

Sunlight-Driven Hydrogen Peroxide Production from Water and Molecular Oxygen by Metal-Free Photocatalysts**

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Abstract: Design of green, safe, and sustainable process for the synthesis of hydrogen peroxide (H_2O_2) is a very important subject. Early reported processes, however, require hydrogen (H_2) and palladium-based catalysts. Herein we propose a photocatalytic process for H_2O_2 synthesis driven by metal-free catalysts with earth-abundant water and molecular oxygen (O_2) as resources under sunlight irradiation ($\lambda > 400$ nm). We use graphitic carbon nitride ($g-C_3N_4$) containing electron-deficient aromatic diimide units as catalysts. Incorporating the diimide units positively shifts the valence-band potential of the catalysts, while maintaining sufficient conduction-band potential for O_2 reduction. Visible light irradiation of the catalysts in pure water with O_2 successfully produces H_2O_2 by oxidation of water by the photoformed valence-band holes and selective two-electron reduction of O_2 by the conduction band electrons.

Hydrogen peroxide (H_2O_2) is a clean oxidant that emits only water as a byproduct and is widely used for pulp bleaching, disinfection, and organic synthesis.^[1] H_2O_2 has also received much attention as an energy carrier for fuel cells, offering an alternative to H_2 because it is soluble in water and can be used in a one-compartment cell for electricity generation.^[2] H_2O_2 is currently manufactured in industry by the anthraquinone method based on oxidation of anthrahydroquinone by O_2 ,^[3] however, it requires a regeneration of anthrahydroquinone by hydrogenation of the formed anthraquinone with H_2 on palladium-based catalysts. Alternative to the high-energy-consuming two-step process, an one-step H_2O_2 synthesis with H_2 and O_2 has been studied extensively with Pd^[4] or Au–Pd bimetallic catalysts.^[5] This direct synthesis quantitatively produces H_2O_2 , but requires extreme care because of the potentially explosive nature of H_2/O_2 mixed

gases. A new method capable of producing H_2O_2 without H_2 is therefore desired.

Photocatalytic H_2O_2 production on semiconductor materials, such as titanium dioxide (TiO_2), has also been studied.^[6] The reactions are usually carried out by UV irradiation ($\lambda < 400$ nm) of an O_2 -saturated water with TiO_2 in the presence of alcohols as the electron and proton donor. Photoexcitation of TiO_2 produces the electron (e^-) and positive hole (h^+) pairs. The h^+ oxidize alcohol and produce aldehyde and protons, while the e^- promote two-electron reduction of O_2 and produce H_2O_2 [Eq. (1) and (2)].



These reactions proceed without H_2 at room temperature, therefore are a safe H_2O_2 synthesis. The selectivity for H_2O_2 formation is, however, very low ($< 6\%$). This is because one-electron reduction of O_2 occurs mainly and produces a superoxide ($\cdot OOH$) radical [Eq. (3)],^[7] thus suppressing two-electron reduction of O_2 [Eq. (2)].



Earlier, we found that graphitic carbon nitride ($g-C_3N_4$), a metal-free polymeric semiconductor with a graphitic stacking structure of melem sheets,^[8] promotes selective two-electron reduction of O_2 and produces H_2O_2 with greater than 90 % selectivity under sunlight irradiation ($\lambda > 400$ nm).^[9] The selective two-electron reduction of O_2 is due to the efficient formation of 1,4-endoperoxide species on the melem unit (Scheme 1). The photoformed e^- are localized at the C1 and N4 positions of melem (Scheme 1a). The e^- reduces O_2 and creates a superoxo radical (Scheme 1b). This is rapidly reduced by another e^- at the *para* position and produces 1,4-endoperoxide species (Scheme 1c), which is readily transformed to H_2O_2 . The rapid endoperoxide formation [Scheme 1b→c] suppresses the $\cdot OOH$ radical formation [Scheme 1b→d; Eq. (3)], thus promoting selective two-electron reduction of O_2 [Eq. (2)].

A green and sustainable process for photocatalytic H_2O_2 synthesis requires the use of earth-abundant water in place of alcohol. If this is achieved, oxidation of water by the photoformed h^+ produces O_2 and protons [Eq. (4)], while the e^- promote two-electron reduction of O_2 [Eq. (2)]. H_2O_2 can therefore be synthesized from water and O_2 under sunlight irradiation with 100 % atom efficiency [Eq. (5)].



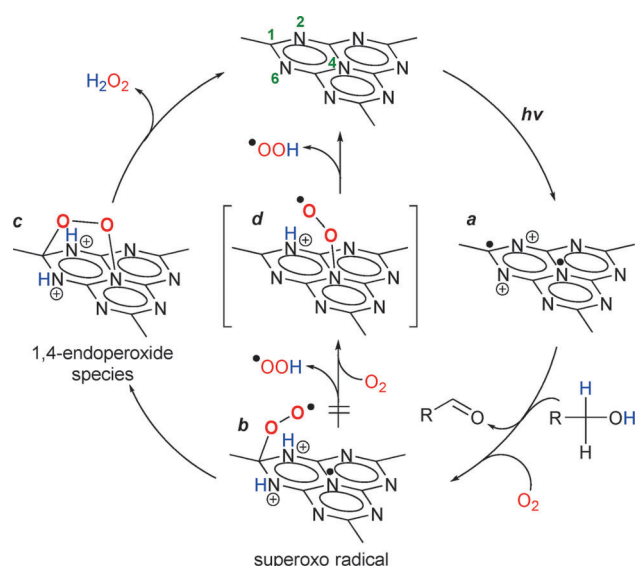
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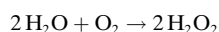
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Scheme 1. Selective H_2O_2 production on $\text{g-C}_3\text{N}_4$ under visible light irradiation. For more details on (a)–(d) see text.



The $\text{g-C}_3\text{N}_4$ catalyst is, however, unsuccessful for H_2O_2 production from water and O_2 ,^[9] because the top of the valence band (VB) lies at approximately 1.4 V (versus the normal hydrogen electrode (NHE), pH 7),^[10] which is insufficient for water oxidation (ca. 0.8 V)^[11] because of the small thermodynamic driving force. Improving $\text{g-C}_3\text{N}_4$ to promote water oxidation while maintaining high selectivity for two-electron reduction of O_2 is necessary.

Herein we report that a simple modification of $\text{g-C}_3\text{N}_4$ facilitates H_2O_2 production from water and O_2 . Aromatic diimides are an important class of n-type organic semiconductors for application to organic field-effect transistors (OFETs) owing to their high electron mobility and stability.^[12] Incorporating the diimides into the semiconductors positively shifts the oxidation and reduction potentials due to their high electron affinity.^[13] We incorporated pyromellitic diimide (PDI), a simple aromatic diimide, into the $\text{g-C}_3\text{N}_4$ network by a facile thermal condensation (Scheme 2). The obtained $\text{g-C}_3\text{N}_4/\text{PDI}$ catalysts, when activated by visible light, successfully oxidize water owing to the positively shifted VB levels, while maintaining high selectivity for two-electron reduction of O_2 . This thus facilitates H_2O_2 synthesis from water and O_2 under sunlight irradiation.

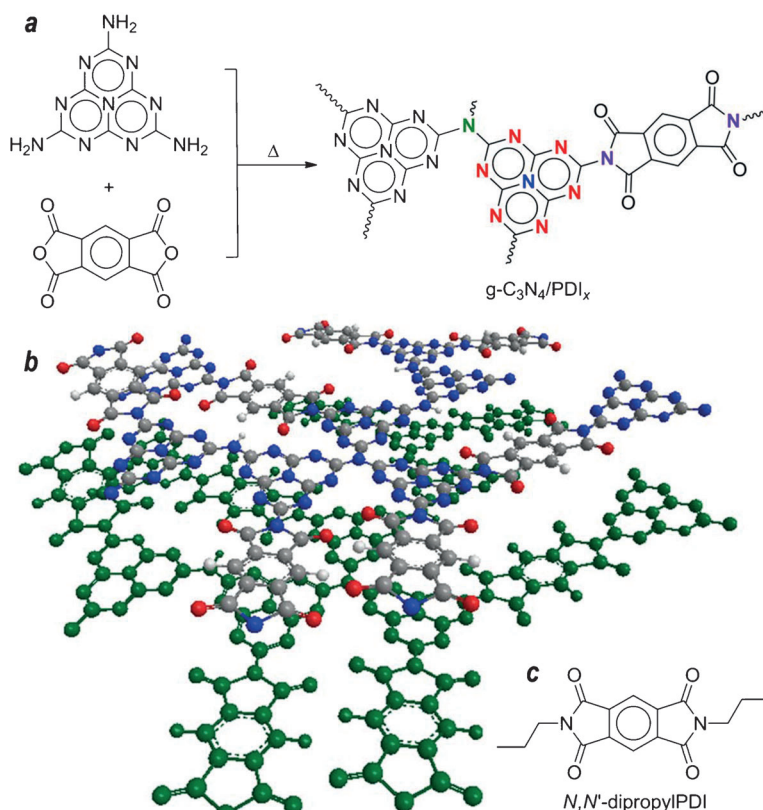
The $\text{g-C}_3\text{N}_4/\text{PDI}_x$ catalysts containing different amounts of PDI units (x [mol %] = 33, 51, and 59) were prepared by calcinating a mixture of melem and pyromellitic dianhydride at 598 K (Scheme 2a), according to procedure for related

materials.^[14] As summarized in Table 1, the gray-brown powders of $\text{g-C}_3\text{N}_4/\text{PDI}_x$ obtained have surface areas similar to $\text{g-C}_3\text{N}_4$ ($5\text{--}8\text{ m}^2\text{ g}^{-1}$). As shown in Figure S1 in the Support-

Table 1: Results for photocatalytic H_2O_2 production^[a]

Entry	Catalyst	Surface area [$\text{m}^2\text{ g}^{-1}$] ^[b]	H_2O_2 [μmol] ^[c]
1	TiO_2 ^[d]	57	< 0.2
2	Au/TiO_2 ^[e]	-	< 0.2
3	F- TiO_2	-	< 0.2
4	$\text{g-C}_3\text{N}_4$	7.8	< 0.2
5	mpg- C_3N_4	190	< 0.2
6	$\text{g-C}_3\text{N}_4/\text{PDI}_{33}$	5.6	22.4
7	$\text{g-C}_3\text{N}_4/\text{PDI}_{51}$	7.1	50.6
	1st reuse ^[f]	-	50.2
	2nd reuse ^[f]	-	50.3
8	$\text{g-C}_3\text{N}_4/\text{PDI}_{59}$	6.7	39.4
9	N,N' -dipropylPDI ^[g]	-	< 0.2
10	$\text{g-C}_3\text{N}_4 + N,N'$ -dipropylPDI ^[h]	-	< 0.2

[a] Reaction conditions: water (30 mL), catalyst (50 mg), O_2 (1 atm), $\lambda > 420\text{ nm}$ (intensity at 420–500 nm: 26.9 W m^{-2}), time (48 h). [b] BET surface area. [c] Determined by redox titration with KMnO_4 (detection limit: $0.2\text{ }\mu\text{mol}$). [d] JRC-TIO-4 TiO_2 supplied from the Catalyst Society of Japan (equivalent to Degussa P25; anatase/rutile = ca. 83/17). [e] The amount of Au loaded is 1 wt %, and the average diameter of Au particles is $3.4 \pm 0.9\text{ nm}$. [f] Catalyst was reused after simple washing with water followed by drying in vacuo. [g] 50 mg. [h] $\text{g-C}_3\text{N}_4$ (25 mg) and N,N' -dipropylPDI (25 mg).



Scheme 2. a) Synthesis of $\text{g-C}_3\text{N}_4/\text{PDI}_x$, b) their proposed structure, and c) the structure of N,N' -dipropylPDI. C gray, H white, N blue, and O red spheres; the second layer is shown in green for clarity.

ing Information, transmission electron microscopy (TEM) images of the catalysts show sheet-like structures, as is the case for g-C₃N₄.^[15] X-ray diffraction (XRD) of g-C₃N₄ (Figure S2) shows a peak at $2\theta = 27.4$ ($d = 0.325$ nm) assigned to (002) packing of the melem sheets.^[16] Increasing the amounts of PDI units decreases its intensity, along with a formation of new two peaks at $2\theta = 19.0$ ($d = 0.467$ nm) and 29.6 ($d = 0.302$ nm). These are assigned to π , π -stacking of PDI units^[17] and donor-acceptor interaction between melem and PDI units,^[18] respectively. These data suggest that, as shown in Scheme 2b, the PDI units are randomly incorporated within the melem sheet and the sheets are layered multiply. As shown in Figure S3, X-ray photoelectron spectroscopy (XPS) of g-C₃N₄ (N1s level) shows three peaks assigned to sp²-hybridized N atoms of melem at 398.5 eV (red, Scheme 2a), trigonal N atoms of the melem center at 399.4 eV (blue, Scheme 2a), and terminal amine N atoms at 401.0 eV (green, Scheme 2a), respectively.^[19] Incorporating PDI units creates a new peak at 400.1 eV, assigned to imide N atoms of the PDI units (purple, Scheme 2).^[20] Integrating these signals therefore allows rough determination of the mole fraction of PDI units (x) within g-C₃N₄/PDI _{x} .

Diffuse-reflectance UV/Vis spectra of g-C₃N₄/PDI _{x} (Figure S4) show absorption in the visible region, as is the case for g-C₃N₄; their band-gap energies are 2.4–2.8 eV. Electrochemical Mott–Schottky plots of g-C₃N₄/PDI _{x} (Figure S5) show typical n-type character. The obtained flat band potentials and band-gap energies provide the band structures of g-C₃N₄/PDI _{x} (Figure 1). Both conduction band (CB) and VB levels

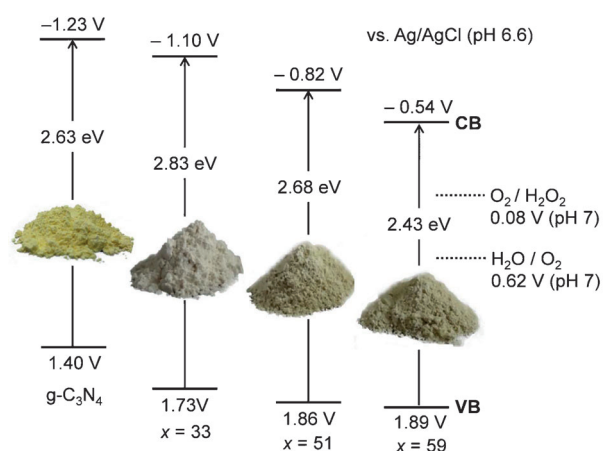


Figure 1. Electronic band structures of g-C₃N₄ and g-C₃N₄/PDI _{x} . Photographs show the corresponding powders of the samples.

become more positive by the incorporation of PDI units owing to their high electron affinity,^[13] with the CB levels still more negative than the reduction potential of O₂ (0.08 V).^[11] These data suggest that g-C₃N₄/PDI _{x} may possess enhanced capability for water oxidation with sufficient potentials for O₂ reduction.

Photocatalytic reactions were performed by photoirradiation of pure water (30 mL) containing respective catalysts (50 mg) by a Xe lamp ($\lambda > 420$ nm) with magnetic stirring under O₂ atmosphere (1 atm) at 298 K. Table 1 summarizes

the results obtained by 48 h reaction. Bare TiO₂ (entry 1) scarcely produces H₂O₂ (less than detection limit, 0.2 μ mol). TiO₂ loaded with Au^[6f] or modified with fluoride,^[6d] which have been proposed for H₂O₂ production, are inactive (entries 2 and 3). g-C₃N₄ (entry 4) does not produce H₂O₂. Mesoporous g-C₃N₄ (mpg-C₃N₄) with a large surface area (190 m² g⁻¹) prepared by a silica-templated polymerization^[21] is also inactive (entry 5). In contrast, g-C₃N₄/PDI _{x} produce very large amounts of H₂O₂ (entries 6–8); the amount of H₂O₂ formed on g-C₃N₄/PDI₅₁ (50.6 μ mol) is more than 250-fold of that obtained with g-C₃N₄ (< 0.2 μ mol). As shown by entries 9 and 10, *N,N'*-dipropylPDI (Scheme 2c), a reference compound for PDI, and a mixture of g-C₃N₄ and *N,N'*-dipropylPDI scarcely produces H₂O₂. These data suggest that incorporating PDI units within the g-C₃N₄ network facilitates H₂O₂ production from water and O₂.

Table S1 shows the results of photoreaction on g-C₃N₄/PDI _{x} with 2-PrOH as a sacrificial electron donor. The selectivity for the amount of H₂O₂ formed relative to the amounts of photooxidation products (acetone and CO₂) is about 90 %, which is similar to that obtained with g-C₃N₄. This suggests that g-C₃N₄/PDI _{x} selectively promote two-electron reduction of O₂ as does g-C₃N₄.^[9] Figure S6 shows the change in the amounts of H₂O₂ formed during reaction in a water/O₂ system with g-C₃N₄/PDI _{x} . The rate of H₂O₂ evolution is almost constant even after prolonged irradiation, indicating that the catalysts produce H₂O₂ without loss of activity. The g-C₃N₄/PDI₅₁ catalyst, when reused for further reaction (entry 7, Table 1), shows almost the same activity as the fresh sample. In addition, the recovered catalyst shows similar X-ray diffraction (XRD) pattern to that of the fresh one (Figure S2). These data suggest that the catalyst is stable and reusable for further reaction.

Figure S7 shows the action spectrum^[22] for H₂O₂ formation on g-C₃N₄/PDI₅₁. The apparent quantum yields (Φ_{AQY}) agree with the absorption spectrum of the catalyst, indicating that its band-gap excitation promotes water oxidation and O₂ reduction. Note that Φ_{AQY} at 420 nm is 2.6 %, which is similar to that for overall water splitting on a highly active solid-solution catalyst (ca. 2.5 % at 420 nm).^[23] Ab initio calculations based on the density functional theory (DFT) were performed within the Gaussian03 program to clarify the effect of PDI unit on the electronic structure of g-C₃N₄ with simple melem and melem-PDI models (Figure 2). Their main electronic transitions ($S_0 \rightarrow S_1$) are HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO + 2, respectively. Incorporating PDI units decreases both S_0 and S_1 levels; this agrees with the observed VB and CB levels (Figure 1). The electrons on both HOMO and LUMO + 2 of the melem-PDI model are located mainly at the melem unit with partial distribution to the PDI units. This is reflected by the high electron affinity of PDI unit.^[13] The electrons on HOMO are located at the N2 and N6 positions of the melem unit, and those on LUMO + 2 are at the C1 and N4 units. These data suggest that these respective atoms on the melem units behave as the oxidation (N2 and N6) and reduction (C1 and N4) sites, as is the case for g-C₃N₄.^[9] (Scheme 1).

The mechanism for H₂O₂ formation on the photoexcited g-C₃N₄/PDI can be explained as Scheme 3.^[24] Photoexcitation

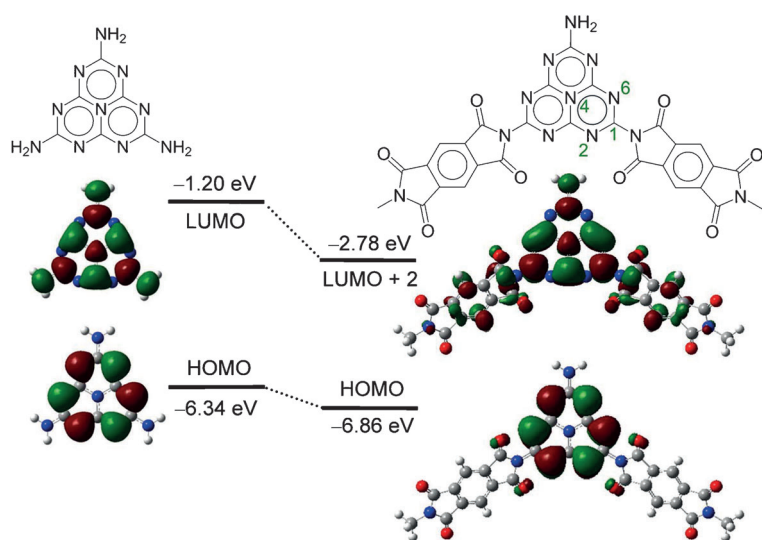


Figure 2. Energy diagrams and interfacial plots of main orbitals for melem (left) and melem-PDI (right) models calculated at the DFT level (B3LYP/6-31g(d)).

by two photons creates two sets of e^-/h^+ pairs (Scheme 3a). The formed e^- are localized at the C1 and N4 positions of the melem unit, whereas h^+ are at the N2 and N6 positions. The h^+ oxidizes water (Scheme 3b), and the e^- on either C1 or N4 position reduces O_2 , producing a superoxo radical (Scheme 3c). This radical is rapidly reduced by the e^- at the *para* position, producing 1,4-endoperoxide species (Scheme 3d). Protonation of the species produces H_2O_2 .

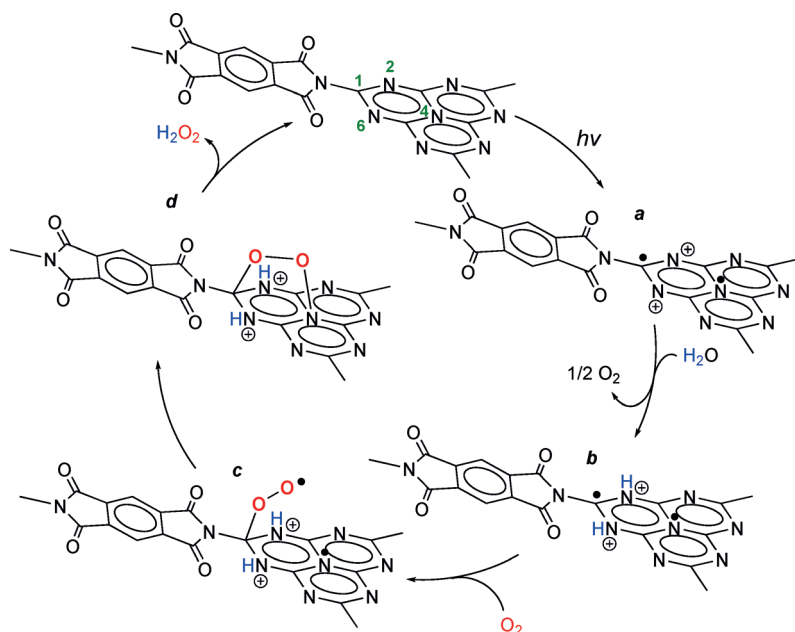
The 1,4-endoperoxide formation on $g-C_3N_4$ /PDI (Scheme 3d) is confirmed by Raman spectroscopy. As shown in Figure 3A, fresh $g-C_3N_4$ /PDI₅₁ exhibits four bands at 645, 709, 753, and 982 cm^{-1} . The 645 cm^{-1} band is assigned

to in-plane bending mode of imide moiety.^[25] Both the 709 and 982 cm^{-1} bands are assigned to breathing mode of melem, and the 753 cm^{-1} band is assigned to out-of-plane bending mode of melem.^[26] Figure 3a shows the Raman shift of the melem-PDI model obtained by DFT calculation. The four bands obtained (619, 665, 766, and 1004 cm^{-1}) are similar to the observed ones (Figure 3A), indicating that the calculation precisely represents the electronic structure of $g-C_3N_4$ /PDI. Figure 3B shows the Raman spectrum of $g-C_3N_4$ /PDI₅₁ recovered after photoreaction in a 2-PrOH/ O_2 system. A new broad band appears at 892 cm^{-1} . Figure 3b depicts the calculated Raman shift of 1,4-endoperoxide species adsorbed on the melem-PDI system. The three bands obtained (837, 890, and 906 cm^{-1}) are assigned to the C1–O symmetric, O–O stretching, and C1–O asymmetric vibrations of the endoperoxide species, respectively. They agree reasonably with the observed broad band at 892 cm^{-1} (Figure 3B). Figure 3C shows the Raman spectrum of $g-C_3N_4$ recovered after photoreaction.

A similar band appears at 891 cm^{-1} , assigned to the 1,4-endoperoxide species. These data indicate that two-electron reduction of O_2 is indeed promoted on the $g-C_3N_4$ /PDI surface (Scheme 3).

The activity of H_2O_2 formation increases with the incorporation of PDI units (Table 1). The reaction consists of water oxidation and O_2 reduction. To clarify the activity of these half reactions, water oxidation with $AgNO_3$ as an electron acceptor and O_2 reduction with 2-PrOH as an electron donor were carried out. As shown in Figure S8 and S9, the activity of both reactions increases with the amount of PDI units. The rate of water oxidation with $AgNO_3$ on $g-C_3N_4$ /PDI₅₁ is 0.8 $\mu mol h^{-1}$. This is much smaller than that of O_2 reduction with 2-PrOH (42 $\mu mol h^{-1}$) but similar to that of H_2O_2 formation in a water/ O_2 system (1.1 $\mu mol h^{-1}$, Figure S6). This result suggests that water oxidation is the rate-determining step for H_2O_2 formation. The positive shift of the VB level by incorporating PDI units (Figure 1) therefore facilitates water oxidation and promotes H_2O_2 formation.

Of the catalysts, $g-C_3N_4$ /PDI₅₁ shows the highest activity (Table 1). The catalyst containing a larger amount of PDI units ($g-C_3N_4$ /PDI₅₉) shows decreased activity despite its more positive VB level. The half reactions show similar tendency of the activity (Figure S8 and S9). As shown in Figure 1, incorporating PDI units also positively shifts the CB level. One of the possible reasons for the low activity is therefore the insufficient reduction capability. In addition, as shown in Scheme 3, the melem unit acts as the active sites for both water oxidation and O_2 reduction. Incorporating larger amounts of PDI units decreases the number of melem units exposed on the catalyst. This may be another possible reason for the low activity. The $g-C_3N_4$ /



Scheme 3. Proposed mechanism for H_2O_2 formation on the photoactivated $g-C_3N_4$ /PDI from water and O_2 .^[24] For more details on (a)–(d) see text.

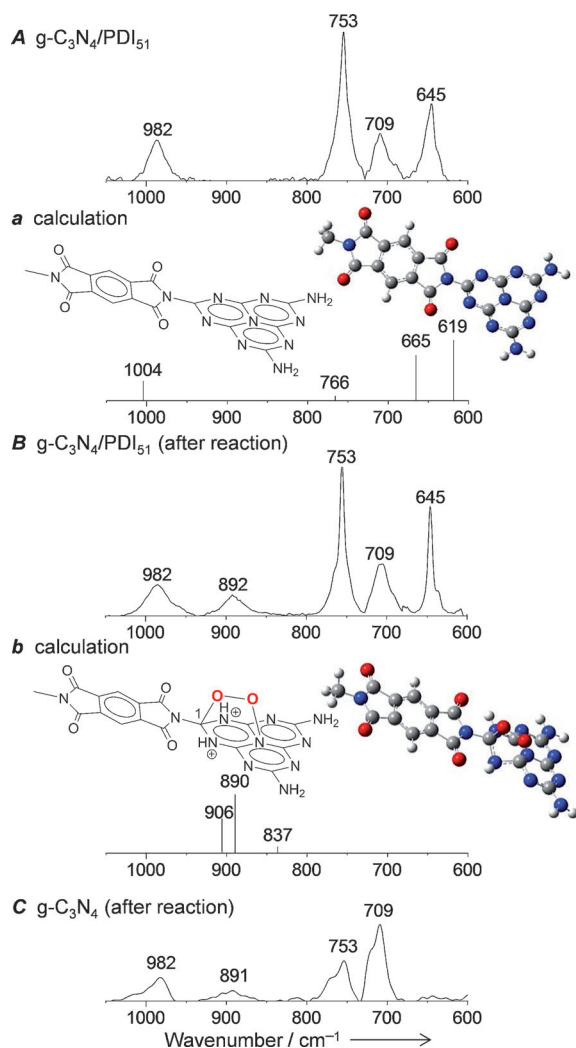


Figure 3. Raman spectra for A) fresh g-C₃N₄/PDI₅₁, and B) g-C₃N₄/PDI₅₁ recovered after photoreaction, and C) g-C₃N₄ recovered after photoreaction (12 h) in a 2-PrOH solution with O₂. Calculated shift for a) the melem-PDI model and b) the model with 1,4-endoperoxide species (B3LYP/6-31g(d)).

PDI₅₁ catalyst has appropriate VB and CB levels and relatively large number of active sites (melem units), thus facilitating efficient H₂O₂ production.

Efficient H₂O₂ formation on g-C₃N₄/PDI requires visible light irradiation ($\lambda > 400$ nm); UV irradiation decreases the efficiency. Photoreaction with a solar simulator as a light source confirms this. As shown in Figure 4a, spectral irradiance of the simulator (Figure 4a, orange) ranges from UV to visible region and is similar to that of sunlight (Figure 4a, green). Figure 4b shows the time-dependent change in H₂O₂ evolution with g-C₃N₄/PDI₅₁ in a water/O₂ system under irradiation by a solar simulator. Irradiation of entire wavelength light (Figure 4b, orange) successfully produces H₂O₂ at the early stage, but the formation rate decreases with time. This is due to the decomposition of the formed H₂O₂ by absorbing UV light ($\lambda < 400$ nm).^[9,27,28] In contrast, irradiation of $\lambda > 420$ nm light using a glass filter (Figure 4b, blue) produces H₂O₂ without a decrease in the formation rate.

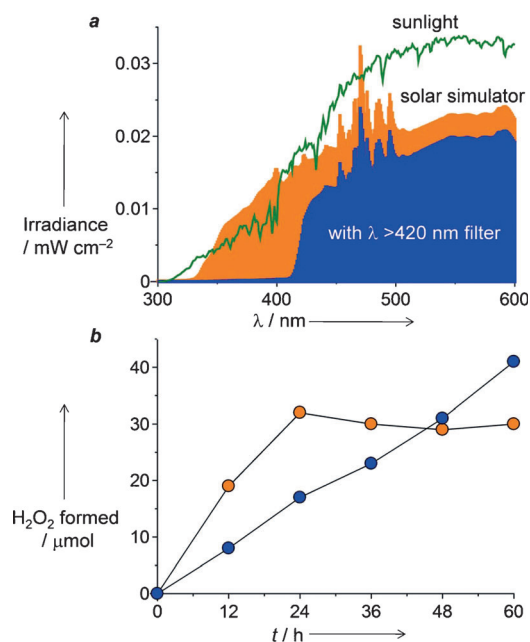


Figure 4. a) Spectral irradiance for sunlight (green, Nov 23, 2013 at 8:00–17:00, north latitude 34.7°, east longitude 135.5°; light intensity at 300–500 nm, 2.8 mW cm⁻²) and solar simulator (orange) without and (blue) with $\lambda > 420$ nm filter (light intensity at 300–500 nm and 420–500 nm are 2.9 and 1.3 mW cm⁻², respectively). b) Time-dependent change in H₂O₂ evolution during photoreaction with g-C₃N₄/PDI₅₁ in a water/O₂ system under irradiation by solar simulator (orange) without and (blue) with $\lambda > 420$ nm filter.

These data suggest that g-C₃N₄/PDI is successfully activated by visible region light within sunlight and promotes efficient H₂O₂ production.

In summary, we found that sunlight activation of g-C₃N₄/PDI produces H₂O₂ from water and O₂. This promotes water oxidation and two-electron reduction of O₂, facilitating efficient production of H₂O₂. At present, the catalytic activity is insufficient; the amount of H₂O₂ formed by 48 h reaction is approximately 30 μmol (1 mM). Activity improvement is necessary for practical application. Nevertheless, the present photoprocess has significant advantages: 1) metal-free catalyst, 2) cost-free light (sunlight), 3) earth-abundant resources (water and O₂), and 4) mild reaction conditions (atmospheric pressure and ambient temperature). The basic concept presented herein based on the band engineering of g-C₃N₄ with aromatic diimide may contribute to the design of safe, green, and sustainable H₂O₂ synthesis by sunlight.

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