Effects of g-C_3N_4 Heterogenization into Intrinsically Microporous Polymers on the Photocatalytic Generation of Hydrogen Peroxide

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ABSTRACT: Graphitic carbon nitride (g-C_3N_4) is known to photogenerate hydrogen peroxide in the presence of hole quenchers in aqueous environments. Here, the g-C_3N_4 photocatalyst is embedded into a host polymer of intrinsic microporosity (PIM-1) to provide recoverable heterogenized photocatalysts without loss of activity. Different types of g-C_3N_4 (including Pt@g-C_3N_4, Pd@g-C_3N_4, and Au@g-C_3N_4) and different quenchers are investigated. Exploratory experiments yield data that suggest binding of the quencher either (i) directly by adsorption onto the g-C_3N_4 (as shown for α-glucose) or (ii) indirectly by absorption into the microporous polymer host environment (as shown for Triton X-100) enhances the overall photochemical H_2O_2 production process. The amphiphilic molecule Triton X-100 is shown to interact only weakly with g-C_3N_4 but strongly with PIM-1, resulting in accumulation and enhanced H_2O_2 production due to the microporous polymer host.

KEYWORDS: disinfection, hydrogen generation, adsorption, bipolar photocatalysis, hydrogen peroxide

1. INTRODUCTION

Hydrogen peroxide is a crucial chemical reagent in many fields of application including green epoxidation chemistry, pollutant treatment, surface cleaning, solar disinfection, bleaching of pulp, health and wound cleaning, or for electrochemical and colorimetric biosensor applications. Hydrogen peroxide is employed in nature/biological systems, for example, during inflammation and in peroxisome processes. The production of hydrogen peroxide is possible from molecular oxygen by chemical reduction, for example, the BASF anthraquinone process based on anthraquinol and air or by direct electrochemical reduction on carbon electrodes. Direct reaction of hydrogen and oxygen gas has been demonstrated over heterogeneous catalysts to yield up to 56 mM H_2O_2 in aqueous media. Many sacrificial reducing agents (or pollutants) react in the presence of catalyst with molecular oxygen to give hydrogen peroxide. In nature, peroxidases are able to generate H_2O_2 and/or to use H_2O_2 in oxidation reactions. Reports have emerged on the photochemical production of hydrogen peroxide from water and O_2. However, thermodynamically, hydrogen peroxide is unstable and likely to dismute back into H_2O and one-half O_2.

Photocatalytic production of H_2O_2 is commonly observed when oxygen is allowed to interact with the photocatalyst in the presence of hole quencher materials (e.g., alcohols, oxalic acid, or other organic donors).
material. Particulate g-C₃N₄ can be employed as suspended particles or 2D nanoparticles, coated onto surfaces, associated with other photocatalysts, or embedded into polymers or porous host materials. It has been reported that g-C₃N₄ in conjunction with graphene can be employed to photogenerate H₂O₂. Defect engineering has been employed to increase rates of H₂O₂ production.

Polymers of intrinsic microporosity (PIMs) are molecularly stiff materials composed of contorted ladder-like structures (e.g., the most-studied PIM-1 and PIM-EA-TB in Figure 1). This leads to good solvent processability (due to molecular interactions in the solid being weak), and uniformly microporous film deposits cast from solution with typically 1 nm diameter pores. Applications for PIMs have emerged in gas permeation and separation, as well as in liquid phase processes, or electrochemical energy storage. Both PIM-1 and PIM-EA-TB have been employed previously for embedding catalysts with the aim of minimizing catalyst surface blocking by avoiding detrimental PIM-catalyst interactions (due to molecular rigidity in the polymer backbone) and maximizing catalyst performance (due to a fully accessible catalyst surface). We have recently demonstrated photocatalytic hydrogen production with a co-catalyst-modified g-C₃N₄ embedded into a PIM.

Here, we investigate g-C₃N₄ photocatalysts for H₂O₂ generation (i) suspended in aqueous solution, (ii) coated with a PIM material and suspended as particles, or (iii) heterogenized when embedded into PIM-1 or PIM-EA-TB and deposited onto a filter paper substrate. In this study, the heterogenization of g-C₃N₄ photocatalysts into polymers of intrinsic microporosity is demonstrated to give highly active films (recoverable from solution) with reactivity similar to that of suspension systems. Filter paper is employed as a simple substrate for photocatalyst–polymer composites to form uniform, stable, and recoverable/reusable films. The important role of hole quencher adsorption (both directly onto g-C₃N₄ and indirectly into PIM-1 micropores) in the photocatalytic reaction is highlighted. Glucose is employed as quencher of choice due to its prevalence in digested biomass, for example, from cellulose. In the presence of amphiphilic molecules such as Triton X-100, PIM-1 is shown to bind the quencher and, in this way, introduce a localized high-concentration environment for enhancing photoreaction and H₂O₂ production.

2. EXPERIMENTAL SECTION

2.1. Reagents. Melamine, glucose, sodium oxalate, potassium hexachloroplatinate(IV), palladium(II) chloride, and potassium gold(III) chloride were purchased from Sigma-Aldrich and used without further purification. Sodium acetate trihydrate was purchased from BDH Chemicals Ltd. Triton X-100 (C₁₀H₃₂O₄(C₂H₄O₂)₉) was obtained from Biopol GmbH. PIM-1, PIM-EA-TB, and g-C₃N₄ were prepared following literature recipes. Ultrapure (18.2 MΩ cm at 18 °C) water from a Thermo Fisher water purification system was used for all solutions.

2.2. Instrumentation. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 Plus instrument with a 200 kV maximum accelerating voltage. Energy dispersive X-ray analysis (EDX) data was collected using an Oxford Instruments X-Max™ silicon drift detector. Scanning electron microscopy (SEM) images were captured with a JEOI JSM-7900F FESEM instrument at an accelerating voltage of 5 kV. Powder X-ray diffraction (PXRD) patterns were recorded in transmission mode on a STOE STADI P equipped with a Multi-Mythen detector using monochromated Cu Kα radiation (1.54060 Å). Raman spectroscopy was performed at wavelengths of 325, 332, and 785 nm excitation with a Renishaw inVia confocal Raman microscope. Mass spectrometry analysis was carried out with an Automated Agilent QTOF (Walkup) used with HPLC (four chromatography columns) and a variable wavelength detector. Nitrogen gas adsorption analysis (Brunauer–Emmett–Teller or BET) for g-C₃N₄ and PIM-1 powder was performed with an Autosorb-iQ-C instrument by Quantachrome. NMR spectra were acquired on a 400 MHz Bruker Neo spectrometer equipped with an iProbe. Spectra were acquired unlocked in H₂O at 298 K, and an automated shimming routine was carried out on the ¹H signal. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Fisher K-Alpha+ facility using a monochromated Cu Kα radiation (1.54060 Å). The light source in photochemical experiments was a Thorlabs M385LP1 with nominal 1200 mW 385 nm light. The intensity is 80 mW cm⁻² at a distance of 2 cm from the light source. Graphitic carbon nitride was obtained by heating melamine at 550 °C in a tube furnace for 4 h in a crucible with lid in ambient air. The yellow product was ground in a mortar to give a uniform product.
aqueous solution and employed in photochemical reactions. In air, the composite-immobilized film was washed with water and dried.

2.3.2. Embedding Photocatalysts into Films. To immobilize g-C3N4@PIM-1 composite onto a filter paper, g-C3N4 and PIM-1 with a 5:1 weight ratio were added into chloroform (5 mg g-C3N4 and 1 mg PIM-1 in 1 cm³) and suspended by ultrasonication for 15 min. The composite was drop-cast deposited onto a filter paper (Whatman, pore size less than 2 μm, cut into a size of 4 cm × 1 cm strips). After drying in air, the composite-immobilized filter paper was immersed in aqueous solution and employed in photochemical reactions.

2.3.3. PIM-1 Particles and g-C3N4@PIM-1 Particles. PIM-1 nanoparticles were synthesized with an anti-solvent precipitation method according to a literature method with a slight modification. Typically, 3 mL of PIM-1 solution in chloroform (with a concentration of approx. 15 mg mL⁻¹) was added dropwise into 20 mL of methanol with vigorous stirring. The stirring was continued for 4 h. Then, the obtained suspension was centrifuged at 5000 rpm for 30 min. Excess methanol was removed, and the solid phase was dried in an oven at 80 °C overnight. SEM images reveal aggregated particles with typically 100–200 nm diameter (Figure 2b). Particles of g-C3N4@PIM-1 were prepared by anti-solvent precipitation in 20 mL of methanol using g-C3N4 and PIM-1 in a weight ratio of 5:1 in chloroform. An SEM image in Figure 2c shows aggregated g-C3N4 with PIM-1. Surface analysis by nitrogen gas absorption (BET; see Supporting Information) suggests for g-C3N4 a surface area of 36.4 m² g⁻¹ and for PIM-1 a surface area of 875 m² g⁻¹. Therefore, in composites, PIM-1 is likely to dominate in terms of adsorption behavior.

2.3.4. Photochemical Reactions. A glass vial with 20 mL of solution was charged either with g-C3N4 powder (5 mg) or with g-C3N4-modified filter paper (5 mg of g-C3N4 with 1 mg of PIM deposited onto a 1 cm × 4 cm area). Photochemical reactions were performed at ambient temperature and pressure (20% oxygen) unless stated otherwise. Magnetic stirring was applied when exposed to LED light (Thorlabs, M385LP1 with 1200 mW, 385 nm light in an approx. 2 cm distance; intensity of approx. 80 mW cm⁻²). For Ar/O₂ control experiments, the photochemical solution was purged with Ar/O₂ for 30 min prior to irradiation. During the photoelectrochemical experiment, a continuous gas flow (Ar/O₂) was maintained.

2.3.5. Detection of Hydrogen Peroxide. Quantitative analysis of the hydrogen peroxide concentration was performed following a literature method. Briefly, H₂O₂ was reacted with para-nitrophenylboronic acid to give para-nitrophenol, which was quantified by mass spectrometry coupled to HPLC (Automated Agilent QTOF; see details in the Supporting Information).

3. RESULTS AND DISCUSSION

3.1. Photogeneration of Hydrogen Peroxide I: Effect of PIM Host Materials. Initial experiments were performed with glucose as the quencher for photogenerated holes in g-C3N4. The g-C3N4 material employed here has been reported previously and is based on a disordered layered structure probably containing heptazine units or more condensed and defective layers. A detailed identification of structural motifs is difficult but has been suggested as an example based on 13C-MAS-NMR methods. Here, X-ray diffraction data in Figure S5 confirm the main diffraction peaks for the 100 and 002 planes. Transmission electron microscopy (Figure S6) and electron diffraction are consistent with X-ray diffraction. Raman data in Figure S7 were obtained with 325 nm excitation (data obtained with 532 and 785 nm excitation suffer from strong fluorescent backgrounds). The main Raman bands are consistent with literature reports for g-C3N4. Diffuse-reflectance UV/Vis data (Supporting Information, Figure S8) and XPS data (Supporting Information, Figure S9) are consistent with the literature reports.

Figure 3a shows data for the production of H₂O₂ with time and with increasing glucose concentration. With 5 mg of g-C3N4 suspended in 20 mL of solution and with 100 mM glucose in solution under constant stirring and illumination (LED, λ = 385 nm), a maximum of 216 μM H₂O₂ is observed after 6 h of reaction. A higher glucose concentration or a longer reaction time did not increase the yield. Next, the experiment was repeated but with 5 mg of g-C3N4 immobilized...
When employing g-C3N4@PIM-1 immobilization on the paper substrate, 51 μM H2O2 is produced with same amount of reagents. The production of hydrogen peroxide is observed without glucose in the solution and as a function of time for (i) 5 mg of g-C3N4 immobilized onto 4 cm × 1 cm filter paper, and (ii) 6 mg of g-C3N4@PIM-EA-TB (containing 5 mg of g-C3N4) immobilized onto 4 cm × 1 cm filter paper (in 20 mL of solution with stepwise addition of glucose; 385 nm LED). (b) As above, (i) 6 mg of g-C3N4@PIM-1 on 4 cm × 1 cm filter paper, (ii) 12 mg of g-C3N4@PIM-1 on 4 cm × 1 cm filter paper, and (iii) 12 mg of g-C3N4@PIM-1 on 4 cm × 2 cm filter paper. (c) Plot of H2O2 concentration versus time with (i) 5 mg of g-C3N4 suspension, (ii) 6 mg of g-C3N4@PIM-1 (containing 5 mg of g-C3N4) immobilized onto 4 cm × 1 cm filter paper, and (iii) 6 mg of g-C3N4@PIM-EA-TB (containing 5 mg of g-C3N4) immobilized onto 4 cm × 1 cm filter paper immersed in 20 mL of 0.1 M glucose solution. Estimated errors in all data points are ±20%.

Figure 3. (a) Photogeneration of H2O2 with (i) 5 mg of g-C3N4 in suspension, (ii) 6 mg of g-C3N4@PIM-1 (containing 5 mg of g-C3N4) immobilized onto 4 cm × 1 cm filter paper, and (iii) 6 mg of g-C3N4@PIM-EA-TB (containing 5 mg of g-C3N4) immobilized onto 4 cm × 1 cm filter paper. (b) As above, (i) 6 mg of g-C3N4@PIM-1 on 4 cm × 1 cm filter paper, (ii) 12 mg of g-C3N4@PIM-1 on 4 cm × 1 cm filter paper, and (iii) 12 mg of g-C3N4@PIM-1 on 4 cm × 2 cm filter paper. (c) Plot of H2O2 concentration versus time with (i) 5 mg of g-C3N4 suspension, (ii) 6 mg of g-C3N4@PIM-1 (containing 5 mg of g-C3N4) immobilized onto 4 cm × 1 cm filter paper, and (iii) 6 mg of g-C3N4@PIM-EA-TB (containing 5 mg of g-C3N4) immobilized onto 4 cm × 1 cm filter paper immersed in 20 mL of 0.1 M glucose solution. Estimated errors in all data points are ±20%.

For the photochemical process to be effective, both glucose(aq) and O2(aq) have to interact closely with the g-C3N4 surface. Both reagents also have to permeate through the PIM host materials. To explore the effects of the film thickness and catalyst loading, further glucose addition experiments were performed. In Figure 3b, data are shown comparing (i) 5 mg of g-C3N4 in PIM-1 over 4 cm2 with (ii) 10 mg of g-C3N4 in PIM-1 over 4 cm2 and with (iii) 10 mg of g-C3N4 in PIM-1 over 8 cm2. Only when using an area of 8 cm2 is the H2O2 production doubled, and therefore, the active geometric area is important. This suggests that for thicker g-C3N4@PIM-1 film deposits, not all the photocatalyst in the film is fully active (potentially due to limited light penetration or due to transport limitations with O2 or glucose not reaching all of the catalyst surface in the immobilized film).

Figure 3c shows H2O2 production data for 100 mM glucose solution and as a function of time for (i) 5 mg of g-C3N4 suspension, (ii) 5 mg of g-C3N4 in PIM-1, and (iii) 5 mg of g-C3N4 in PIM-EA-TB. All three systems allow H2O2 production, but the catalyst in PIM-1 appears to lose some activity after 6 h of continuous photocatalytic reaction. It was recently reported that PIM-1 is itself photochemically active and that some photodegradation of PIM-1 is possible and probably the cause for detrimental changes in porosity and transport.66,67 However, PIM-EA-TB appears to exhibit a more stable reactivity (consistent with that of an equivalent amount of photocatalyst in a stirred suspension) under these conditions. More extensive long-term photocatalyst stability testing is under investigation and will be reported separately.

The production of hydrogen peroxide is observed without glucose and with the presence of PIM-1 or PIM-EA-TB, and a plateauing of reactivity with increased glucose concentration occurs in all cases. This has recently been suggested to be linked to binding (assumed Langmuirian)43 of the hole quencher (here glucose) onto the g-C3N4 surface (vide infra). A further factor in the plateauing of H2O2 production can be the decomposition of H2O2 (competing with H2O2 production) either in solution or under conditions of photocatalysis in the catalyst film. Further data for H2O2 production are summarized in Table 1. With 5 mg of g-C3N4 suspended and without glucose quencher, no significant production of H2O2 occurs. However, for g-C3N4 in PIM-1 even without glucose, some H2O2 is produced. Therefore, it seems likely that some degradation of the PIM-1 host polymer may occur under these conditions.

In the presence of 100 mM glucose, typically 66 μM H2O2 is detected within the suspension after 1 h of photocatalysis. Doubling the amount of photocatalyst doubles the H2O2 yield. When employing g-C3N4@PIM-1 immobilization on the filter paper substrate, 51 μM H2O2 is produced with same concentration of glucose, which is very similar to the yield for suspended g-C3N4. When using 100 mM sodium acetate as the quencher, both g-C3N4 suspension and g-C3N4@PIM-1 immobilization on the filter paper produce similar amounts of H2O2 (but lower compared to those produced with glucose).
Clearly, each type of quencher produces specific effects that are linked to either the transport in the microporous environment and/or the interaction of the quencher with the photocatalyst. Control experiments under Ar/O2 flow were performed to explore the role of oxygen during photochemical reactions. When 5 mg of photocatalyst was immobilized on the filter paper with 1 mg of PIM-1, no hydrogen peroxide was detected after 1 h of photocatalysis in the argon-saturated glucose solution. With the same concentration of glucose in solution and saturated with pure O2 prior to irradiation, g-C3N4@PIM-1 immobilized on filter paper generates an increased amount of H2O2 (77 ± 15 μM) when compared with that generated in ambient air (39 ± 8 μM). It can be concluded that the presence of oxygen played a crucial role in the photochemical reactions to form hydrogen peroxide.

3.2. Photogeneration of Hydrogen Peroxide II: Effect of Glucose Adsorption onto g-C3N4. To better understand the photocatalytic mechanism in the presence of glucose, a binding assay for glucose onto g-C3N4 was performed with the help of 1H-NMR tools. A solution of glucose in water (H2O) was spiked with a small amount of DMSO (as an internal 1H-NMR standard). The concentration of glucose in H2O was then determined (employing water signal suppression pulses) as a function of added g-C3N4 or added PIM-1 particles. Figure 4a shows data for the concentration changes for both α-glucose (approx. 30%) and β-glucose (approx. 70%) as a function of added g-C3N4. A significant change in α-glucose concentration is observed with a theory line added based on (i) the BET surface area, (ii) an assumed binding area of 12.7 ± 10−2 m2, and (iii) the assumption of a simple Langmuirian binding constant (estimated based on a competitive binding model for α- and β-glucose competing for the same binding sites) of approx. Kβ-glucose = 200 (± 50) mol−1 dm3.

The effect on the β-glucose concentration was much less obvious, and no binding constant was obtained. The preferred adsorption of α-glucose onto g-C3N4 is inconsistent with the reported binding preference of β-glucose (the more polar and therefore dominant species in water) toward boronic acid-modified surfaces or toward mineral surfaces. This behavior may be linked to specific interactions of α/β-glucose to the g-C3N4 surface. The binding constant Kβ-glucose suggests α-glucose half-covering at 5 mM α-glucose (or, based on a theoretical equilibrium content of 36% α-glucose, this suggests a total glucose concentration of 14 mM for half-coverage). This fits very well with the observed onset of photoactivity in the glucose concentration range of 1 to 10 mM.

Similarly, it is possible to investigate the interaction of glucose with the PIM-1 host material (added as particles to give a PIM-1 suspension). Figure 4b shows data for the binding of glucose into PIM-1. Both α-glucose and β-glucose show only weak/insignificant interaction and no quantifiable binding isotherm. Therefore, for glucose photocatalysis, the direct interaction of α-glucose with the g-C3N4 photocatalyst appears to be essential for effective hole quenching and H2O2 production. Further surface binding effects to the photocatalyst may also affect the formation/decay of reaction intermediates/products (which are currently unknown) from glucose photodegradation.

3.3. Photogeneration of Hydrogen Peroxide III: The Effect of Photocatalyst Modification. To improve/modify the photocatalytic reactivity, metal co-catalysts can be employed. In particular, for the photoelectrochemical production of hydrogen, the presence of Pt nanoparticles was shown to be important and attributed to the noble metal-capturing photoexcited electrons during charge separation. Here, the effects of photogenerated nano-Pt, nano-Pd, and nano-Au attached to the g-C3N4 particles are evaluated for the production of H2O2. Figure 5 shows TEM images of (a) bare

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**Table 1. Comparison of g-C3N4 Photocatalyst Performance for Photosynthesis of Hydrogen Peroxide**

| catalyst (5 mg g-C3N4) | reaction method | quencher | reaction condition | H2O2 concentration |
|------------------------|-----------------|----------|--------------------|-------------------|
| g-C3N4                 | suspension      | H2O      | ambient            | none              |
| g-C3N4                 | suspension      | 0.1 M glucose | ambient            | 66 ± 13 μM        |
| g-C3N4 (10 mg g-C3N4)  | suspension      | 0.1 M glucose | ambient            | 130 ± 26 μM       |
| g-C3N4                 | suspension      | 0.1 M acetate | ambient            | 30 ± 6 μM         |
| g-C3N4 with PIM-1      | immobilized on filter paper | H2O | ambient            | 37 ± 7 μM         |
| g-C3N4 with PIM-1      | immobilized on filter paper | 0.1 M glucose | ambient            | 51 ± 10 μM        |
| g-C3N4 with PIM-1      | immobilized on filter paper | 0.1 M acetate | ambient            | 41 ± 8 μM         |
| g-C3N4 with PIM-1      | immobilized on filter paper | 0.1 M glucose | under Ar          | none              |
| g-C3N4 with PIM-1      | immobilized on filter paper | 0.1 M glucose | under Ar          | 39 ± 8 μM         |
| g-C3N4 with PIM-1      | immobilized on filter paper | 0.1 M glucose | under O2          | 77 ± 15 μM        |

α = 385 nm, 80 mW cm−2, reaction time: 1 h, stirred solution. Errors estimated are ±20%.

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**Figure 4.** (a) Plot of glucose concentration (α-, β-, and total glucose) versus added g-C3N4 powder (determined by 1H-NMR). Lines correspond to best fit trends based on the competitive Langmuirian binding of α- and β-glucose with Kα-glucose = 200 (± 50) mol−1 dm3 and Kβ-glucose < 10 (± 5) mol−1 dm3. (b) As above, but for the addition of PIM-1 nanoparticles. No significant binding of glucose to PIM-1 is observed. Estimated error in all data points is ±20%.
g-C$_3$N$_4$ and (b) nano-Pt-, (c) nano-Pd-, (d) nano-Au-modified g-C$_3$N$_4$. The morphology of g-C$_3$N$_4$ before and after metal deposition remains the same, showing a typical layered structure. Clearly, dark spots can be observed in Figure 5b,c, which are identified as metal nanoparticles with diameters of around 2−3 nm for Pt@g-C$_3$N$_4$ and Pd@g-C$_3$N$_4$. Energy dispersive X-ray (EDX) mapping analysis further confirmed the successful photochemical metal deposition on the g-C$_3$N$_4$ sheets. For the gold-modified g-C$_3$N$_4$, only bigger particles typically of 100 nm diameter are observed localized in edge regions. EDX analysis confirms gold on the g-C$_3$N$_4$ surface. Gold may nucleate less readily on the g-C$_3$N$_4$ surface, and this may lead to the formation of bigger nanoparticles. Analysis by PXRD (see Figure S5 in the Supporting Information) confirms successful photochemical metal deposition for Pt, Pd, and Au.

Table 2 summarizes data for H$_2$O$_2$ production, employing suspensions of g-C$_3$N$_4$ and co-catalyst-modified materials Pt@g-C$_3$N$_4$, Pd@g-C$_3$N$_4$, and Au@g-C$_3$N$_4$. For Pt- and Pd-modified g-C$_3$N$_4$, a loss of reactivity relative to g-C$_3$N$_4$ is observed. The production of H$_2$O$_2$ has been suggested to rely
on the rapid formation of the 1,4-endoperoxide species on g-C₃N₄, which results in selectivity for the two-electron reduction of oxygen. The loading of metal co-catalyst can increase the charge separation process by allowing the transfer of photoexcited electrons from the g-C₃N₄ conduction band to the metal particles. Although charge separation may be improved, the production of H₂O₂ may be less effective with metal loading as endo-peroxides have to form directly on the g-C₃N₄ surface and not on the metal. This conclusion agrees with previous studies. A decrease in photoactivated 1,4-endoperoxide species was inferred from the EPR measurement for Pt@g-C₃N₄. Only Au@g-C₃N₄ exhibits significant H₂O₂ production reactivity in the presence of 100 mM glucose. Gold is known to (electro)chemically produce H₂O₂ from O₂ at intermediate/mild reduction potentials. In fact, the presence of gold seems to double the yield of H₂O₂. However, considering the more complex preparation of Au@g-C₃N₄, the focus in this report remains on photocatalysis with pure g-C₃N₄ and without a co-catalyst.

3.4. Photogeneration of Hydrogen Peroxide IV: Effect of Triton X-100 Quencher. Next, the importance of binding hole quencher systems was further investigated by selecting the amphiphilic surfactant Triton X-100. Low concentrations of surface-active quencher material could be sufficient to help produce hydrogen peroxide. To explore the effects of g-C₃N₄ and PIM-1 in this photocatalytic reaction, three types of materials are compared: (i) g-C₃N₄ suspension, (ii) g-C₃N₄@PIM-1 immobilized on filter paper, and (iii) g-C₃N₄@PIM-1 particles (see the Experimental Section).

Triton X-100 (see molecular structure in Figure 6a) is a neutral polyethylene glycol-based surfactant with a CMC range of 0.22 to 0.24 mM. Data in Figure 6a suggest that at low concentrations of Triton X-100, H₂O₂ production occurs either with (i) g-C₃N₄ suspension, with (ii) immobilized g-C₃N₄ in a PIM-1 host, and with (iii) g-C₃N₄@PIM-1 particles. Figure 6b shows data for the H₂O₂ production as a function of time for 0.2 mM Triton X-100 in 20 mL of water. The presence of PIM-1 clearly improves the performance, and in particular, suspended g-C₃N₄@PIM-1 particles appear effective. Figure 2 shows SEM images for the g-C₃N₄@PIM-1 particles. The reactivity of the photocatalyst in the presence of PIM-1 is substantially higher. The g-C₃N₄@PIM-1 particles in suspension produce twice as much H₂O₂, and the onset of photochemical reactivity is low.

Data in Figure 6c displays the reactivity trends for two different concentrations of Triton X-100 after 1 h of illumination. Even with concentrations as low as 0.2 mM Triton X-100, the production of H₂O₂ is observed. With pure g-C₃N₄, only a Triton X-100 concentration higher than the CMC produces hydrogen peroxide possibly due to a lack of adsorption at lower concentrations. With g-C₃N₄@PIM-1 immobilized on filter paper and with g-C₃N₄@PIM-1 particles, an increase in the rate of H₂O₂ production is observed. For the 1 mM concentration of Triton X-100, the beneficial effects from PIM-1 are not obvious. Overall, the photocatalyst g-C₃N₄@PIM-1 in suspension appears to be the most effective system for both below- and above-CMC concentrations. This raises the question of whether the binding of Triton X-100

Table 2. Comparison of Metal-Deposited g-C₃N₄ Performance for the Photogeneration of Hydrogen Peroxide

| catalyst | amount | reaction method | quencher | reaction time | H₂O₂ concentration |
|----------|--------|-----------------|----------|--------------|-------------------|
| g-C₃N₄  | 5 mg   | suspension      | 0.1 M glucose | 1 h          | 66 ± 13 μM        |
| Pt@g-C₃N₄ | 5 mg | suspension | 0.1 M glucose | 1 h | none |
| Pd@g-C₃N₄ | 5 mg | suspension | 0.1 M glucose | 1 h | none |
| Au@g-C₃N₄ | 5 mg | suspension | 0.1 M glucose | 1 h | 138 ± 30 μM |

“In 20 mL solution, suspension, 1 h, λ = 385 nm LED light, 80 mW cm⁻². Errors estimated at ±20%.

Figure 6. Molecular structure of Triton X-100 and (a) photogeneration of H₂O₂ with (i) 5 mg of g-C₃N₄ in suspension, (ii) 6 mg of g-C₃N₄@PIM-1 (containing 5 mg of g-C₃N₄) immobilized on 4 cm × 1 cm filter paper, and (iii) 6 mg of g-C₃N₄@PIM-1 particles (containing 5 mg of g-C₃N₄) in suspension (in 20 mL of solution; stepwise addition of Triton X-100; λ = 385 nm LED light). (b) Plot of H₂O₂ concentration versus reaction time for (i) 5 mg of g-C₃N₄ in suspension, (ii) 6 mg of g-C₃N₄@PIM-1 (containing 5 mg of g-C₃N₄) immobilized on 4 cm × 1 cm filter paper, and (iii) 6 mg of g-C₃N₄@PIM-1 particles (containing 5 mg of g-C₃N₄) in 1 mM Triton X-100. (c) Comparison of photocatalytic H₂O₂ production over (i) 5 mg of g-C₃N₄ in suspension, (ii) 6 mg of g-C₃N₄@PIM-1 (containing 5 mg of g-C₃N₄) immobilized on 4 cm × 1 cm filter paper, and (iii) 6 mg of g-C₃N₄@PIM-1 particles (containing 5 mg of g-C₃N₄) in suspension at two distinct Triton X-100 concentrations, below and above CMC concentration, after 1 h reaction time. Estimated error in all data points is ±20%.
occurs directly to the g-C₃N₄ photocatalyst surface or alternatively into the PIM-1 as the microporous host.

3.5. Photogeneration of Hydrogen Peroxide V: Effect of Triton X-100 Adsorption to PIM-1. To further study the ability of Triton X-100 to bind to g-C₃N₄ or to PIM-1, additional ¹H-NMR experiments were performed. Figure 7 shows data based on monitoring the Triton X-100 concentrations with ¹H-NMR when adding g-C₃N₄ (Figure 7a) and when adding PIM-1 particles (Figure 7b). When starting with a solution of 10.5 μmol in 15 mL (corresponding to a Triton X-100 concentration of approx. 0.7 mM), essentially no binding occurs with g-C₃N₄. Upon continued addition of g-C₃N₄, the solution concentration remains nearly constant. This could be linked to the insufficiently strong binding of Triton X-100 to the g-C₃N₄ surface. In contrast, data in Figure 7b suggest substantial interaction between the Triton X-100 and PIM-1 particles. The initial amount of 9.5 μmol in 15 mL of solution (corresponding to a Triton X-100 concentration of 0.6 mM) decreases essentially linearly with PIM-1 addition. The uptake is approx. one molecule of Triton X-100 for every four PIM-1 particles (consistent with a water/PIM-1 partitioning process). Note that the partitioning process was slow at 20 °C but more clearly resolved at 50 °C. This is a substantial binding effect and a sign for effective quencher-filling of the microporous space (note that all data points are initially 15 mL; removal of 0.6 mL for each data point). Trendlines added only as a guide to the eyes. Estimated error in all data points is ±20%.

4. CONCLUSIONS

It has been shown that adsorption (for both (i) onto the photocatalyst or (ii) into the microporous host) is an important step in the photocatalytic H₂O₂ production with g-C₃N₄. For glucose, adsorption of α-glucose (Kₐ-glucose = 200 ± 50 mol⁻¹ dm³) is observed in ¹H-NMR experiments with α-glucose binding being significantly stronger compared to β-glucose. In contrast, adsorption of glucose into PIM-1 was shown to be insignificant. Data for glucose-driven hydrogen peroxide production are therefore consistent with the binding of α-glucose to the photocatalyst before hole quenching processes are possible. In contrast, for Triton X-100, adsorption onto g-C₃N₄ was shown to be insignificant although Triton X-100 binding into PIM-1 is significant (with partitioning of one Triton X-100 molecule for every four PIM-1 monomeric repeat units). Production of hydrogen peroxide in the presence of Triton X-100 is enhanced in g-C₃N₄@PIM-1 (either immobilized in a film on filter paper or suspended as composite particles) when compared to bare g-C₃N₄. These are two distinct mechanistic cases with (i) adsorption directly onto the photocatalyst and (ii) adsorption indirectly into a host material with embedded photocatalysts.

The production of H₂O₂ is possible with suspended catalyst particles, but just as effective is the use of PIM-embedded photocatalyst immobilized, for example, on filter paper as substrate. The immobilized photocatalyst is easily fabricated and recoverable. The fact that PIM materials are molecularly rigid prevents them from directly interacting with the photocatalyst, although some photodegradation of PIM-1 and the resulting formation of H₂O₂ have been observed. In these preliminary experimental results, PIM-EA-TB represents a more photostable microporous polymer host. More experiments with PIM-EA-TB (and other types of PIMs) have to be performed in the future to provide a detailed comparison of adsorption effects and effects on photochemical reaction kinetics. Embedded into PIMs, photocatalyst surfaces are not obstructed and therefore able to interact with molecular quencher systems permeating/accumulating from solution into the microporous host. This study is exploratory in nature and may provide a starting point for the further development of photocatalysts in microporous PIM environments. The molecular structure of the PIM host will provide an opportunity to modify or enhance/tune photocatalytic activity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c23960.

Quantitative analysis of hydrogen peroxide concentration; binding assays with ¹H-NMR; nitrogen-binding (BET) surface analysis; X-ray diffraction analysis; TEM and electron diffraction; Raman spectroscopy analysis; diffuse-reflectance UV/Vis data; XPS data (PDF)
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Notes
The authors declare no competing financial interest.

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