

Supporting Information

Photochemical Conversion of Nitrate to Ammonium Ion by a Newly Developed Photo- Reductive Titanium Dioxide Catalyst: Implications on Nitrogen Recovery

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Table S1. Composition of synthetic groundwater used in this study.

Chemical composition*	Concentration (mg/L)
Nitrate	100
Chloride	13
Bicarbonate	38
Sulfate	33
Silica	37
Sodium	14
Potassium	4
Calcium	24
Magnesium	6
TOC	4.5
pH	8.0

* The synthetic groundwater chemical composition was based on reported values in literature (Ottofuelling, S.; Von Der Kammer, F.; Hofmann, T. Commercial Titanium Dioxide Nanoparticles in Both Natural and Synthetic Water: Comprehensive Multidimensional Testing and Prediction of Aggregation Behavior. *Environ. Sci. Technol.* **2011**, 45 (23), 10045–10052.)

Table S2. Nitrate removal efficiency by photo-reduction TiO_2 in DI water and synthetic groundwater matrix.*

Water Matrix	Nitrate Removal Efficiency (%)	Selectivity of ammonium ion (%)	Formation of nitrite (%)
DI Water	95	70	Not detected
Synthetic Groundwater	99	60	Not detected

*Nitrate removal, nitrite formation and ammonia selectivity data represent samples collected at 5 hours of the photocatalytic reaction.

Text S1. Ammonia Measurements

Phenol Reagent is prepared by adding 1.1 mL of liquified phenol to 9.9 mL of 200 proof ethanol in a tube. Sodium Nitroprusside is prepared by transferring 500 mg of sodium nitroprusside to a 100 mL flask and transferring the solution to a stock bottle. Alkaline Citrate is prepared by adding 10 g of sodium citrate anhydrous to a 50 mL volumetric flask, followed by 500 mg of sodium hydroxide. 10 mL of this solution is added to 2.5 mL of sodium hypochlorite to prepare a solution of hypochlorous alkaline citrate. 85 μ L of sample is added to 765 μ L of DI water, followed by 34 μ L of phenol solution, 34 μ L of sodium nitroprusside and 85 μ L of hypochlorous alkaline citrate solution. The sample is kept for 1 hour and read at 640 nm.

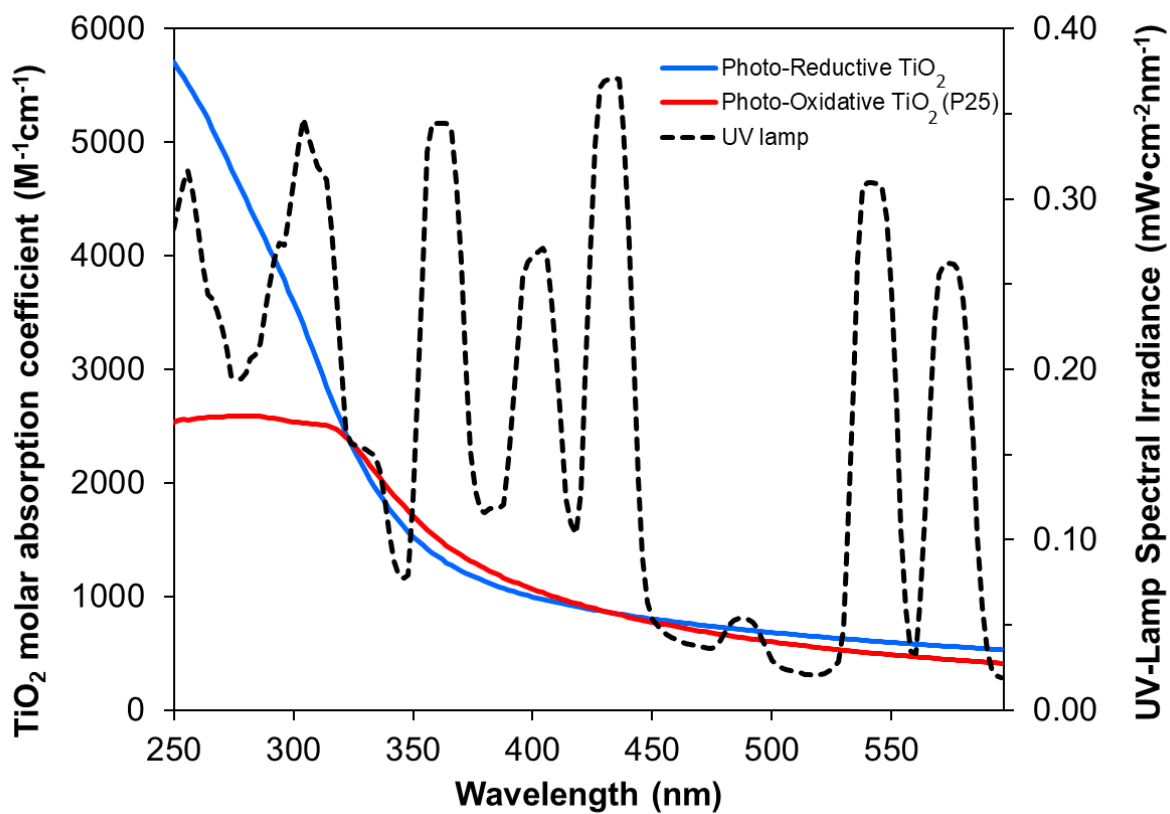


Figure S1. UV-Vis for DEG-doped TiO₂ nanoparticles synthesized at 230°C and for industrial TiO₂ catalyst P25 both at 50 mg/L and irradiance spectra output for the medium-pressure UV lamp used to conduct all experiments.

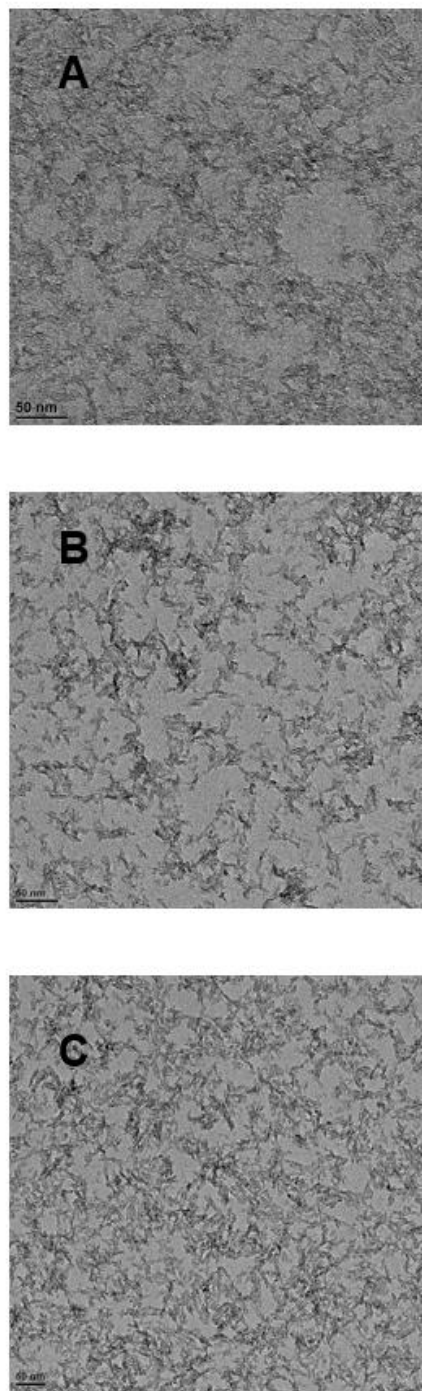


Figure S2. Transmission Electron Microscopy micrograph of synthesized photo-reductive TiO_2 nanocrystals with different heating time for hydrolysis at 230°C . (A) 3 hours; (B) 6 hours; (C) 9 hours.

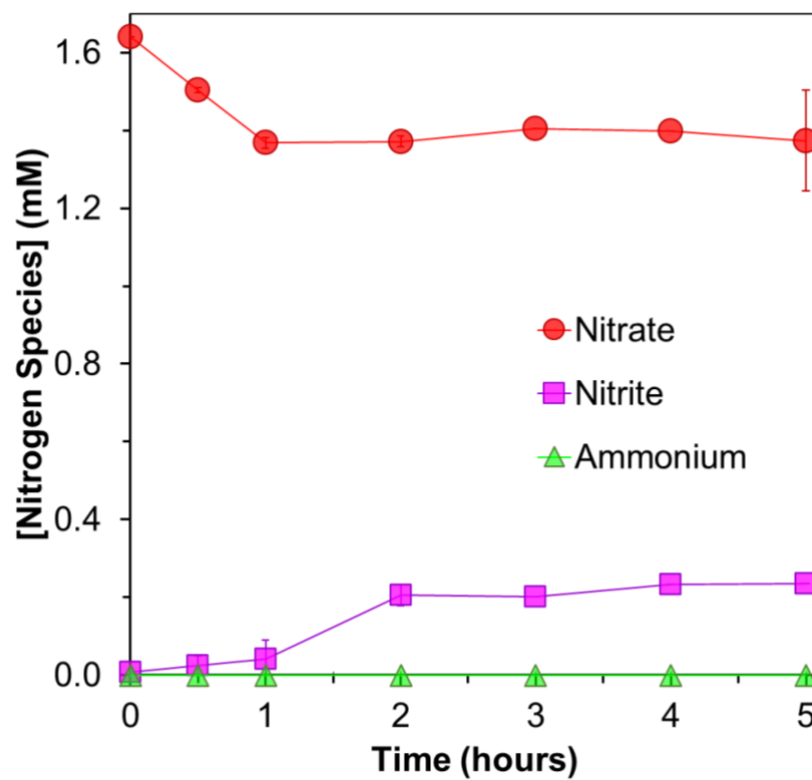


Figure S3. Nitrogen speciation profile during photochemical nitrate reactions in the presence of photo-oxidative P25 Degussa TiO_2 catalyst. $[\text{Nitrate}] = 1.6 \text{ mM}$, $[\text{TiO}_2] = 50 \text{ mg/L}$. $\text{pH} = 7$.

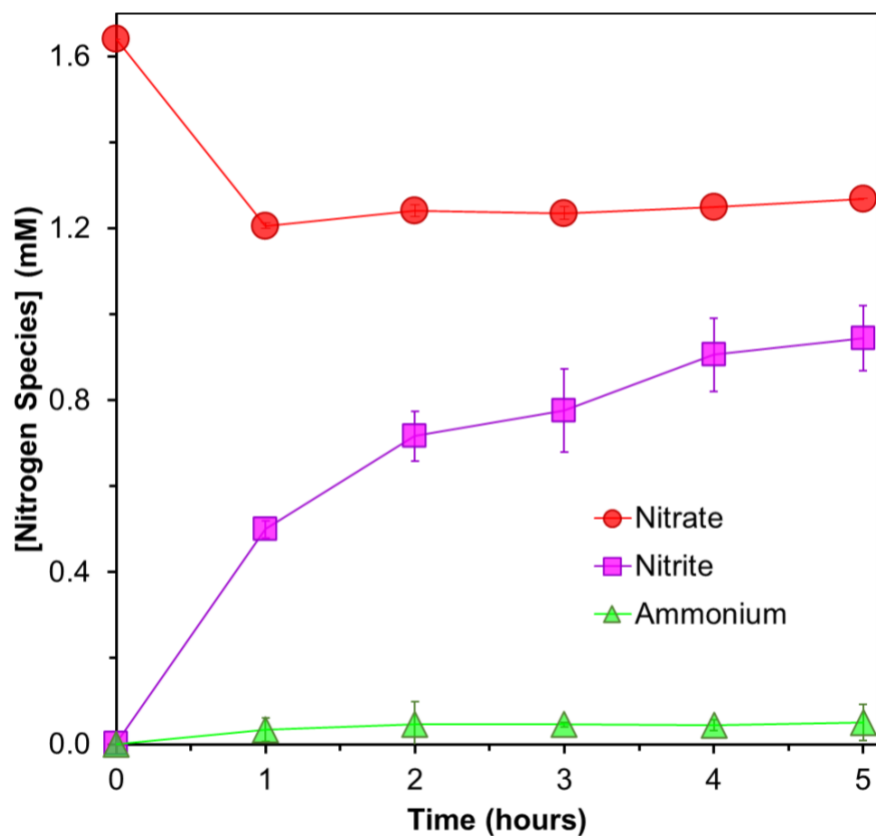


Figure S4. Nitrogen speciation profile for nitrate solution in the catalyst control experiment in the absence of photocatalyst and only with UV irradiation. [Nitrate] = 1.6 mM, [TiO₂] = 50 mg/L, pH = 7.

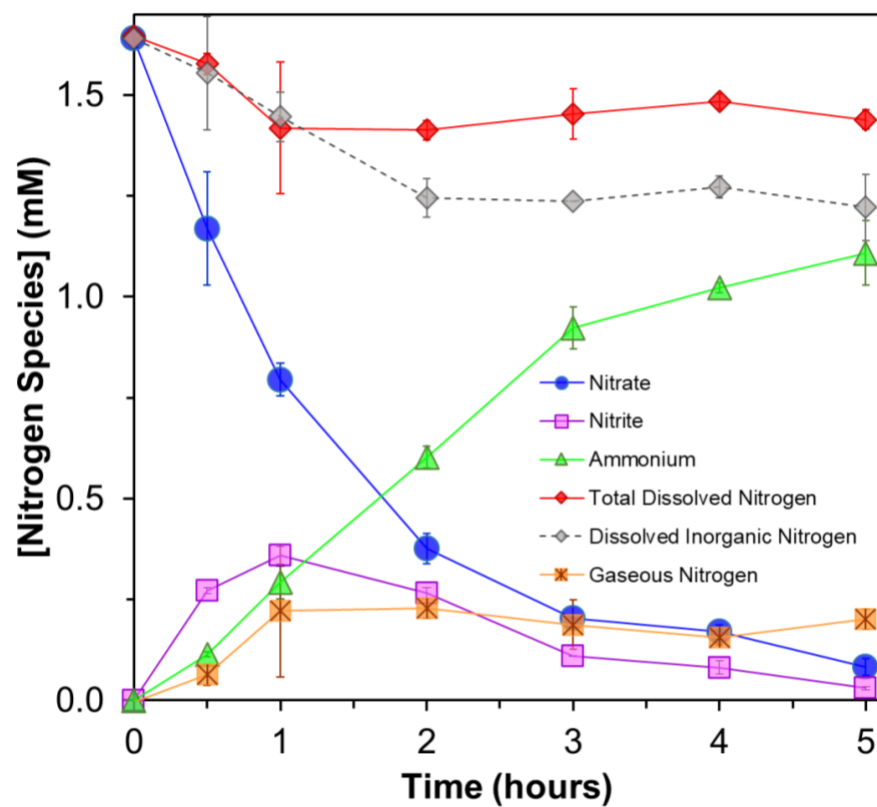


Figure S5. Nitrogen speciation profile for nitrate solution during photochemical reactions in the presence of synthesized DEG-TiO₂ catalyst. Synthesis temperature = 230°C, [Nitrate] = 1.6 mM, [TiO₂] = 50 mg/L, pH = 7.