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# Nanophase-photocatalysis: loading, storing, and release of H<sub>2</sub>O<sub>2</sub> using graphitic carbon nitride†

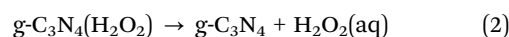
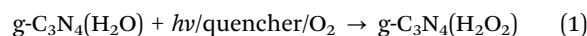
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**A blue light mediated photochemical process using solid graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) in ambient air/isopropanol vapour is suggested to be linked to “nanophase” water inclusions and is shown to produce approx. 50 μmol H<sub>2</sub>O<sub>2</sub> per gram of g-C<sub>3</sub>N<sub>4</sub>, which can be stored in the solid g-C<sub>3</sub>N<sub>4</sub> for later release for applications, for example, in disinfection or anti-bacterial surfaces.**

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>, see Fig. 1A, first synthesised by Berzelius and named by Liebig<sup>1</sup>) has a layered structure with many defects that can be produced at low cost and is employed in a number of important applications.<sup>2,3</sup> Here, we explore the potential of g-C<sub>3</sub>N<sub>4</sub> for the formation, storage, and release of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The photocatalytic formation of H<sub>2</sub>O<sub>2</sub> has been widely reported<sup>4</sup> and is useful to disinfect,<sup>5</sup> bleach,<sup>6</sup> or clean environments.<sup>7</sup> In addition to effective production of H<sub>2</sub>O<sub>2</sub> based on photo-catalysis<sup>8</sup> from ambient oxygen and a hole quencher, there are reports of piezo-catalysis,<sup>9</sup> which is indicative of a broader range of molecular activation

processes for g-C<sub>3</sub>N<sub>4</sub> at the microscopic scale. Singlet oxygen formation with g-C<sub>3</sub>N<sub>4</sub> has been observed.<sup>10</sup>

Previously, when exploring the photochemical reactivity of g-C<sub>3</sub>N<sub>4</sub> (as a solid powder or when immobilising g-C<sub>3</sub>N<sub>4</sub> particles into an intrinsically microporous host material PIM-1)<sup>11</sup> immersed in a liquid phase, we observed H<sub>2</sub>O<sub>2</sub> 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-C<sub>3</sub>N<sub>4</sub> powder exposed to light in ambient air. H<sub>2</sub>O<sub>2</sub> is released only later in the absence of light upon contact to water (eqn (1) and (2)).



In a typical experiment,‡ 50 mg of yellow g-C<sub>3</sub>N<sub>4</sub> powder, possessing a flaky layered morphology (Fig. 1B), with surface area = 36.4 m<sup>2</sup> g<sup>-1</sup> (based on nitrogen adsorption data),<sup>11</sup> was placed into a Petri dish with a transparent cover and illuminated with a blue light source (Thorlabs M385LP1 with typically 80 mW cm<sup>-2</sup> 385 nm light in approx. 2 cm distance).<sup>11</sup> 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-C<sub>3</sub>N<sub>4</sub> (for disordered heptazine-based polymer organized in layers with a separation of 0.326 nm).<sup>12</sup> 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,<sup>13</sup> 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

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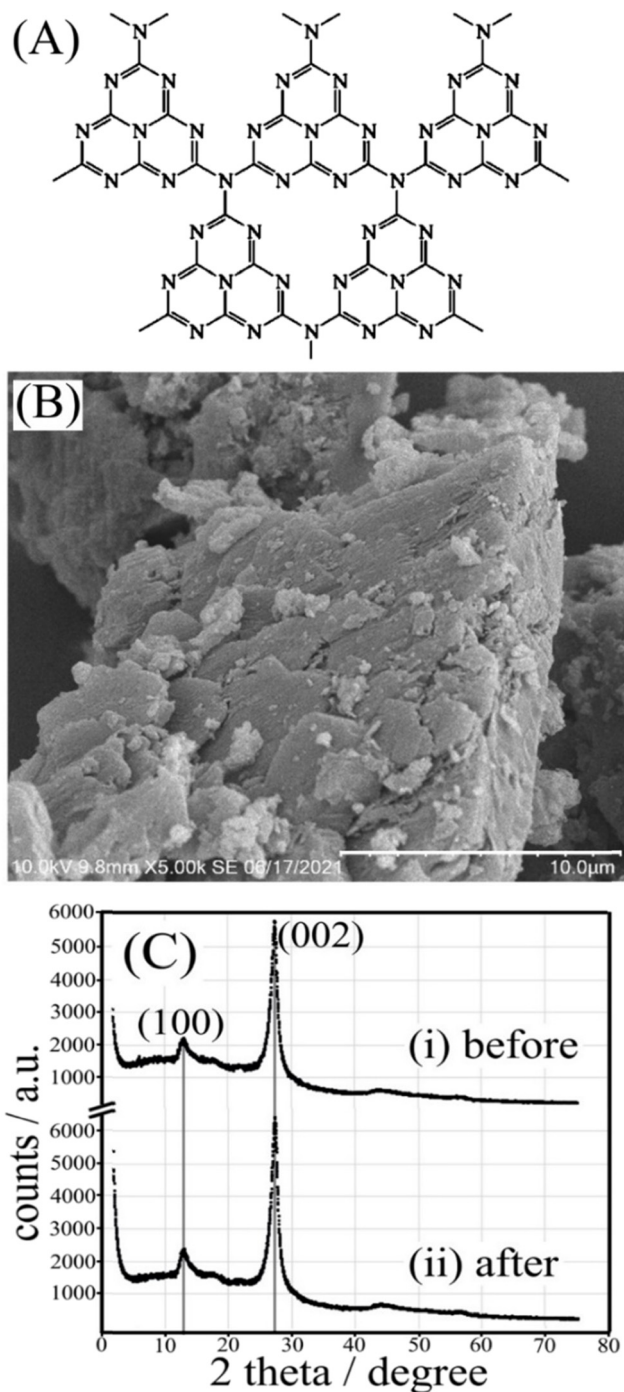
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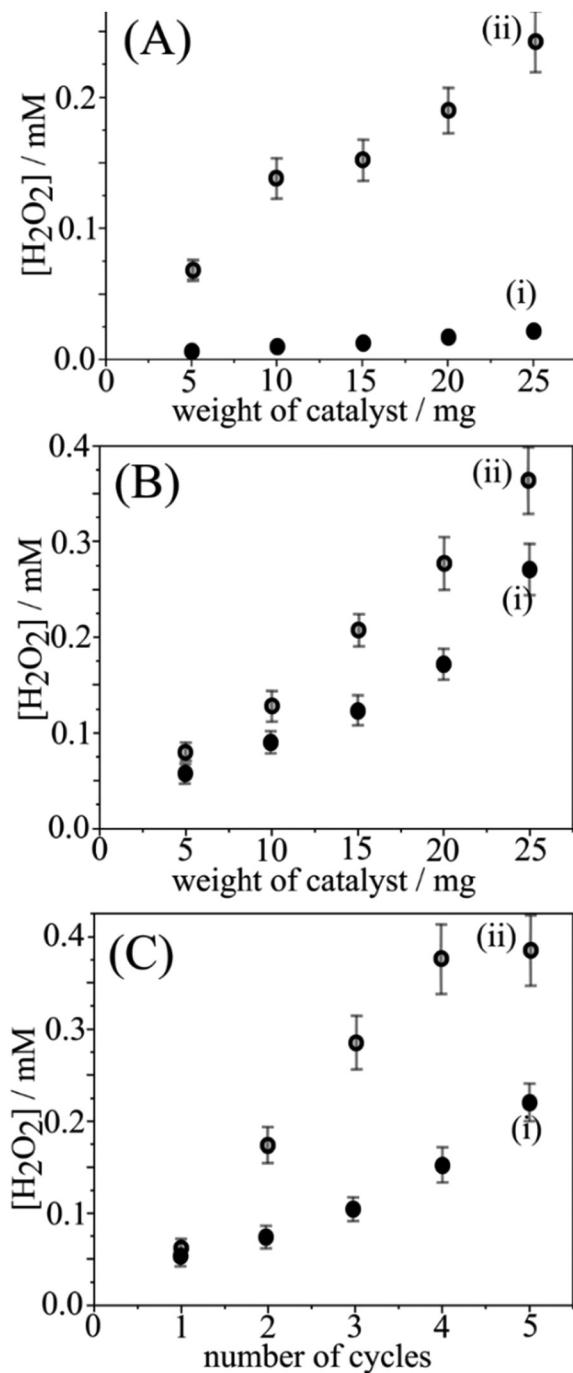




**Fig. 1** (A) Molecular structure (idealised) for g-C<sub>3</sub>N<sub>4</sub>. (B) Scanning electron micrograph for g-C<sub>3</sub>N<sub>4</sub> powder. (C) X-ray diffraction data for g-C<sub>3</sub>N<sub>4</sub> (i) before and (ii) after blue light treatment in the presence of isopropanol vapour.

the g-C<sub>3</sub>N<sub>4</sub> 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<sub>3</sub>N<sub>4</sub> surface.

Data in Fig. 2A demonstrate the production of H<sub>2</sub>O<sub>2</sub> (determined with *para*-nitrophenol and LC/MS detection; ESI†) when



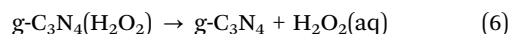
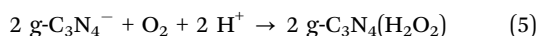
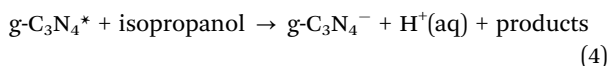
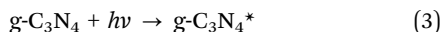
**Fig. 2** (A) Production of H<sub>2</sub>O<sub>2</sub> with g-C<sub>3</sub>N<sub>4</sub> powder suspended in 2 mL water (after 5 minutes) (i) as prepared catalyst and (ii) blue light/isopropanol vapour treated g-C<sub>3</sub>N<sub>4</sub> (30 minutes). (B) H<sub>2</sub>O<sub>2</sub> release (i) with g-C<sub>3</sub>N<sub>4</sub> and (ii) with g-C<sub>3</sub>N<sub>4</sub>@PIM-1 dispersed in 2 mL water (5 minutes) both after blue light treatment. (C) Repeat measurements with g-C<sub>3</sub>N<sub>4</sub>@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 ±10%.

placing the photoactivated g-C<sub>3</sub>N<sub>4</sub> powder into pure water. For the activated g-C<sub>3</sub>N<sub>4</sub>, typically 100–200 μM H<sub>2</sub>O<sub>2</sub> in 2 cm<sup>3</sup> water are released, whereas only traces of H<sub>2</sub>O<sub>2</sub> are released without prior photoactivation. The release of H<sub>2</sub>O<sub>2</sub> occurs immediately



upon immersion and does not continue with time. Adding more  $g\text{-C}_3\text{N}_4$  increases the  $\text{H}_2\text{O}_2$  concentration in an approximately linear fashion. The number of moles of  $\text{H}_2\text{O}_2$  released suggests approx. one  $\text{H}_2\text{O}_2$  molecule for every 300 heptazine units in the  $g\text{-C}_3\text{N}_4$  powder (or 0.06 wt%  $\text{H}_2\text{O}_2$ ) assuming a bulk reaction. Fig. 2B shows data for the release of  $\text{H}_2\text{O}_2$  (i) for  $g\text{-C}_3\text{N}_4$  powder and (ii) for  $g\text{-C}_3\text{N}_4$ @PIM-1 composite (employing 17 wt% intrinsically microporous polymer PIM-1 to give a film on filter paper; see ESI†). As in previous studies,<sup>11,14</sup> 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  $g\text{-C}_3\text{N}_4$  powder and polymer-embedded  $g\text{-C}_3\text{N}_4$  exhibit similar  $\text{H}_2\text{O}_2$  release.

The data in Fig. 2C demonstrate the re-use of  $g\text{-C}_3\text{N}_4$ @PIM-1 with/without additional blue light treatment for up to five cycles. The intermittent blue light treatment clearly enhances the  $\text{H}_2\text{O}_2$  release so that 0.5 mM  $\text{H}_2\text{O}_2$  can be produced with only a few reaction cycles. The formation and release of  $\text{H}_2\text{O}_2$  under blue light conditions can be discussed in terms of the following reaction steps:



Photoexcitation of  $g\text{-C}_3\text{N}_4$  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,<sup>15</sup> can combine with ambient oxygen and protons to give trapped  $\text{H}_2\text{O}_2$  (eqn (5)). The  $g\text{-C}_3\text{N}_4(\text{H}_2\text{O}_2)$  material can be stored for several weeks without significant loss of  $\text{H}_2\text{O}_2$  content (Fig. 3B), and its eventual immersion into water releases  $\text{H}_2\text{O}_2$  (eqn (6)). Thermogravimetric analysis of  $g\text{-C}_3\text{N}_4$  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  $\text{H}_2\text{O}_2$ ). Heating the  $g\text{-C}_3\text{N}_4(\text{H}_2\text{O}_2)$  sample to 150 °C removes  $\text{H}_2\text{O}$  and immediately destroys the  $\text{H}_2\text{O}_2$ . Intriguingly, a vacuum treatment (2h, approx. 10 mTorr) at room temperature also removes the  $\text{H}_2\text{O}_2$ .

The release of  $\text{H}_2\text{O}_2$  into aqueous media can be visualised with the 3,3',5,5'-tetramethylbenzidine (TMB) colour reaction.<sup>16</sup> The  $g\text{-C}_3\text{N}_4$  treated with blue light and isopropanol was added 2 cm<sup>3</sup> 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  $\text{CH}_3\text{COOH}$ . Fig. 3A shows photographs of the test solutions (i) without and (ii) with 50 μM  $\text{H}_2\text{O}_2$  intentionally added as reference. Samples (iii) to (viii) correspond to added weights (0, 5, 10, 15, 20, 25 mg) of  $g\text{-C}_3\text{N}_4$

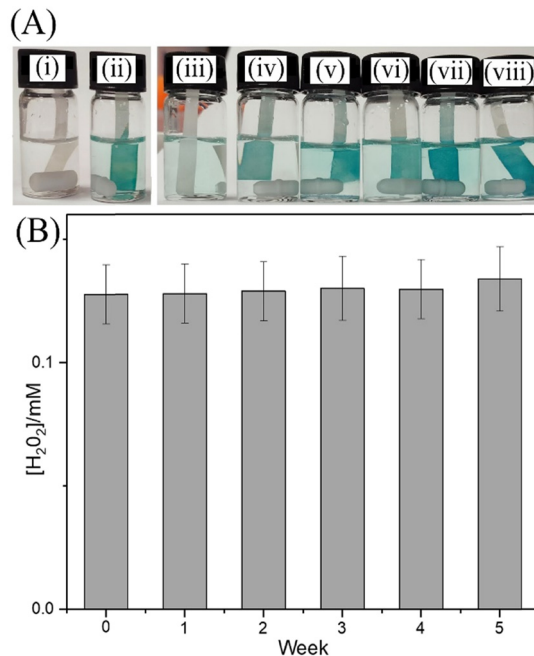


Fig. 3 (A) Test solutions containing 2.5 mL water, 0.5 mL DMSO, 0.1 M  $\text{CH}_3\text{COOH}$ , 0.5 mM TMB, with (i) no addition, with (ii) 50 μM  $\text{H}_2\text{O}_2$  as a reference, and with (iii) 0 mg, (iv) 5 mg, (v) 10 mg, (vi) 15 mg, (vii) 20 mg, (viii) 25 mg of photoactivated  $g\text{-C}_3\text{N}_4$ . (B) Plot of release of  $\text{H}_2\text{O}_2$  (10 mg  $g\text{-C}_3\text{N}_4$  in 2 mL water) versus time after blue light/isopropanol treatment (error bars based on one standard deviation and triplicate measurements).

photochemically charged  $g\text{-C}_3\text{N}_4$ . 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  $\text{H}_2\text{O}_2$  concentration by mass spectrometry and suggests  $\text{H}_2\text{O}_2$  release in the 50 to 500 μM range.

In conclusion, active sites for photo-generated  $\text{H}_2\text{O}_2$  binding/storage in the solid  $g\text{-C}_3\text{N}_4$  material appear to exist (approx. one bound  $\text{H}_2\text{O}_2$  per 300 heptazine units), which are probably associated with nanophase water. Once bound,  $\text{H}_2\text{O}_2$  in  $g\text{-C}_3\text{N}_4$  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  $\text{H}_2\text{O}$  and any trapped  $\text{H}_2\text{O}_2$ .

Coatings of  $g\text{-C}_3\text{N}_4$  could be employed to release  $\text{H}_2\text{O}_2$  upon contact with water, for example as a disinfectant in hospital environments.<sup>20</sup> Further studies of the nature of the  $\text{H}_2\text{O}_2$  binding interaction, the effects of humidity and the nature of the hole quencher, and further  $g\text{-C}_3\text{N}_4$  structural engineering provide future potential to achieve higher levels of  $\text{H}_2\text{O}_2$  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.

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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.

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## Conflicts of interest

There are no conflicts of interest to declare.

## Notes and references

‡ Experimental: g-C<sub>3</sub>N<sub>4</sub> was prepared as reported previously.<sup>17</sup> PIM-1 was prepared following a literature method.<sup>18,19</sup> Films of g-C<sub>3</sub>N<sub>4</sub>@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 cm<sup>3</sup> 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 cm<sup>2</sup>. The sample was air dried to leave a layer of g-C<sub>3</sub>N<sub>4</sub>@PIM-1 on the filter paper (thickness approx. 0.25 mm). Further experimental details are provided in the ESI.†

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