Supporting Information

Understanding the Formation of Nitrate from Nitrogen at the Interface of Gas-Water Microbubbles

Sandeep Bose, Yu Xia, * Richard N.Zare*

*Department of Chemistry, Stanford University, CA 94305 United States

Email: zare@stanford.edu

Table of Contents

Determination of H_2O_2

Potassium titanium oxalate (PTO) was used for the colorimetric detection of H_2O_2 in the sample. A 1:1 mixture of an aqueous solution of 0.1M PTO and the sample was kept for 15 minutes. After that, the absorbance was measured by UV-Vis spectrometer with a characteristic absorption peak at 400 nm. For H_2O_2 quantification in the samples, the calibration curve was prepared using standard H_2O_2 solution. The whole experiment for H_2O_2 was replicated three times. The average value of three different measurements were reported and plotted in the graph. The error bars represent the standard error and it

measures the amount of variation from the mean value. The standard error (SE) was calculated using the equation, $SE = \sigma/\sqrt{n}$, where, σ = Standard deviation, and n = number of measurements.

Determination of NO_3^- using Spectrophotometry

The concentration of nitrates in the solution was determined spectrophotometrically by diazotization of sulfanilamide. For quantification, sulfanilamide solution was prepared by dissolving 1% (w/v) of sulfanilamide in 1% (v/v) HCl. 0.1 mL of sulfanilamide solution and 2 mL of HCl was added to 2 mL of the nitrate containing samples. The solutions were incubated in boiling water for 5 min for diazotization of sulfanilamide. The sample was cooled to room temperature and 0.2 mL of N-1-(napthyl)-ethylenediamine dihydrochloride (NEDA) solution (1% (w/v) of NEDA in 1% (v/v) HCl) was added to it. Addition of NEDA solution resulted in the formation of an azo dye (chromophore). The sample was kept in that condition at room temperature for 30 min and the color developed was monitored spectrophotometrically at 540 nm using a UV-Vis spectrophotometer. The concentration-absorbance curves were calibrated using standard sodium nitrate ($NaNO_3$) solution. The whole experiment for NO_3^- was replicated three times. The average value of three different measurements were reported and plotted in the graph. The error bars represent the standard error and it measures the amount of variation from the mean value. The standard error (SE) was calculated using the equation, $SE = \sigma/\sqrt{n}$, where, σ = Standard deviation, and n = number of measurements.

Spin Trap Experiment

5,5-dimethyl-1-pyrroline-N-oxide (DMPO), a spin trap was purchased from Sigma Aldrich. For the intermediate capture experiment, 2 mM of DMPO was added to aqueous Fe^{2+} solution before bubbling N_2. After 2 h of reaction, the samples were tested using an Orbitrap mass spectrometer based on the nanoESI ionization method at a positive potential of 1.5 kV.

Determination of $H_2N_2O_2$ intermediate in the microbubbled solution

^{1}H-NMR was performed on a Bruker 600 MHz spectrometer for the detection of $H_2N_2O_2$. The microbubbing experiment was performed for 30 min and then immediately measured by NMR within less than 5 min due to the rapid decomposition of the $H_2N_2O_2$. The chemical shift value was confirmed by using standard $H_2N_2O_2$, which was prepared from commercially available $Na_2N_2O_2$.

DFT calculations

Geometry optimizations and frequency calculations for reactants, products, reaction intermediates (IMs), and transition states (TSs) were conducted using the density functional theory (DFT) within the Gaussian 16 software package.[1] The CAM-B3LYP functional with Def2TZVP basis sets was employed for all calculations.[2-4] Each stationary point on the potential energy surface (PES) was characterized by vibrational frequency analysis to confirm its identity as either a minimum or a saddle point. All reported energies include zero-point vibrational energy (ZPE) corrections.
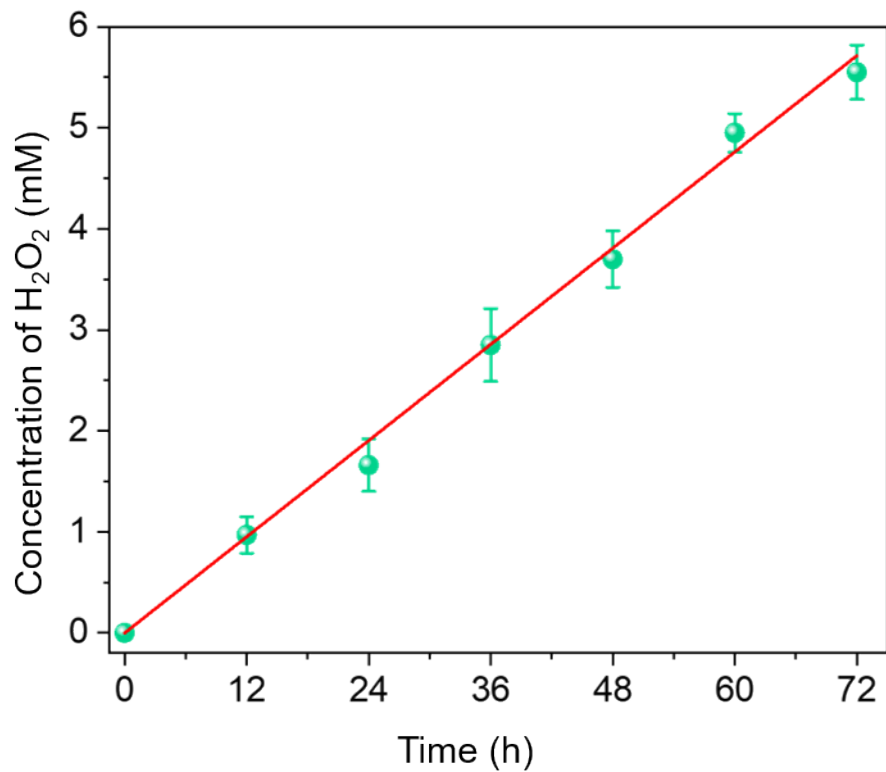
Figure S1. H_2O_2 production as a function of N_2 bubbling time. The rate of H_2O_2 yield is found to be 79.3 ± 1.3 µM h^{-1}.
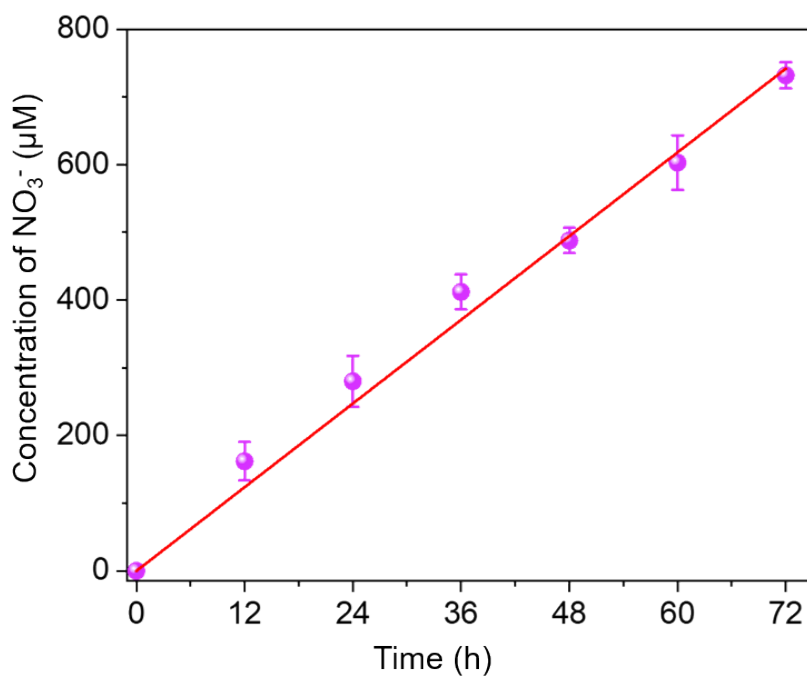
Figure S2. NO_3^- production as a function of N_2 bubbling time. The rate of NO_3^- yield is found to be 10.3 ± 0.19 µM h^{-1}.
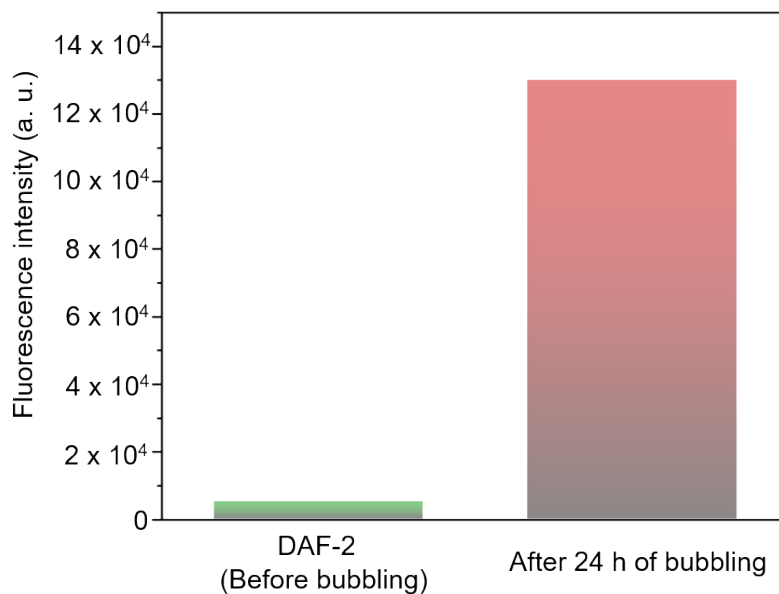
Figure S3. Comparison of fluorescence intensity of the solution containing DAF-2 before N_2-bubbling and after 24 h of N_2-bubbling. After 24 h, the intensity increases due to the formation of DAF-2T.
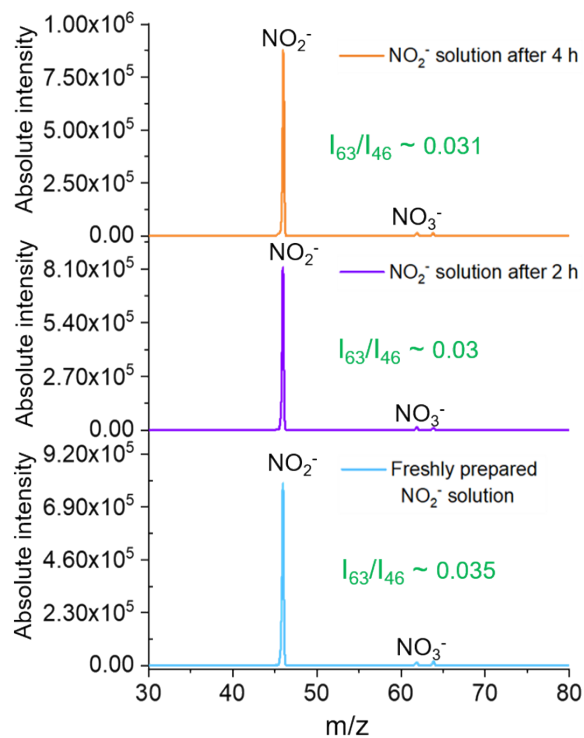

Figure S4. A comparison of the mass spectrum of the freshly prepared NO_2^- and NO_2^- solution kept for 2 h and 4 h without any bubbling. No evolution of NO_3^- peak shows the stability of NO_2^- in the solution.

References

1   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox. Gaussian 09, Revision B.01. Gaussian Inc., Wallingford, 2009**.**

2   C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B. Condens. Matter* 1988, **37**, 785–789.

3   A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648–5652.

4   F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297–3305.