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

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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 µmol H_2O_2 per gram of g-C_3N_4, which can be stored in the solid g-C_3N_4 for later release for applications, for example, in disinfection or anti-bacterial surfaces.

Graphitic carbon nitride (g-C_3N_4, see Fig. 1A, first synthesised by Berzelius and named by Liebig[1]) 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-C_3N_4 for the formation, storage, and release of hydrogen peroxide (H_2O_2). The photocatalytic formation of H_2O_2 has been widely reported[4] and is useful to disinfect,[5] bleach,[6] or clean environments.[7] In addition to effective production of H_2O_2 based on photo-catalysis[8] from ambient oxygen and a hole quencher, there are reports of piezo-catalysis,[9] which is indicative of a broader range of molecular activation 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-C_3N_4 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)).

$$\text{g-C}_3\text{N}_4(\text{H}_2\text{O}) + h\nu/\text{quencher}/\text{O}_2 \rightarrow \text{g-C}_3\text{N}_4(\text{H}_2\text{O}_2) \quad (1)$$

$$\text{g-C}_3\text{N}_4(\text{H}_2\text{O}_2) \rightarrow \text{g-C}_3\text{N}_4 + \text{H}_2\text{O}_2(\text{aq}) \quad (2)$$

In a typical experiment,‡ 50 mg of yellow g-C_3N_4 powder, possessing a flaky layered morphology (Fig. 1B), with surface area = 36.4 $m^2\ g^{-1}$ (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-C_3N_4 (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

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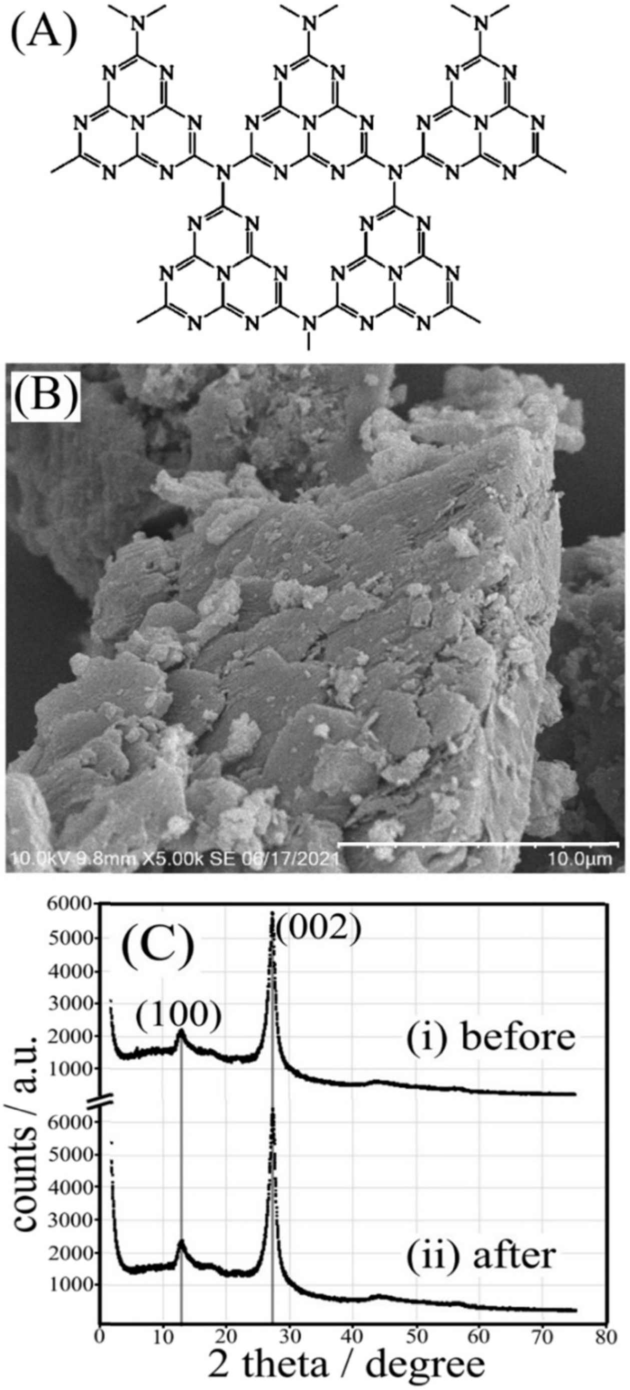

Fig. 1 (A) Molecular structure (idealised) for g-C_3N_4. (B) Scanning electron micrograph for g-C_3N_4 powder. (C) X-ray diffraction data for g-C_3N_4 (i) before and (ii) after blue light treatment in the presence of isopropanol vapour.

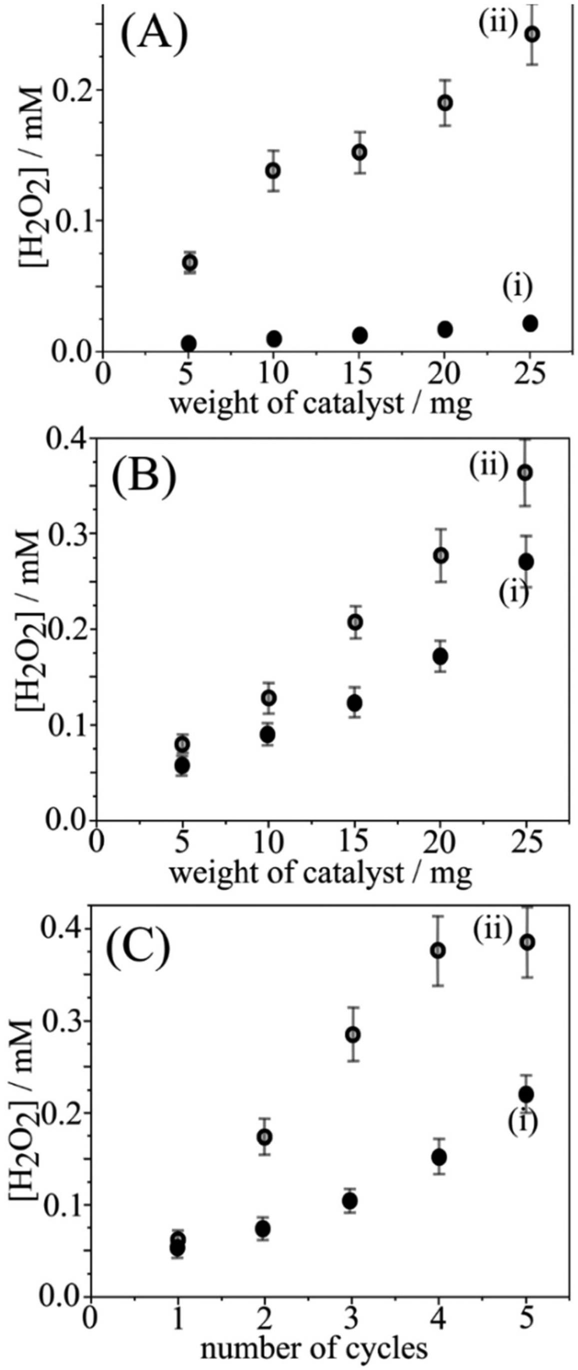

Fig. 2 (A) Production of H_2O_2 with g-C_3N_4 powder suspended in 2 mL water (after 5 minutes) (i) as prepared catalyst and (ii) blue light/isopropanol vapour treated g-C_3N_4 (30 minutes). (B) H_2O_2 release (i) with g-C_3N_4 and (ii) with g-C_3N_4@PIM-1 dispersed in 2 mL water (5 minutes) both after 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 ±10%.

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 placing the photoactivated g-C_3N_4 powder into pure water. For the activated g-C_3N_4, typically 100–200 μM H_2O_2 in 2 cm^3 water are released, whereas only traces of H_2O_2 are released without prior photoactivation. The release of H_2O_2 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:

$$\text{g-C}_3\text{N}_4 + h\nu \rightarrow \text{g-C}_3\text{N}_4{}^* \qquad (3)$$

$$\text{g-C}_3\text{N}_4{}^* + \text{isopropanol} \rightarrow \text{g-C}_3\text{N}_4{}^- + \text{H}^+(\text{aq}) + \text{products} \qquad (4)$$

$$2\ \text{g-C}_3\text{N}_4{}^- + \text{O}_2 + 2\ \text{H}^+ \rightarrow 2\ \text{g-C}_3\text{N}_4(\text{H}_2\text{O}_2) \qquad (5)$$

$$\text{g-C}_3\text{N}_4(\text{H}_2\text{O}_2) \rightarrow \text{g-C}_3\text{N}_4 + \text{H}_2\text{O}_2(\text{aq}) \qquad (6)$$

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-$C_3N_4(H_2O_2)$ material can be stored for several weeks without significant loss of H_2O_2 content (Fig. 3B), and its eventual immersion into water releases H_2O_2 (eqn (6)). Thermogravimetric analysis of g-C_3N_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 H_2O_2. Heating the g-$C_3N_4(H_2O_2)$ sample to 150 °C removes H_2O and immediately destroys the H_2O_2. Intriguingly, a vacuum treatment (2h, approx. 10 mTorr) at room temperature also removes the H_2O_2.

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-C_3N_4 treated with blue light and isopropanol was added 2 cm^3 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 CH_3COOH. Fig. 3A shows photographs of the test solutions (i) without and (ii) with 50 μM H_2O_2 intentionally added as reference. Samples (iii) to (viii) correspond to added weights (0, 5, 10, 15, 20, 25 mg) of g-C_3N_4 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 μM range.

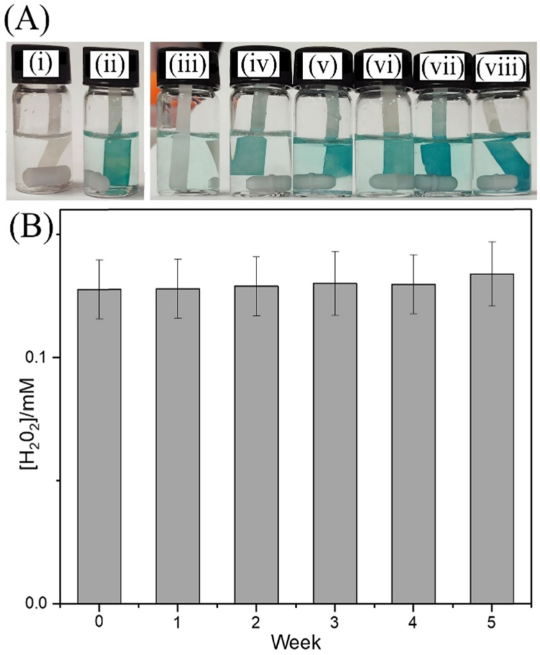

Fig. 3 (A) Test solutions containing 2.5 mL water, 0.5 mL DMSO, 0.1 M CH_3COOH, 0.5 mM TMB, with (i) no addition, with (ii) 50 μM H_2O_2 as a reference, and with (iii) 0 mg, (iv) 5 mg, (v) 10 mg, (vi) 15 mg, (vii) 20 mg, (viii) 25 mg of photoactivated g-C_3N_4. (B) Plot of release of H_2O_2 (10 mg g-C_3N_4 in 2 mL water) *versus* time after blue light/isopropanol treatment (error bars based on one standard deviation and triplicate measurements).

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.

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Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

‡ Experimental: g-C_3N_4 was prepared as reported previously.[17] PIM-1 was prepared following a literature method.[18,19] Films of g-C_3N_4@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^3 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^2. The sample was air dried to leave a layer of g-C_3N_4@PIM-1 on the filter paper (thickness approx. 0.25 mm). Further experimental details are provided in the ESI.†

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