질소 순환 시스템 효율/안정성 유지 이슈
Efficiency and Stability Issues in Nitrogen Cycle Reaction System

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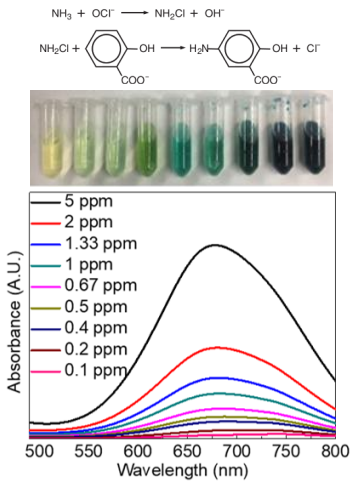
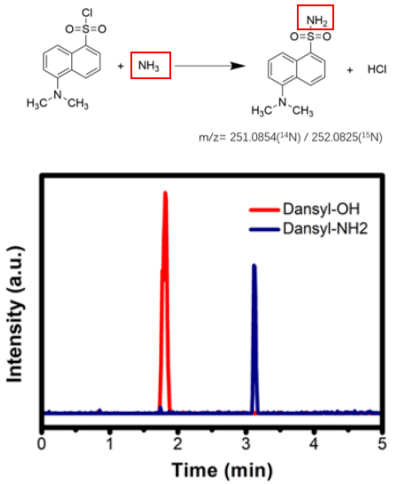
Nanomaterials for Energy & Environment Laboratory
www.uksim.org

Detection of Ammonia Production

- **Ex-situ analysis**

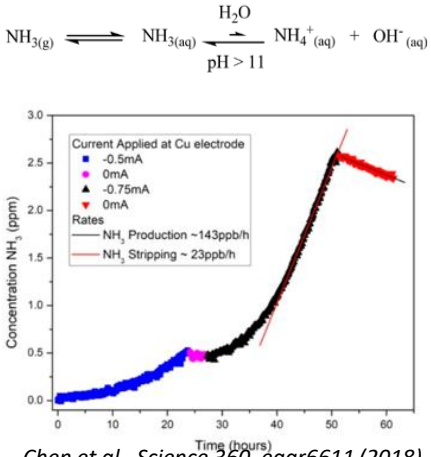


Colorimetric method



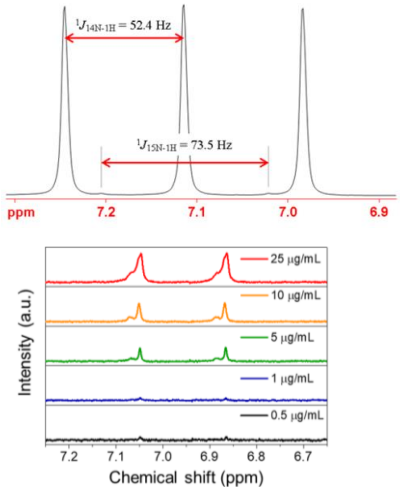
ACS Energy Lett. 2020, 5, 1532−1536

LC-MS



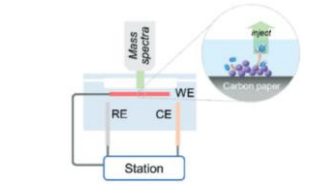
Chen et al., Science 360, eaar6611 (2018)

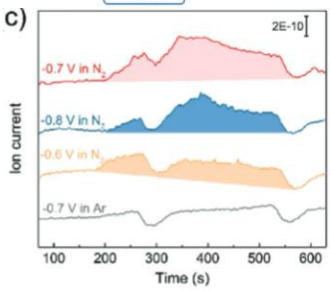
GC



NMR

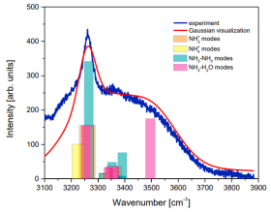
- **in-situ analysis**

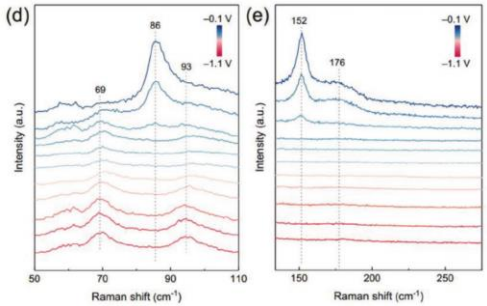




Adv. Energy Mater. 2020, 10, 2001289

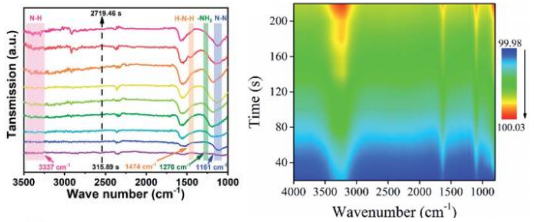
DEMS

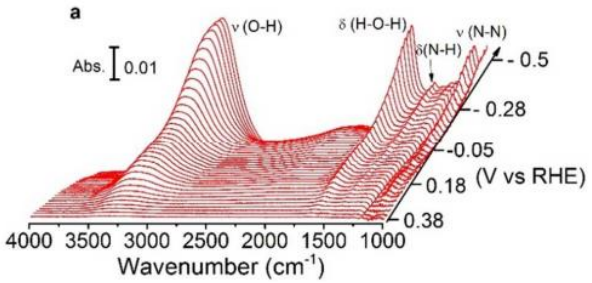




iScience 23, 101757, November 20, 2020

Raman





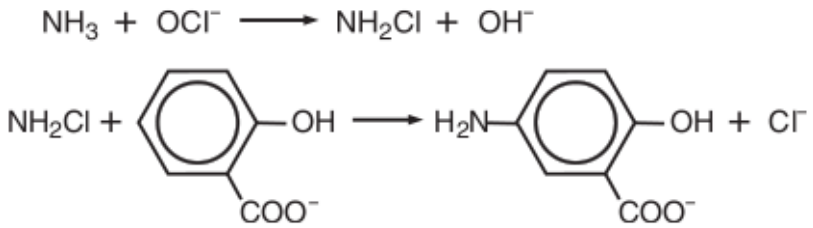
J. Am. Chem. Soc. 2018, 140, 4, 1496−1501

FT-IR

Salicylate Test and UV/Vis Spectroscopy

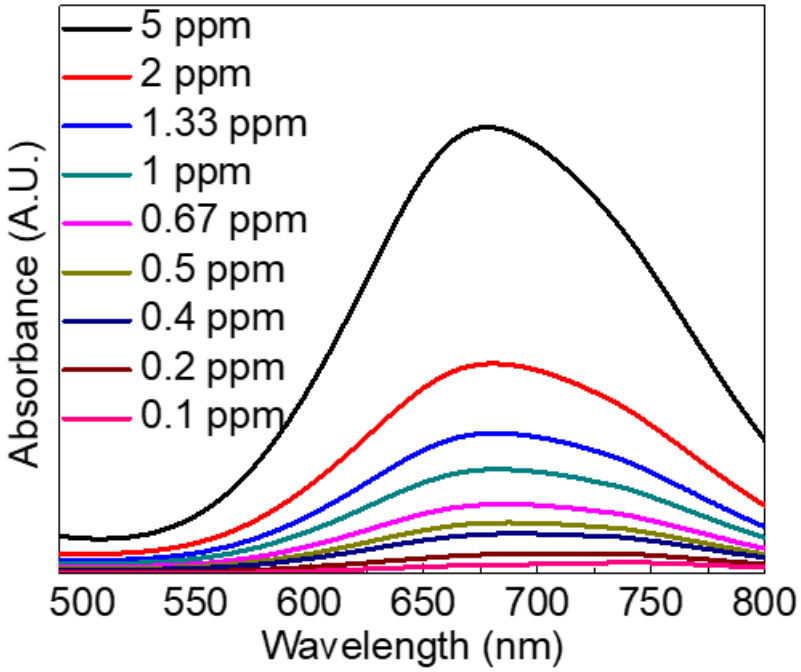
- **NH_3/NH_4^+ test**
  - API Ammonia Test Kit
  - Polyethylene glycol (<90wt%) and sodium salicylate (<10wt%)
  - Ammonia levels from 0 to 8 ppm

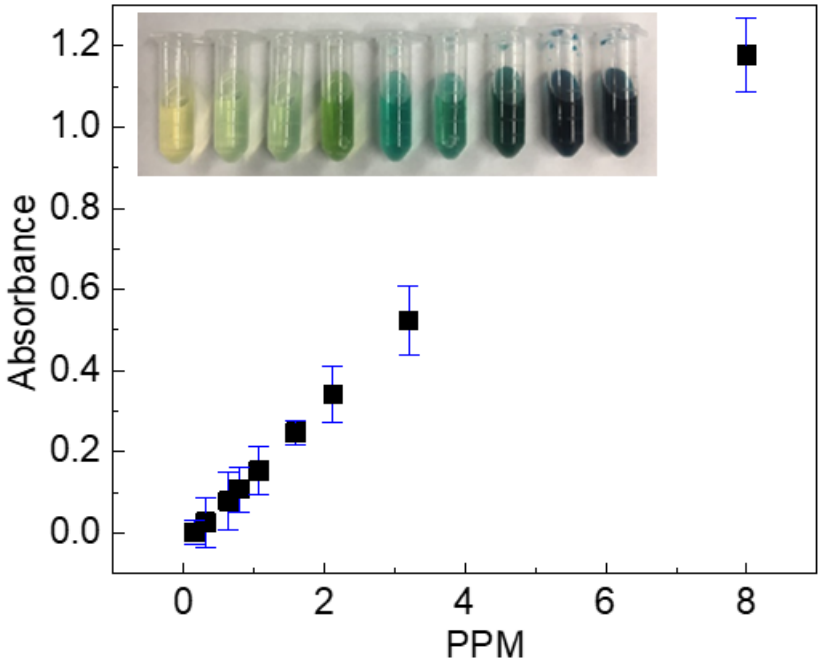
- **Reaction sequence**



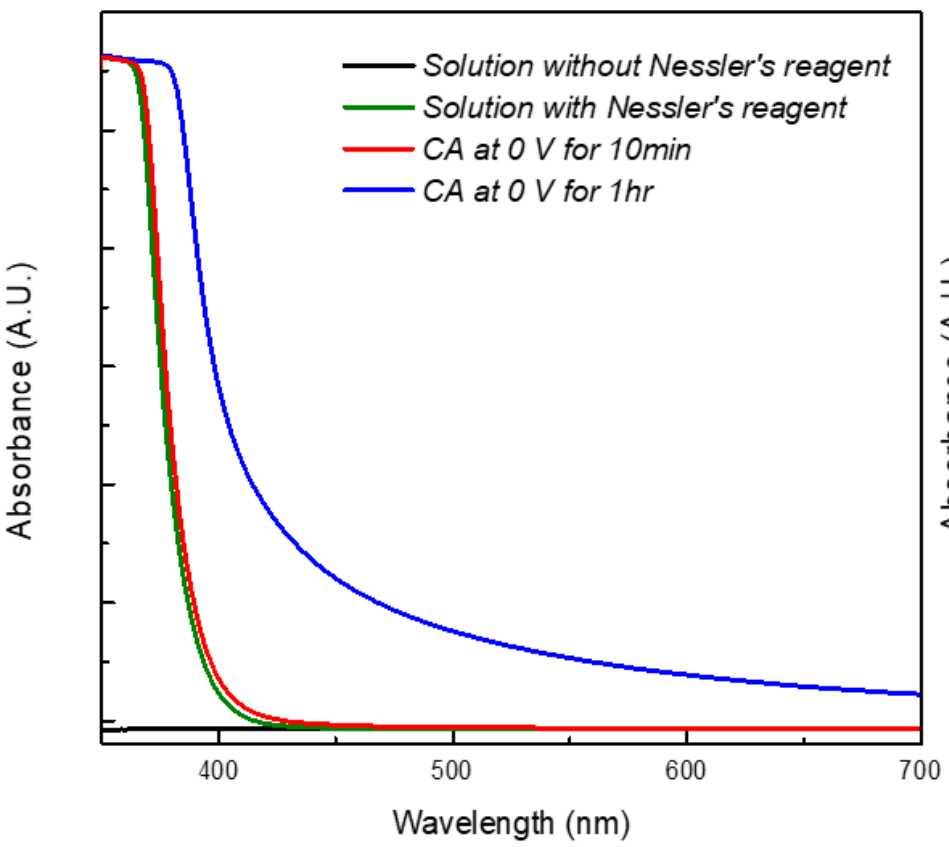
1. Conversion of ammonia to monochloroamine
2. Monochloroamine reacts with salicylate to form 5-aminosalicylate.
3. 5-aminosalicylate is oxidized in the presence of sodium nitroferricyanide to form a blue-green colored dye that absorbs light at 650 nm.

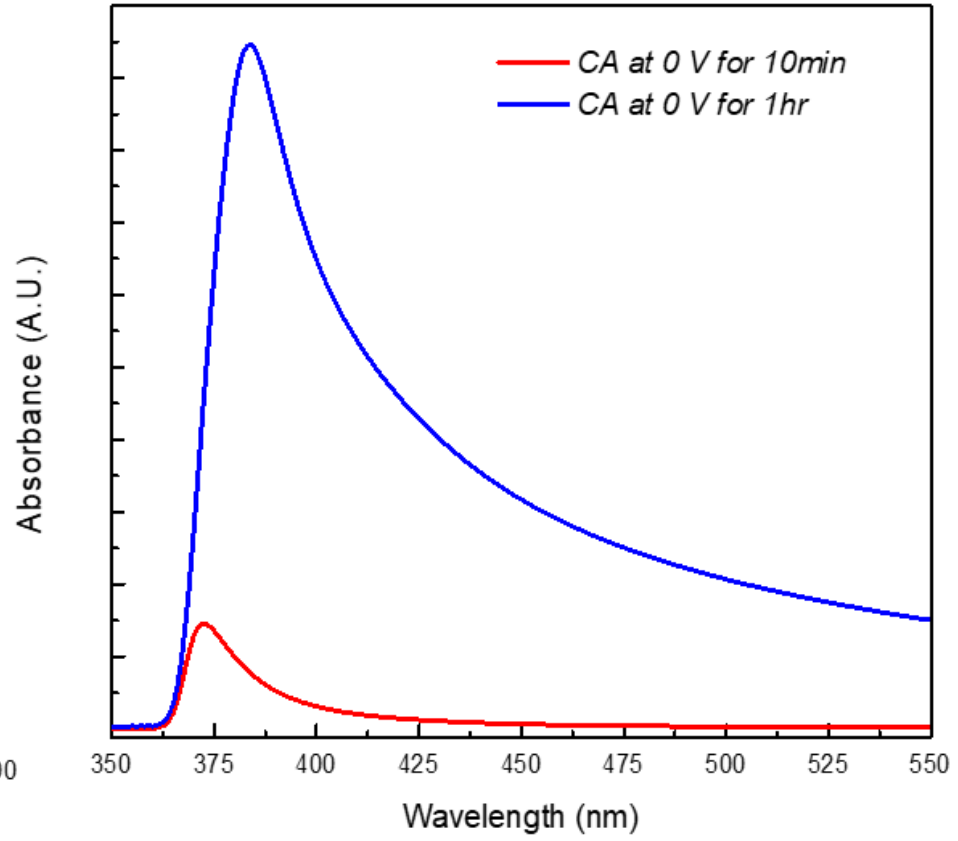
Calibration data





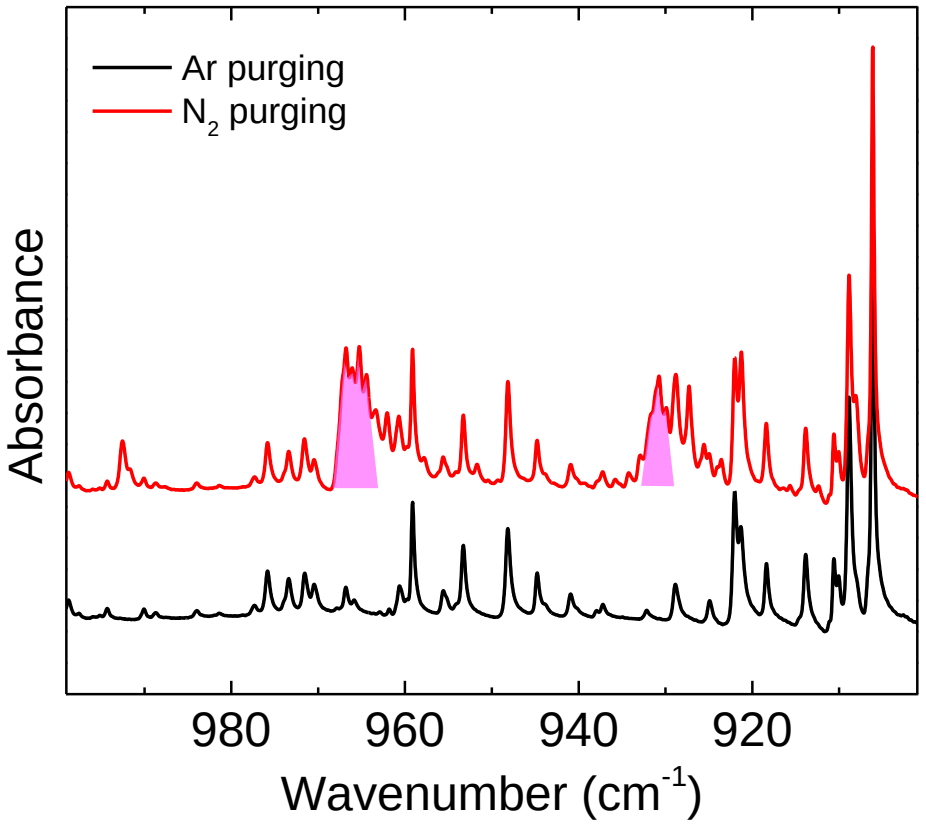
Nessler’s reagent

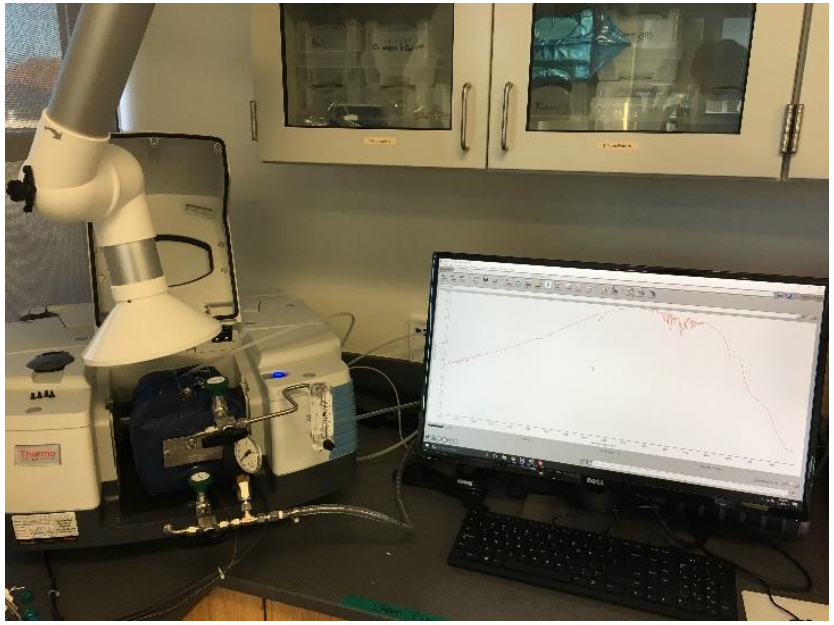




- Nessler’s reagent : Potassium tetraiodomercurate (II) ($K_2[HgI_4]$)
- $NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \rightarrow \mathbf{HgO{\cdot}Hg(NH_2)I} \downarrow + 7I^- + 3H_2O$

FTIR result





FTIR with MCT detector

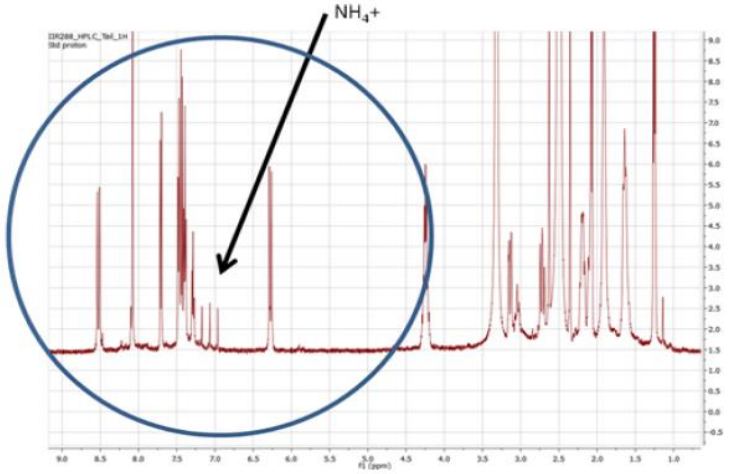
NMR confirmation

* **^{14}Nitrogen J coupling.**

^{14}N is the most natural abundant nitrogen isotope, 99.6 %. It has a spin I=1. If coupled to a ^{1}H, NH, the ^{1}H line should split into (2I+1)=3 lines with equal intensities.

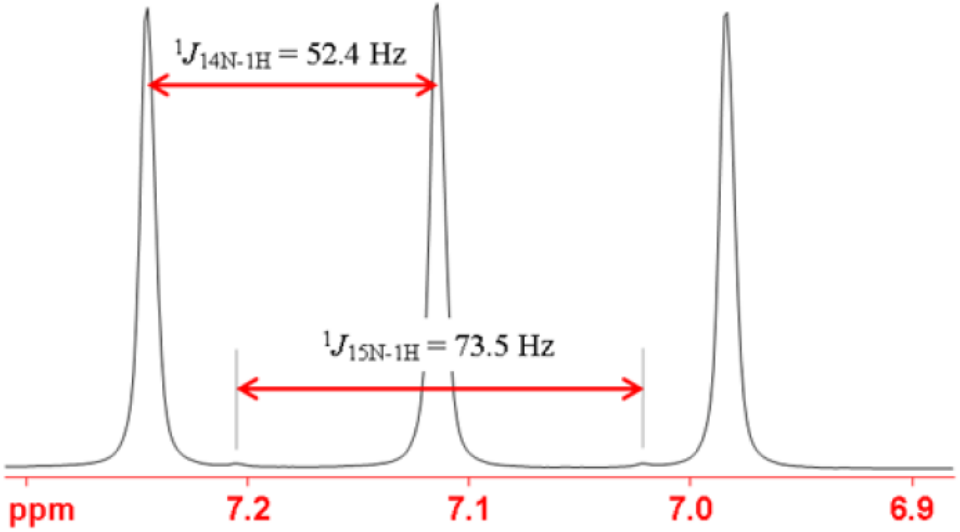
Most of the time though, due to quadrupolar relaxation effects, no ^{14}N splitting of the ^{1}H line is observed.

Now, when N is in a highly symmetric environment, like NH_4^+ the ^{14}N splits the proton signal into a triplet as shown in the following spectrum,



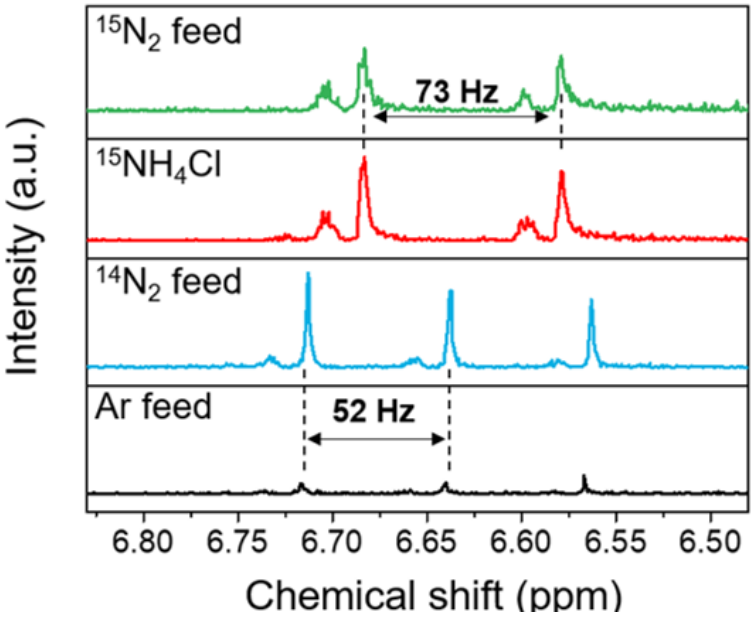
The following information on N-H couplings was found in the literature,

^{1}H spectrum of natural abundance NH_4Cl (1.5 M) in 1M HCl/H_2O showing coupling to ^{14}N as a (spin 1) triplet and coupling to ^{15}N as a weak doublet. Note that the ^{14}N coupling constant is smaller than that of ^{15}N because of ^{14}N's lower resonant frequency.



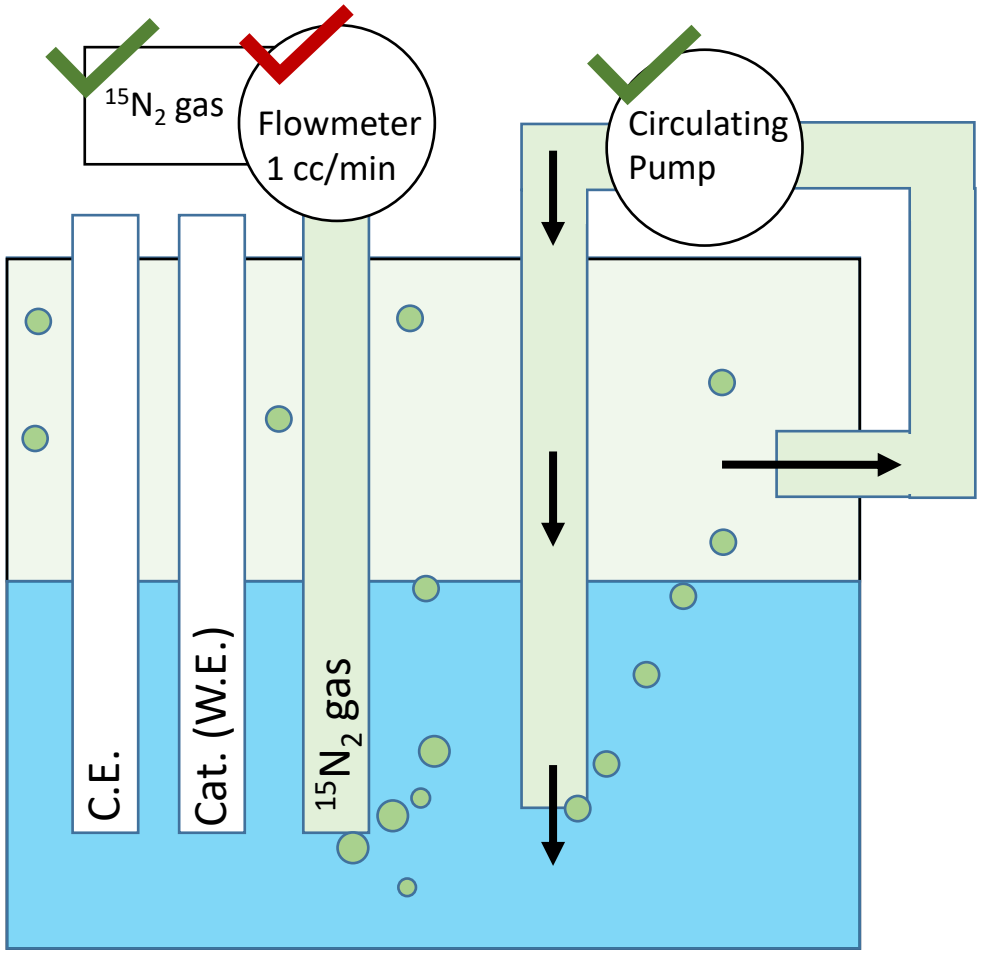
NMR confirmation

NMR analysis



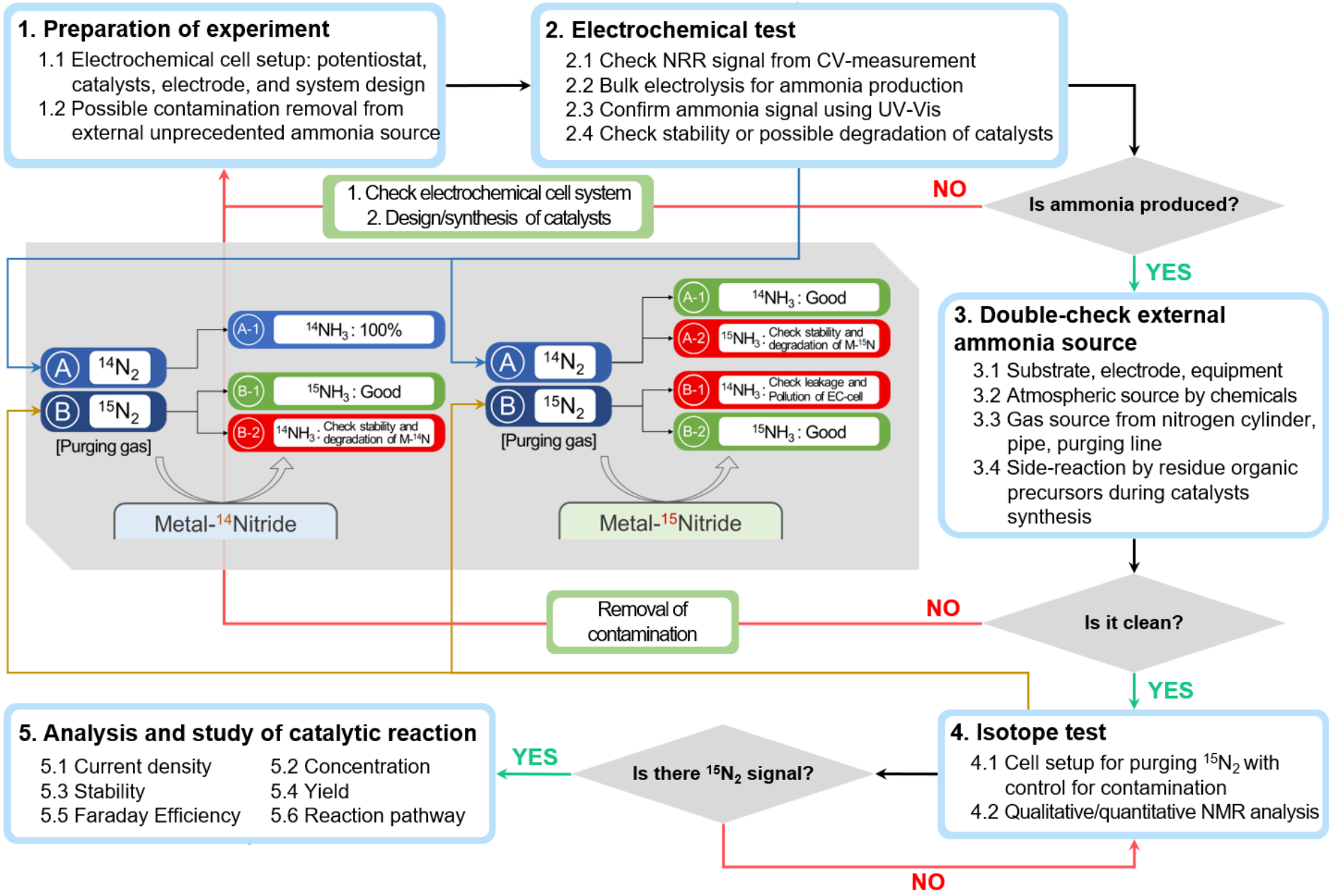
Stability test

- Long-term stability have low F.E.
- (about 2 %, 12 h and 20 h)
- cycle stability test is ongoing.



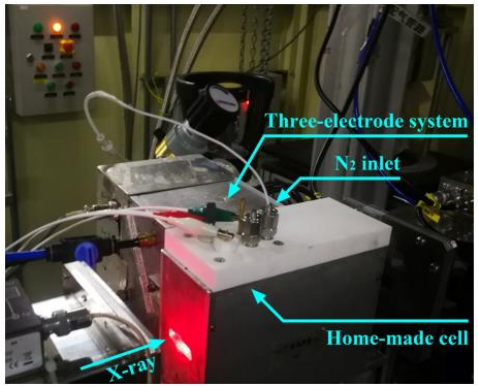
- NMR analysis using $^{15}N_2$ and N_2 is being performed to verify the nitrogen reduction performance of the catalyst.
- The triple peaks occurred when nitrogen is purged, where its interval is 52 Hz corresponding to ammonia signal.
- Double peaks are indicated when using $^{15}NH_4Cl$ to standard data, which interval is 73 Hz.
- Analysis using $^{15}N_2$ gas is ongoing.

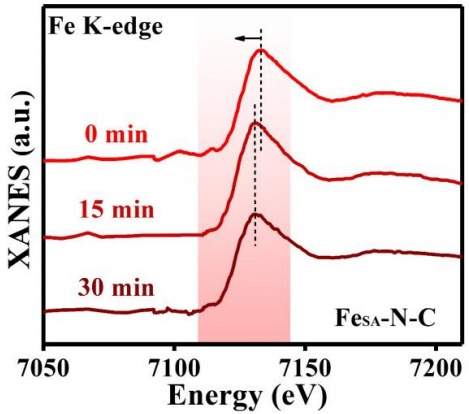
Assessment protocol

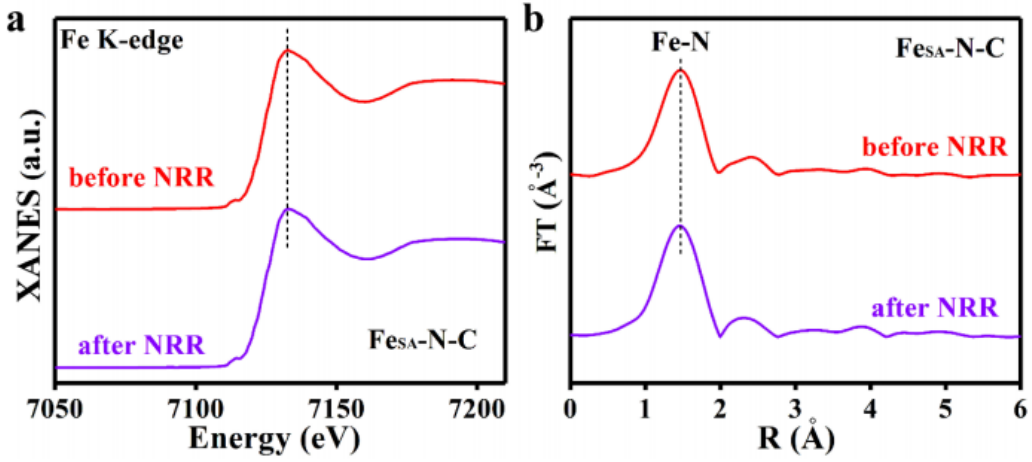


In-situ method in NRR

In-situ XAS







- Potentiostatic testing was carried out at 0 V vs. RHE and the XANES results of the Fe K-edge were collected at different times.
- Once the reaction proceeds, the peak shifted from 7133 eV to a lower energy of 7131 eV after 15 min, suggesting a decreased valence state of Fe.
- During the NRR process, N_2 molecules are fixed to bond with Fe sites by donating electrons to the unoccupied d orbitals of Fe.

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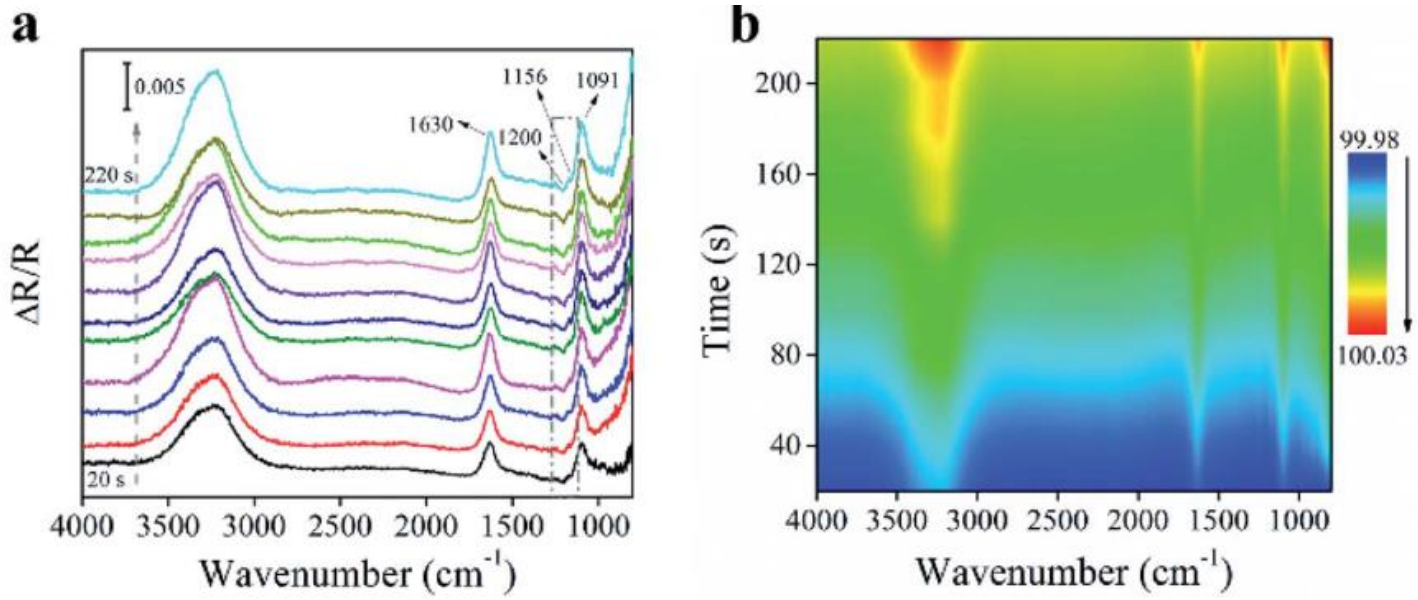
In-situ method in NRR

In-situ FTIR



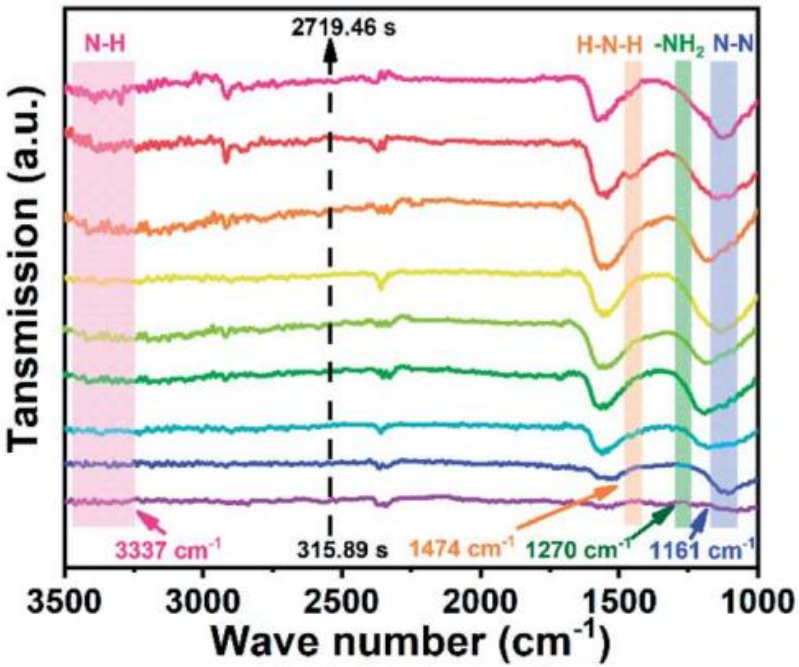
- In situ electrochemical FTIR experiments are also conducted to elucidate the reaction mechanism of the NRR over the NiFe–MoS_2 NCs at - 0.3 V vs. RHE in 0.1 M Na_2SO_4 solution.

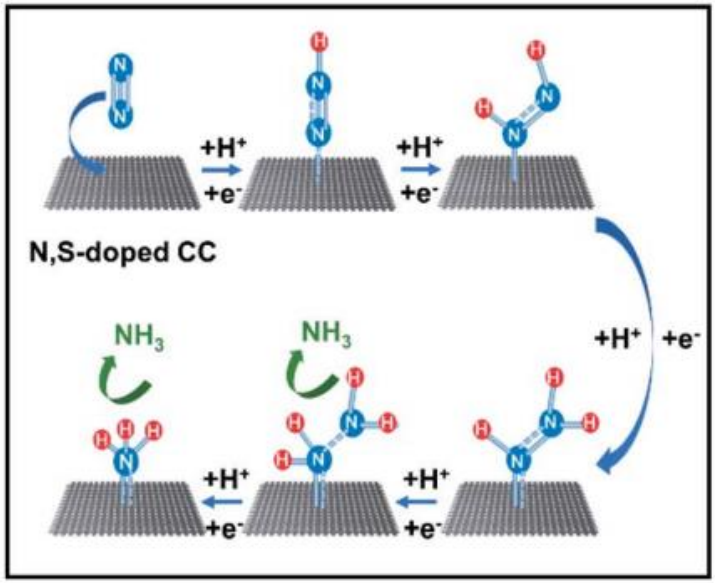
- Two negative-going peaks located at 1200 and 1156 cm^{-1} are observed, which are attributed to the **N–H** stretching and **–NH_2** rocking vibration mode of the symmetrically coordinated NH_3.

J. Mater. Chem. A, 2020, 8, 7339–7349

In-situ method in NRR

In-situ FTIR

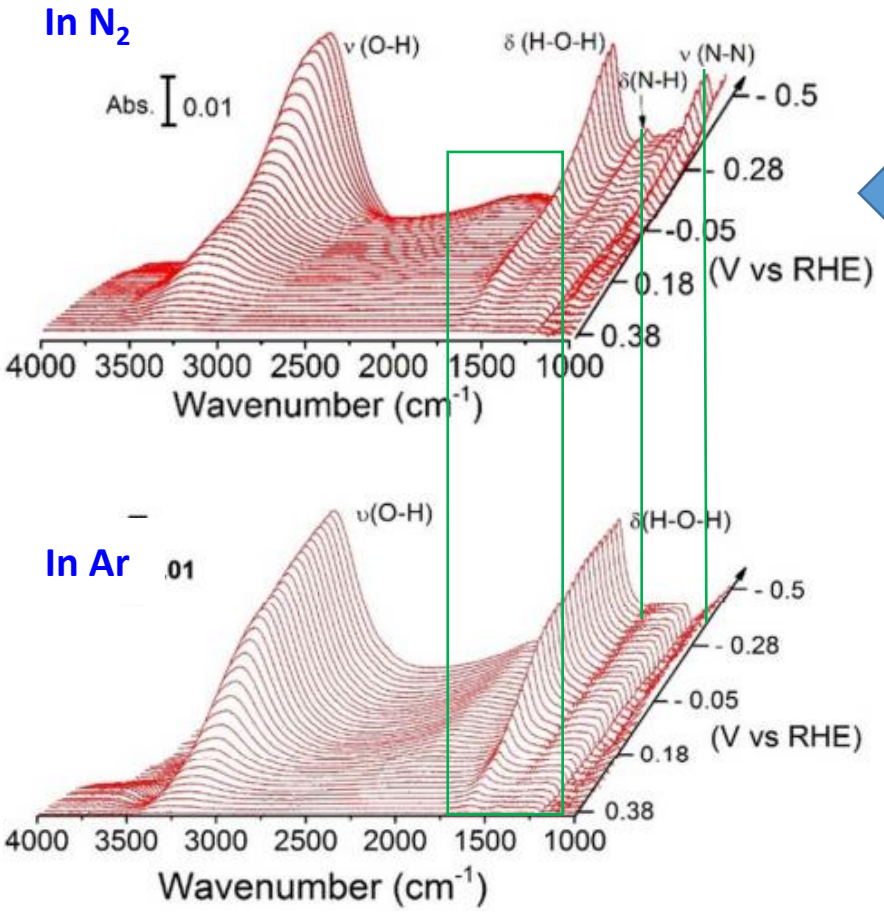




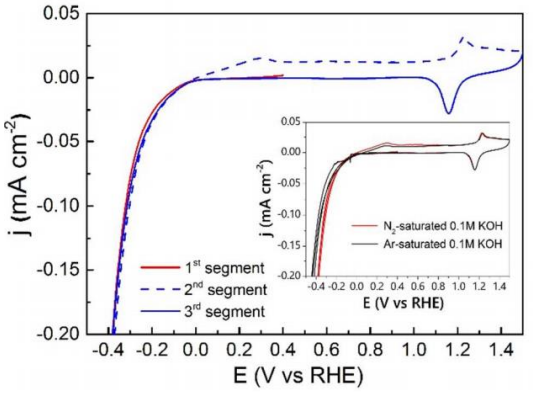
- The absorption at 1161 cm^{-1} is assigned to the N–N stretching, the intensity of which increased with increasing reaction time.
- Simultaneously, three weak absorptions at 1270, 1474, and 3337 cm^{-1} were observed, which are attributed to -NH_2 wagging, H–N–H bending, and N–H stretching of H–N–H bending, respectively.

In-situ method in NRR

In-situ FTIR



In situ

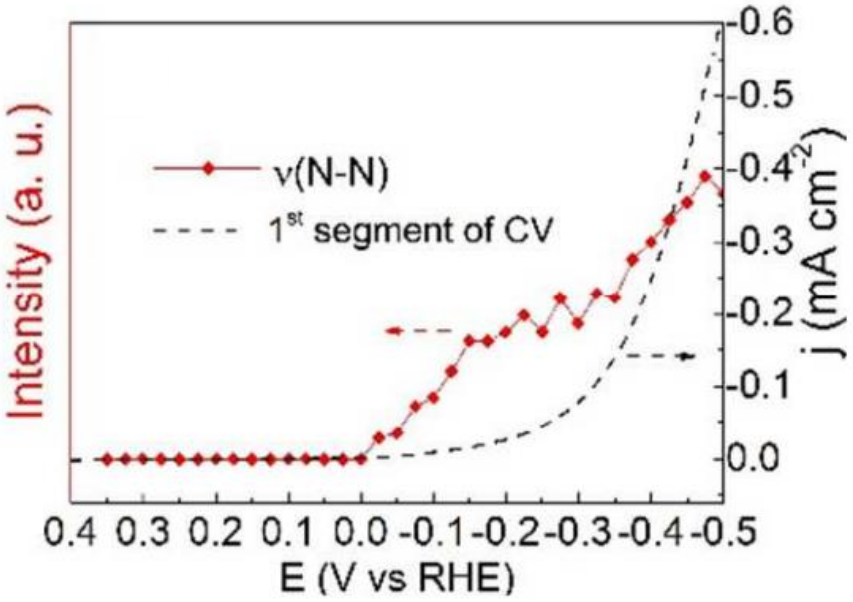


J. Am. Chem. Soc. 2018, 140, 4, 1496–1501

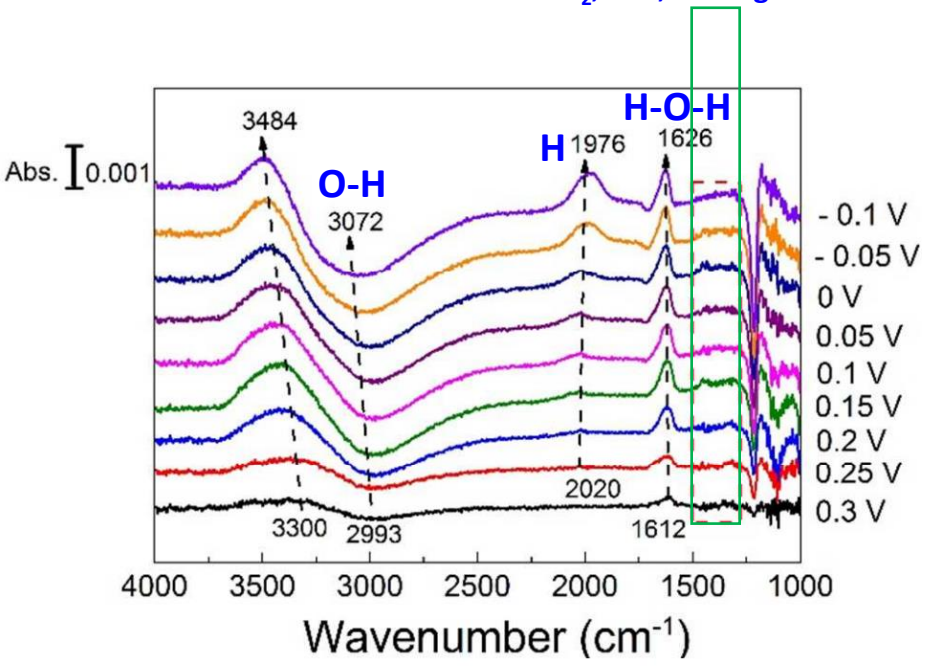
- The FTIR spectra collected in the 1st scan from 0.4 V to -0.5 V.
- A broad positive band at ~ 2088 cm^{-1} that appeared with the reduction current in figure attributes to the adsorbed H atoms.
- Three weak bands at 1450 cm^{-1}, 1298 cm^{-1} and 1109 cm^{-1} attribute to the H-N-H bending, -NH_2 wagging and N-N stretching of adsorbed N_2H_y species, respectively.

In-situ method in NRR

In-situ FTIR



No -NH_2, N-H, N-N signal on Pt film



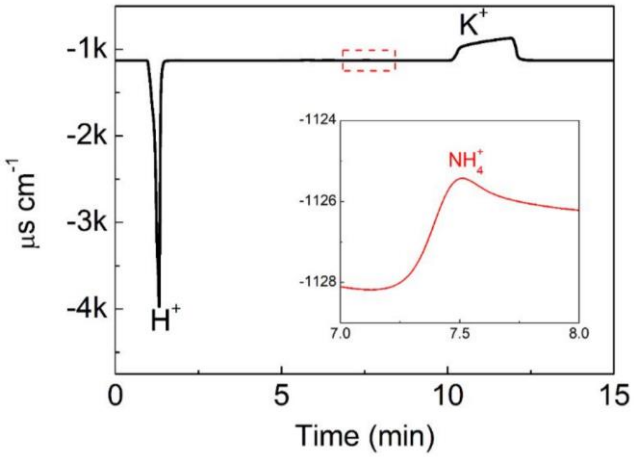
J. Am. Chem. Soc. 2018, 140, 4, 1496–1501

- The potential dependence of the strongest band among the three (N-N stretching at 1109 cm^{-1}) and the corresponding 1st segment of the CV (black dashed line).
- The band started to appear at potentials below 0 V and increased with potential decreasing, accompanying with the increase of the reduction current in the 1st segment of the CV.
- The results of FTIR on Pt film can be due to the low faradic efficiency of NRR on Pt surfaces compared with HER resulting in a much lower signal from N_2H_y if there is any. (right data)

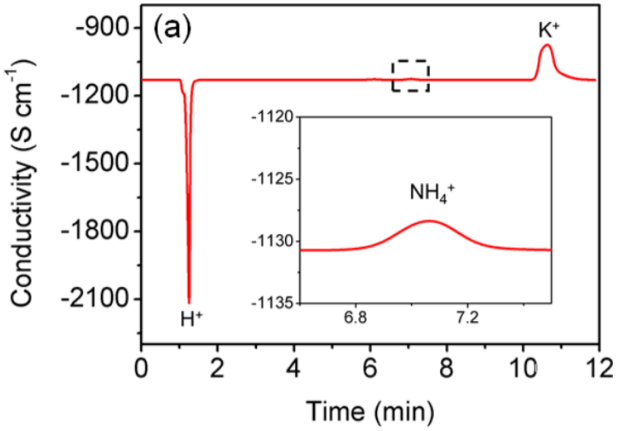
Detecting of Ammonia

Ion chromatography (IC)

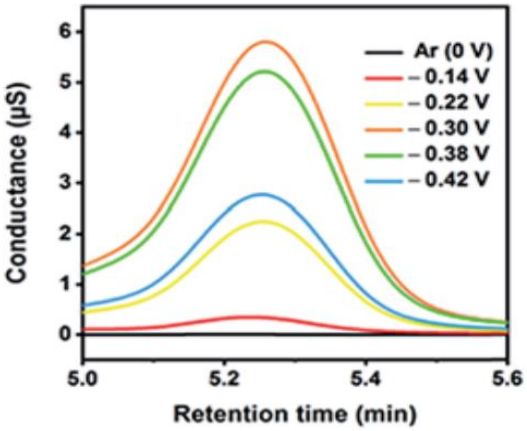
Nature Comm. (2019), 10:4380



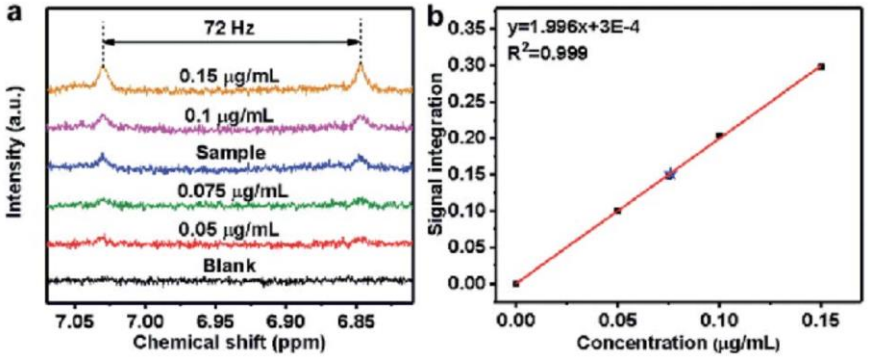
J. Am. Chem. Soc. 2019, 141, 14976−14980



J. Mater. Chem. A, 2019, 7, 19977–19983



Nuclear magnetic resonance (NMR)

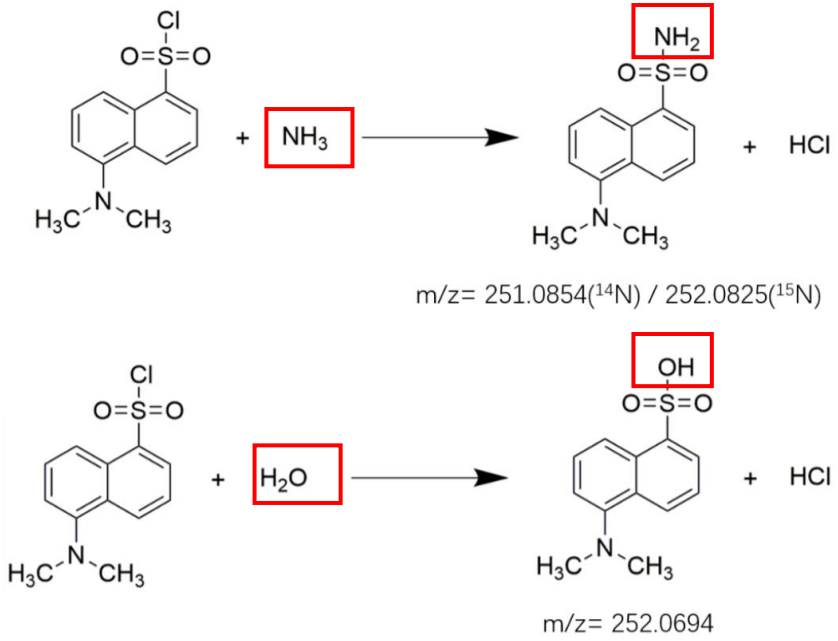


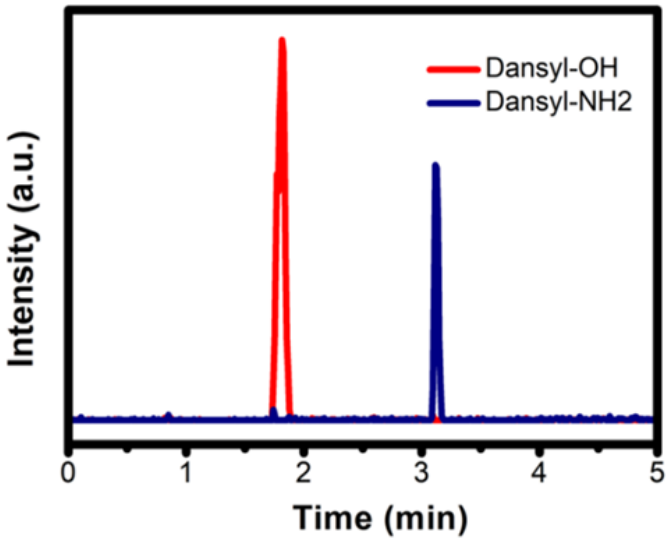
J. Mater. Chem. A, 2019, 7, 26371–26377 | 26373

- Condition : with water suppression Bruker Avance3 400 MHz
- $^{15}NH_4Cl$ solutions were prepared with 0.1 M HCl

Detecting of Ammonia

Liquid Chromatography-Mass Spectrometry (LC-MS)



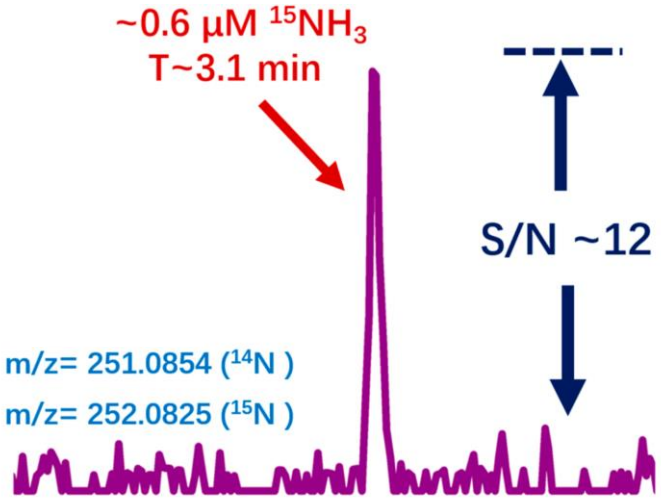


- Despite their similar masses, the initial UPLC step separates the DNS-OH and DNS-NH_3 products by eluting them from the column at substantially different times. The mass-selected chromatograms for **DNS-OH and DNS-NH_3** displayed two distinct peaks (1.8 and 3.1 min, respectively).

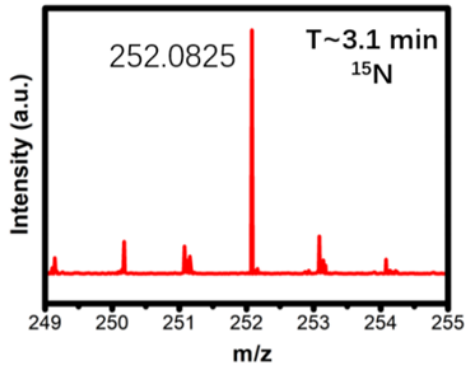
ACS Energy Lett. 2020, 5, 1532−1536

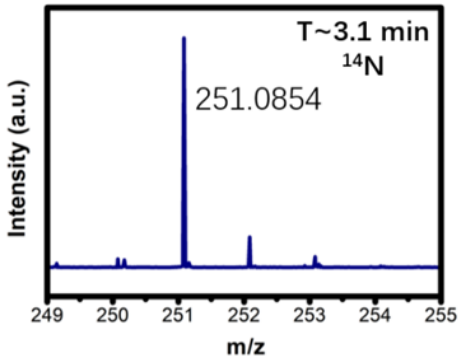
Detecting of Ammonia

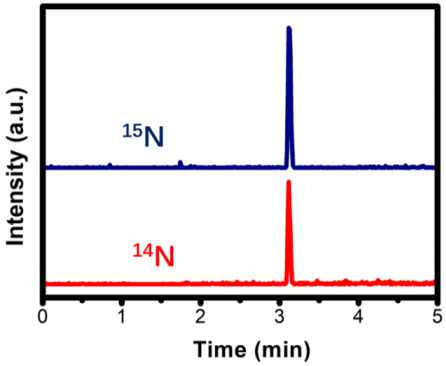
Liquid Chromatography-Mass Spectrometry (LC-MS)



- Mass-selected chromatogram for a 0.6 μM $^{15}NH_3$ sample derivatized by dansyl chloride, demonstrating a high S/N ratio of ~12 and a short elution time of ~3.1 min.
- The presence of ammonia and its heavy isotopologue can be distinguished and quantified by their MS peak areas at m/z= 251.0854 (^{14}N) and m/z=252.0825 (^{15}N).
- Dansyl chloride is widely used in derivatization of amino acids for fluorescence and mass spectrometry analysis.



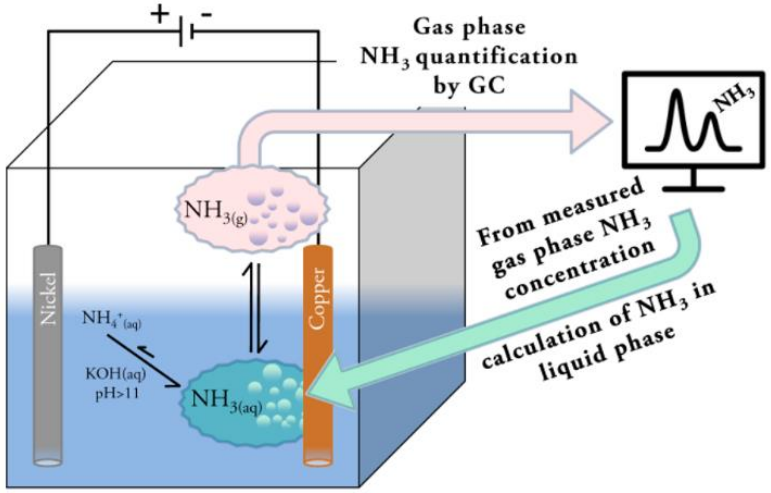




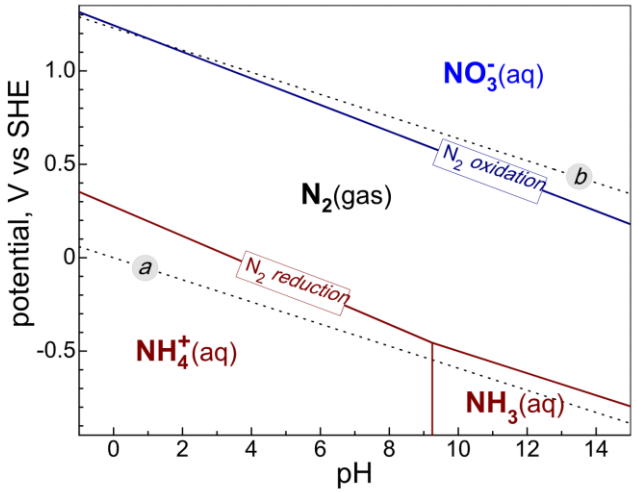
ACS Energy Lett. 2020, 5, 1532−1536

Detecting of Ammonia

Gas Chromatography (GC)



Chen et al., Science 360, eaar6611 (2018)



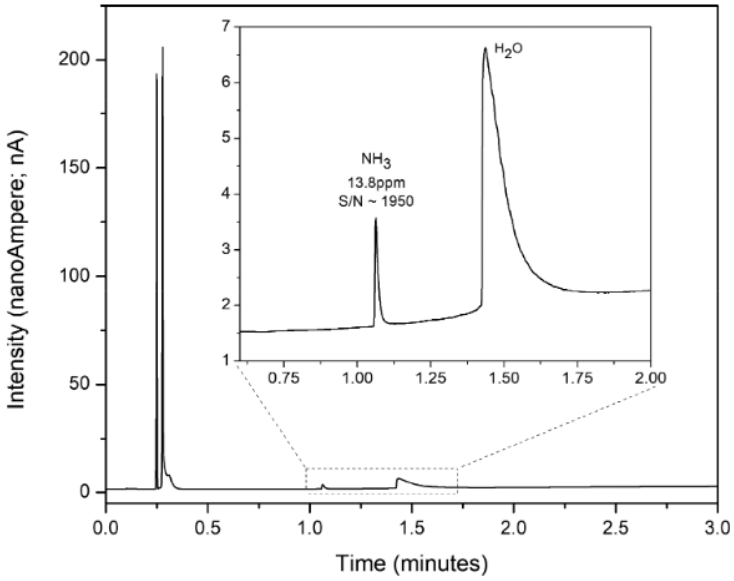
$$NH_{3(g)} \rightleftharpoons NH_{3(aq)} \underset{pH > 11}{\overset{H_2O}{\rightleftharpoons}} NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

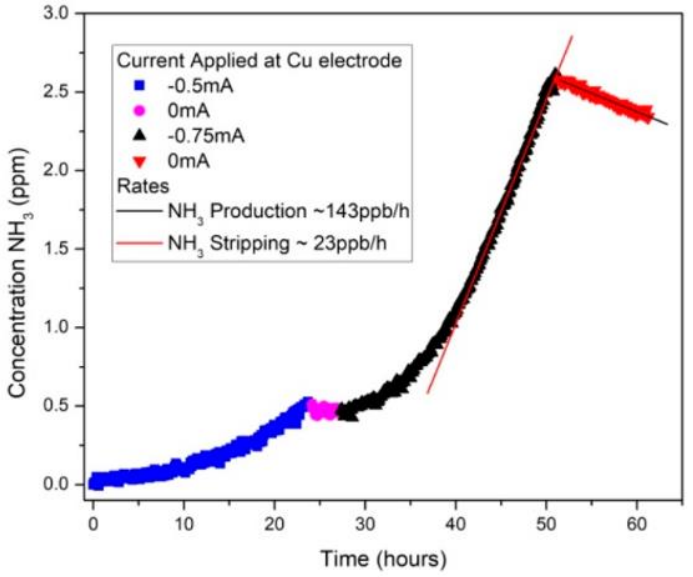
- Relevant equilibrium to be considered is between ammonia in the gas phase ($NH_{3(g)}$) and ammonia as dissolved gas ($NH_{3(aq)}$)
- Electrochemcial ammonia generation device and equilibrium between dissolved ammonia ($NH_{3(aq)}$) and gas-phase ammonia ($NH_{3(g)}$) provided pH is basic.
- Gas-phase ammonia concentration is addressed directly by GC, while dissolved ammonia concentration is calculated from gas-phase ammonia concentration.
- When pH is greater than 11, the equilibrium is fully shifted to the left side of the equation.

ACS Energy Lett. 2020, 5, 3773−3777

Detecting of Ammonia

Gas Chromatography (GC)





- Permanent gases are eluted at 0.25 min, ammonia at 1.1 min, and water at 1.3 min.
- This peak increases in time, indicating ammonia is generated electrocatalytically in solution and it quickly equilibrates with its gaseous head space as the high pH ensures that NH_3 is present in solution rather than NH^{4+}.
- The ammonia production rate in the gas phase reahed about 143 ppb/h.
- When the current is stopped while maintaining the nitrogen carrier gas flow active, NH_3 concentration slowly decrease.

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