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Nitric oxide emission during the reductive heterogeneous photocatalysis of aqueous nitrate with TiO_2^\dagger

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For the first time, nitric oxide (NO), a precursor of nitrogen dioxide (NO₂, a NIOSH-listed atmospheric pollutant), has been found to be one of the final products of the photocatalytic reduction of nitrate in water using TiO₂ and formic acid as hole scavenger.

INTRODUCTION

Heterogeneous photocatalysis (HP) constitutes a potential alternative for removal of nitrate from water or brines produced by remediation technologies.¹ Most scientific studies concerning the use of HP for water treatment monitor exclusively the aqueous phase and are focused either on the transformation of a toxic metal or metalloid to a harmless species or, in the case of organic compounds, on their complete mineralization yielding water, simple inorganic acids and CO₂. However, in many cases, HP can generate other gas phase products that might be harmful to humans and the environment; the photocatalytic arsenic reduction over TiO₂ generating arsine is an example.² Therefore, the determination of the composition of the gas phase is crucial, not only considering potential health impacts and environmental implications, but also to contribute to a better understanding of the mechanism of removal of pollutants from the aqueous phase.

Nitrate is an essential nutrient for protein synthesis in plants and it is formed and retained by well-known bacteria mediated processes in the environment: nitrogen fixation and nitrification.³ However, it is used as fertilizer in intensive farming, leading to a sustained increase in its surface and groundwater concentration and to an acceleration of the nitrogen cycle resulting in aquatic and terrestrial eutrophication and global acidification.⁴ In relation with human health, nitrate ion is not considered harmful, but intestinal tract bacteria can easily convert it into NO₂⁻, potentially affecting

O₂ transport by oxidation of Fe²⁺ in hemoglobin.⁵ For that reason, the WHO established a guideline value for drinking water of 50 mg L⁻¹.⁵

Removal of nitrate by HP has led to an abundant literature that pointed at NH₃ (or NH₄⁺) and N₂ as final products. TiO₂ (Degussa or Evonik P25) presents values for the flatband potential of the conduction band (CB) and valence band (VB) as -0.3 V and +2.9 V (at pH 0), respectively. After UV irradiation of the semiconductor, conduction band electrons (e_{CB}⁻) and valence band holes (h_{VB}⁺) are created; e_{CB}⁻ can reduce electron acceptors (A) of suitable redox potential, while h_{VB}⁺ can oxidize electron donors (D) or water, generating hydroxyl radicals (HO[•]):



If monoelectronic pathways are proposed in HP reactions, direct nitrate photocatalytic reduction by e_{CB}⁻ would not be possible because the redox potential for nitrate to the nitrate radical anion ($E^0_{(\text{NO}_3^-/\text{NO}_3^{\bullet-})} = -0.89 \text{ V}$)^{6,7} hinders e_{CB}⁻ attack. Actually, poor reactivity for nitrate reduction or no reaction at all has been observed using bare TiO₂ in pure water (see e.g. references^{8,9} and references therein). Therefore, an electron donor or hole scavenger like an alcohol or a carboxylic acid (RH), able to generate reducing radicals (R[•]) after reaction with h_{VB}⁺ or HO[•], has to be added to allow indirect reduction through the following reactions:



where R_{ox} is the final organic oxidation product in solution.

Formic acid has been used as hole scavenger in previous studies^{8,10-13} leading to significantly higher nitrate conversions compared with other reagents. In addition, noble metal modified TiO₂ has been reported to promote a high efficient reaction and an acceptable selectivity towards N₂ formation.^{8,10,11,14} Several authors^{10,14} indicated different selectivities to N₂ formation using bare TiO₂ and using electron donors but, in fact, none of them have actually measured N₂ in those conditions, and the gas phase has been incompletely characterized. To the best of our knowledge, only two groups have reported the quantification of N₂ emissions from nitrate treatment with HP: Zhang et al.,¹¹ in a single point characterization, reported 99% selectivity to N₂ when removing NO₃⁻ with Ag-modified TiO₂, while Kominami et al.¹⁵ measured N₂ emissions when using different metal-loaded TiO₂, yielding 98% of N₂ selectivity, calculated based on consumption of photogenerated electrons.

In this work, we demonstrate for the first time the emission of harmful concentrations of NO during the photocatalytic reduction of nitrate in water using TiO₂ and formic acid as hole scavenger.

RESULTS AND DISCUSSION

Intermediates and final products of the photocatalytic removal of nitrate in the presence of formic acid. The concentration profiles for nitrate, formic acid and the intermediate (NO₂⁻) and final products (NH₄⁺, NO) as a function of time during the reductive TiO₂-HP of nitrate were obtained for experiments starting with [NO₃⁻]₀ = 0.08 mM in the presence of [HCOOH]₀ = 0.1 mM (at pH 2.8). As shown in Fig. 1(a), a simultaneous decrease of the NO₃⁻ concentration with complete degradation of HCOOH takes place during the reaction.

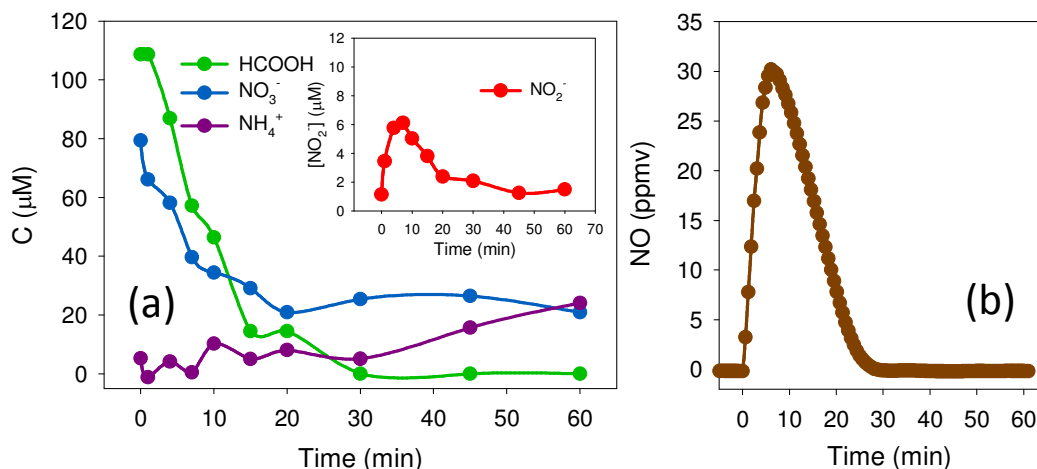


Fig. 1. Time profiles of (a) $[\text{NO}_3^-]$, $[\text{NH}_4^+]$ and $[\text{HCOOH}]$ in the aqueous phase during the photocatalytic reaction of nitrate over P25 and (b) NO evolution in the gas phase. Initial conditions: $[\text{NO}_3^-]_0 = 0.08 \text{ mM}$ and $[\text{HCOOH}]_0 = 0.1 \text{ mM}$, pH 2.8 and $T = 25 \text{ }^\circ\text{C}$. Inset: Time profile of $[\text{NO}_2^-]$.

The role of NO_2^- as aqueous reaction intermediate can be observed in Fig. 1(a) (inset), and its consumption occurs in parallel with the increase of the NH_4^+ concentration, the final and stable product in solution at the end of the reaction, as reported previously.^{1,11,13,14,16} On the other hand, NO (Fig. 1(b)) is emitted from the system and its total produced amount (NO_T) was calculated using eqn (7):

$$\text{NO}_T = \int_0^{t_f} F^{\text{N}_2} \times \frac{[\text{NO}]}{\bar{V}} \times dt \quad (7)$$

where NO_T is the amount of moles of NO emitted in the system, F^{N_2} is the N_2 flow rate (600 mL min^{-1}), $[\text{NO}]$ is the temporal concentration of NO in ppmv given by the NO_x analyzer, and \bar{V} the molar volume of NO.

At the end of the experiment (60 min), 26% of the nitrate remains in solution and the rest of the mass of nitrogen initially present as nitrate is distributed as follows: 30% of NH_4^+ in solution (Fig. 1), 30% of NO in the gas phase (calculated with eqn (7),

representing the area below the curve in Fig. 1(b)), and the remaining 14% is supposed to be N₂ or a mixture of N₂ and N₂O, as reported previously¹⁷ and suggested elsewhere.^{1,10,13,16}

In the absence of light, HCOOH or TiO₂, neither NO₃⁻ degradation nor formation of products was observed, indicating that NO is a byproduct of the heterogeneous photocatalytic transformation of NO₃⁻. The similarity between the trends for the variation of [NO₃⁻] and [HCOOH] indicates that the presence of HCOOH dictates the evolution of the other species in the system; HCOOH is the limiting reagent as when it is completely depleted the evolution of the rest of the compounds barely varies. The role of HCOOH becomes evident according to the generation of NO: the reaction initiates very fast but progressively decelerates as HCOOH is consumed, leading to a broad peak with a maximum at around 5 min of reaction (Fig. 1).

As stated previously, the monoelectronic reduction of nitrate by e_{CB}⁻ is not thermodynamically possible. However, formic acid reacts with h_{VB}⁺¹⁸ (eqn (8)) decreasing the electron-hole recombination rate and generating CO₂^{•-}, a very strong reducing radical ($E^0_{(\text{CO}_2/\text{CO}_2^{\bullet-})} = -1.81 \text{ V}$).¹⁸



CO₂^{•-} can then reduce NO₃⁻ to NO₃²⁻ (eqn (9)), this latest species being able to react rapidly in water producing NO₂ (eqn (10))⁷ or, in the presence of O₂, being reoxidized to NO₃⁻, affecting the overall efficiency of the removal process.¹⁹ NO₂ is unstable in water and can either disproportionate (eqn (11)),¹⁹⁻²¹ or react with e_{CB}⁻ forming NO₂⁻ (eqn (12)).²² NO₂⁻ can be reduced by e_{CB}⁻ (eqn (13)) generating NO₂²⁻, and this species can be hydrolyzed generating NO (eqn (14)),²² which can be also formed by NO₂⁻ thermal (eqn (15))²² or photochemical decomposition (eqn (16)).²³





After these reactions, NH_4^+ can be formed by the one-step sequential reduction of NO by e_{CB}^- , with formation of hydroxylamine as intermediate.²² Other authors have also found that the increase on the $\text{HCOOH}/\text{NO}_3^-$ molar ratio in HP experiments of nitrate removal^{1,10} and a working $\text{pH} \leq 3$,^{5,13} enhance the selectivity towards NH_4^+ .

Experiments with different initial concentrations of NO_3^- and HCOOH were performed in order to understand their influence on the distribution of products. The same general behavior observed in Fig. 1 was obtained for the evolution of all species (Figures S2 and S3). Under the studied conditions, the emission of NO was correlated with the formic acid initial concentration (Fig. 2), observing only a minor change in NO_T when increasing $[\text{NO}_3^-]_0$ (inset, Fig. 2), leading to $230 \pm 33 \mu\text{mol}$ of NO_T emitted per mmol of HCOOH .

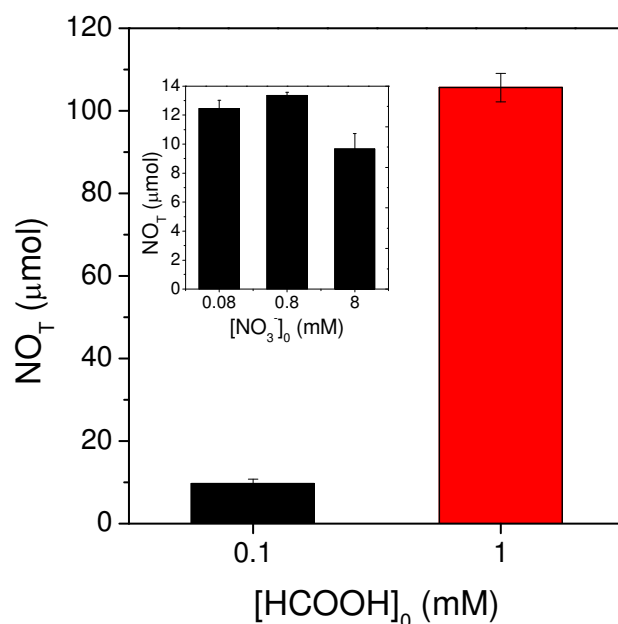


Fig. 2. Total NO emitted (NO_T) after NO_3^- treatment by TiO_2 -HP ($[\text{TiO}_2] = 1 \text{ g L}^{-1}$) in the presence of HCOOH. Experimental conditions: $[\text{NO}_3^-]_0 = 8 \text{ mM}$ and $[\text{HCOOH}]_0 = 0.1$ and 1 mM . Inset: NO_T obtained at different initial NO_3^- concentrations and $[\text{HCOOH}]_0 = 0.1 \text{ mM}$.

Most of the studies of nitrate removal by TiO_2 -HP consider the use of formic acid for making feasible the reaction due to its high electron donor efficiency and, usually, high $[\text{HCOOH}]_0/[\text{NO}_3^-]_0$ ratios are used. As recently proven by Doudrik et al.,¹³ higher formic acid concentration does not always lead to a better nitrate removal efficiency. In addition to that observation, Fig. 2 highlights that an increase in the amount of formic acid also increase NO emissions under the studied conditions. This last consideration needs to be taken into account in the case of the possible scale up of TiO_2 -HP for nitrate removal in water treatment plants, due to the fact that NO is a precursor of NO_2 formation in the atmosphere,²⁴ with NIOSH occupational exposure level of 1 ppm (recommended exposure level over a period of 15 min).²⁵

CONCLUSIONS

The discovery of NO emissions during the removal of nitrate by TiO₂-HP brings valuable information to be considered in future studies associated with treatment of nitrate-polluted water. New TiO₂ based materials, the type of electron donor and the working pH may impact on the amount of NO introduced in the gas phase or even lead to the emission of other more dangerous nitrogen oxides as NO₂ or HONO. Additionally, NO appears as a major product during the removal of nitrate by HP and, therefore, its inclusion in the kinetic description of the system should be also taken into account in further works.

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