

Project Title	Photocatalytic decomposition of nitrous oxide
University (where student will register)	University of Warwick
Which institution will the student be based at?	As above
Theme (Max. 2 selections)	Climate & Environmental Sustainability <input checked="" type="checkbox"/> Organisms & Ecosystems <input type="checkbox"/> Dynamic Earth <input type="checkbox"/>
Key words	Nitrous oxide; Remediation; Photocatalysis; heterogeneous catalysis
Supervisory team (including institution & email address)	PI: Adrian Chaplin; Department of Chemistry, University of Warwick; a.b.chaplin@warwick.ac.uk Co-I: Richard Walton; Department of Chemistry, University of Warwick; r.i.walton@warwick.ac.uk Co-I: Ryan M; School of Life Sciences, University of Warwick; ryan.mushinski@warwick.ac.uk

Project Highlights:

- The project aims to address the remediation of greenhouse gases, specifically focusing on the decomposition of nitrous oxide (N₂O).
- The studentship will explore photochemical promoted heterogeneous catalysis, harnessing solar energy to enhance the catalytic activity of metal oxide materials. This approach offers potential for mitigating N₂O emissions and reducing its impact as a potent greenhouse gas.
- Working collaboratively with supervisors and project partners, the student will develop various catalyst targets. This will foster innovation and creativity in catalyst design, contributing to the advancement of sustainable solutions for greenhouse gas remediation.

Overview

Nitrous oxide (N₂O) is a potent greenhouse gas, with a global warming potential 300 times greater than carbon dioxide, and the dominant ozone depleting substance emitted in the 21st century. Although naturally occurring, increasing anthropogenic N₂O emissions from intensive agricultural fertilisation, industrial processes, and combustion of fossil fuels and biomass are a major cause for concern due to the detrimental impact this will have on our environment. The selective decomposition of N₂O into environmentally benign N₂ and O₂ is a compelling prospect to remediate such emissions but, despite being a thermodynamically favourable reaction, activation of this weakly interacting triatomic gas is encumbered by a considerable degree of kinetic inertness. The overarching aim of this project is to harness solar energy to promote this reaction, using thermally and industrially relevant metal oxide materials as catalysts.

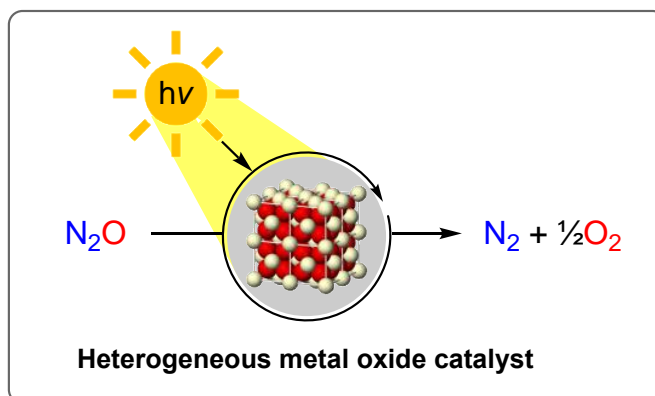


Figure 1: Schematic overview of project aim: the photochemical promoted decomposition of nitrous oxide into dinitrogen and dioxygen using a heterogenous metal oxide catalyst (alt text).

Methodology

Decomposition of N_2O can be promoted thermally using metal oxides but typically requires temperatures $>400\text{ }^\circ\text{C}$ that are not desirable from a remediation perspective. Photocatalytic alternatives that harness solar energy are attractive and potentially viable alternative but are poorly developed. This project will explore this possibility and involve (a) synthesis of established and novel metal-oxide-based photocatalysts, (b) development of analytical procedures for accurately evaluating N_2O decomposition reactions under different regimes (pure N_2O , N_2O and inert gas mixtures, and dilute N_2O in air), and thereafter (c) systematic evaluation of the photocatalysts for N_2O decomposition. Precisely monitoring the decomposition of N_2O into N_2 and O_2 is considerable analytical challenge, and a range of techniques will be explored to determine which is best for a given reaction regime. The use of quantitative head space sampling by gas chromatography will be fully explored in combination with FTIR-based methods.

Training and skills

This PhD project will provide exceptional interdisciplinary training. In addition to the analytical techniques highlighted above, the student working on this project will develop methods for the synthesis and characterisation of technologically relevant solid-state materials; the latter benefiting from the extensive range of analytical techniques available at Warwick such as X-ray diffraction, thermal analysis, and microscopy, with the possibility of developing *operando* versions of these to understand the mechanism of catalysis and stability of catalysts.

Partners and collaboration (including CASE)

Results from the project will be used to engage with relevant industries, working with Warwick Innovations to protect any emerging Intellectual Property.

Possible timeline

Year 1: Synthesis of established metal-oxide-based photocatalysts; optimisation of analytical procedures for analysing gaseous mixture of N_2O , N_2 , and O_2 ; analysis of established metal-oxide-based photocatalysts for the decomposition of pure N_2O .

Year 2: Iterative preparation, catalytic evaluation, and mechanistic investigation of novel metal-oxide-based photocatalysts for the decomposition of pure N_2O and inert gas mixtures of N_2O .

Year 3: Continued iterative preparation, catalytic evaluation, and mechanistic investigation of novel metal-oxide-based photocatalysts for the decomposition of inert gas mixtures of N₂O, and increasingly dilute mixture of N₂O in air.

Further reading

Ravishankara, A.R., Daniel, J.S. & Portmann, R.W., 2009. Nitrous oxide (N₂O): the dominant ozone-depleting substance emitted in the 21st century. *Science*, 326(5949), pp.123–125.

Hansen, J. & Sato, M., 2004. Greenhouse gas growth rates. *Proceedings of the National Academy of Sciences of the United States of America*, 101(46), pp.16109–16114.

Severin, K., 2015. Synthetic chemistry with nitrous oxide. *Chemical Society Reviews*, 44(17), pp.6375–6386.

Gyton, M.R., Leforestier, B. & Chaplin, A.B., 2019. Rhodium(I) Pincer Complexes of Nitrous Oxide. *Angew. Chem. Int. Ed*, 58(43), pp.15295–15298.

Konsolakis, M., 2015. Recent Advances on Nitrous Oxide (N₂O) Decomposition over Non-Noble-Metal Oxide Catalysts: Catalytic Performance, Mechanistic Considerations, and Surface Chemistry Aspects. *ACS Catalysis*, 5(11), pp. 6397–6421.

Ming, T. *et al.*, 2016. Fighting global warming by greenhouse gas removal: destroying atmospheric nitrous oxide thanks to synergies between two breakthrough technologies. *Environ. Sci. Pollut. Res.*, 23(7), pp. 6119–6138.

Further details

Before starting the project, applications must hold an honours degree (at least II.1 or equivalent) in Chemistry, or other relevant discipline.

Enquires are welcomed and applications should be directed to Adrian (a.b.chaplin@warwick.ac.uk); please include a current CV that details any past research work.