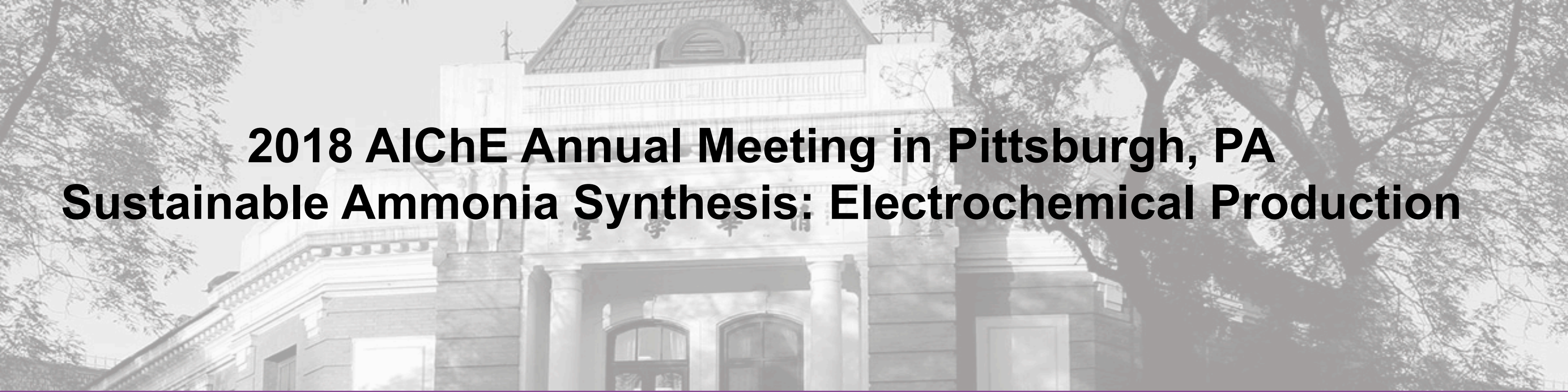


2018 AIChE Annual Meeting in Pittsburgh, PA
Sustainable Ammonia Synthesis: Electrochemical Production

Highly-Selective Electrochemical Reduction of Dinitrogen to Ammonia at Ambient Temperature and Pressure

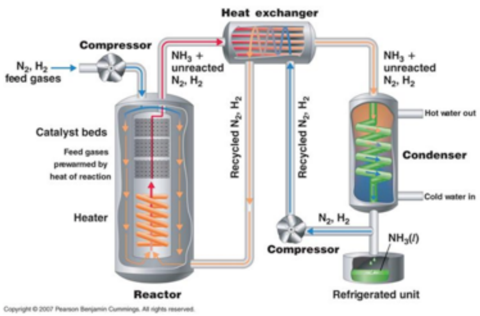
Qiang Zhang (张 强)
Tsinghua University
Email: zhang-qiang@mails.tsinghua.edu.cn

CONTENTS

1. Background

Heterogeneous catalysts

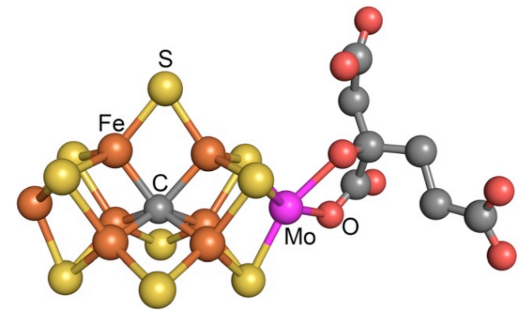
Haber−Bosch Process:



Holly grail

$$N_2 \xrightarrow[\text{room temperature}]{\text{1 atm}} NH_3$$

Biological catalysts



Chem. Rev. 2014, 114, 8, 4041

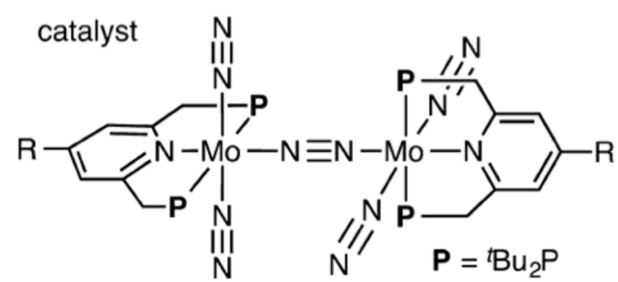
Photocatalytic catalysts & Electrocatalytic catalysts

using water, air and

renewable energy

lower energy consumption

Synthetic molecular catalysts



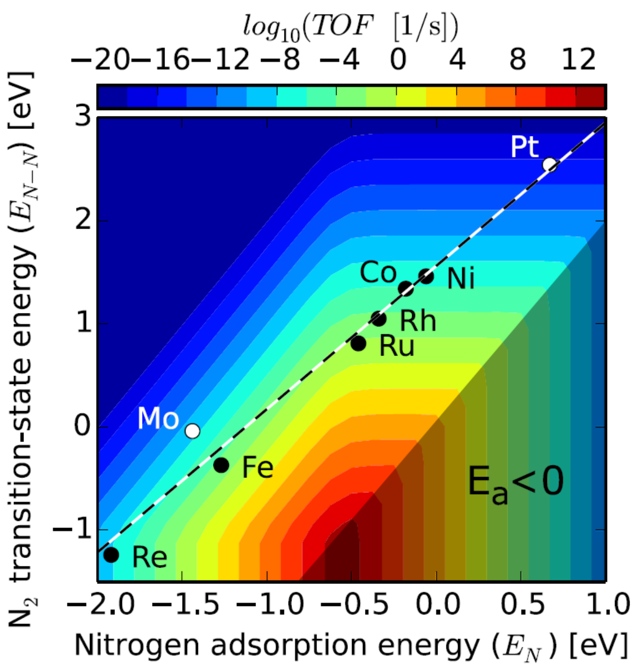
Mater. Horiz., 2018, 5, 9 *Energy Environ. Sci.*, 2018, 11, 45-56
Science, 2018, 360, eaar6611

J. Am. Chem. Soc. 2014, 136, 9719

1. Background

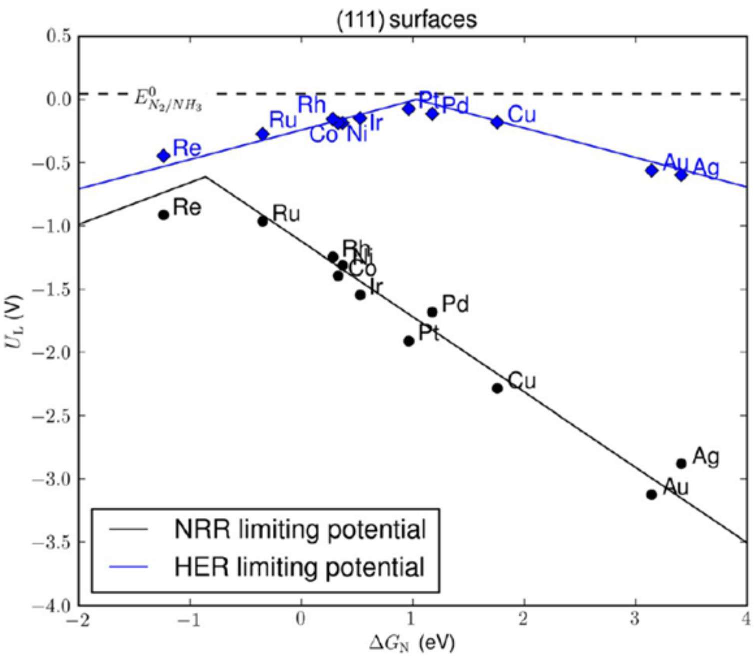
Challenges of heterogeneous nitrogen reduction reaction (NRR)

Limitations of the scaling relations



J. K. Nørskov, *J. Catal.* **2015**, 328, 36-42.

The competing hydrogen evolution reaction（HER）

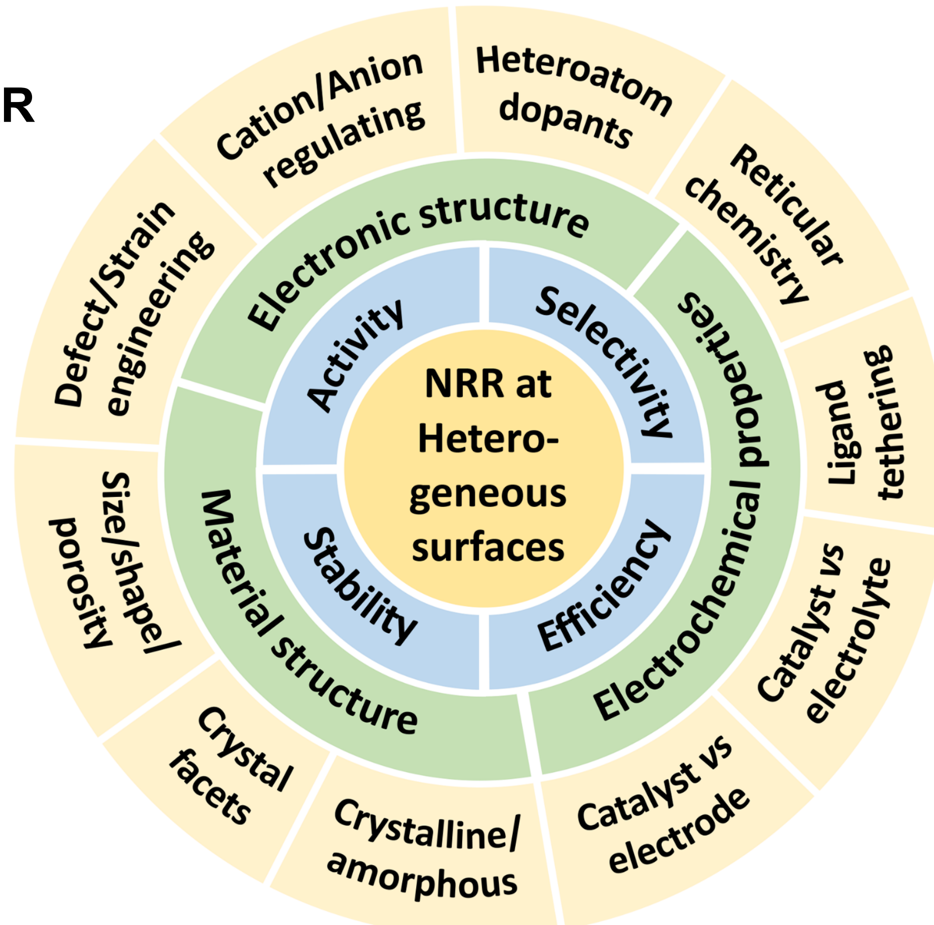


J. K. Nørskov, *ChemSusChem* **2015**, 8, 2180.

2. Review of electrocatalytic NRR

Strategies to enhance heterogeneous NRR under ambient conditions:

Boosting NRR by rational catalyst design



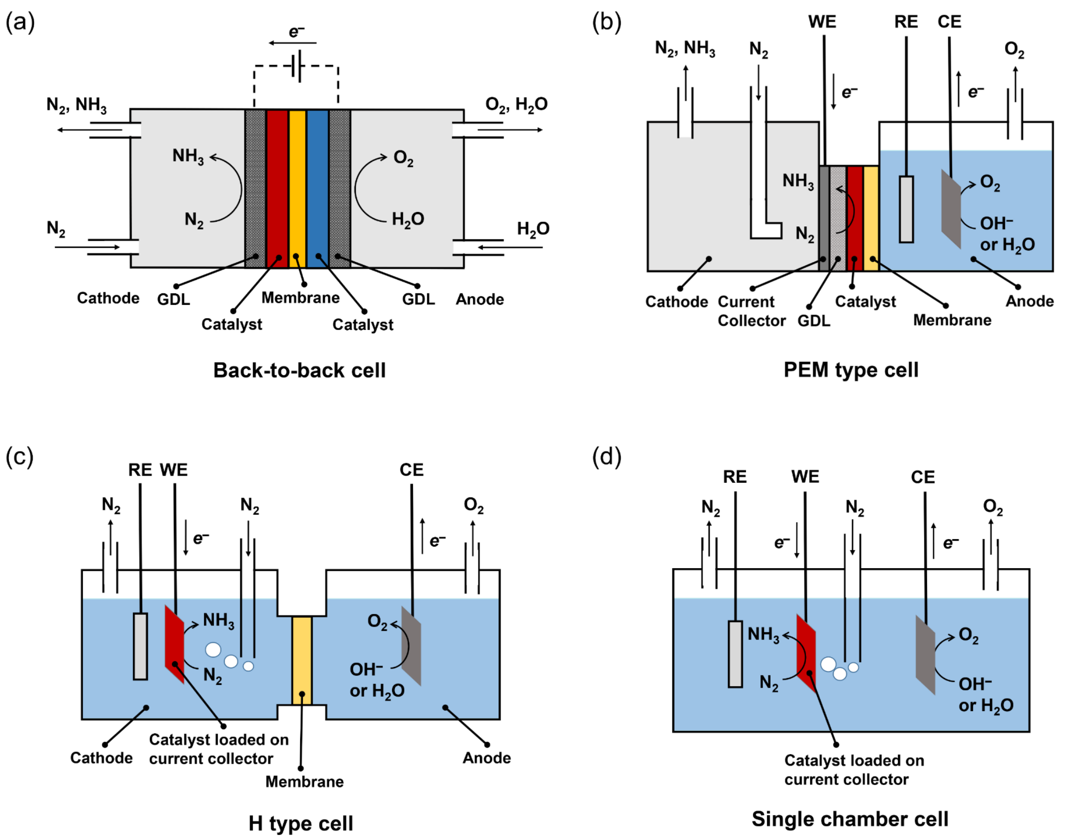
Suppressing HER at the catalyst/ electrolyte interface

Avoiding HER by decoupling N_2 Fixation and NH_3 formation

Adv. Energy Mater. 2018, 1800369

2. Review of electrocatalytic NRR

A summary of electrocatalytic devices for NRR



Adv. Energy Mater. 2018, 1800369

NH_3 determination methods

1. Colorimetric methods:
- Indophenol blue method
- Nessler's reagent method

2. Ion chromatography

3. Ammonia selective electrode (e.g.: Orion 9512HPBNWP)

4. $^{15}N_2$ isotopic methods
- Nuclear magnetic resonance spectrometer (NMR)
- mass spectrometer (MS)
- Infrared spectroscopy (IR)

3. Hematite catalyst toward NRR

Hematite (α-Fe_2O_3) nanoparticles

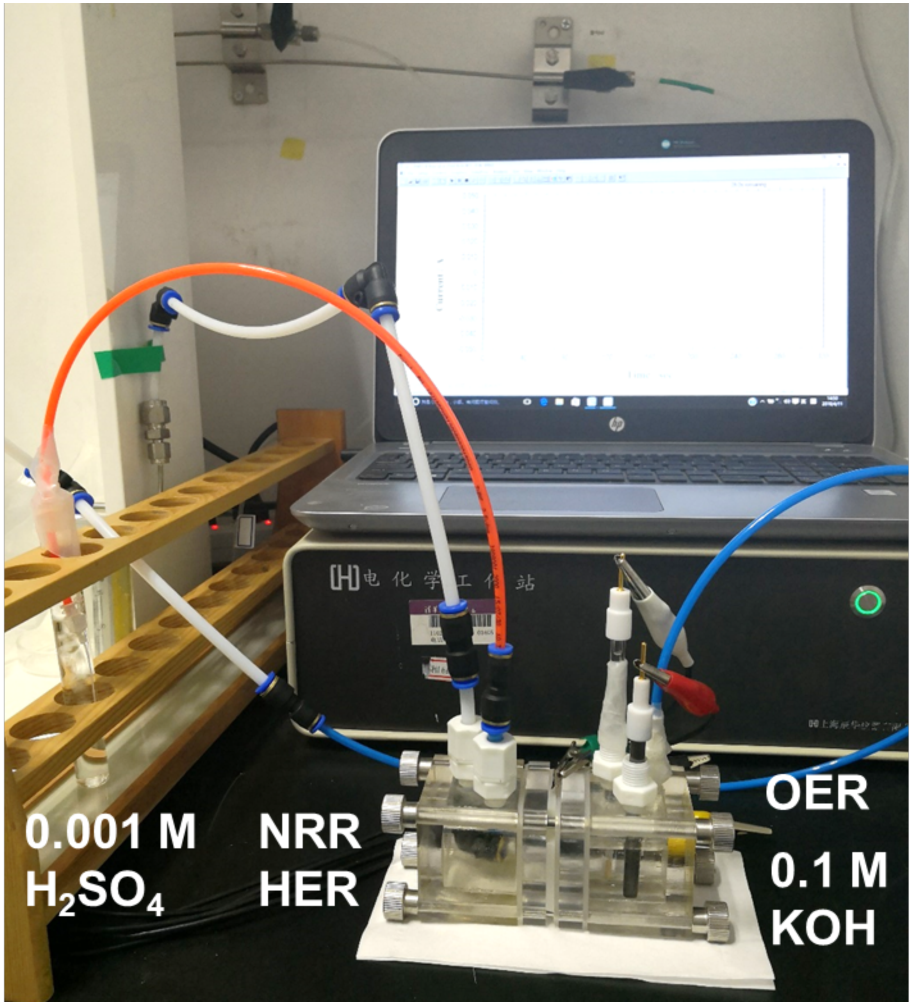
Motivated by *Science* **2014**, 345, 637

Surface modification to boost NRR

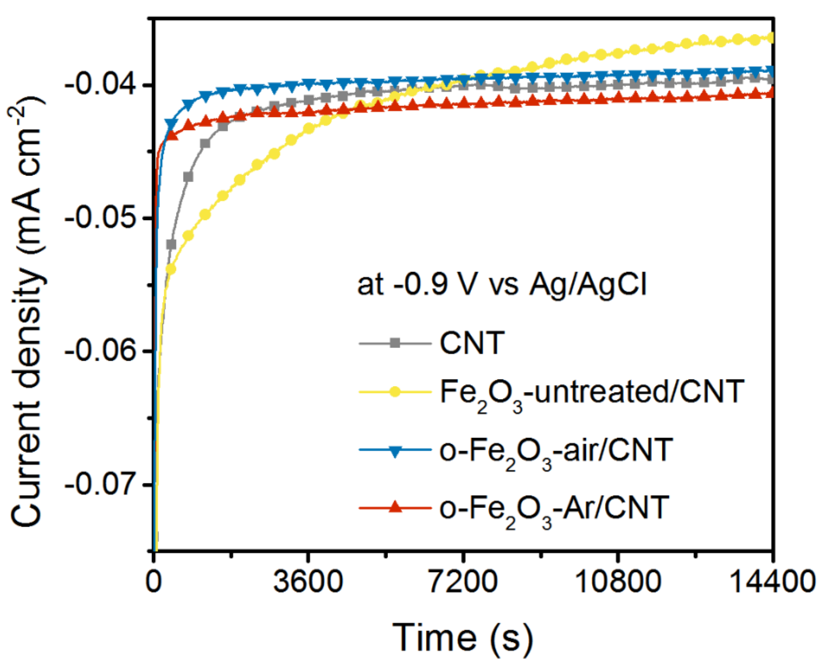
Preparation of catalyst ink and deposit onto carbon paper (CP)
Catalyst loading: 3.4 mg cm^{-2}

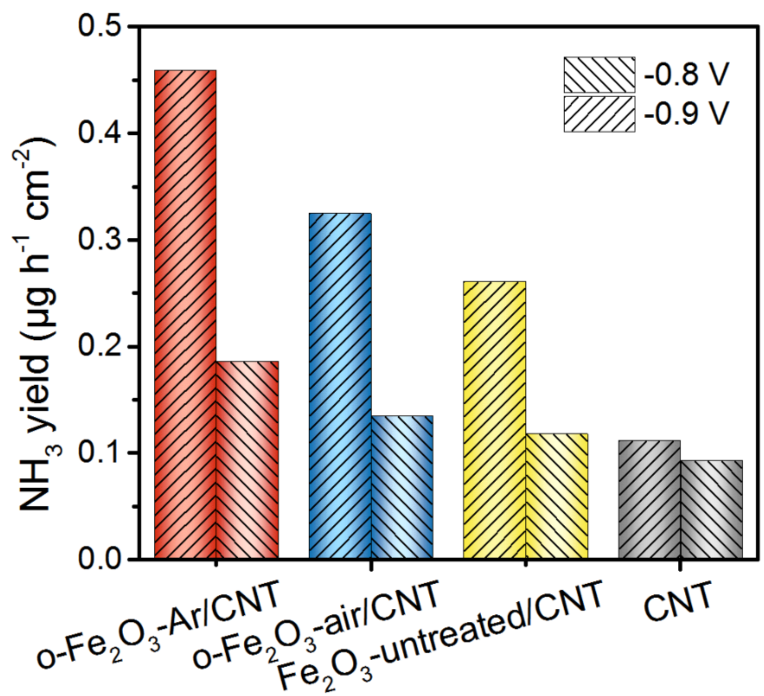
Hot-pressing of Nafion 115 membrane and CP at 130℃ for 5 min to form an MEA

Using the Nessler's reagent method for ammonia determination



3. Hematite nanocatalyst toward NRR





Hematite annealed at 450°C for 1 h in Ar

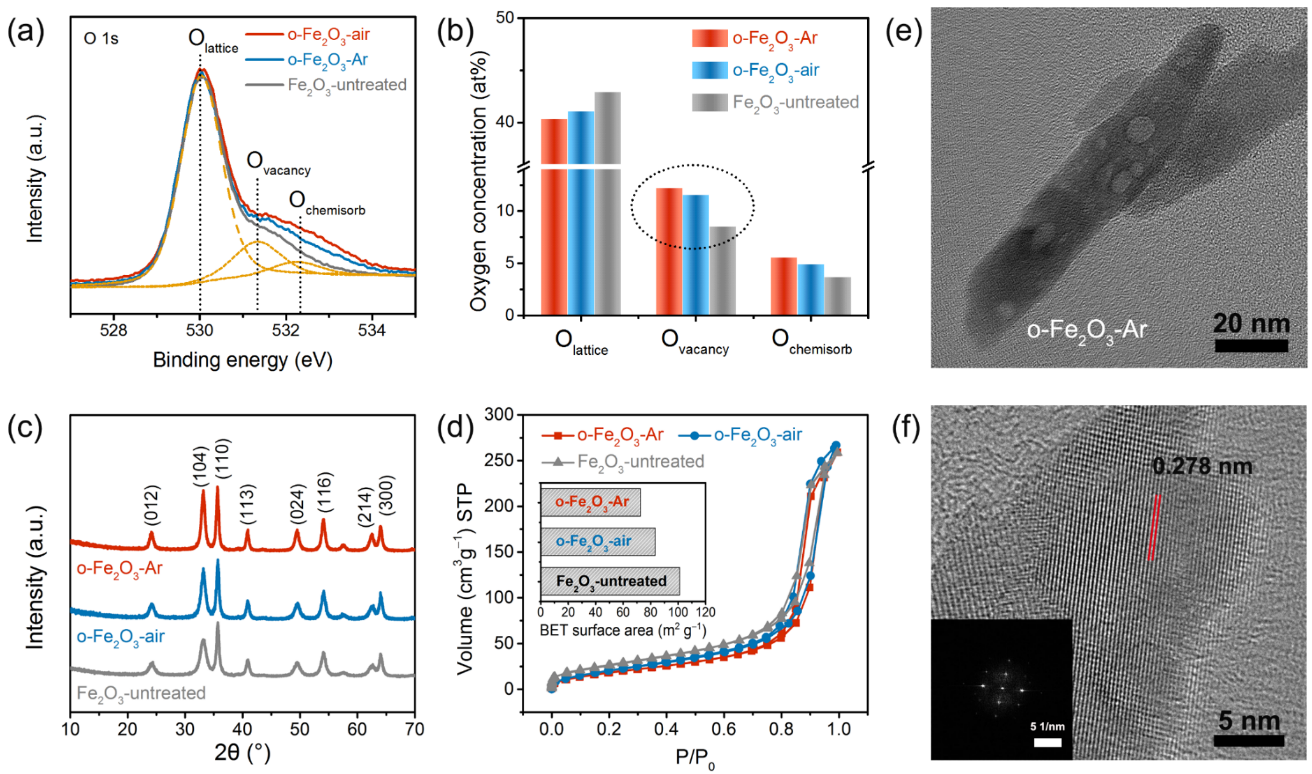
Hematite annealed at 450°C for 1 h in air

Hematite nanoparticles as-received

CNT the conductive additive

X. Cui, et al. *Chem. Eur J.* **2018**, 24, 1. DOI: 10.1002/chem.201800535

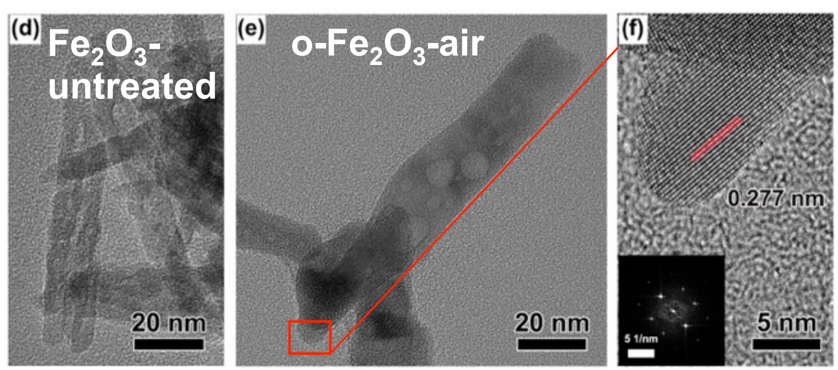
3. Hematite nanocatalyst toward NRR



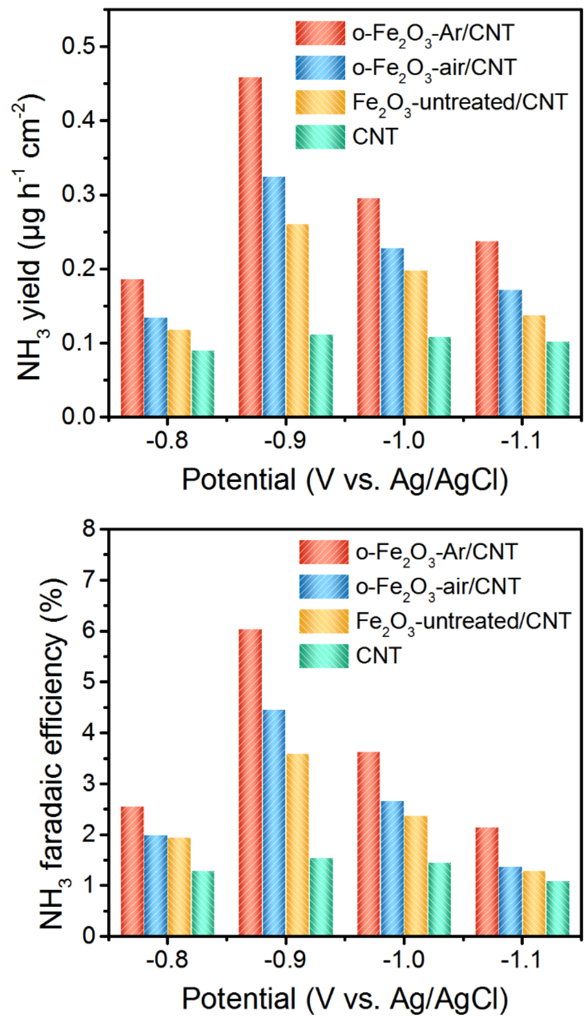
The diameter of the nanorods increased after annealing

The concentration of the surface oxygen vacancies varied while the crystal phase maintained after annealing.

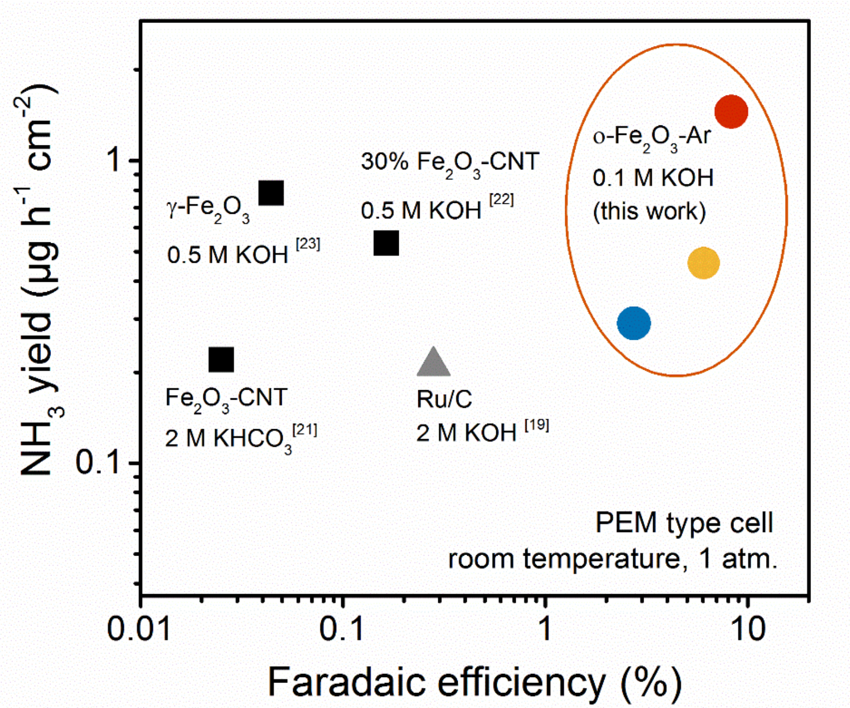
Chem. Eur J. **2018**, 24, 1



3. Hematite catalyst toward NRR



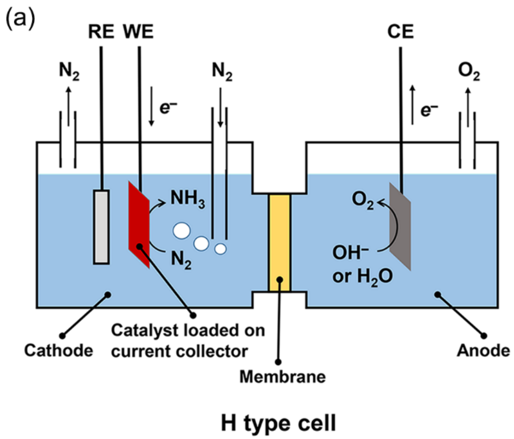
Chem. Eur J. **2018**, 24, 1

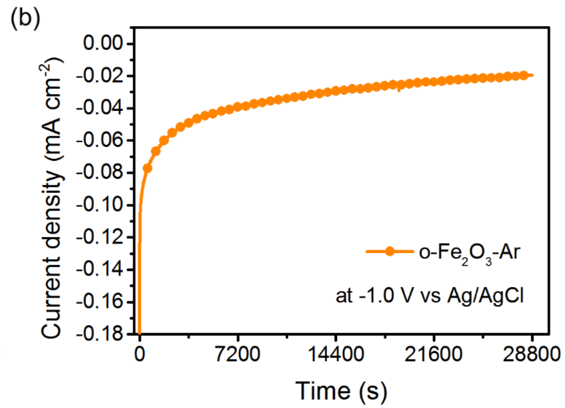


An average r_{NH3} of 1.45 $\mu g \cdot h^{-1} \cdot cm^{-2}$ and NH_3 FE of 8.28% (1h)

An average r_{NH3} of 0.46 $\mu g \cdot h^{-1} \cdot cm^{-2}$ and NH_3 FE of 6.04% (4h)

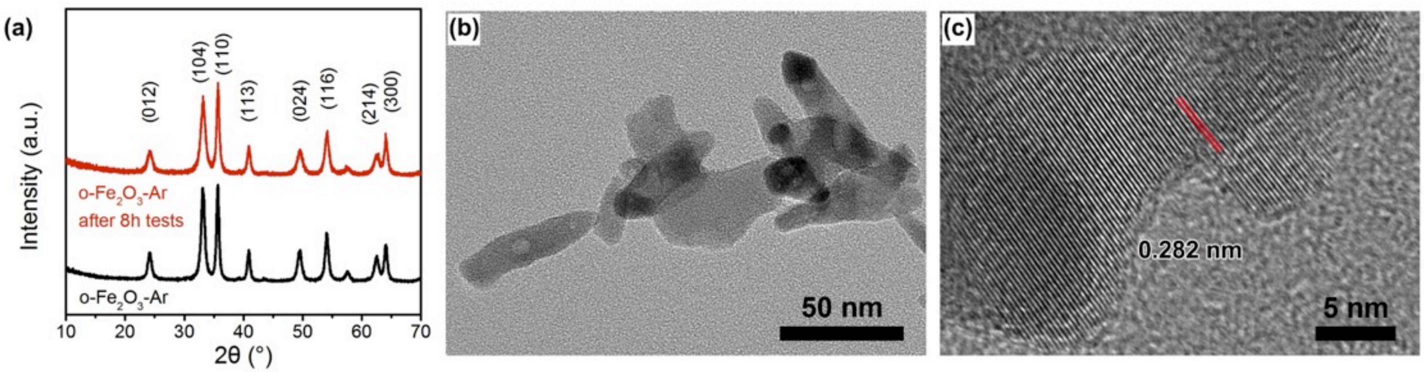
3. Hematite catalyst toward NRR





An average r_{NH3} of 0.183 $\mu g \cdot h^{-1} \cdot cm^{-2}$ and NH_3 FE of 3.09% (8h)

Chem. Eur J. **2018**, 24, 1



- **Both the NH_3 yield and NH_3 faradaic efficiency of NRR under ambient conditions can be improved by modification of the hematite surface.**
- **However, the catalytic activity, selectivity and stability toward NRR in aqueous systems are still far from satisfactory.**

4. Future directions for NRR

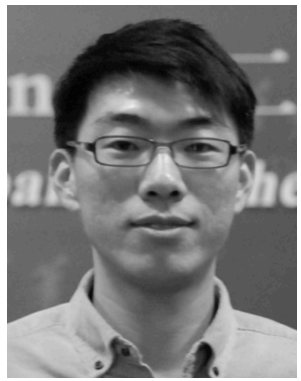
- Rational Design of the Catalysts and the Electrochemical System
- Better Understanding of the NRR Mechanism
- Standard Protocols for the Electrochemical NRR Measurements
- Clarification of the Origin of Nitrogen in the Ammonia Generated
- Advanced Characterization Techniques: in situ and operando studies

4. Acknowledgements

PEOPLE

Dr. Xiaoyang Cui

Dr. Cheng Tang



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Wenjun Ma (undergraduate)

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