ChemComm

COMMUNICATION

ROYAL SOCIETY OF CHEMISTRY

View Article Online

Check for updates

Cite this: Chem. Commun., 2023, 59, 7423

Received 23rd March 2023, Accepted 23rd May 2023

DOI: 10.1039/d3cc01442h

rsc.li/chemcomm

Nanophase-photocatalysis: loading, storing, and release of H_2O_2 using graphitic carbon nitride⁺

Akalya Karunakaran,^{ab} Katie J. Francis,^a Chris R. Bowen,^b Richard J. Ball,^c Yuanzhu Zhao,^a Lina Wang,^a Neil B. McKeown, ^b^d Mariolino Carta, ^b^e Philip J. Fletcher,^f Remi Castaing,^f Mark A. Isaacs, ^b^g Laurence J. Hardwick, ^b^{hi} Gema Cabello,^{hij} Igor V. Sazanovich ^k and Frank Marken ^s^a

A blue light mediated photochemical process using solid graphitic carbon nitride $(g-C_3N_4)$ in ambient air/isopropanol vapour is suggested to be linked to "nanophase" water inclusions and is shown to produce approx. 50 μ mol H₂O₂ per gram of g-C₃N₄, which can be stored in the solid g-C₃N₄ for later release for applications, for example, in disinfection or anti-bacterial surfaces.

Graphitic carbon nitride (g-C₃N₄, see Fig. 1A, first synthesised by Berzelius and named by Liebig¹) has a layered structure with many defects that can be produced at low cost and is employed in a number of important applications.^{2,3} Here, we explore the potential of g-C₃N₄ for the formation, storage, and release of hydrogen peroxide (H₂O₂). The photocatalytic formation of H₂O₂ has been widely reported⁴ and is useful to disinfect,⁵ bleach,⁶ or clean environments.⁷ In addition to effective production of H₂O₂ based on photo-catalysis⁸ from ambient oxygen and a hole quencher, there are reports of piezo-catalysis,⁹ which is indicative of a broader range of molecular activation

- ^a Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK. E-mail: f.marken@bath.ac.uk
- ^b Department of Mechanical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, UK
- ^c Department of Architecture & Civil Engineering, University of Bath, Claverton Down, Bath BA2 7AY, UK
- ^d EaStCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, Scotland EH9 3JF, UK
- ^e Department of Chemistry, Swansea University, College of Science, Grove Building, Singleton Park, Swansea SA2 8PP, UK
- ^fUniversity of Bath, Materials & Chemical Characterisation Facility, MC2, UK
- ^g HarwellXPS, Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot, OX11 0FA, UK
- ^h Stephenson Institute for Renewable Energy, Department of Chemistry, University of Liverpool, Liverpool L69 7ZF, UK
- ⁱ The Faraday Institution, Harwell Campus, Didcot, OX11 0RA, UK
- j Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge CB3 0EL, UK
- ^k Central Laser Facility, Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 OQX, UK
- † Electronic supplementary information (ESI) available. See DOI: https://doi.org/ 10.1039/d3cc01442h

processes for $g-C_3N_4$ at the microscopic scale. Singlet oxygen formation with $g-C_3N_4$ has been observed.¹⁰

Previously, when exploring the photochemical reactivity of $g-C_3N_4$ (as a solid powder or when immobilising $g-C_3N_4$ particles into an intrinsically microporous host material PIM-1)¹¹ immersed in a liquid phase, we observed H_2O_2 production in the aqueous phase in the presence of hole quenchers such as glucose or Triton X-100. Here, isopropanol vapour is employed in order to provide a quencher during the corresponding solid-state photochemical process. In contrast to previous studies, here the photocatalytic process is performed with the g-C₃N₄ powder exposed to light in ambient air. H_2O_2 is released only later in the absence of light upon contact to water (eqn (1) and (2)).

 $g-C_3N_4(H_2O) + h\nu/quencher/O_2 \rightarrow g-C_3N_4(H_2O_2)$ (1)

$$g-C_3N_4(H_2O_2) \rightarrow g-C_3N_4 + H_2O_2(aq)$$
 (2)

In a typical experiment,[‡] 50 mg of yellow g-C₃N₄ powder, possessing a flaky layered morphology (Fig. 1B), with surface area = $36.4 \text{ m}^2 \text{ g}^{-1}$ (based on nitrogen adsorption data);¹¹ was placed into a Petri dish with a transparent cover and illuminated with a blue light source (Thorlabs M385LP1 with typically 80 mW cm⁻² 385 nm light in approx. 2 cm distance).¹¹ A small vial containing liquid isopropanol was placed into the same Petri dish to maintain an atmosphere of isopropanol vapour as a quencher for holes that are generated by photoexcitation. After a 30 minute treatment, the yellow powder was recovered and then stored in a glass vial. Data from X-ray diffraction analysis (Fig. 1C) show essentially the same features before and after photochemical treatment, which is consistent with literature data for layered g-C₃N₄ (for disordered heptazine-based polymer organized in layers with a separation of 0.326 nm).¹² The main (002) peak occurs at 27.5°. Although literature reports indicate that under long term photo-irradiation conditions endo-peroxide signals should be seen,13 the data reported here for Raman analysis, surface enhanced Raman, and XPS surface analysis (see Fig. S2-S8, ESI†) all confirm that there is no significant structural change in the bulk, or on the surface, of



Fig. 1 (A) Molecular structure (idealised) for $g-C_3N_4$. (B) Scanning electron micrograph for $g-C_3N_4$ powder. (C) X-ray diffraction data for $g-C_3N_4$ (i) before and (ii) after blue light treatment in the presence of isopropanol vapour.

the g- C_3N_4 after blue light treatment. Most likely, the endoperoxide content is too low to be detected under these reaction conditions, although a shift from C–N to C–O at% in XPS data (see ESI,[†] Fig. S2) appears to be linked to the formation of products from the photochemical process on the g- C_3N_4 surface.

Data in Fig. 2A demonstrate the production of H_2O_2 (determined with *para*-nitrophenol and LC/MS detection; ESI[†]) when



Fig. 2 (A) Production of H_2O_2 with $g-C_3N_4$ powder suspended in 2 mL water (after 5 minutes) (i) as prepared catalyst and (ii) blue light/isopropanol vapour treated $g-C_3N_4$ (30 minutes). (B) H_2O_2 release (i) with $g-C_3N_4$ and (ii) with $g-C_3N_4$ @PIM-1 dispersed in 2 mL water (5 minutes) both after blue light treatment. (C) Repeat measurements with $g-C_3N_4$ @PIM-1 (5 mg) comparing the effects of (i) just intermittent drying in ambient light and (ii) intermittent treatment with blue light in isopropanol vapour. Error bars estimated $\pm 10\%$.

placing the photoactivated g- C_3N_4 powder into pure water. For the activated g- C_3N_4 , typically 100–200 μ M H₂O₂ in 2 cm³ water are released, whereas only traces of H₂O₂ are released without prior photoactivation. The release of H₂O₂ occurs immediately upon immersion and does not continue with time. Adding more g- C_3N_4 increases the H_2O_2 concentration in an approximately linear fashion. The number of moles of H_2O_2 released suggests approx. one H_2O_2 molecule for every 300 heptazine units in the g- C_3N_4 powder (or 0.06 wt% H_2O_2) assuming a bulk reaction. Fig. 2B shows data for the release of H_2O_2 (i) for g- C_3N_4 powder and (ii) for g- C_3N_4 @PIM-1 composite (employing 17 wt% intrinsically microporous polymer PIM-1 to give a film on filter paper; see ESI†). As in previous studies,^{11,14} PIM-1 is employed as molecularly rigid material to make the photocatalyst easily accessible to the aqueous phase and allows easy recovery for re-use of the catalyst. Fig. 2B shows that both g- C_3N_4 powder and polymer-embedded g- C_3N_4 exhibit similar H_2O_2 release.

The data in Fig. 2C demonstrate the re-use of $g-C_3N_4$ @PIM-1 with/without additional blue light treatment for up to five cycles. The intermittent blue light treatment clearly enhances the H_2O_2 release so that 0.5 mM H_2O_2 can be produced with only a few reaction cycles. The formation and release of H_2O_2 under blue light conditions can be discussed in terms of the following reaction steps:

$$g-C_3N_4 + h\nu \rightarrow g-C_3N_4^* \tag{3}$$

$$g-C_3N_4^* + isopropanol \rightarrow g-C_3N_4^- + H^+(aq) + products$$
(4)

$$2 \text{ g-C}_{3}\text{N}_{4}^{-} + \text{O}_{2} + 2 \text{ H}^{+} \rightarrow 2 \text{ g-C}_{3}\text{N}_{4}(\text{H}_{2}\text{O}_{2})$$
(5)

$$g-C_3N_4(H_2O_2) \rightarrow g-C_3N_4 + H_2O_2(aq)$$
 (6)

Photoexcitation of $g-C_3N_4$ leads to an excited state (eqn (3)), which after charge separation produces a hole and an electron. The hole reacts with the isopropanol quencher to give protons and products (eqn (4)). The electrons, which have been reported to generate a strong electron paramagnetic resonance and blue coloration,¹⁵ can combine with ambient oxygen and protons to give trapped H_2O_2 (eqn (5)). The g-C₃N₄(H_2O_2) material can be stored for several weeks without significant loss of H2O2 content (Fig. 3B), and its eventual immersion into water releases H_2O_2 (eqn (6)). Thermogravimetric analysis of g-C₃N₄ before and after photoreaction (see ESI,† Fig. S9) reveals the presence of water (approx. 2.5 wt%), which is likely to be present as a "nanophase" in between layers and likely to play a crucial role (see eqn (4) during the solid state photochemical formation of H_2O_2 . Heating the g-C₃N₄(H_2O_2) sample to 150 °C removes H_2O_2 and immediately destroys the H₂O₂. Intriguingly, a vacuum treatment (2h, approx. 10 mTorr) at room temperature also removes the H₂O₂.

The release of H_2O_2 into aqueous media can be visualised with the 3,3',5,5'-tetramethylbenzidine (TMB) colour reaction.¹⁶ The g-C₃N₄ treated with blue light and isopropanol was added 2 cm³ of deionized water. After 5 minutes, the solution was filtered with a 0.2 µm filter. The solution is added to the vial containing TMB and 0.1 M CH₃COOH. Fig. 3A shows photographs of the test solutions (i) without and (ii) with 50 µM H₂O₂ intentionally added as reference. Samples (iii) to (viii) correspond to added weights (0, 5, 10, 15, 20, 25 mg) of g-C₃N₄



Fig. 3 (A) Test solutions containing 2.5 mL water, 0.5 mL DMSO, 0.1 M CH₃COOH, 0.5 mM TMB, with (i) no addition, with (ii) 50 μ M H₂O₂ as a reference, and with (iii) 0 mg, (iv) 5 mg, (v) 10 mg, (vi) 15 mg, (vii) 20 mg, (viii) 25 mg of photoactivated g-C₃N₄. (B) Plot of release of H₂O₂ (10 mg g-C₃N₄ in 2 mL water) *versus* time after blue light/isopropanol treatment (error bars based on one standard deviation and triplicate measurements).

photochemically charged g- C_3N_4 . A Nafion-impregnated filter paper was employed to bind the cationic oxidised form of TMB to amplify the blue colour signal. The colour reaction is consistent with the analysis of H_2O_2 concentration by mass spectrometry and suggests H_2O_2 release in the 50 to 500 μ M range.

In conclusion, active sites for photo-generated H_2O_2 binding/storage in the solid g- C_3N_4 material appear to exist (approx. one bound H_2O_2 per 300 heptazine units), which are probably associated with nanophase water. Once bound, H_2O_2 in g- C_3N_4 remains stable over prolonged periods of time (Fig. 3B). However, a short vacuum treatment at room temperature or a heat treatment at 150 °C removes both the liquid nanophase H_2O and any trapped H_2O_2 .

Coatings of g- C_3N_4 could be employed to release H_2O_2 upon contact with water, for example as a disinfectant in hospital environments.²⁰ Further studies of the nature of the H_2O_2 binding interaction, the effects of humidity and the nature of the hole quencher, and further g- C_3N_4 structural engineering provide future potential to achieve higher levels of H_2O_2 to be bound, stored, and released. Other types of photochemical gas conversions could be performed under illumination in solid state and with aqueous nanophase entrapment.

Akalya Karunakaran: data curation; formal Analysis; investigation; methodology; writing – review & editing. Katie J. Francis: data curation; investigation. Chris R. Bowen and Richard J. Ball: conceptualization; methodology; supervision; writing – review & editing. Yuanzhu Zhao and Lina Wang: data curation; investigation; writing – review & editing. Neil B. McKeown and Mariolino Carta: conceptualization; supervision; writing – review & editing. Philip J. Fletcher, Remi Castaing, and Mark Isaac: data curation; investigation; writing – review & editing. Laurence J. Hardwick: formal analysis; supervision; writing – review & editing. Gema Cabello and Igor V. Sazanovich: data curation; formal analysis; investigation; methodology; writing – review & editing. Frank Marken: conceptualization; project administration; resources; supervision; writing – original draft.

A. K. thanks the National Overseas Scholarship-India. L. J. H. and G. C. were supported by the UK Faraday Institution (EPSRC EP/S003053/1) through the Degradation Project (grant numbers FIRG001 and FIRG024). STFC is acknowledged for beam time on the ULTRA facility to carry out Kerr-gated experiments. We thank Alexander Cowan (University of Liverpool) for helpful discussion.

Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

 \ddagger Experimental: g-C₃N₄ was prepared as reported previously.¹⁷ PIM-1 was prepared following a literature method.^{18,19} Films of g-C₃N₄@PIM-1 were obtained by drop casting. An amount of 5 mg of graphitic carbon nitride (measured with a Ohaus PX224 analytical balance) was added to the 1 cm³ solution of 1 mg PIM-1 in chloroform and sonicated for 15 minutes. The solution was drop-casted on filter paper with a size of 2×2 cm². The sample was air dried to leave a layer of g-C₃N₄@PIM-1 on the filter paper (thickness approx. 0.25 mm). Further experimental details are provided in the ESI.†

- 1 J. V. Liebig, Ann. Pharm., 1834, 10, 10.
- 2 Y. Wang, X. C. Wang and M. Antonietti, *Angew. Chem.*, *Int. Ed.*, 2012, **51**(1), 68–89.
- 3 K. Z. Qi, S. Y. Liu and A. Zada, J. Taiwan Inst. Chem. Eng., 2020, 109, 111-123.

- 4 J. Q. Wen, J. Xie, X. B. Chen and X. Li, *Appl. Surf. Sci.*, 2017, **391**, 72–123.
- 5 L. L. Chen, W. P. Shi, T. D. Zhang, R. B. Zhou, X. Q. Jin, Y. Q. Zhou, W. J. Lin, W. H. Guo and D. C. Yin, 2D Mater., 2022, 9(4), 045034.
- 6 Z. Haider, H. I. Cho, G. H. Moon and H. I. Kim, *Catal. Today*, 2019, 335, 55–64.
- 7 F. Ding, D. Yang, Z. W. Tong, Y. H. Nan, Y. J. Wang, X. Y. Zou and Z. Y. Jiang, *Environ. Sci.: Nano*, 2017, 4(7), 1455–1469.
- 8 S. W. Cao, J. X. Low, J. G. Yu and M. Jaroniec, Adv. Mater., 2015, 27(13), 2150-2176.
- 9 C. Hu, F. Chen, Y. G. Wang, N. Tian, T. Y. Ma, Y. H. Zhang and H. W. Huang, *Adv. Mater.*, 2021, 33(24), 2101751.
- 10 M. Tamtaji, A. Tyagi, C. Y. Young, P. R. Galligan, H. W. Liu, Z. J. Liu, R. Karimi, Y. T. Cai, A. P. Roxas, H. L. Wong and Z. T. Luo, ACS Appl. Nano Mater., 2021, 4(8), 7563–7586.
- 11 Y. Z. Zhao, L. N. Wang, R. Malpass-Evans, N. B. McKeown, M. Carta, J. P. Lowe, C. L. Lyall, R. Castaing, P. J. Fletcher, G. Kociok-Kohn, J. Wenk, Z. Y. Guo and F. Marken, ACS Appl. Mater. Interfaces, 2022, 14(17), 19938–19948.
- 12 F. Fina, S. K. Callear, G. M. Carins and J. T. S. Irvine, *Chem. Mater.*, 2015, 27(7), 2612–2618.
- 13 Y. Shiraishi, S. Kanazawa, Y. Sugano, D. Tsukamoto, H. Sakamoto, S. Ichikawa and T. Hirai, *ACS Catal.*, 2014, **4**, 774–780.
- Y. Z. Zhao, J. Dobson, C. Harabajiu, E. Madrid, T. Kanyanee, C. Lyall, S. Reeksting, M. Carta, N. B. McKeown, L. Torrente-Murciano, K. Black and F. Marken, *Bioelectrochemistry*, 2020, 134, 107499.
- 15 D. Hollmann, M. Karnahl, S. Tschierlei, K. Kailasam, M. Schneider, J. Radnik, K. Grabow, U. Bentrup, H. Junge, M. Beller, S. Lochbrunner, A. Thomas and A. Brückner, *Chem. Mater.*, 2014, 26(4), 1727–1733.
- 16 L. N. Wang, M. Carta, R. Malpass-Evans, N. B. McKeown, P. J. Fletcher, P. Estrela, A. Roldan and F. Marken, *J. Catal.*, 2011, 416, 253–266.
- 17 Y. Z. Zhao, N. A. Al Abass, R. Malpass-Evans, M. Carta, N. B. McKeown, E. Madrid, P. J. Fletcher and F. Marken, *Electrochem. Commun.*, 2019, **103**, 1–6.
- 18 P. M. Budd, E. S. Elabas, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. Tattershall and D. Wang, *Adv. Mater.*, 2004, **16**, 456–457.
- 19 P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib and C. E. Tattershall, *Chem. Commun.*, 2004, 230–231.
- 20 Z. Y. Teng, N. L. Yang, H. Y. Lv, S. C. Wang, M. Z. Hu, C. Y. Wang, D. Wang and G. X. Wang, *Chemistry*, 2019, 5, 664–680.