Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information for

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

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Experimental section

Chemicals

KNO_3 (> 99%, Mallinkrodt), concentrated $HClO_4$ (70%, Biopack) and HCOOH (88%, Biopack) were used without further purification. Analytical calibration standards of KNO_3, $NaNO_2$ and NH_4Cl where obtained from ChemLab and TiO_2 Aeroxide P25 was provided by Evonik. All experiments were done with MilliQ water (resistivity = 18 MΩ cm) and all mentioned chemicals were analytical grade or superior.

Photocatalytic experiments

Photocatalytic removal of nitrate was carried out in a recirculating batch reactor (Figure S1) consisting in a glass jacketed reservoir, a recirculation peristaltic pump and a tubular Pyrex® glass photoreactor with annular section, equipped with a 15 W actinic lamp (Phillips TL-D, $\lambda_{max} = 366$ nm). In each experiment, 500 mL of TiO_2 suspension at pH 2.8 (adjusted with $HClO_4$), with the desired concentrations of KNO_3 ($[NO_3^-]_0 = 80\text{-}8000$ μM) and HCOOH ($[HCOOH]_0 = 100\text{-}1000$ μM), was added into the reactor, recirculated during 30 min in the dark to reach the adsorption equilibrium on the catalyst surface, and then irradiated for at least 60 min. Adsorption of nitrate and formic acid on the photocatalyst was negligible, as found previously by Wehbe et al. [1] All the experiments were made at 25.0 ± 0.1 ºC and under continuous N_2 bubbling at 600 mL min^{-1}.

Samples were periodically withdrawn, filtered through 0.22 μm cellulose acetate filters and conditioned to determine $[NO_3^-]$, $[NO_2^-]$, $[NH_4^+]$ and [HCOOH]. The concentrations of NO_3^-, NO_2^- and NH_4^+ were measured spectrophotometrically using the standard methods SM−4500−NO3−E,[2] SM−4500−NO2−B[3] and SM−4500−NH3−F,[4] respectively, employing a HP8453A spectrophotometer (Hewlett−Packard) with UV detection. HCOOH concentration was determined using a Shimadzu 5000 A TOC analyzer in the non-purgeable organic carbon (NPOC) mode.

NO_x concentration during the photocatalytic runs was monitored using a Horiba PG-250 gas phase analyzer based on the chemiluminescent reaction between NO and O_3.[5]

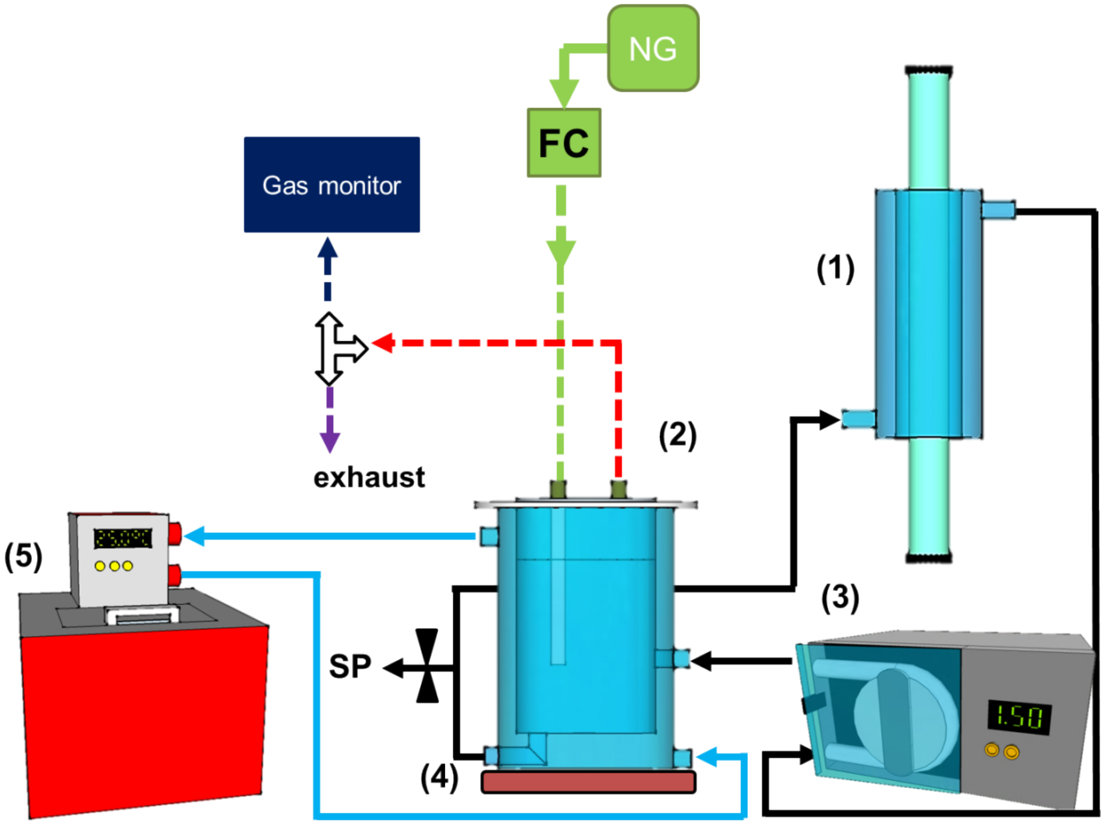

Figure S1. Recirculating batch reactor: (1) Pyrex® tubular photoreactor, (2) glass jacketed reservoir, (3) peristaltic pump, (4) magnetic stirrer, (5) thermocirculator. FC is the flow controller, NG the nitrogen generator and SP is the liquid sampling port used to collect samples during the photocatalytic runs.

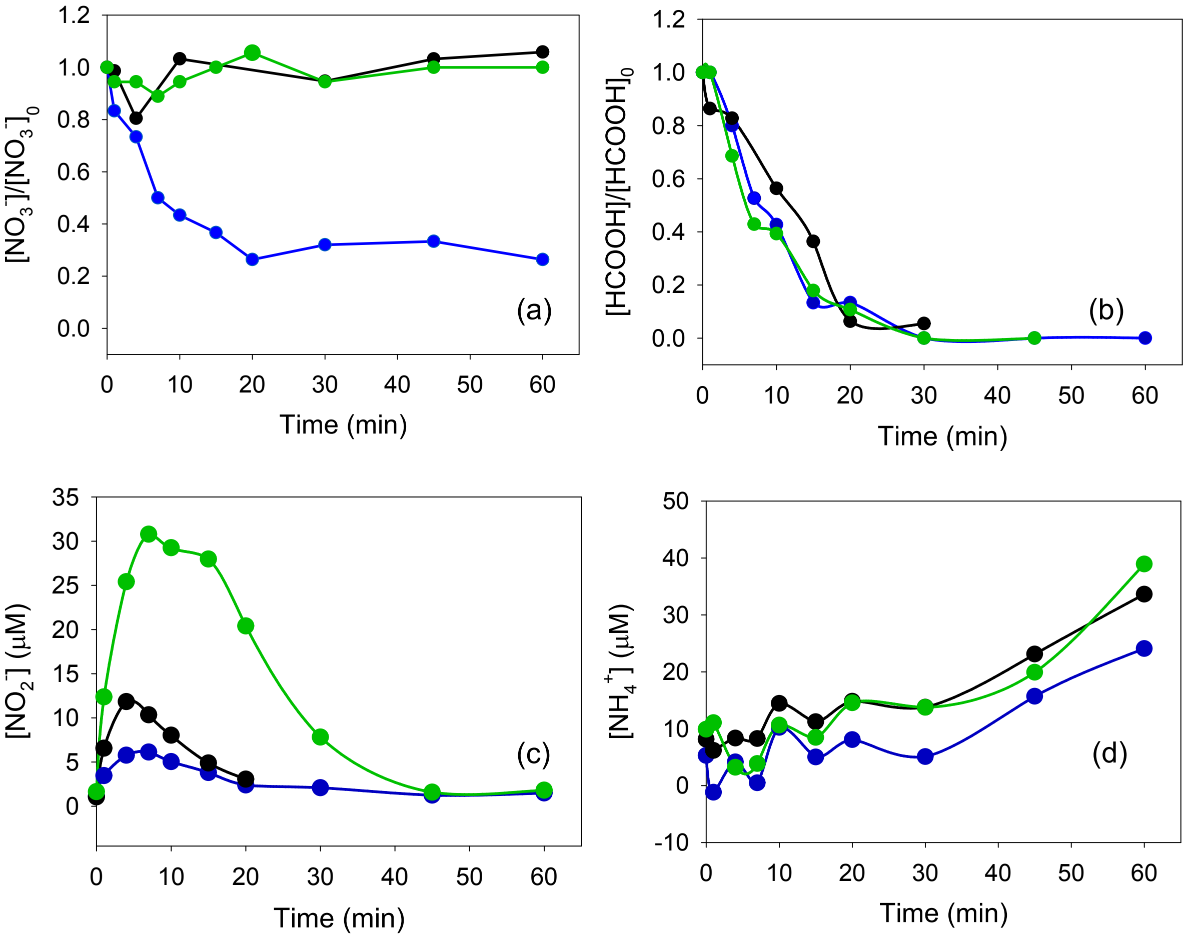

Figure S2. Time evolution for (a) $[NO_3^-]/[NO_3^-]_0$, (b) [HCOOH]/[HCOOH]$_0$, (c) $[NO_2^-]$ and (d) $[NH_4^+]$ during the treatment of NO_3^- by HP in aqueous phase with TiO_2 in the presence of [HCOOH] = 0.1 mM and $[NO_3^-]_0$ = 0.08 mM (blue), 0.8 mM (black) and 8 mM (green).

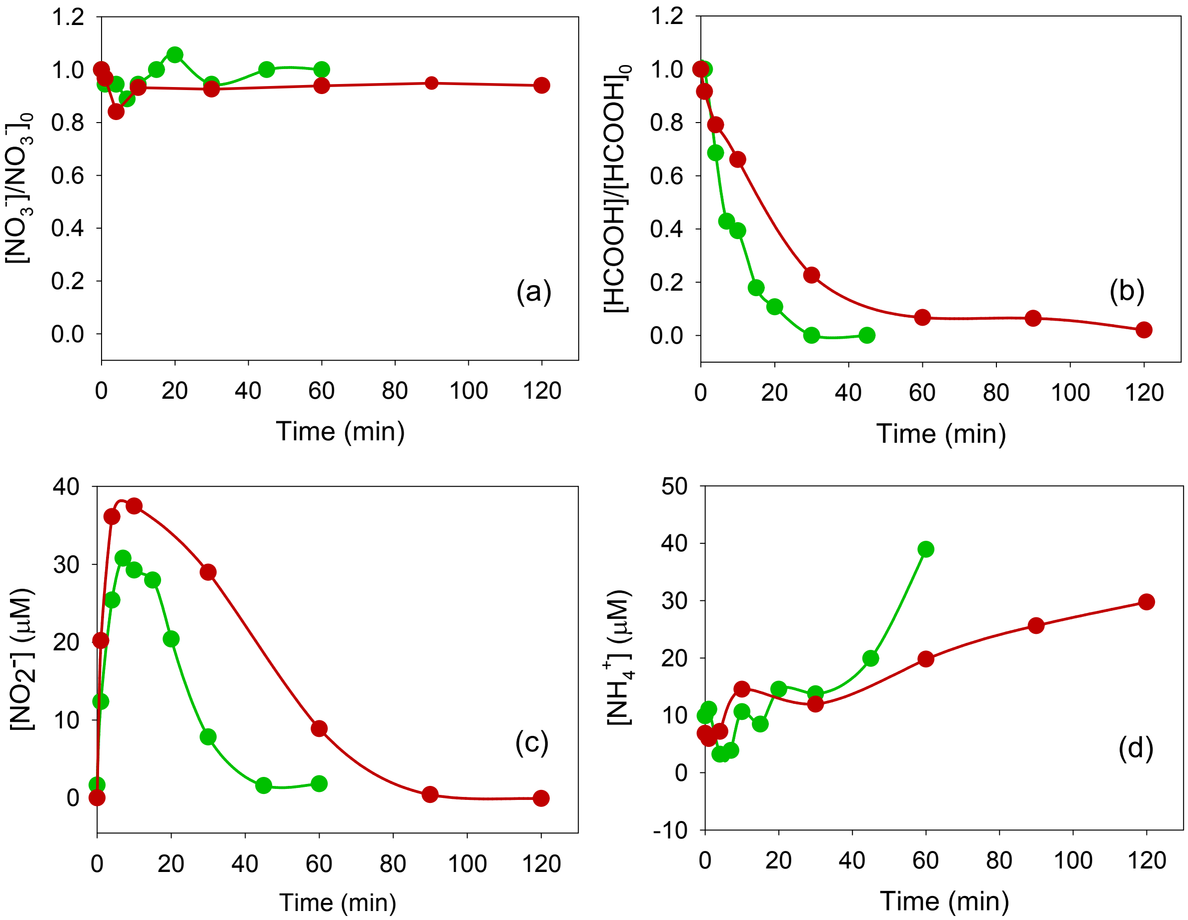

Figure S3. Time evolution for (a) $[NO_3^-]/[NO_3^-]_0$, (b) $[HCOOH]/[HCOOH]_0$, (c) $[NO_2^-]$ and (d) $[NH_4^+]$ during the treatment of NO_3^- by HP in aqueous phase with TiO_2 in the presence of $[HCOOH]_0$ = 0.1 (green) and 1 mM (red) and $[NO_3^-]_0$ = 8 mM.

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