

Sustainable nitrate production out of thin air: The photocatalytic oxidation of molecular nitrogen

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Supporting Information

Experimental Details

Photocatalytic experiments were performed in a set-up according to ISO 22197-1 described in detail by Patzsch et al.¹⁷. Approximately 1.5 g of photocatalyst powder (TiO₂, Evonik Aeroxide P25) was placed in a 5 x 10 cm² sample holder, slightly pressed on with a flat plunger to achieve an even surface, and placed inside a reactor made from PEEK with a borosilicate window at the top. Synthetic air was used as gas phase N₂ source and was streamed over the sample with total flow rate of 1 L min⁻¹. Regulated by digital mass-flow-controllers, part of the flow was diverted through a washing bottle to achieve the desired relative humidity (r.h.), prior to re-mixing the gas flows before the reactor inlet. Relative humidity and gas temperature were measured directly at the reactor outlet. Illumination was performed from the top of the reactor through the window *via* a high-power UV-LED-Lamp (Opsytek Dr. Göbel GmbH, peak emission at 365 nm) with a calibrated tuneable light intensity of up to 1000 mW cm⁻² at the position of the sample. The gas phase was analysed for NO_x (NO and NO₂) by using an environmental NO_x analyzer (Horiba APNA-370, 0.5 ppb limit of detection). The reactions were performed at room temperature (23 ± 1 °C). During the illumination, the gas stream temperature measured at the outlet increased by 1 to 2 °C as a result of the intense radiation. Using an IR thermometer, the temperature of the catalyst in the reaction zone was estimated at 80 °C under prolonged 250 mW/cm² irradiation.

After the photocatalytic experiments, the powder samples were collected in 50 mL falcon tubes, mixed with 20 mL deionised water and agitated for 24 hours (900 rpm) at 22 °C in a Thermo Mixer (MKR13, HLC BioTech). After filtration through a syringe Filter (PVDF, 0.25 µm), aliquots of 5 mL were used to determine the nitrate content *via* Ion Chromatography (Dionex Aquion, Thermo Scientific; IC Column Dionex IonPac AS22). As a reference, fresh photocatalyst samples were subjected to the same procedure to determine the amount of nitrate on the material prior to the experiments. This baseline (0.121 ± 0.003 µmol g⁻¹), accounting for the exact mass of catalyst employed in the given experiment, was then subtracted from the post-reaction values to obtain the amount of nitrate deposited (or converted) during the experiment (see Table S1).

Control Experiments

In each experiment, the concentration of NO_x was monitored in the dark for several minutes prior to switching on the lamps. Only background noise (corresponding to approx. 0.05 μmol in 5 hours) and no production of NO_x was observed during this period in any experiment, indicating that in the absence of light, no reaction takes place. The observed background noise of NO and NO₂ was subtracted from all values given for fixed nitrogen.

As shown in Fig. S1, additional control experiments were conducted under irradiation but in the absence of a photocatalyst with both synthetic air and argon (Control 1 and Control 2 respectively) as well as with the irradiated photocatalyst but with Ar instead of N₂ atmosphere (Control 3).

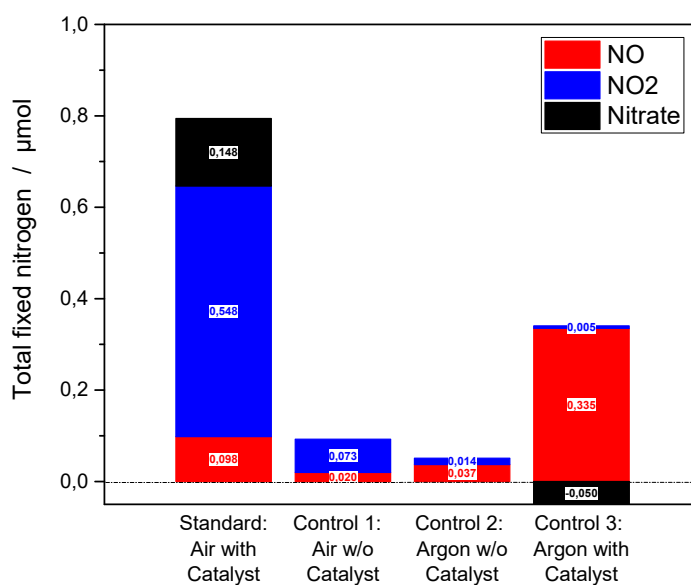


Figure S1: The observed formation of the fixed nitrogen compounds NO (red), NO₂ (blue) and nitrate (black) in the different control experiments in comparison with our standard conditions: P25 photocatalyst, 1 L min⁻¹ synthetic air flow rate, 50 % r.h., 250 mW cm⁻² irradiance, 50 cm² irradiated area. In case of negative values for nitrate this means that less nitrate was found on the catalyst after the reaction than before.

Determination of formed or converted nitrate

Table S1: Overview of the different experiments showing the employed catalyst mass, light intensity, gas phase makeup (SA = synthetic air, unless mentioned otherwise with 50 % r.h.), reaction time as well as the nitrate found on the catalyst after the experiment and the resulting nitrate balance (after subtracting the catalyst baseline value). ¹r.h. 3%, ² r.h.95%

No.	Catalyst mass / g	Light intensity / mW cm^{-2}	Gas phase makeup	Reaction time / h	Nitrate found after the experiment / μmol	Nitrate balance / μmol
1	1.365	250	SA	5	0.313	0.148
2	1.624	250	Ar	5	0.146	-0.050
3	1.531	250	SA	10	0.360	0.175
4	1.468	250	SA	20	0.357	0.179
5	1.726	250	SA ¹	5	0.298	0.089
6	1.719	250	SA ²	5	0.284	0.077
7	1.491	500	SA	5	0.243	0.063
8	1.686	750	SA	5	0.119	-0.085
9	2.350	1000	SA	5	0.195	-0.088

Analysis of the activity increase with varied light intensity

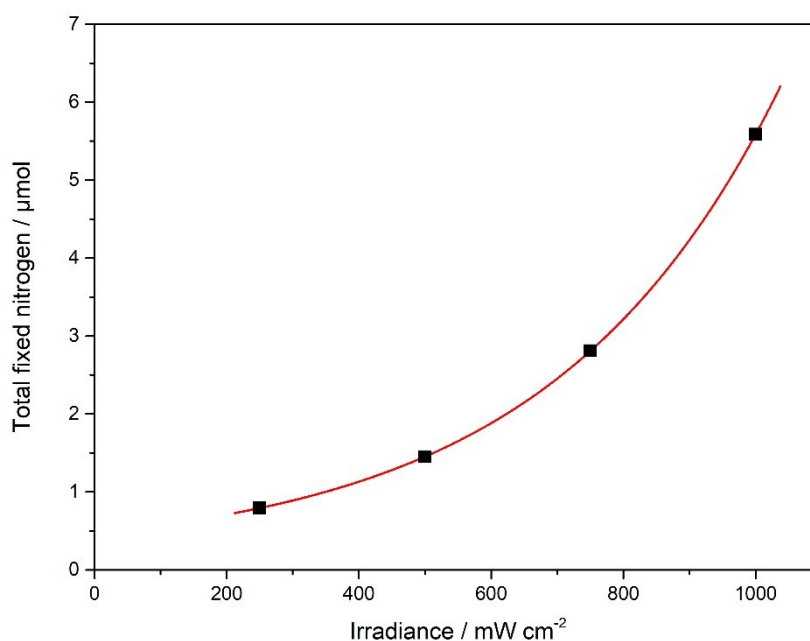


Figure S2: The observed formation of total fixed nitrogen (sum of NO, NO₂ and nitrate) in dependence of the irradiance. The red line represents the best fit for an exponential growth function ($y = 0.3052 \cdot \exp(x/347.59789) + 0.16625$, $R^2 \geq 0.999$). Conditions: P25 photocatalyst, 1 L min⁻¹ synthetic air flow rate, 50 % r.h., 50 cm² irradiated area.