

Sustainable nitrate production out of thin air:

The photocatalytic oxidation of molecular nitrogen

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Abstract: Novel processes for the sustainable production of fertilizers are highly sought after to combat climate change. Herein, we demonstrate that by irradiating with strong UVA-light, TiO_2 is able to photocatalytically oxidize molecular nitrogen in the gas phase under ambient conditions to NO_x and nitrate. The reaction produces predominantly nitrogen dioxide with a high selectivity of up to 93% which could be captured afterwards to produce nitric acid or nitrates and used as sustainable (solar) fertilizer.

Keywords: Photocatalysis, titanium dioxide, nitrogen fixation, sustainable production, solar fertilizer.

While molecular nitrogen (N_2) is very abundant and makes up the majority of our atmosphere, only a relatively small part of the nitrogen on Earth is fixed in the form of other compounds.¹ The reason for this is the very stable N-N triple bond (942 kJ mol^{-1} bond energy) which is exceptionally difficult to break. Yet, fixed nitrogen compounds such as ammonia, amines, nitrates are needed in many chemical production processes. They also play a major role in plant growth and in nutrition in the form of amino acids and proteins.²⁻⁴ Ammonia- and nitrate-based fertilizers are therefore essential for our industrialized agriculture and in consequence, to keep humanity fed.³

At the beginning of the 20th century, the exponentially growing needs of agriculture and industry for fixed nitrogen could no longer be met by natural sources, sparking the quest for a synthetic process.^{5,6} An extraordinary effort of scientists and engineers eventually resulted in the development of the Haber-Bosch ammonia production process which is still the industrial standard today.⁶ However, this process alone is responsible for 1-2 % of the worldwide CO_2 emissions as the large amount of hydrogen gas consumed is produced almost exclusively from fossil sources. The emission reductions required to combat climate change consequently demand greener alternatives, particularly as the demand for fixed nitrogen continues to grow.⁷ In addition to water electrolysis to supply the hydrogen for Haber-Bosch, novel sustainable processes are highly sought after. And so, the quest for artificial nitrogen fixation processes has once again begun and received renewed attention in the last years.⁸⁻¹⁰

In addition to plasma- and electrochemical methods which can be powered sustainably by renewable electricity, photocatalysis also presents an option to utilize sunlight directly.⁸ The photocatalytic fixation of nitrogen to ammonia has already been observed as early as 1941¹¹ but only studied in more detail three decades later by Schrauzer and Guth.^{12,13} This process also occurs naturally over certain minerals and may thereby even be responsible for a significant share of the nitrogen fixed on Earth.¹⁴

Next to ammonia and urea, other important nitrogen compounds are nitric acid and nitrates. These are currently produced in the Ostwald process, in which ammonia is oxidized by oxygen to nitrogen oxides. This very exothermic process ($-225.5 \text{ kJ mol}_{\text{NO}}^{-1}$)¹⁵ consumes a significant share of the worldwide ammonia production and converts the majority of the ammonia energy content to heat.⁷

As this presents a major energetic detour, the direct formation of nitrate from molecular nitrogen and oxygen could therefore be an attractive, resource- and energy-saving alternative. In fact, the first industrial process for nitrogen fixation, the Birkeland-Eyde process, was based on the oxidation of air to NO_x in an electrical discharge plasma.⁹ Interestingly, photocatalysis can also be used to oxidize molecular nitrogen to nitrogen oxides (NO_x) and eventually, nitrate. There are relatively few but quite promising reports observing this reaction in illuminated aqueous photocatalyst suspensions.^{13,16–18}

A major challenge for photocatalytic conversion of N₂ lies in the fact that its solubility in water is rather poor (approx. 0.6 mM at room temperature)¹⁹ which may result in significant mass transfer limitations. It also leads to an unfavourable high H₂O/N₂ ratio which may present a problem since water effectively competes for the photogenerated electrons and holes. There is also the issue that the nitrate accumulating during the reaction is a strong electron scavenger which may lead to parasitic reactions and limit the achievable concentrations.²⁰

The easiest solution would be to just work in the gas phase. Here, the ratio of the reactants N₂, O₂ and possibly H₂O can be freely controlled and mass-transfer limitations effectively overcome. When formed as nitrogen oxides, the products can also be easily removed from the system and captured in a water absorber column to directly yield nitric acid. Since we could not find any reports in the literature about the photocatalytic oxidation of molecular nitrogen in the gas phase, we conducted this proof-of-principle study on the topic.

For the experiments we used a setup originally designed for analysing the photocatalytic oxidation of nitrogen oxides for air remediation purposes (cf. ISO 22197-1).^{21,22} Here, we just used pure (NO_x-free) synthetic air as the test gas, which continuously flowed over the catalyst, and analysed the NO_x gases formed during the photocatalytic reaction induced by a strong UVA-LED light source. As catalyst, we employed the well-known Evonik Aeroxide P25, a titania material composed of both the anatase and rutile crystal phases.²³

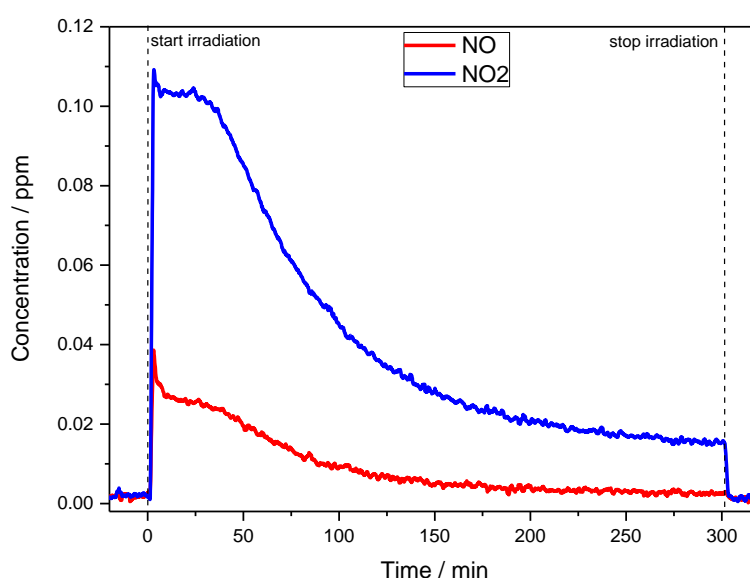


Figure 1: Exemplary reaction profile for the photocatalytic oxidation of molecular nitrogen with release of NO (red) and NO₂ (blue) into the gas phase. Conditions: P25 photocatalyst, 1 L min⁻¹ synthetic air flow rate, 50 % r.h., 250 mW cm⁻² irradiance, 50 cm² irradiated area.

The first results showed that the formation of NO_x can be observed immediately upon switching on the light source (Figure 1). Most of the NO_x detected is in the form of NO₂ while NO makes up about

15 %. It is well known from research into photocatalytic NO_x abatement that TiO₂ can easily oxidize NO to NO₂ under the conditions employed here^{24,25} so an abundance of NO₂ is expected even if the primarily formed product is NO. There seems to be some form of initial catalyst deactivation present as from the time-course of the experiments it is evident that the reaction rate decreases with prolonged time on stream but later stabilizes on a lower level after about 3-5 hours.

Unless carefully prepared and handled exclusively under inert conditions the catalyst materials will likely already have some nitrate on them both from prior photocatalytic oxidation of NO_x and potentially N₂ during storage and handling as well as residues from their production. As nitrate can be easily converted to NO_x both by reduction and oxidation (renoxification),^{20,26} this presents a significant source of false results. We therefore determined the amount of nitrate on the catalyst prior to and after the experiments to exclude nitrate conversion as the primary source of NO_x emission during the experiments. In almost all cases presented here, the amount of nitrate found on the photocatalyst was higher after the reaction than before, indicating that additional nitrate was deposited during the reaction (presumably from overoxidation or disproportionation of NO₂). The values presented for fixed nitrogen are consequently a combination of the NO_x detected in the gas phase during the irradiation plus the difference of nitrate found on the photocatalyst materials after the experiment.

For nitrogen fixation experiments, rigorous control experiments are mandatory due to the ubiquitous nature of nitrogen compounds and the typically low observed concentrations.^{27,28} In the present case, no significant product formation was observed without irradiation or under irradiation but without a photocatalyst (details in the SI). In presence of photocatalyst, changing the gas supply from air to argon led to significantly reduced but still measurable NO_x production rates under irradiation (Figure S1), which in this case were exclusively in the form of NO. Part of this emission originated from nitrate on the photocatalyst as evidenced by a negative nitrate balance. Also, the employed setup was never designed to be absolutely gas-tight so there are likely low levels of nitrogen still present in the gas stream which may account for the observed product formation.

Figure 2 shows the product distribution for different run times, accounting for gas-phase NO and NO₂ as well as for nitrate deposited on the surface during the experiment. It is apparent that the formation rate decreases over time as already mentioned above, indicating a slow catalyst deactivation. However, within experimental error the product distribution appears to remain constant over a reaction time of 20 hours with the majority being present as NO₂ (66-69 %). By-products are NO (12-17 %) in the gas phase and nitrate (15-19 %) being deposited on the surface as evidenced by a higher nitrate content of the catalyst powder after vs. prior to the experiment. The invariant selectivity indicates that whatever effect decreases the activity over time does not affect the reaction mechanism.

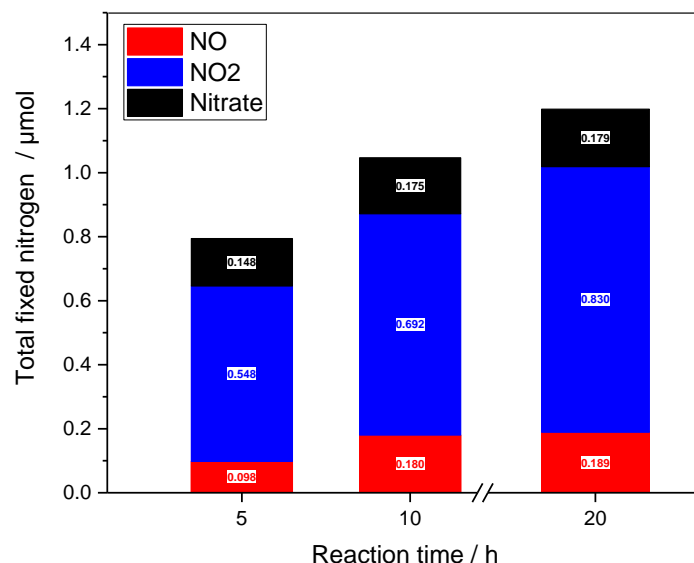


Figure 2: Influence of the reaction time on the formation of the fixed nitrogen compounds NO (red), NO₂ (blue) and nitrate (black). Conditions: P25 photocatalyst, 1 L min⁻¹ synthetic air flow rate, 50 % r.h., 250 mW cm⁻² irradiance, 50 cm² irradiated area.

To study the effect of water on the reaction, we performed experiments also with low and high humidity. While increasing the water content from 50 to 95 % relative humidity (r.h.) slightly increased the overall reaction rate, almost no conversion was observed in the case of dry (3 % r.h.) air (Figure 3, left hand side). This indicates that water is essential for the reaction mechanism; probably because in the absence of any suitable other options, water is required as electron donor. Alternatively, the hydroxyl radicals formed by water oxidation may be part of the reaction mechanism. In any case, this rules out that N₂ is directly oxidized using valence band holes as in this case neither another electron donor nor hydroxyl radicals would be needed.

The selectivity is also affected by the humidity. With higher humidity, there is a notable shift towards a higher NO fraction, mostly at the expense of nitrate (Figure 3, left hand side). When increasing the relative humidity from 3 to 95 %, the NO selectivity increases from 3.7 to 22.7 % while that of nitrate decreases from 50.9 to 9.1%. At the same time, the NO₂ fraction stays approximately the same and is only slightly increased. This may be explained by the fact that both the photocatalytic oxidation of NO to NO₂ and subsequently to nitrate show a lowered reaction rate at high humidity.²⁹ So there is a lower fraction of NO converted into NO₂ but its conversion is also lower which results in an approximately stable NO₂ fraction.

With respect to product separation, a high selectivity towards NO₂ would be preferable as it can be easily extracted from the gas phase in a water absorber while NO would first have to be oxidized and nitrate would have to be removed from the catalyst. Therefore, an intermediate humidity (e.g. 50 % r.h.) appears to be ideal, as it achieves both a high overall reaction rate and a high selectivity towards NO₂.

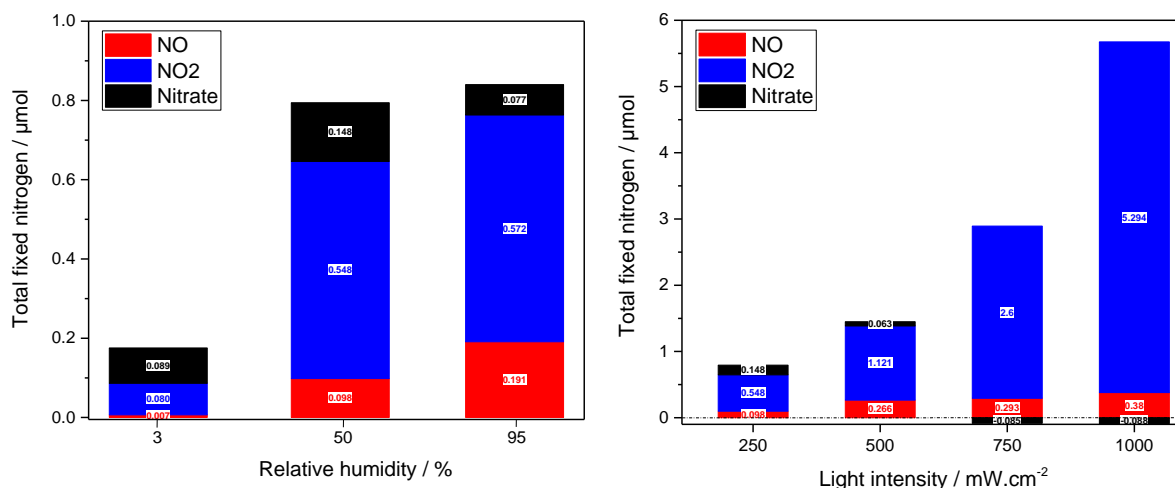
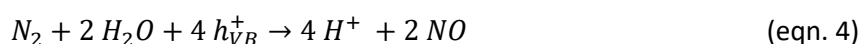


Figure 3: Influence of the relative humidity (left) and light intensity (right) on the formation of the fixed nitrogen compounds NO (red), NO₂ (blue) and nitrate (black). Conditions (unless varied in the experiment as labelled): P25 photocatalyst, 1 L min⁻¹ synthetic air flow rate, 50 % r.h., 250 mW cm⁻² irradiance, 50 cm² irradiated area, 5 h reaction time. In case of negative values for nitrate this means that less nitrate was found on the catalyst after the reaction than before.

This agrees well with quantum-chemical calculations from Yuan et al., which proposed both a reductively activated pathway via superoxide (eqns. 1-3) and an oxidative pathway via hydroxyl radicals (eqn. 4).¹⁶ At the moment we cannot conclude which of these is more likely or if possibly, both mechanisms occur simultaneously. Detailed spectroscopic studies will have to be done to shed more light on the exact reaction mechanism.



Increasing the light intensity also increases the observed NO_x formation rate, further confirming that light is the driving force for the reaction (Figure 3, right hand side). The selectivity shifts to lower NO and nitrate and consequently higher NO₂ yield with increased light intensity. At the highest intensity, the selectivity is 93.3 % for NO₂ and 6.7 % for NO. In this case, no nitrate accumulation on the surface was observed but a slight decrease, which however only accounts for a very small fraction of the total products (1.6%). A possible explanation for this phenomenon is that the rate of photocatalytic NO oxidation to NO₂ increases faster with higher light intensity than both the N₂ and NO₂ oxidation reactions. Unfortunately, while there are some studies on light dependency of the photocatalytic NO oxidation, no such information is available on the other two reactions. Another possibility is a thermal effect (*vide infra*) causing the individual reaction rates to deviate. In any case, this finding is very promising as it enables the production of NO₂ with an excellent selectivity.

Interestingly, the activity increase is exponential, affording an astonishing 7-fold increase when going from 250 to 1000 mW cm⁻². The maximum observed reaction rate translates into 223.4 μmol m⁻² h⁻¹ or 13.85 mg m⁻² h⁻¹ as nitrate equivalent which is more than 3 times the highest value reported to far.¹⁶ A possible explanation for the exponential increase is that the reaction may require several charge carriers to be present and transferred simultaneously. A similar behaviour has been observed for example for the water oxidation reaction, in which 4 electrons need to be transferred.³⁰ However,

none of the reaction mechanisms proposed so far for photocatalytic N₂ oxidation featured concerted multi-electron transfers. Another possibility is a thermal effect; while the temperature of the gas stream passing over the catalyst only increased mildly by few K during the reaction, the catalyst bed heats up considerably as a result of the intense radiation.

While being one of the decisive factors in catalysis, thermal effects in photocatalysis have long been overlooked or considered insignificant. However, recently more and more studies also consider elevated temperatures to achieve higher efficiency, particularly under intensified reaction conditions.^{31–34} Evident for example in the case of water oxidation with almost unity quantum yield it has been shown that this can have dramatic effects, particularly for catalytically demanding reactions (which N₂ oxidation most certainly is).^{33,35} Quantum-chemical calculations also predict a strong positive influence of higher temperature on the proposed reductive pathway for N₂ oxidation.¹⁶ Unfortunately, our employed setup was unsuitable to properly study variations in reaction temperature. Further studies are currently planned to investigate in detail how the reaction temperature influences this reaction and what efficiency gains can be achieved this way.

Overall, we could show that molecular nitrogen can be directly converted in the gas phase to nitrogen oxides over an illuminated titanium dioxide photocatalyst. While the rates and efficiency observed herein are still quite modest (approx. 14 mg m⁻² h⁻¹ nitrate equivalent and 0.01 % apparent quantum yield), we expect there are significant advances possible with catalyst design which has not yet been addressed at all in this proof-of-principle study.

Although the exact reaction mechanism is still unclear, we could show that water plays an essential role and that increasing the light intensity affords an exponential activity increase, possibly through an overlying thermal effect. The latter may be facilitated by just conducting the reaction at higher temperature to begin with or by using concentrated sunlight. Optimizing these reaction conditions will certainly also lead to higher overall efficiency.

If the process can be optimized to better efficiency and yield this could present a very appealing low-cost option to produce sustainable nitrate-based fertilizers just from air and sunlight. This could be realized in a decentralized manner, directly at the place of use (e.g. in rural areas) and thus also safe costs and emissions from transportation and storage.³⁶

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