% |

- Peptide ligands can be used to control Fe nanoparticle composition and morphology

## Morphology and Phase

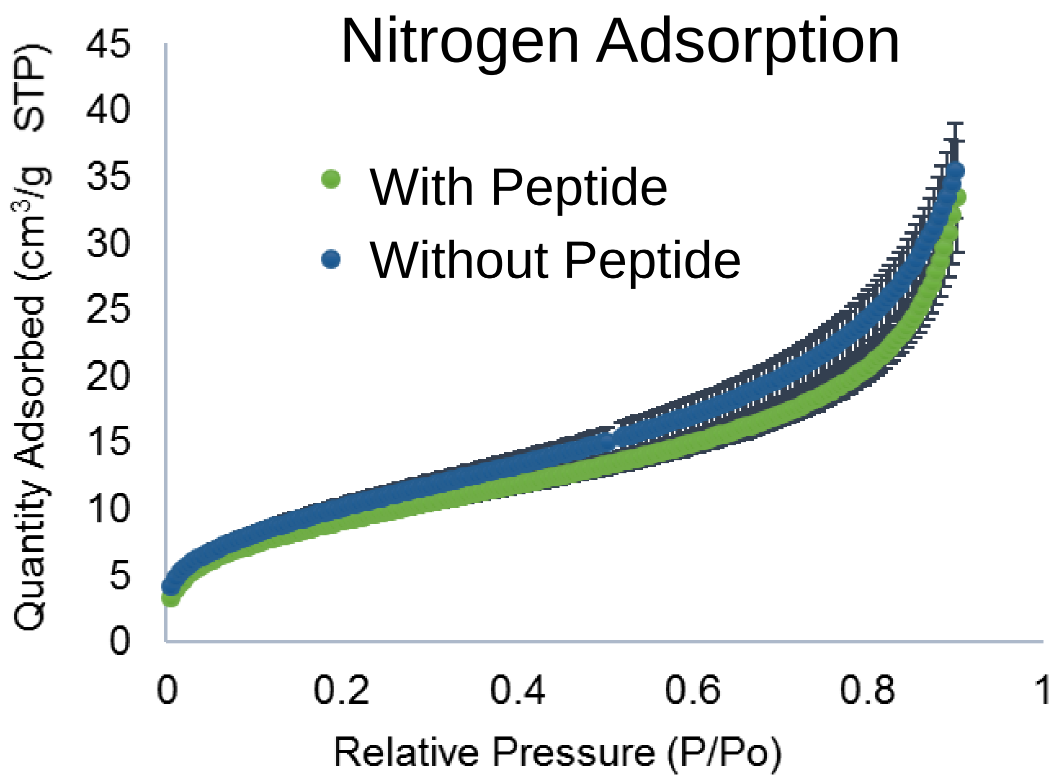


# Peptide Binding and Gas Adsorption

Peptide Binding

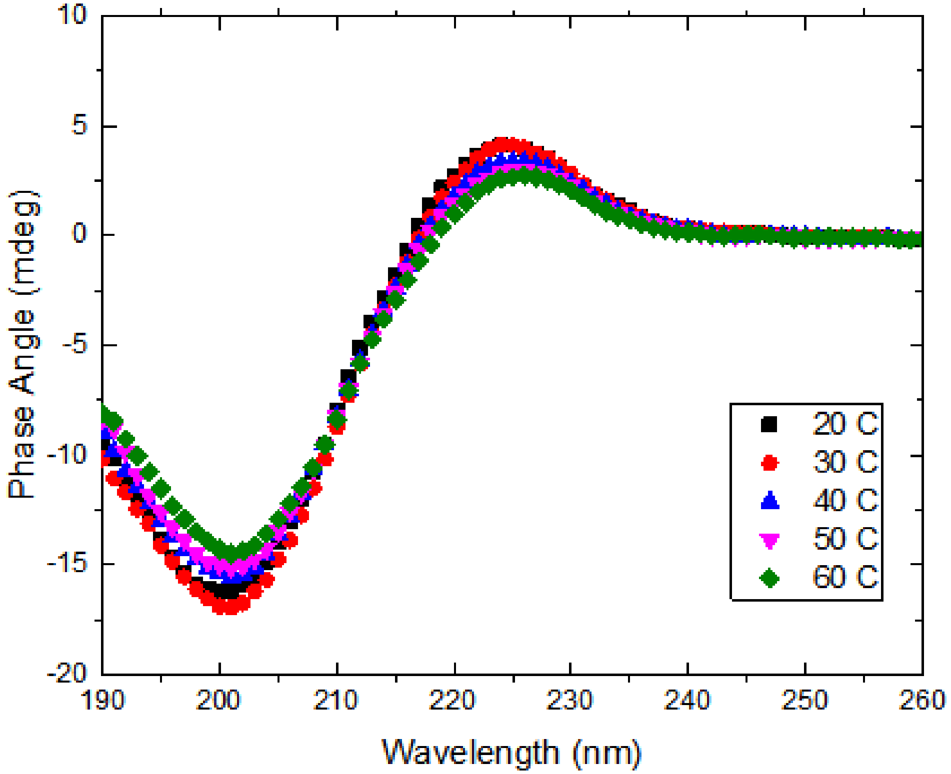
| Sample | Peptide Loading (% mass) |
|---|---|
| Peptide 1 | 8.90 ± 0.03 |
| Peptide 1 (Double Loaded) | 16.51 ± 0.01 |
| Peptide 2 | 8.94 ± 0.03 |
| Peptide 3 | 8.87 ± 0.07 |
| Peptide 4 | 9.91 ± 0.06 |



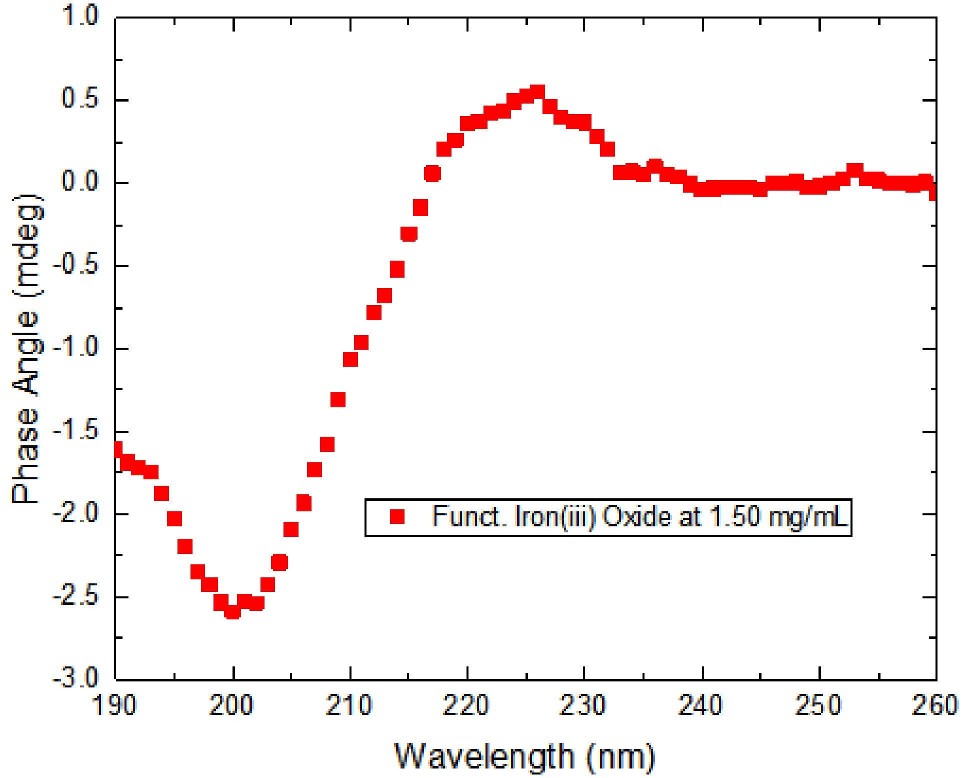

- Repeatable and controllable peptide binding to commercial nanoparticles
- Nitrogen gas adsorption isotherms statistically similar
  - Importantly not blocking nitrogen
  - BET surface area ~16 $m^2/g$

# Secondary Structure Analysis

Peptide in Solution

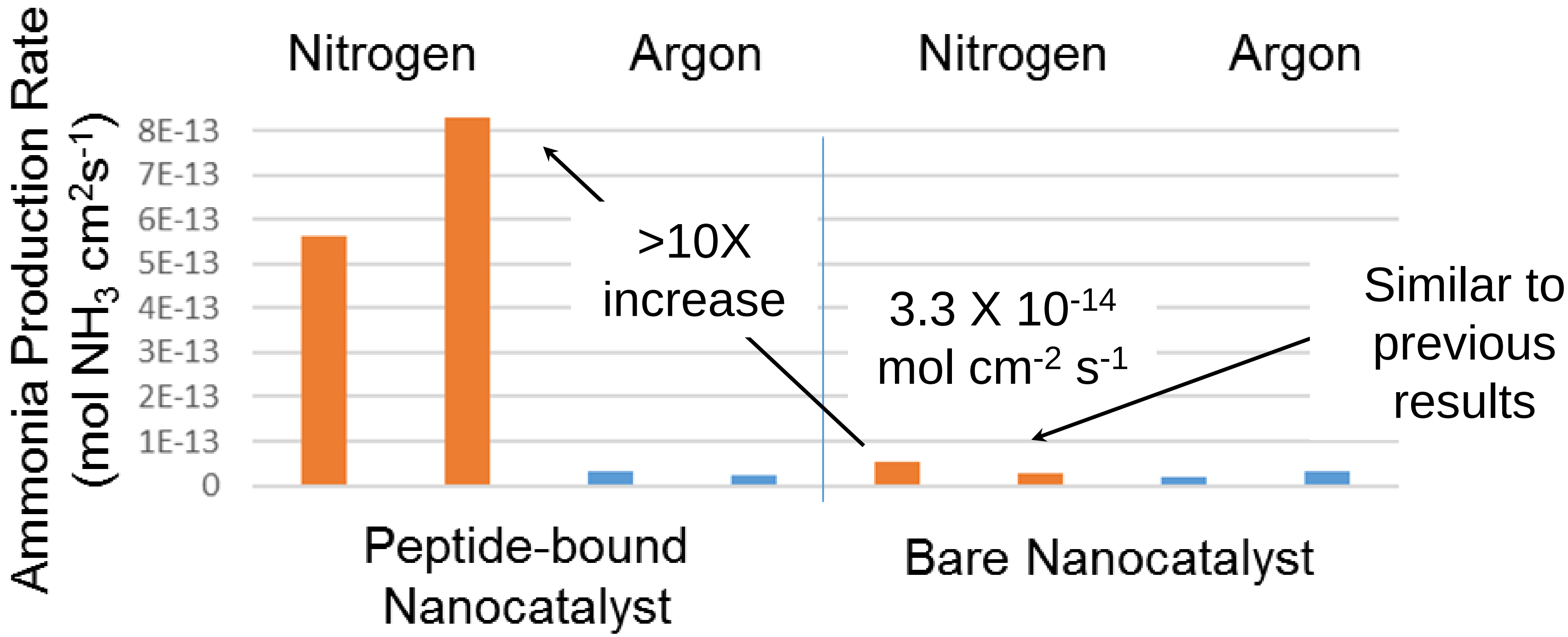



Bound Peptide




- Peptide structure is heat stable
- Peptide structure maintains binding to the iron (III) oxide nanoparticles

# Peptide Effect on Ammonia Production




| Current Efficiency: | 0.04% | 0.001% |
|---|---|---|

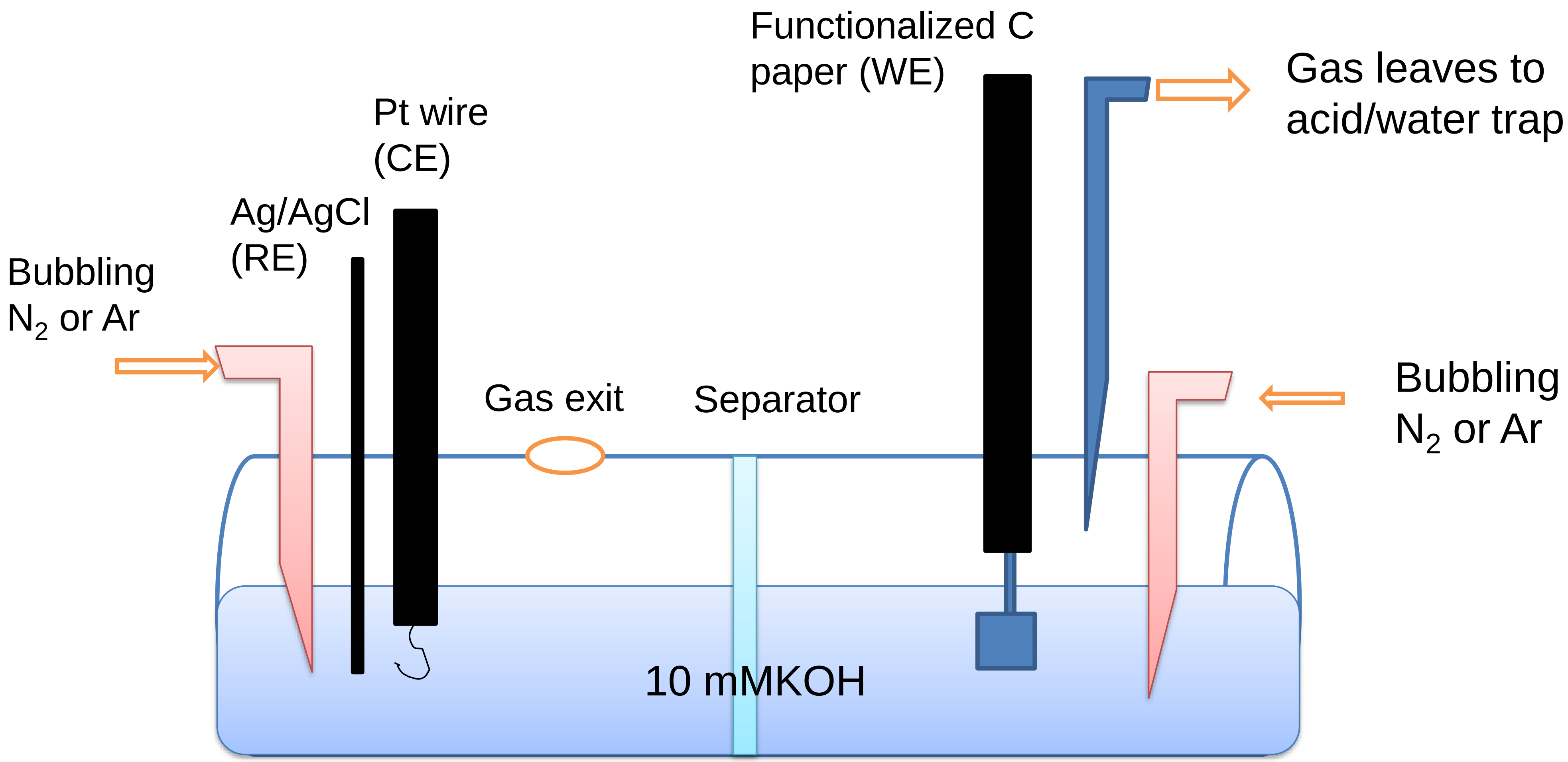
- >10X increase in ammonia production rate
- >10X increase in current efficiency
- Repeatable results, with argon control



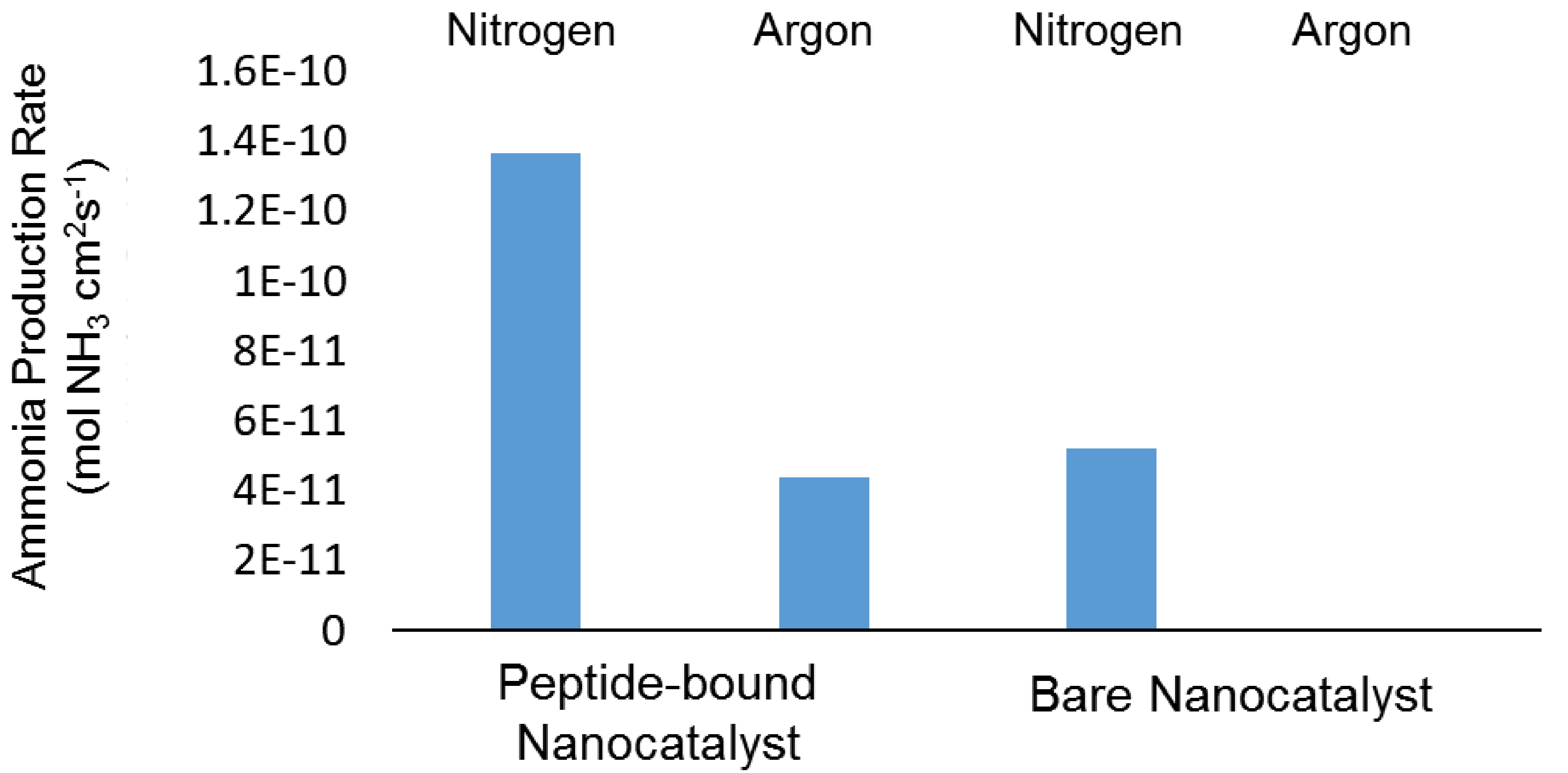
Conditions: 3 hour of operation at -2.5 V, IrOx counter electrode, 50°C

# Aqueous Separated Cell

- Repeating studies done at Proton OnSite
- Ammonia assay used to analyze ammonia in acid trap and electrolyte



# Preliminary Results




- Current efficiency ~1% for peptide subtracting Ar
- Still see an enhancement with the peptide
- Working on contamination issues and labeled controls

Conditions: 6 hour of operation at -2.0 V (vs. Ag/AgCl), Pt counter electrode, 25°C

# Conclusions and Future Work

## Conclusions

- AEM-based electrochemical systems are a promising
  - Ammonia production is shown above Ar controls with non-noble metals in multiple systems
  - Careful experimental set up and protocol is important
- Biologically inspired catalyst approaches are promising
  - Increased production rates and efficiency 10X in solid state cell, and promising preliminary data in liquid separated cell
  - Control of nanoparticle formation possible

## Future Work

- Understand mechanisms behind increased performance in peptide-bound nanocatalysts

# Acknowledgements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