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# A rotating ring disc electrode study of photo(electro)catalyst for nitrogen fixation

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There are numerous reports of photo(electro)catalysts demonstrating activity for nitrogen reduction to ammonia and a few reports of photo(electro)catalysts demonstrating activity for nitrogen oxidation to nitric acid. However, progress in advancing solar-to-fertilizer applications is slow, due in part to the pace of catalyst screening. Most evaluations of photo(electro)catalysts activity occur using batch reactors. This is because common product analyses require accumulation of ammonia or nitric acid in the reactor to overcome instrument detection limits. The primary aim here is to examine the use of an electroanalytical method, rotating ring disk electrode voltammetry (RRDE), to detect ammonia produced by a nitrogen fixing photo(electro)catalyst. To examine the potential for RRDE, we investigated a photo(electro)catalyst known to reduce nitrogen to ammonia (titania), while varying the applied electrochemical potential and degree of illumination on the disk. We show that the observed ammonia oxidation at the ring electrode corresponds strongly with ammonia measurements obtained from the bulk electrolyte. Indicating that RRDE may be effective for catalyst screening. The chief limitation of this approach is the need for an alkaline electrolyte. In addition, this approach does not rule out the presence of adventitious ammonia.

## 1. Introduction

Ammonia is one of the most important commodity chemicals in today's chemical industry, representing a key feedstock for synthesis of nitrogen based fuels and fertilizers.[1,2] The standard method of producing ammonia at an industrial scale is through the Haber–Bosch Process.[3] The process is impressive, producing more than 140 million tonnes of ammonia per year with a thermochemical efficiency of 70%.[4] However, the scale of the process leads to a massive energy consumption of 2.5 extrajoules per year. The hydrogen feedstock required for this process also has a carbon footprint of 340 million tonnes of $CO_2$ per year, making the Haber–Bosch

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process detrimental to the environment.[5] To circumvent these problems, enormous research efforts have been directed toward alternative catalytic pathways which activate $N_2$ under milder conditions.[3,6] One of the alternatives is photocatalytic nitrogen fixation.[7–10] This approach is ideal, as it enables the synthesis of ammonia from abundant feedstock (dinitrogen and water) using only renewable energy (sun).

Examining the activity of a photocatalyst requires information regarding the rate of ammonia production. Since most photo(electro)catalyst experiments use water as the proton source, ammonia is produced in the aqueous phase as dissolved ammonia or ammonium. Common product analysis of ammonia and ammonium is largely limited to colorimetric methods (*e.g.* indophenol blue method and Nesslers' reagent), ionic chromatography, and NMR spectroscopy.[11,12] These methods are well-established, however periodic replacement of chemical reagents, lamps, and ion-exchange columns make the measurement methods complicated and time consuming. Therefore, the development of alternative techniques to rapidly detect ammonia is of growing importance for catalyst development.

Electroanalytical methods are another under-explored approach whereby ammonia is detectable using current and voltage responses. Rotating ring disk electrode (RRDE) voltammetry is one example of an electroanalytical approach which can detect products *in situ*. Rotating ring-disk electrode voltammetry is commonly used to evaluate products of the oxygen evolution and oxygen reduction reactions; however, it has yet to be thoroughly examined for use in ammonia detection.[13,14] In the RRDE experimental set up, a shaft houses a double working electrode. A non-conductive barrier separates the disk electrode from the ring electrode. Typically, evaluation of a photo(electro)catalyst occurs through depositing the catalyst on the center disk electrode. There, the disk can be illuminated to examine photochemical reactions and/or an applied potential can induce electrochemical reactions on the catalyst. During voltammetry experiments, the system is rotated to induce laminar flow to the disk. Due to the hydrodynamics that arise during the rotation, products formed at the disk are transported to the outer ring. Through polarizing the ring at a desired potential, the products can be detected if the product can be electrochemically reacted (reduced or oxidized). Ammonia electro-oxidation is well established for many noble metals,[15] and thus exploring product analysis through quantifying the rate of ammonia oxidation (current) could allow for more rapid catalyst screening.

Here we investigate the use of rotating ring disk voltammetry under illumination and in the dark, to evaluate the photo(electro)chemical nitrogen fixing activity. We use a platinum ring electrode to monitor ammonia produced on the disk. We also examine the products measured in the bulk cell and compare that with the observed ammonia oxidation rate. Finally, through tuning the applied potential of the disk (reducing and oxidizing) we aim to evaluate the reaction mechanism by which ammonia is formed.

# 2. Method

## 2.1. Catalyst preparation

A commercial rutile titanium dioxide was purchased by US Research Nanomaterials Inc. The resulting suspension was centrifuged at 13 000 rpm five times to remove the residue ethanol on the surface of the catalyst. The ink was prepared by mixing 10 mg catalyst ($TiO_2$) with 40 μL of 5 wt% of Nafion solution (Sigma Aldrich) which was dissolved into 1 mL DI water and 1 mL of isopropanol. After ultrasonification for 1 h, 20 μL of the well-dispersed ink was coated onto the surface of a glassy carbon electrode (GCE). This allowed for the formation of photo(electro)catalyst films on the surface of GCE. Dispersed films were dried under air as the shaft was rotated at 1000 rpm.

### 2.2. Rotating ring disk voltammetry procedure

The characterization of nitrogen reduction activity of the catalysts was conducted with the rotating ring disk electrode system (Pine Research). A 300 W xenon lamp was positioned under the quartz reactor normal to the catalyst surface to provide illumination (Fig. 1a). All electrochemistry was conducted in 0.1 M of KOH. The electrolyte was continuously sparged with nitrogen or argon gas (control). The gas was washed prior to entering the electrochemical cell through an acid trap. This aided in removing possible contamination from within the gas tank. A potentiostat (Biologic) was used to apply a fixed potential to the disc, which varied from 1.9 $V_{RHE}$ to $-0.6$ $V_{RHE}$. Prior to the experiments, both the disc and platinum ring were clean through scanning the potential from $-1.3$ V to 1.3 V at a scan rate of 200 mV $s^{-1}$ for 50 cycles. All cleaning was conducted under an argon-gas environment. The catalyst was conditioned under a fixed potential for 1 h before testing, while the shaft was rotated at a rotating speed of 1000 rpm. This was completed for the nitrogen-light (photo-active), nitrogen-dark (control), and argon-light (control) conditions.

The platinum ring is cleaned through scanning from $-1.3$ V to 1.3 V in a new electrolyte. Ammonia oxidation experiments were conducted on a platinum ring over a potential window of 0.05 $V_{RHE}$ to 0.85 $V_{RHE}$ under nitrogen light and dark and argon light, to detect free ammonia. Linear sweep voltammetry is conducted under a rotating ring disk electrode system at a scan rate of 5 mV $s^{-1}$ under a rotation speed of 1000 rpm.

### 2.3. Indophenol blue method

A comparison using the indophenol blue method is conducted through extracting 1 mL of solution after 1 h potential bias and illumination. In detail, 1 mL of

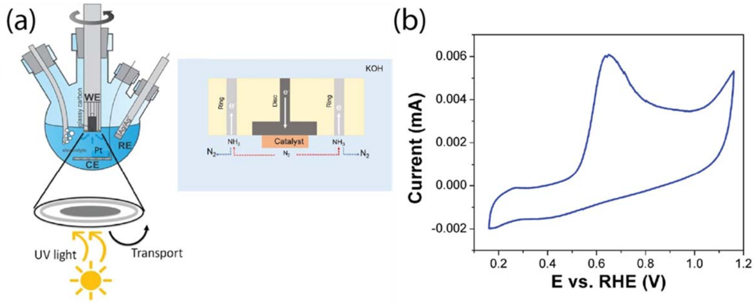

Fig. 1 (a) Schematic of RRDE ammonia measurement equipment where the catalyst is supported on the disk and the ring detects ammonia. (b) Cyclic voltammogram demonstrating ammonia oxidation peak with known ammonia in electrolyte.

solution was removed from the reaction vessel. Then 1 mL of 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, followed by addition of 1 mL of 0.05 M NaClO and 0.2 mL of an aqueous solution of 1 wt% $C_5FeN_6Na_2O$ (sodium nitroferricyanide). After 2 h at room temperature, the absorption spectrum was measured using an ultraviolet-visible spectrophotometer (Avantes). The formation of indophenol blue was determined using the absorbance at a wavelength of 655 nm.[16]

## 3. Results and discussion

Here, our general goal is to use the ammonia oxidation reaction to detect ammonia formed by a nitrogen fixing photo(electro)catalyst. By ascribing the ring current to the ammonia oxidation reaction, then Faraday's law can allow for the determination of ammonia concentration. Ammonia oxidation on platinum has been well studied, and the reaction is known to be structure sensitive, with ammonia oxidation occurring on Pt(100) sites. Hydroxide is important for the ammonia oxidation reaction process, as it is critical for each immediate process (eqn (1)–(4)).[17–19]

$$NH_3 + OH^- \rightarrow NH_{2,ad} + H_2O + e^- \tag{1}$$

$$NH_{2,ad} + OH^- \rightarrow NH_{ad} + H_2O + e^- \tag{2}$$

$$NH_{ad} + OH^- \rightarrow N_{ad} + H_2O + e^- \tag{3}$$

$$N_{ad} \rightarrow N_2 \tag{4}$$

However, hydroxide can also strongly bind to platinum under some potentials, and can also inhibit ammonia oxidation,[16,20] effectively blocking ammonia from the ring. For this reason, we chose to use an alkaline electrolyte (0.1 M KOH) for all experiments; however, keeping below 0.8 V *vs.* RHE in order to minimize this effect.

On the disk, we deposited our photo(electro)catalyst. Alkaline electrolytes are commonly used in electrocatalytic applications, especially when suppression of the hydrogen evolution reaction is desired, however, many photocatalysts operate in near neutral pH electrolytes or in DI water. Thus, we note that all experiments here are under elevated pH conditions (*e.g.* $pH = 14$). Titania can also react with KOH, however, during the short duration of the experiment and the dilute base we did not see instability issues with the titania; however, this should be investigated further.

The nitrogen reduction reaction is the primary reaction pathway proposed for ammonia production from the photo(electro)catalyst and ambient pressure electrocatalyst (eqn (5)).

$$N_{2(g)} + 6H_{aq}^{\ +} + 6e^- \rightarrow 2NH_{3(g)} \tag{5}$$

Here, the nitrogen reduction occurs through an associative mechanism to form ammonia directly at the conduction edge. However, on a photocatalyst, where electrons and holes are present, some have speculated that nitrogen fixation may actually occur through an oxidative reaction (hole-driven process) at the conduction band (eqn (6)).[7] Detection of ammonia then may be due to nitrate reducing to ammonia at the valence band (eqn (7)).

$$N_{2(g)} + 12OH^- \rightarrow 2NO_3^- + 6H_2O + 10e^- \quad (6)$$

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O \quad (7)$$

Due to this uncertainty around whether nitrogen is fixed through an oxidative or reductive pathway, here we examined both, through biasing the disk at both reducing and oxidizing potentials.

We start out by examining ammonia oxidation on the ring through a series of control experiments with the rutile titania photocatalyst. During the control experiments, known concentrations of ammonia were added to the supporting electrolyte. Specifically, 0.1 M of $NH_4Cl$ standard solution was added to the supporting electrolyte and the ring potential was swept from 0.05 $V_{RHE}$ to 0.85 $V_{RHE}$ (Fig. 1b). The ammonia oxidation peak on the platinum ring should occur around 0.7 $V_{RHE}$ in alkaline solution.[21,22] This peak was clearly observed in the CV, and this peak location was used as the reference for the photo(electro)catalytic nitrogen fixation experiments.

After identifying the peak location for ammonia oxidation on the ring electrode, we next examined the titania catalyst under light conditions in nitrogen gas (Fig. 2a), dark conditions with nitrogen gas (Fig. 2b), and light conditions with argon gas (Fig. 2c). We started each experiment by illuminating the photo(electro) catalyst with a 300 W xenon lamp and under a bias for 1 h. We examined reducing potentials (*e.g.* −0.1 and −0.6 $V_{RHE}$), oxidizing potential (*e.g.* 1.9 $V_{RHE}$) and open circuit conditions (*e.g.* photocatalysis). As described above, the need to examine various biased conditions was used to determine if ammonia formation occurred through an oxidative or reductive pathway on the photo(electro)catalyst. Under each condition we then perform cyclic voltammetry between 0.05 $V_{RHE}$ to 0.85 $V_{RHE}$ on the platinum ring electrode to examine the ammonia oxidation peak.

For the experiment with nitrogen gas under illumination, the ammonia oxidation peak current increased as the disk applied potential became more negative (*e.g.*, from −0.1 to −0.6 V *vs.* RHE) (Fig. 2a – red and green dotted lines). We should note that the ammonia oxidation peak was not distinguishable under open circuit conditions, indicating that no ammonia was detected using titania as a photocatalyst. However, by applying an external bias to the photocatalyst, the catalyst is able to operate as a photo(electro)catalyst. This also allowed us to

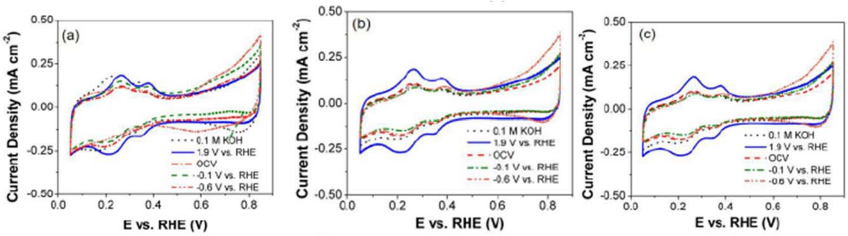

Fig. 2 Cyclic voltammetry of rutile $TiO_2$ under (a) $N_2$ and light, (b) $N_2$ and darkness (c) Ar and light, with various applied potentials.

control the position of the conduction band. The increasing ammonia oxidation current with an increased bias, indicates that the nitrogen reduction reaction may be able to take place on the titania photocatalyst. For the $N_2$ dark and argon light conditions (controls), a small increase in current was observed near the ammonia oxidation potential as the reductive potential of the disk was decreased (Fig. 2b and c). However, it was unclear if this was an indication of contamination (adventitious ammonia) or if this was due to increased hydroxide adsorption, as the hydroxide adsorption potential region also resulted in an increase in current. Despite some degree of contamination, the ammonia oxidation peak of the rutile titania was ∼20% higher, indicting that the catalyst may have some photoactivity.

After examining the ammonia production and ammonia oxidation under reducing potentials, we examined the oxidizing potential (*e.g.* 1.9 V *vs.* RHE) through biasing the catalyst in a positive direction. Here, our primary aim was to investigate the hypothesis that photogenerated holes can interact with nitrogen on titania producing fixed nitrogen. However, in all tests with rutile titania under oxidizing conditions, we saw no ammonia oxidation current. This result indicates that ammonia production may only be possible through an electron mediated process rather than a hole driven process (Fig. 2b and c).

Next, we aimed to correlate the ammonia oxidation rate with the measured ammonia production. To do this, we ran identical conditions as for the rotating ring disk electrochemistry; however, instead of measuring the ammonia oxidation at the ring, we collected 1 mL samples for each experiment with and without biasing to measure the ammonia concentration using the conventional colorimetric method (*e.g.* indophenol blue).

To accomplish this, we ran the RRDE with known concentrations of ammonium chloride and measured the peak current at the ammonia oxidation peak (Fig. 3a and b). Due to the non-linear relationship between oxidizing current and ammonia concentration we created two calibration curves for the low and high concentrations. The ammonia current correlates to the ammonia concentration in the RRDE tests, calculated by the oxidation current subtracted from the blank test where no ammonia is added inside the solution. When making these calibration curves, there is a clear linear relationship between ammonia oxidation current and ammonia concentration, with a $R^2$ value of 0.98.

In addition to developing calibration curves which converted current density to ammonia concentration, we also created calibration curves for the colorimetric methods (Fig. 3d and e). Here, ammonium in the supporting electrolyte is mixed with the indophenol reagents, and the absorbance of the resulting mixture is used to indicate the concentration of ammonia in the mixture. Similarly, the ammonia absorbance correlates to ammonia concentration in the indophenol blue method, calculated by absorbance value subtracted from the blank test where no ammonia is added inside the sample. The conversion of current density is based on the geometrical area of platinum ring (0.11 $cm^2$). The limit of detection (LOD) for rotating ring disk voltammetry is 2 μM and the LOD for indophenol blue method is 2.01 μM.

Based on the above two ammonia quantification methods, rutile phase titania showed similar ammonia production when measured using the rotating ring disc voltammetry in comparison to the indophenol blue method (Fig. 4a and b). However, the concentration under the best conditions (*e.g.* $-0.6$ V $N_2$, light), were still near the detection limit of the UV-vis measurement techniques. This

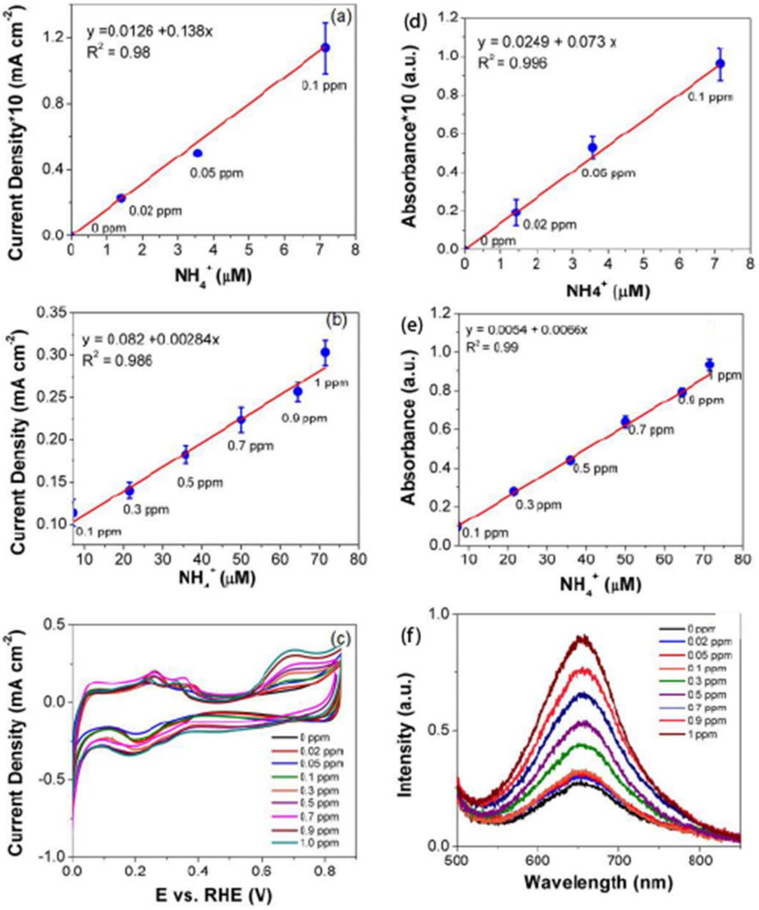

**Fig. 3** Calibration curve of rotating ring disc voltammetry through electrochemical ammonia oxidation *via* Pt ring: (a) 0–0.1 ppm, (b) 0.1–1 ppm, and (c) cyclic voltammetry. Calibration curve of indophenol blue ammonia measurement methods: (d) 0–0.1 ppm, (e) 0.1–1 ppm, and (f) absorbance curves.

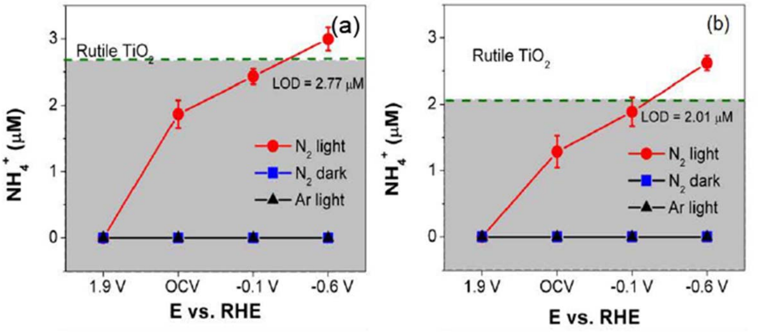

**Fig. 4** (a) Calibrated ammonia concentration of rutile titania using the rotating ring disc voltammetry under electricity biasing at $-0.6\ V_{RHE}$, (b) calibrated ammonia concentration of rutile titania using the indophenol blue method under electricity biasing at $-0.6\ V_{RHE}$.

indicates that although the measurement technique was measuring ammonia, the catalyst is not highly active. It should be noted that this technique does not rule out adventitious sources of contamination. This means that some of the ammonia oxidation and measured ammonia could be due to trace amounts of ammonia found in the catalyst or glassware. Despite this limitation, the potential for using RRDE may be effective for evaluating a highly active catalyst, as the approach provided high consistency between batch measurements and the electroanalytical methods.

## 4. Conclusions

In summary, our aim was to develop a one-step electrochemical analytical ammonia measurement method which aims to reduce the time and expense of current state-of-the-art ammonia measurement methods (*e.g.* colorimetric method, ionic chromatography). Our results indicate that RRDE voltammetry provides a nearly identical ammonia measurement for a common photocatalyst titania. However, we also noted several limitations of this approach. First, ammonia oxidation on a platinum ring electrode only occurs under alkaline conditions. This contrasts with the favorable environment of nitrogen fixation (neutral environments). It would be ideal to find an electrolyte which could not only activate ammonia oxidation but also maintain the favorable environment of nitrogen fixation. Furthermore, it is known that hydroxide ions are easily poisoned on the platinum ring.[20,23] Hence, while applying a fixed potential on the disc and simultaneously conducting cyclic voltammetry on the platinum ring, the ammonia oxidation current will be suppressed if no proper cleaning takes place. Finally, this approach may only be viable for highly active catalysts which produce significantly more ammonia than the weight of the catalyst, as recommended in a recent review.[24] This is because the method is not able to eliminate contamination, and thus for this technique to be helpful, the contamination must be minimized with respect to the total yield.

## Conflicts of interest

There are no conflicts to declare.

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