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Construction of Conjugated Organic Polymers for Efficient Photocatalytic Hydrogen Peroxide Generation with Adequate Utilization of Water Oxidation

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Abstract: The visible-light-driven photocatalytic production of hydrogen peroxide (H₂O₂) is currently an emerging approach for transforming solar energy into chemical energy. In general, the photocatalytic process for producing H₂O₂ includes two pathways: the water oxidation reaction (WOR) and the oxygen reduction reaction (ORR). However, the utilization efficiency of ORR surpasses that of WOR, leading to a discrepancy with the low oxygen levels in natural water and thereby impeding their practical application. Herein, we report a novel donor–bridge–acceptor (D–B–A) organic polymer conjugated by the Sonogashira–Hagihara coupling reaction with tetraphenylethene (TPE) units as the electron donors, acetylene (A) as the connectors and pyrene (P) moieties as the electron acceptors. Notably, the resulting TPE–A–P exhibits a remarkable solar-to-chemical conversion of 1.65% and a high BET-specific surface area (1132 m²·g^{−1}). Furthermore, even under anaerobic conditions, it demonstrates an impressive H₂O₂ photosynthetic efficiency of 1770 μmol g^{−1} h^{−1}, exceeding the vast majority of previously reported photosynthetic systems of H₂O₂. The outstanding performance is attributed to the effective separation of electrons and holes, along with the presence of sufficient reaction sites facilitated by the incorporation of alkynyl electronic bridges. This protocol presents a successful method for generating H₂O₂ via a water oxidation reaction, signifying a significant advancement towards practical applications in the natural environment.

Keywords: environmental chemistry; hydrogen peroxide; photocatalysis; water oxidation reaction



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1. Introduction

With the increasing concern about environmental degradation and in situ surface water remediation, the renewable energy conversion has become a pillar supporting the advancement of sustainable development in the field of modern energy [1]. As one of the world's 100 most used chemicals, hydrogen peroxide (H₂O₂) has been extensively utilized as an efficient green oxidant in chemical synthesis, wastewater treatment, paper bleaching and disinfection [2,3]. Owing to a comparable energy density to compressed hydrogen, H₂O₂ as a liquid fuel substitute for H₂ is easier in storage and transportation [4]. To date, the industrial-scale production of H₂O₂ through the anthraquinone (AQ) oxidation process often involves drawbacks such as energy consumption and the generation of hazardous waste [5]. Therefore, it is highly desired to develop an alternative method for H₂O₂ manufacturing based on an efficient, affordable, green and eco-friendly process.

As a promising alternative towards sustainability, the photocatalytic production of H₂O₂ with remarkable efficiency and selectivity is of great interest. The ideal artificial photosynthesis of H₂O₂ driven by sunlight can straightforwardly exploit earth-abundant

water and air as raw materials, enabling the full utilization of both the water oxidation and oxygen reduction half-reactions to activate the photocatalyst [6]. Recently, various non-metal photocatalysts, such as graphitic carbon nitride (g-C₃N₄) and their derivatives, resorcinol formaldehydes (RFs), as well as covalent triazine frameworks (CTFs), have been widely investigated for enhancing H₂O₂ photosynthesis [7–9]. Nonetheless, most of the reported works still encounter the following obstacles: (i) the valence band of photocatalyst cannot match the prerequisites of water oxidation reaction (WOR), resulting in only using a single mode of oxygen reduction reaction (ORR), which severely hinders the application of this technology in natural water [10,11]. (ii) Sacrificial agents such as AgNO₃ or alcohol are employed to quench the electrons or holes, which instigates the inevitable introduction of additional substances and the generation of byproducts in the reaction system [12], and (iii) the existing photocatalysts for the synthesis of H₂O₂ typically have a low BET specific surface area, which obstructs the exposure of catalytic sites and is not conducive to transfer mass [13]. Moreover, preliminary investigations remain unsatisfactory due to the inadequate selectivity and unsuitable photo-redox capability to meet the stringent requirements of highly efficient full reactions for H₂O₂ production [14]. Accordingly, it is crucial to develop remarkable photocatalysts for overall H₂O₂ production via WOR and ORR dual channels with 100% atomic utilization.

Pyrene compounds are classic polycyclic aromatic hydrocarbons with a large π -conjugated plane and unique photophysical properties [15]. The easily modifiable structure of pyrene molecules and the unique planarity of the pyrene skeleton are conducive to enhancing the π - π interactions between layers, promoting the rapid separation and transfer of photo-generated charge carriers [16]. Through the donor–bridge–acceptor (D-B-A) molecular strategy containing redox moieties, the binding energy of excitons in a photocatalyst is significantly reduced, and the recombination of holes and electrons can be effectively suppressed [17].

Here, we precisely designed alternately linked electron donor–bridge–acceptor-conjugated polymeric semiconductor (termed TPE-A-P) with electron-rich tetraphenylethene moieties serving as electron donors, acetylene as the bridges and high-electron-affinity pyrene moieties acting as electron acceptors. For comparison, another photocatalyst (termed TPE-P) without alkynyl electron bridges was also successfully constructed. The activation energy of excitons in TPE-A-P photocatalyst is only 95 meV, far lower than the 141 meV for TPE-P, which was attributed to the significant role of alkynyl electron bridges. Without sacrificial agents, TPE-A-P exhibits the highest H₂O₂ production rate of 3028 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in open air, pure water, and solar light irradiation, which outperforms the majority of reported non-metallic photocatalysts. Meanwhile, the valence band potential of TPE-A-P reaches as high as 2.32 eV, giving rise to the great capacity for 2e[−] WOR. Correspondingly, the efficiency of H₂O₂ production was still maintained at 1770 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in the absence of oxygen for TPE-A-P. Further TD-DFT calculations and in situ infrared characterization disclosed the mechanism and reactive sites of TPE-A-P and TPE-P. This study provides new insights into the molecular design of donor–bridge–acceptor photocatalysts for the full reaction of H₂O₂ production under anaerobic conditions.

2. Materials and Methods

All reagents and solvents were purchased from Sigma Aldrich or Bide pharm Co. (Shanghai, China).

2.1. Synthesis of TPE-A-P

1,1,2,2-Tetrakis(4-ethynylphenyl)ethene (42.85 mg, 0.1 mmol), 1,3,6,8-tetrabromopyrene (51.78 mg, 0.1 mmol), CuI (1.9 mg, 0.1 mmol), (PPh₃)₂PdCl₂ (7.02 mg, 0.1 mmol), triethylamine (10 mL) and *N,N*-dimethylformamide (10 mL) were added to a 100 mL reaction flask. The mixture was degassed with nitrogen for 30 min at room temperature. Then, the mixture was heated to 80 °C and refluxed for 48 h under nitrogen atmosphere. After that, the mixture was cooled to room temperature, and the precipitate was collected by filtration.

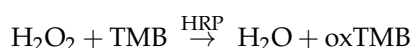
The crude product was then washed with *N,N*-dimethylformamide, dichloromethane and ethanol. The final product was dried at 60 °C overnight to give an orange power.

2.2. Synthesis of TPE-P

1,1,2,2-Tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (83.63 mg, 0.1 mmol), 1,3,6,8-tetrabromopyrene (51.78 mg, 0.1 mmol), Pd(PPh₃)₄ (6 mg, 0.05 mmol), *N,N*-dimethylformamide (10 mL) and 2 M potassium carbonate aqueous solution (1 mL) were added to a 50 mL reaction flask. The mixture was degassed with nitrogen for 30 min at room temperature. Then, the mixture was heated to 150 °C and refluxed for 48 h under nitrogen atmosphere. After that, the mixture was cooled to room temperature, and the precipitate was collected by filtration. The crude product was then washed with *N,N*-dimethylformamide, dichloromethane, water and ethanol. The final product was dried at 80 °C overnight to give a green power.

2.3. Photocatalytic Experiments

Photocatalyst (1 mg) was dispersed in 50 mL deionized water in a 100 mL beaker. After ultrasonicated for 30 min in darkness, a Xe lamp (100 mW·cm^{−2}, λ > 400 nm) was used to irradiate the catalyst under magnetic stirring. At certain 30 min intervals, 1 mL of suspension was sampled and filtered with a 0.22 μm filter to remove the photocatalysts. Finally, the concentration of H₂O₂ was determined by using a TMB-H₂O₂-HRP enzymatic assay. The reaction between H₂O₂ and TMB was as follows:



3,3',5,5'-Tetramethylbenzidine (TMB) solution was prepared as follows: 15 mg of TMB was dissolved in 0.3 mL of DMSO, followed by the addition of 5 mL of glycerol. Moreover, 45 mL of deionized water containing 20 mg of ethylenediaminetetraacetic acid (EDTA) and 95 mg of citric acid was added to the above solution. Finally, the solution was filled to 500 mL with deionized water.

Horseradish peroxidase (HRP) solution was prepared as follows: 2 mg of peroxidase (from horseradish) was dissolved in 10 mL of deionized water.

Determination of the calibration curve was as follows: The standard H₂O₂ (0, 0.3, 0.6, 1.5, 3, 7.5 and 15 mM) solutions were prepared. Moreover, 10 μL of the above-known concentration H₂O₂ solution was taken, followed by the addition of 10 μL of HRP solution and 200 μL of TMB solution. After 3 min, 10 μL of concentrated hydrochloric acid was added to the above solution. The concentration of the H₂O₂ was calculated based on the absorbance at 450 nm by a UV–vis spectrophotometer. According to the linear relationship between signal intensity and H₂O₂ concentration, the H₂O₂ standard curve was drawn for subsequent H₂O₂ concentration calibration.

3. Results and Discussion

3.1. Chemical and Physical Characterization

TPE-A-P (Figure 1a) was firstly synthesized via the classic Sonogashira–Hagihara cross-coupling reaction between 1,1,2,2-tetrakis(4-ethynylphenyl)ethene (TPE) and 1,3,6,8-tetrabromopyrene (P) with acetylene as connectors, while TPE-P was prepared by the Suzuki coupling reaction between 1,3,6,8-tetrabromopyrene (P) and 1,1,2,2-tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (TTMBPE).

The powder X-ray diffraction (XRD) patterns of target TPE-A-P and TPE-P photocatalysts displayed the features of amorphous carbon (Figure S1). The compositions and structures of both materials were further characterized by Fourier-transform infrared (FTIR) and ¹³C solid-state NMR spectroscopy (¹³C ssNMR). The peak at 3275 cm^{−1}, assigned to the ≡C–H stretching vibrations from the TPE terminal alkyne, vanished in the FTIR spectra of TPE-A-P (Figure S2), indicating the successful construction of TPE-A-P. Meanwhile, the complete disappearance of the characteristic B–O peak at 1359 cm^{−1} suggested the

successful preparation of TPE-P [18]. The characteristic alkynyl peak at ≈ 90 ppm was observed in the solid-state ^{13}C NMR spectrum of TPE-A-P (Figure 1b), confirmed by the $\text{C}\equiv\text{C}$ peak at 2209 cm^{-1} in the Raman spectra (Figure 1c) [19]. In contrast, no alkynyl signals were detected in those of TPE-P (Figure S3). X-ray photoelectron spectroscopic (XPS) analysis was performed to investigate the electronic structure and elemental composition of materials. As expected, Figure S4 showed that only the existence of the C element was observed in both samples. In the C 1s spectra, two peaks appearing at 283.7 and 284.6 eV can be attributed to C–C and C=C in TPE-A-P (Figure S4a), while a single peak at 284.6 eV was deconvoluted from the C 1s spectra of TPE-P (Figure S4b). Collectively, these chemical characterizations offered robust evidence supporting the successful synthesis of TPE-A-P and TPE-P [20].

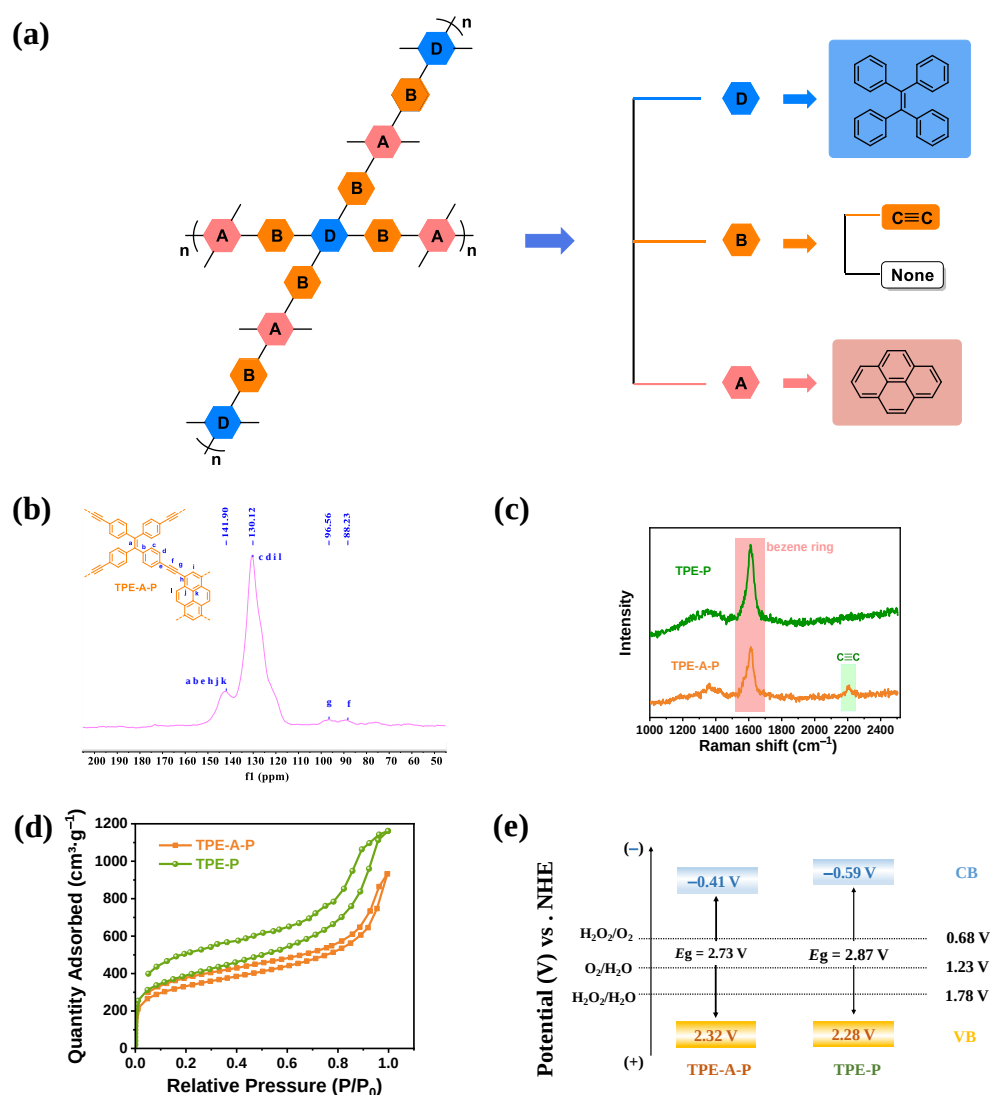


Figure 1. Structure and characterization of TPE-A-P and TPE-P. (a) Molecular structures of TPE-A-P and TPE-P. (b) Solid state ^{13}C CP-MAS NMR spectra of TPE-A-P. (c) Raman spectra of TPE-A-P and TPE-P. (d) N_2 adsorption-desorption isotherms of TPE-A-P and TPE-P. (e) Schematic illustration of the electronic structure of TPE-A-P and TPE-P.

Nitrogen adsorption-desorption isotherms were measured at 77 K to evaluate the porous porosities of TPE-A-P and TPE-P (Figure 1d). The Brunauer-Emmett-Teller (BET)-specific surface areas were determined to be 1132 and $1334\text{ m}^2\cdot\text{g}^{-1}$ for TPE-A-P and TPE-P, respectively. According to the IUPAC classification, both TPE-A-P and TPE-P possessed type IV adsorption-desorption isotherms, and the corresponding pore sizes

of two materials illustrated in Figure S5 proved that both TPE-A-P and TPE-P possessed mesoporous properties. As shown in Figure S6, field-emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM) revealed that two samples exhibited tightly exfoliated structures on their surfaces. Additionally, Thermogravimetric analysis (TGA) revealed that TPE-A-P possesses excellent thermal stability with a decomposed temperature above 310 °C under N₂ atmosphere (Figure S7a).

The electronic structures of TPE-A-P and TPE-P were also of vital importance in the overall photosynthesis of H₂O₂. The electronic structures of TPE-A-P and TPE-P were determined by Mott–Schottky tests and valence band XPS (VB-XPS) spectra. The conduction band minima (CB_{min}) of TPE-A-P and TPE-P were characterized to be −0.41 and −0.59 eV versus NHE from the Mott–Schottky tests (Figure S8). Moreover, the slopes of TPE-A-P and TPE-P were positive, indicating they were n-type semiconductors. As illustrated in Figure S9, VB-XPS spectra showed that the VB maxima (VB_{max}) of TPE-A-P and TPE-P were 1.92 and 2.09 eV, respectively. The VB-XPS was used to ascertain the energy level difference from VB_{max} to Fermi level, and Kelvin probe force microscopy (KPFM) was employed to determine the energy level difference from Fermi level to vacuum level (Figure S10). Subsequently, the vacuum level to the electrode potential can be converted from the equation $E_{VB} = \Phi + VB_{max} - 4.44$. Here, Φ is the work function of semiconductors detected by KPFM, and 4.44 is the value of the absolute potential of the standard hydrogen electrode [21]. The Φ of TPE-A-P and TPE-P were 4.84 and 4.63 eV, respectively. Consequently, the E_{VB} of TPE-A-P and TPE-P were calculated to be 2.32 and 2.28 eV. Therefore, the bandgaps of TPE-A-P and TPE-P were 2.73 and 2.87 eV. The electronic structures of TPE-A-P and TPE-P are illustrated in Figure 1e, and both photocatalysts mentioned above are thermodynamically sufficient for the photosynthesis of H₂O₂ through both the WOR and ORR pathways [22,23].

3.2. Photocatalytic Performance

The photocatalytic H₂O₂ production was conducted by suspending the as-synthesized TPE-A-P and TPE-P (1 mg) in pure water (50 mL) without any sacrificial agents or continuous O₂ bubbling under Xenon-lamp light with the UV light cutoff (>400 nm, 100 mW·cm^{−2}). Figure 2a showed that the photocatalytic H₂O₂ generation rate for TPE-A-P was 3028 μmol g^{−1} h^{−1}, which was nearly six times that of TPE-P (518 μmol g^{−1} h^{−1}). Remarkably, the amount of photosynthetic hydrogen peroxide remained a rapid increase within 5 h for TPE-A-P in pure water. (Figure S11). Additionally, TPE-A-P maintained its high efficiency after five consecutive cycles (Figure S12), indicating its excellent reusability and stability. By contrast, TPE-P exhibited a significant decrease in catalytic activity after four runs. The apparent quantum yield (AQY) of TPE-A-P reached 22.6%, 12.4%, 9.2% and 4.9% at 420, 470, 550 and 620 nm, respectively, compared to only 10.1% at 420 nm for TPE-P (Figure 2b). The solar–chemical-conversion (SCC) efficiency of TPE-A-P achieved 1.65%, which was about 16 times higher than the average solar-to-biomass conversion efficiency of typical plants (≈0.1%) [24–28]. In addition, the properties of TPE-A-P remained unchanged. The morphology and structure were maintained after 5 h irradiation (Figure S6). Notably, TPE-A-P maintained more than 50% of its activity in H₂O₂ generation even under anaerobic conditions (Figure 2c), which prominently surpassed photocatalysts reported in previous works listed in Figure 2d and Table S1 [29,30].

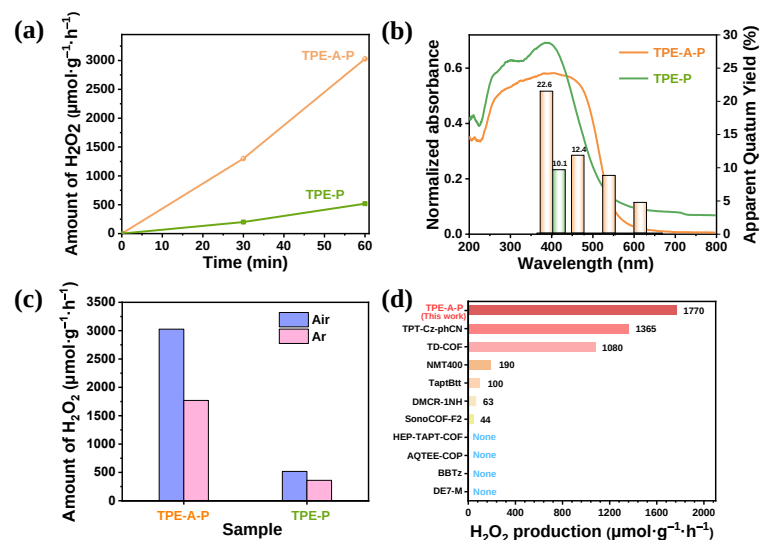


Figure 2. The photocatalytic performance of TPE-A-P and TPE-P for H_2O_2 production. (a) The photocatalytic H_2O_2 generation rate of TPE-A-P and TPE-P in open air and pure water without any additives. (b) UV-vis diffuse reflectance spectra of TPE-A-P and TPE-P and the AQY of TPE-A-P at 420, 470, 550 and 620 nm. (c) Photocatalytic production of H_2O_2 by TPE-A-P and TPE-P in pure water under different atmospheres. (d) Activity comparison between TPE-A-P and other reported photocatalysts for H_2O_2 production in anaerobic conditions.

Our investigation proceeded to explore the reason behind the remarkable photo-synthetic efficiency. Figure S13 showed that the photocurrent density of TPE-A-P was significantly higher than that of TPE-P, which suggested the availability of more light-induced carriers in the photocatalytic reaction. Electrochemical impedance spectroscopy (EIS) measurement was also conducted to explore the interfacial charge transfer resistance of TPE-A-P and TPE-P (Figure S14). According to the Nyquist plots, the smaller semicircle diameter of TPE-A-P indicated the excellent separation of photogenerated electrons and holes, as well as a faster interfacial charge transfer in TPE-A-P. From the steady-state photoluminescence (PL) emission spectra (Figure 3a), the overall recombination efficiency of excitons was relatively low in TPE-A-P, whereas they were still significant in TPE-P, suggesting that the exciton radiative recombination was greatly suppressed in TPE-A-P. Temperature-dependent PL spectroscopy was also conducted to investigate the charge migration dynamics (Figure 3b,c). The exciton activation energy (E_a) of the photoluminescence quenching process was estimated by the Arrhenius equation (Figure 3d,e) [31]. The E_a derived were 95 meV for TPE-A-P and 141 meV for TPE-P. We believed that the lower E_a of TPE-A-P indicated much easier separation of excitons than TPE-P. In addition, the dihedral angles of TPE-A-P and TPE-P were 0.218° and 53.23° , respectively (Figure 3f,g) [32]. The introduction of acetylene as the bridge greatly facilitated the coplanarity of the electron acceptors and electron donors, which was conducive to the charge transfer and exciton dissociation process in the D-B-A structure of TPE-A-P.

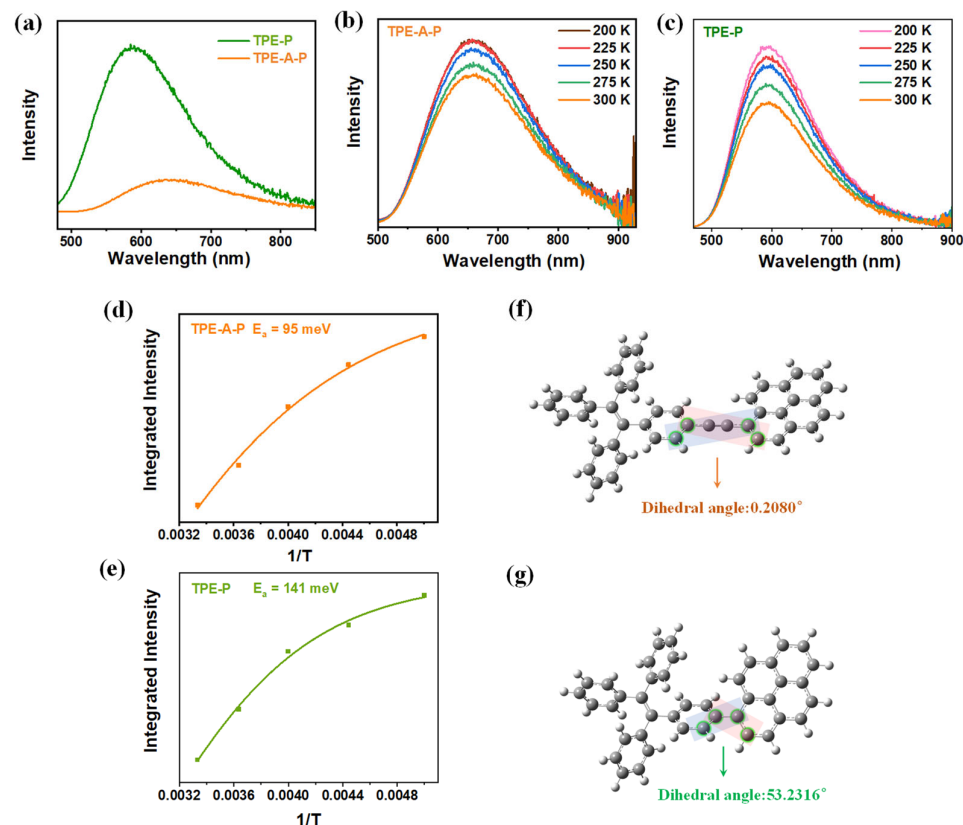


Figure 3. Investigation of the charge separation efficiency in two materials. (a) Photoluminescence spectra of TPE-A-P and TPE-P. Temperature-dependent PL spectra for (b) TPE-A-P and (c) TPE-P. The exciton activation energy of (d) TPE-A-P and (e) TPE-P. The dihedral angles of (f) TPE-A-P and (g) TPE-P.

3.3. Pathways for Photosynthesis of H_2O_2

Control experiments and electrochemical measurements were conducted to investigate the pathways for generating H_2O_2 in photocatalysis. Rotating disk electrode (RDE) voltammetry was executed to explore the average electron transfer number in the ORR process for two materials. The linear sweep voltammetry curves were acquired with different rotating speeds (Figure 4a,b). The Koutecky–Levich (K–L) plots in Figure 4c revealed that the average electron transfer number (n) of TPE-A-P and TPE-P were 1.93 and 0.92, respectively, suggesting varying degrees of selectivity of ORR process when TPE-A-P and TPE-P were utilized [33]. The number of 1.93 was close to the theoretical value for directly and selectively reducing O_2 into H_2O_2 for TPE-A-P, while 0.92 indicated single electron transfer occurred in the presence of TPE-P. In addition, a ring-disk electrode (RRDE) was also conducted to investigate the selective electron transfer during ORR. As shown in Figure S15a, the ring current of TPE-A-P exhibited a rapid enhancement along with the decrease in potential, implying a greater generation of H_2O_2 from the disk part. The n values of TPE-A-P and TPE-P were then calculated to be 2.1 and 1.1, respectively (Figure S15b). In order to further probe the differences in the ORR process, we conducted a series of sacrificial agent experiments (Figure 4d,e). With the existence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as $O_2^{\cdot-}$ sacrificial agents, the yield of photosynthetic H_2O_2 for TPE-A-P decreased slightly, while a noticeable reduction for TPE-P was observed. This result revealed a different majority of intermediates within the ORR process between the two materials. Combined with the RDE test results, TPE-A-P was more inclined to undergo a direct $2e^-$ one-step oxygen reduction ($O_2 \rightarrow H_2O_2$) to produce H_2O_2 . Conversely, TPE-P tended to undergo an indirect sequential $1e^-$ two-step oxygen reduction ($O_2 \rightarrow O_2^{\cdot-} \rightarrow H_2O_2$) [34], where O_2 is first singly reduced to form $O_2^{\cdot-}$, and then the $O_2^{\cdot-}$ acquires another electron to generate H_2O_2 . Unfavorably, $O_2^{\cdot-}$ is easily quenched

and can attack the generated H_2O_2 , causing the decomposition of H_2O_2 and thus resulting in a decrease in yield [35,36]. Therefore, the 2e^- one-step oxygen reduction is more advantageous to the efficiency of the ORR process in photocatalytic H_2O_2 production. The 2e^- one-step ORR selectivity of TPE-A-P guaranteed an exceeding performance. When using EDTA-2Na as a hole scavenger, TPE-A-P exhibited a tiny decrease in the photocatalytic yields of H_2O_2 and in sharp contrast to TPE-P, which further confirmed a better ORR performance for TPE-A-P. Electron paramagnetic resonance (EPR) experiments were performed to detect reactive oxygen species (ROS). Figure 4f demonstrated that the presence of $\text{O}_2^{\cdot-}$ was detected in both TPE-A-P and TPE-P systems with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the spin-trap agent. These results collectively indicated that TPE-A-P followed both a 1e^- two-step ORR and 2e^- one-step ORR pathways for H_2O_2 production, while TPE-P mainly followed a 1e^- two-step ORR pathway.

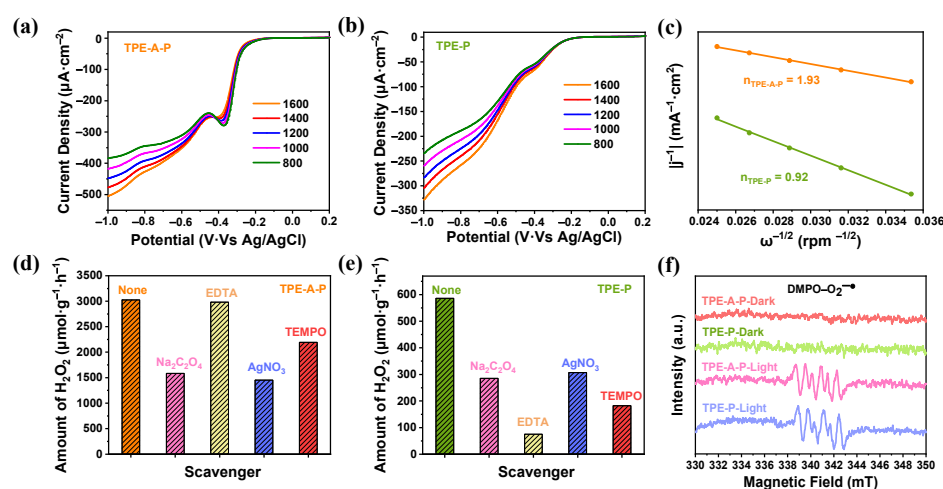


Figure 4. Investigation of pathways for ORR process. Linear-sweep RDE voltammograms of (a) TPE-A-P and (b) TPE-P. (c) Koutecky–Levich plots obtained from RDE measurements. Photosynthesis of H_2O_2 with different scavengers of (d) TPE-A-P, (e) TPE-P. (f) EPR spectra of $\text{DMPO-O}_2^{\cdot-}$ for TPE-A-P and TPE-P.

On the other hand, the WOR process was also vital for the photosynthesis of H_2O_2 since both TPE-A-P and TPE-P maintained more than one-half of the activities in an Ar atmosphere. Correspondingly, both materials were capable of generating H_2O_2 with almost half of the efficiency when silver nitrate (AgNO_3) served as an electron sacrificial agent, confirming an appreciable capacity of WOR (Figure 4d,e). The RRDE tests under nitrogen atmosphere were utilized to determine the products of WOR. TPE-A-P and TPE-P displayed substantial reduction currents at the Pt ring electrode when the applied potentials were set at 0.6 V (Figure 5a), which were identified as the reduction of H_2O_2 [37]. Noticeably, TPE-A-P exhibited better 2e^- WOR performance than TPE-P. Only TPE-P showed distinct reduction currents when the applied potentials were set at -0.23 V (Figure 5b), which was attributed to the reduction of O_2 . This revealed that TPE-P followed both 2e^- and 4e^- WOR pathways, while TPE-A-P mainly followed a 2e^- WOR pathway, indicating an excellent selectivity favoring the photosynthesis for H_2O_2 . In addition, H_2O_2 could also be photosynthesized through indirect 2e^- water oxidation, which involved hydroxyl radicals ($\cdot\text{OH}$) as the intermediate. EPR experiments revealed no detectable $\cdot\text{OH}$ signals by using DMPO as a trapping agent under both light and dark conditions (Figure 5c), indicating no indirect 2e^- pathway of water oxidation for both photocatalysts [38]. Consequently, TPE-A-P and TPE-P facilitated the formation of H_2O_2 via the direct 2e^- pathway of WOR.

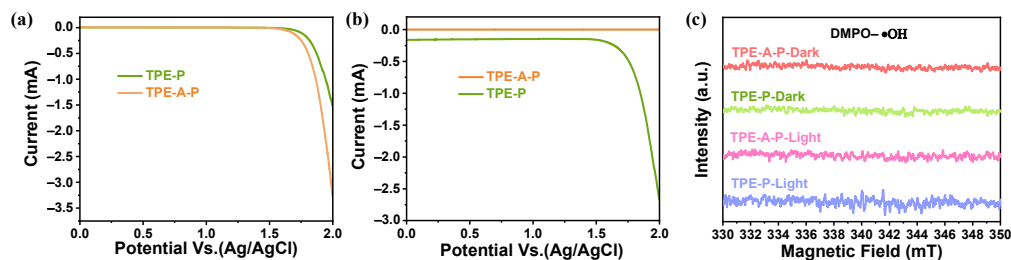


Figure 5. Studies of pathways for WOR process. Rotating ring-disk electrode voltammograms obtained in 0.1 M phosphate buffer solution with a rotation rate of 1600 rpm. (a) The Pt ring was set at 0.6 V to detect H₂O₂. (b) The Pt ring was set at −0.23 V to detect O₂. (c) EPR spectra of DMPO-•OH for TPE-A-P and TPE-P.

3.4. Active Sites for Both ORR and WOR

To have a clear insight into the mechanism of photocatalytic H₂O₂ generation, we conducted theoretical studies based on the model compounds of TPE-A-P and TPE-P. As shown in Table S2, the dominant transition of TPE-A-P and TPE-P was both $S_0 \rightarrow S_1$ with the largest values of oscillator strengths [39]. Therefore, time-dependent density functional theory (TD-DFT) in terms of the transition of $S_0 \rightarrow S_1$ was exploited to investigate the active sites responsible for the photosynthesis of H₂O₂ (Figure S16) [40]. Accordingly, the photoinduced holes of excited TPE-A-P and TPE-P were primarily located at the TPE sites, while the photoinduced electrons were situated at the pyrene sites. Moreover, the electrostatic potential maps in Figure 6a,b depicted the electrical distribution of TPE-A-P and TPE-P, indicating a prominent negative electron charge surface with blue color on pyrene moieties as well as a significant positive charge surface with red color on the TPE sites for both materials. The distribution of the negative and positive charges was compatible with the locations of photoinduced holes and electrons. TPE-A-P possessed unique electron-rich alkynyl electron bridges, which were capable of transferring electrons to oxygen, implying acetylene moieties as the active sites for ORR [41]. Additionally, TPE-A-P exhibited a higher density of positive charges on the TPE sites in comparison to TPE-P. This characteristic facilitated the separation of charges, enabling TPE-A-P to efficiently catalyze the synthesis of H₂O₂ from water oxidation.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements of TPE-A-P and TPE-P were tested to demonstrate the active sites for ORR and WOR. As exhibited in Figure 6c,d, under a continuous steam-saturated O₂ flow and when the system was irradiated for 60 min, new vibrations corresponding to O–O (855 cm^{−1}), O₂^{•−} (1129 cm^{−1}), OOH (1246 cm^{−1}) for TPE-P emerged owing to the formation of intermediates from the 1e[−] two-step ORR process [42]. For TPE-A-P, vibrations corresponding to O–O (874 cm^{−1}), O₂^{•−} (1179 cm^{−1}), OOH (1245 cm^{−1}) also appeared. However, the variation in the intensity of these signals for TPE-A-P was relatively low, implying a different selectivity for ORR pathways. It is noteworthy that the peak intensity corresponding to C≡C (2209 cm^{−1}) showed a gradual enhancement after illumination, which elaborated alkynyl electron bridges served as active sites in the ORR reaction. Furthermore, the characteristic signals attributed to the benzene rings (1516 cm^{−1} for TPE-A-P and 1497 cm^{−1} for TPE-P) gradually intensified under irradiation, which further confirmed the benzene rings as active sites in the ORR process [43]. In combination with the calculation results of hole and electron contribution rates in TD-DFT, the benzene rings located at pyrene moieties were involved in H₂O₂ production via ORR reaction.

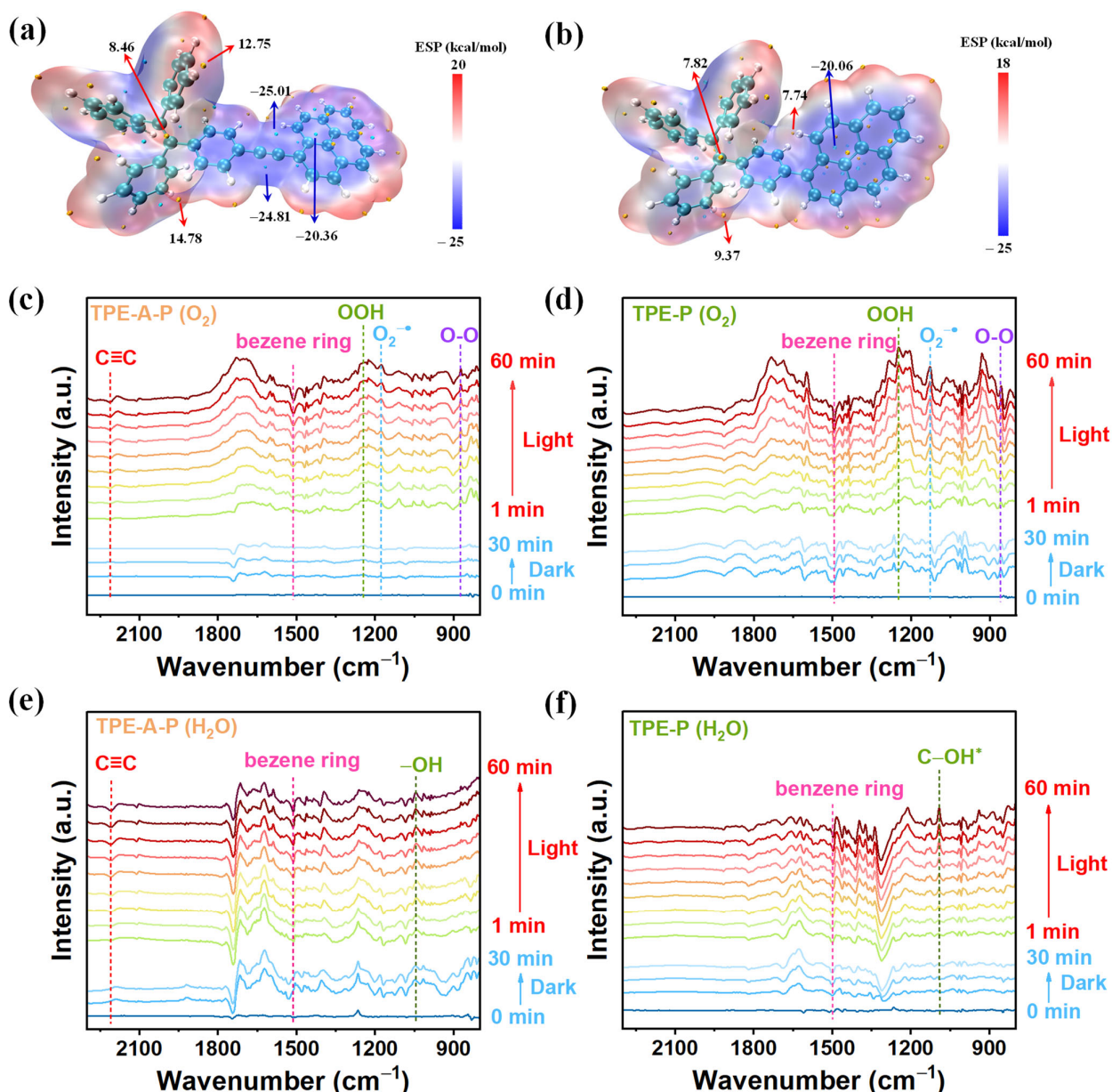


Figure 6. Active sites of TPE-A-P and TPE-P for H_2O_2 production. Electrostatic potential maps for (a) TPE-A-P and (b) TPE-P. The yellow dots represent the points of maximum surface potential, and the green dots represent the points of minimum surface potential. In situ DRIFTS spectra of (c) TPE-A-P under O_2 , (d) TPE-P under O_2 , (e) TPE-A-P under H_2O , (f) TPE-P under H_2O .

The active sites for WOR were further demonstrated by in situ IR spectrometry measurements after a continuous steam-saturated H_2O (Figure 6e,f). Under light irradiation, the formation of a new infrared signal corresponding to $-\text{OH}$ (1045 cm^{-1} for TPE-A-P) and $\text{C}-\text{OH}^*$ (1092 cm^{-1} for TPE-P) evidenced the adsorption of H_2O and subsequent oxidation reactions [44]. Additionally, the enhancement of the characteristic peak of $\text{C}\equiv\text{C}$ (2209 cm^{-1} for TPE-A-P) during the illumination process indicated the involvement of acetylene sites to produce H_2O_2 via WOR reaction. Moreover, the peak at 1513 cm^{-1} for TPE-A-P and 1483 cm^{-1} for TPE-P, assigned to the vibration of benzene rings, showed a rising signal intensity [45]. Binding with the analysis of the distribution of the photoinduced holes in TD-DFT, the benzene rings situated at TPE moieties served as active sites for the WOR reaction.

These results emphasized variation in active sites for WOR and ORR between TPE-A-P and TPE-P. Based on the experimental and computational results, the primary mechanism of TPE-A-P photocatalytic H_2O_2 production was proposed as follows: under visible-light illumination, the photoinduced electrons were primarily trapped at the pyrene sites, whereas the holes predominantly collected on the TPE units. Particularly due to the capacity of adsorbing both water and oxygen, alkynyl electron bridges served as active sites for both WOR and ORR. These led to the production of H_2O_2 through a direct $2e^-$ one-step ORR on the pyrene and acetylene moieties as well as a direct $2e^-$ WOR pathway at TPE and acetylene sites.

4. Conclusions

In summary, we synthesized an effective D-B-A conjugated organic polymer for photosynthetic H_2O_2 . The photosynthetic rate of H_2O_2 reaches $3028 \mu\text{mol g}^{-1} \text{h}^{-1}$ under ambient conditions. More importantly, the activity was maintained for more than one-half, even under argon conditions. Our investigations show that the incorporation of alkynyl electron bridges can effectively diminish exciton excitations, thereby suppressing the radiative recombination of excitons. Meanwhile, the differences in the ORR pathways between TPE-A-P and TPE-P lead to a gap of performance in photocatalytic H_2O_2 production, where TPE-A-P mainly exhibited a $2e^-$ one-step ORR pathway and TPE-P followed a $1e^-$ two-step pathway. Additionally, TPE-A-P exhibited direct $2e^-$ water oxidation selectivity and better performance in WOR than TPE-P. In addition to possessing TPE as the active sites for water oxidation reaction and pyrene units as the sites for oxygen reduction reaction in both materials, the acetylene groups in TPE-A-P also participate in both WOR and ORR process, leading to an overall increase in H_2O_2 production performance. This work introduces a novel D-B-A protocol for the photocatalytic production of H_2O_2 in oxygen-limited conditions and holds an important implication for natural water remediation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma17112709/s1>, Figure S1: PXRD patterns of TPE-A-P and TPE-P; Figure S2: FTIR of TPE-A-P, TPE-P, TPE and TTMBPE; Figure S3: Solid state ^{13}C CP-MAS NMR spectra of TPE-P; Figure S4: C(1s) spectra of (a) TPE-A-P, (b) TPE-P; Figure S5: The pore size distributions of (a) TPE-A-P, (b) TPE-P; Figure S6: SEM images of (a) TPE-A-P, (b) TPE-A-P after 5-h irradiation, (c) TPE-P, (d) TPE-P after 5-h irradiation. TEM images of (e) TPE-A-P, (f) TPE-A-P after 5-h irradiation, (g) TPE-P, (h) TPE-P after 5-h irradiation; Figure S7: Thermogravimetric analysis (TGA) profiles of (a) TPE-A-P and (b) TPE-P ranging from room temperature to 800°C at $10^\circ\text{C}\cdot\text{min}^{-1}$; Figure S8: Mott Schottky plots of (a) TPE-A-P, (b) TPE-P; Figure S9: VB-XPS spectra of (a) TPE-A-P, (b) TPE-P; Figure S10: KPFM images of (a) HOPG, (b) TPE-A-P, (c) TPE-P; Figure S11: Photosynthetic amount of H_2O_2 generation from TPE-A-P and TPE-P in pure water under 5-h irradiation; Figure S12: Cycle experiments of TPE-A-P and TPE-P in deionized water; Figure S13: Current-Time (I-t) curves under visible light illumination of (a) TPE-A-P and TPE-P in Ar, (b) TPE-A-P and TPE-P in O_2 ; Figure S14: Nyquist plot of TPE-A-P and TPE-P; Figure S15: (a) ORR polarization curves of photocatalysts on RRDE at 1600 rpm in O_2 -saturated phosphate buffer solution. (b) The corresponding number (n) of electron transfer as a function of the applied potential; Figure S16: The distribution of electrons and holes in excited state of (a) TPE-A-P and (b) TPE-P; Table S1: The efficiency comparison between TPE-A-P and previous reported photocatalysts for H_2O_2 production in anaerobic conditions; Table S2: Oscillator strengths of excited states of monomers from TPE-A-P and TPE-P. References [6,30,42,46–67] are cited in the Supplementary Materials.

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References

1. Rani, E.; Talebi, P.; Cao, W.; Huttula, M.; Singh, H. Harnessing photo/electro-catalytic activity via nano-junctions in ternary nanocomposites for clean energy. *Nanoscale* **2020**, *12*, 23461–23479. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Ciriminna, R.; Albanese, L.; Meneguzzo, F.; Pagliaro, M. Hydrogen peroxide: A key chemical for today's sustainable development. *ChemSusChem* **2016**, *9*, 3374–3381. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Jin, Y.; Shi, Y.; Chen, Z.; Chen, R.; Chen, X.; Zheng, X.; Liu, Y.; Ding, R. Enhancement of solar water disinfection using H₂O₂ generated in situ by electrochemical reduction. *Appl. Catal. B Environ.* **2020**, *267*, 118730. [\[CrossRef\]](#)
4. Mase, K.; Yoneda, M.; Yamada, Y.; Fukuzumi, S. Seawater usable for production and consumption of hydrogen peroxide as a solar fuel. *Nat. Commun.* **2016**, *7*, 11470. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Guo, Y.; Dai, C.; Lei, Z.; Chen, B.; Fang, X. Synthesis of hydrogen peroxide over Pd/SiO₂/COR monolith catalysts by anthraquinone method. *Catal. Today* **2016**, *276*, 36–45. [\[CrossRef\]](#)
6. Yue, J.; Song, L.; Fan, Y.F.; Pan, Z.X.; Yang, P.; Ma, Y.; Xu, Q.; Tang, B. Thiophene-containing covalent organic frameworks for overall photocatalytic H₂O₂ synthesis in water and seawater. *Angew. Chem. Int. Ed.* **2023**, *62*, e202309624. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Moon, G.-H.; Kim, W.; Bokare, A.D.; Sung, N.-E.; Choi, W.Y. Solar production of H₂O₂ on reduced graphene oxide–TiO₂ hybrid photocatalysts consisting of earth-abundant elements only. *Energy Environ. Sci.* **2014**, *7*, 4023–4028. [\[CrossRef\]](#)
8. Chu, C.H.; Huang, D.H.; Zhu, Q.H.; Stavitski, E.; Spies, J.A.; Pan, Z.H.; Mao, J.; Xin, H.L.; Schmuttenmaer, C.A.; Hu, S.; et al. Electronic tuning of metal nanoparticles for highly efficient photocatalytic hydrogen peroxide production. *ACS Catal.* **2019**, *9*, 626–631. [\[CrossRef\]](#)
9. Zeng, X.K.; Liu, Y.; Kang, Y.; Li, Q.Y.; Xia, Y.; Zhu, Y.L.; Hou, H.L.; Uddin, M.H.; Gengenbach, T.R.; Xia, D.H.; et al. Simultaneously tuning charge separation and oxygen reduction pathway on graphitic carbon nitride by polyethylenimine for boosted photocatalytic hydrogen peroxide production. *ACS Catal.* **2020**, *10*, 3697–3706. [\[CrossRef\]](#)
10. Baek, J.H.; Gill, T.M.; Abroshan, H.; Park, S.; Shi, X.J.; Nørskov, J.; Jung, H.S.; Siahrostami, S.; Zheng, X.L. Selective and efficient Gd-doped BiVO₄ photoanode for two-electron water oxidation to H₂O₂. *ACS Energy Lett.* **2019**, *4*, 720–728. [\[CrossRef\]](#)
11. Xu, J.W.; Zheng, X.L.; Feng, Z.P.; Lu, Z.Y.; Zhang, Z.W.; Huang, W.; Li, Y.B.; Vuckovic, D.; Li, Y.Q.; Dai, S.; et al. Organic wastewater treatment by a single-atom catalyst and electrolytically produced H₂O₂. *Nat. Sustain.* **2021**, *4*, 233–241. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Chen, L.; Wang, L.; Wan, Y.Y.; Zhang, Y.; Qi, Z.M.; Wu, X.J.; Xu, H.X. Acetylene and diacetylene functionalized covalent triazine frameworks as metal-free photocatalysts for hydrogen peroxide production: A new two-electron water oxidation pathway. *Adv. Mater.* **2020**, *32*, 1904433. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Ye, Y.X.; Wen, C.; Pan, J.H.; Wang, J.W.; Tong, Y.J.; Wei, S.B.; Ke, Z.F.; Jiang, L.; Zhu, F.; Zhou, N.B.; et al. Visible-light driven efficient overall H₂O₂ production on modified graphitic carbon nitride under ambient conditions. *Appl. Catal. B Environ.* **2021**, *285*, 119726. [\[CrossRef\]](#)
14. Luo, Y.; Zhang, B.P.; Liu, C.C.; Xia, D.H.; Ou, X.W.; Cai, Y.P.; Zhou, Y.; Jiang, J.; Han, B. Sulfone-modified covalent organic frameworks enabling efficient photocatalytic hydrogen peroxide generation via one-step two-electron O₂ reduction. *Angew. Chem. Int. Ed.* **2023**, *62*, e202305355. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Dong, X.Y.; Zhang, F.L.; Wang, Y.X.; Huang, F.W.; Lang, X.J. Selective oxidation of sulfides with oxygen over a pyrene covalent organic framework photocatalyst with TEMPO. *Appl. Catal. B Environ.* **2024**, *345*, 123660. [\[CrossRef\]](#)
16. Sun, J.; Sekhar Jena, H.; Krishnaraj, C.; Singh Rawat, K.; Abednatanzi, S.; Chakraborty, J.; Laemont, A.; Liu, W.; Chen, H.; Liu, Y.Y.; et al. Pyrene-based covalent organic frameworks for photocatalytic hydrogen peroxide production. *Angew. Chem. Int. Ed.* **2023**, *62*, e202216719. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Yan, H.J.; Shen, M.H.; Shen, Y.; Wang, X.D.; Lin, W.; Pan, J.H.; He, J.; Ye, Y.X.; Yang, X.; Zhu, F.; et al. Spontaneous exciton dissociation in organic photocatalyst under ambient conditions for highly efficient synthesis of hydrogen peroxide. *Proc. Natl. Acad. Sci. USA* **2022**, *119*, e2020913119. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Yan, H.J.; Deng, Y.C.; Shen, M.H.; Ye, Y.X.; Yang, X.; Zhu, F.; Ouyang, G.F. Regulation the reactive oxygen species on conjugated polymers for highly efficient photocatalysis. *Appl. Catal. B Environ.* **2022**, *314*, 121488. [\[CrossRef\]](#)
19. Zhou, W.X.; Cheng, Y.Y.; Ye, Y.X.; Wei, X.Q.; Tong, Q.; Dong, L.; Ouyang, G.F. Metal-free photocatalytic CO₂ reduction to CH₄ and H₂O₂ under non-sacrificial ambient conditions. *Angew. Chem. Int. Ed.* **2023**, *62*, e202313392. [\[CrossRef\]](#)
20. Ye, Y.X.; Pan, J.H.; Shen, Y.; Shen, M.H.; Yan, H.J.; He, J.; Yang, X.; Zhu, F.; Xu, J.Q.; He, J.G.; et al. A solar-to-chemical conversion efficiency up to 0.26% achieved in ambient conditions. *Proc. Natl. Acad. Sci. USA* **2021**, *118*, 2115666118. [\[CrossRef\]](#)
21. Luo, J.; Liu, Y.N.; Fan, C.Z.; Tang, L.; Yang, S.J.; Liu, M.L.; Wang, M.; Feng, C.Y.; Ouyang, X.L.; Wang, L.L.; et al. Direct attack and indirect transfer mechanisms dominated by reactive oxygen species for photocatalytic H₂O₂ production on g-C₃N₄ possessing nitrogen vacancies. *ACS Catal.* **2021**, *11*, 11440–11450. [\[CrossRef\]](#)

22. Zhao, C.; Wang, X.Y.; Yin, Y.F.; Tian, W.M.; Zeng, G.; Li, H.T.; Ye, S.; Wu, L.M.; Liu, J. Molecular level modulation of anthraquinone-containing resorcinol-formaldehyde resin photocatalysts for H₂O₂ production with exceeding 1.2% efficiency. *Angew. Chem. Int. Ed.* **2023**, *62*, e202218318. [[CrossRef](#)]
23. Haripriya, P.; Anjana, T.; Sreelakshmi, K.; Madhu, N.T.; Anjana, M.; Suneesh, P.V.; Ravi Kumar, D.V. Effect of alkali metal cation doping in graphitic carbon nitride towards photocatalytic generation of hydrogen peroxide under direct sunlight. *Catal. Commun.* **2024**, *187*, 106909. [[CrossRef](#)]
24. Hirakawa, H.; Hashimoto, M.; Shiraishi, Y.; Hirai, T. Photocatalytic conversion of nitrogen to ammonia with water on surface oxygen vacancies of titanium dioxide. *J. Am. Chem. Soc.* **2017**, *139*, 10929–10936. [[CrossRef](#)]
25. Xiao, C.L.; Hu, H.; Zhang, X.Y.; MacFarlane, D.R. Nanostructured gold/bismutite hybrid heterocatalysts for plasmon-enhanced photosynthesis of ammonia. *ACS Sustain. Chem. Eng.* **2017**, *5*, 10858–10863. [[CrossRef](#)]
26. Shiraishi, Y.; Shito, S.; Kofuji, Y.; Hashimoto, M.; Chishiro, K.; Hirakawa, H.; Tanaka, S.; Ichikawa, S.; Hirai, T. Nitrogen fixation with water on carbon-nitride-based metal-free photocatalysts with 0.1% solar-to-ammonia energy conversion efficiency. *ACS Appl. Energy Mater.* **2018**, *1*, 4169–4177. [[CrossRef](#)]
27. Zhang, N.; Jalil, A.; Wu, D.; Chen, S.; Liu, Y.; Gao, C.; Ye, W.; Qi, Z.; Ju, H.; Wang, C.; et al. Refining defect states in W₁₈O₄₉ by Mo doping: A strategy for tuning N₂ activation towards solar-driven nitrogen fixation. *J. Am. Chem. Soc.* **2018**, *140*, 9434–9443. [[CrossRef](#)]
28. Li, X.H.; Chen, W.L.; Tan, H.Q.; Li, F.R.; Li, J.P.; Li, Y.G.; Wang, E.B. Reduced state of the graphene oxide@polyoxometalate nanocatalyst achieving high-efficiency nitrogen fixation under light driving conditions. *ACS Appl. Mater. Interfaces* **2019**, *11*, 37927–37938. [[CrossRef](#)] [[PubMed](#)]
29. Ren, P.; Zhang, T.; Jain, N.; Ching, H.V.; Jaworski, A.; Barcaro, G.; Monti, S.; Silvestre-Albero, J.; Celorrio, V.; Chouhan, L.; et al. An atomically dispersed Mn-photocatalyst for generating hydrogen peroxide from seawater via the water oxidation reaction (WOR). *J. Am. Chem. Soc.* **2023**, *145*, 16584–16596. [[CrossRef](#)]
30. Yan, H.; Peng, Y.; Huang, Y.; Shen, M.; Wei, X.; Zou, W.; Tong, Q.; Zhou, N.; Xu, J.; Zhang, Y.; et al. Enhancing photosynthesis efficiency of hydrogen peroxide by modulating side chains to facilitate water oxidation at low-energy barrier sites. *Adv. Mater.* **2024**, *36*, 2311535. [[CrossRef](#)]
31. Misra, P.; Sharma, T.K.; Kukreja, L.M. Temperature dependent photoluminescence processes in ZnO thin films grown on sapphire by pulsed laser deposition. *Curr. Appl. Phys.* **2009**, *9*, 179. [[CrossRef](#)]
32. Xing, X.J.; Zhu, P.; Pang, E.; Zhao, S.J.; Tang, Y.; Hu, Z.Y.; Ouyang, Q.C.; Lan, M.H. D-A-D-structured boron-dipyrromethene with aggregation-induced enhanced phototherapeutic efficiency for near-infrared fluorescent and photoacoustic imaging-guided synergistic photodynamic and photothermal cancer therapy. *Chin. Chem. Lett.* **2023**, 109452. [[CrossRef](#)]
33. Kofuji, Y.; Isobe, Y.; Shiraishi, Y.; Sakamoto, H.; Tanaka, S.; Ichikawa, S.; Hirai, T. Carbon nitride–aromatic diimide–graphene nanohybrids: Metal-free photocatalysts for solar-to-hydrogen peroxide energy conversion with 0.2% efficiency. *J. Am. Chem. Soc.* **2016**, *138*, 10019–10025. [[CrossRef](#)]
34. Kou, M.; Wang, Y.; Xu, Y.; Ye, L.; Huang, Y.; Jia, B.; Li, H.; Ren, J.; Deng, Y.; Chen, J.; et al. Molecularly engineered covalent organic frameworks for hydrogen peroxide photosynthesis. *Angew. Chem. Int. Ed.* **2022**, *61*, e202200413. [[CrossRef](#)]
35. Sun, J.; Jeet, C.; Deng, M.; Laemont, A.; Feng, X.; Liu, Y.Y.; Van Der Voort, P. Metal–organic frameworks and covalent organic frameworks as photocatalysts for H₂O₂ production from oxygen and water. *J. Mater. Chem. A* **2023**, *11*, 21516–21540. [[CrossRef](#)]
36. Shu, C.; Yang, X.J.; Liu, L.J.; Hu, X.L.; Sun, R.X.; Yang, X.; Cooper, A.I.; Tan, B.; Wang, X.Y. Mixed-linker strategy for the construction of sulfone-containing D–A–A covalent organic frameworks for efficient photocatalytic hydrogen peroxide production. *Angew. Chem. Int. Ed.* **2024**, *136*, e202403926. [[CrossRef](#)]
37. Wu, C.B.; Teng, Z.Y.; Yang, C.; Chen, F.S.; Yang, H.B.; Wang, L.; Xu, H.X.; Liu, B.; Zheng, G.F.; Han, Q. Polarization engineering of covalent triazine frameworks for highly efficient photosynthesis of hydrogen peroxide from molecular oxygen and water. *Adv. Mater.* **2022**, *34*, 2110266. [[CrossRef](#)] [[PubMed](#)]
38. Pan, G.D.; Hou, H.S.; Liu, Z.Y.; Yang, C.K.; Long, J.L.; Huang, G.C.; Bi, J.H.; Yu, Y.; Li, L.Y. The hydration-initiated pathway of water oxidation over photoexcited covalent organic frameworks. *ACS Catal.* **2022**, *12*, 14911–14917. [[CrossRef](#)]
39. Wang, H.Z.; Yang, C.; Chen, F.S.; Zheng, G.F.; Han, Q. A crystalline partially fluorinated triazine covalent organic framework for efficient photosynthesis of hydrogen peroxide. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202328. [[CrossRef](#)]
40. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305. [[CrossRef](#)]
41. Wu, W.D.; Wang, A.P.; Luo, J.; Liu, T.L. A highly stable, capacity dense carboxylate viologen anolyte towards long-duration energy storage. *Angew. Chem. Int. Ed.* **2023**, *62*, e202216662. [[CrossRef](#)]
42. Yang, C.; Wan, S.J.; Zhu, B.C.; Yu, J.G.; Cao, S.W. Calcination-regulated microstructures of donor-acceptor polymers towards enhanced and stable photocatalytic H₂O₂ production in pure water. *Angew. Chem. Int. Ed.* **2022**, *61*, e202208438. [[CrossRef](#)]
43. Hu, X.L.; Zhan, Z.; Zhang, J.Q.; Hussain, I.; Tan, B. Immobilized covalent triazine frameworks films as effective photocatalysts for hydrogen evolution reaction. *Nat. Commun.* **2021**, *12*, 6596. [[CrossRef](#)]
44. Lu, J.N.; Liu, J.J.; Dong, L.Z.; Lin, J.M.; Yu, F.; Liu, J.; Lan, Y.Q. Synergistic metal-nonmetal active sites in a metal-organic cage for efficient photocatalytic synthesis of hydrogen peroxide in pure water. *Angew. Chem. Int. Ed.* **2023**, *62*, e202308505. [[CrossRef](#)] [[PubMed](#)]

45. Zhang, Y.N.; Pan, C.S.; Bian, G.M.; Xu, J.; Dong, Y.M.; Zhang, Y.; Lou, Y.; Liu, W.X.; Zhu, Y.F. H₂O₂ generation from O₂ and H₂O on a near-infrared absorbing porphyrin supramolecular photocatalyst. *Nat. Energy* **2023**, *8*, 361–371. [\[CrossRef\]](#)
46. Frisch, M.J. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
47. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104. [\[CrossRef\]](#) [\[PubMed\]](#)
48. *GaussView*, version 6.1.1; Shawnee: Mission, KS, USA, 2019.
49. Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–6170. [\[CrossRef\]](#)
50. Zheng, J.; Xu, X.; Truhlar, D.G. Minimally augmented Karlsruhe basis sets. *Theor. Chem. Acc.* **2011**, *128*, 295–305. [\[CrossRef\]](#)
51. Papajak, E.; Zheng, J.; Xu, X.; Leverentz, H.R.; Truhlar, D.G. Perspectives on basis sets beautiful: Seasonal plantings of diffuse basis functions. *J. Chem. Theory Comput.* **2011**, *7*, 3027–3034. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Yanai, T.; Tew, D.P.; Handy, N.C. A new hybrid exchange–correlation functional using the coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57. [\[CrossRef\]](#)
53. Francl, M.M.; Pietro, W.J.; Hehre, W.J.; Binkley, J.S.; Gordon, M.S.; DeFrees, D.J.; Pople, J.A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **1982**, *77*, 3654–3665.
54. Ditchfield, R.; Hehre, W.J.; Pople, J.A. Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules. *J. Chem. Phys.* **1971**, *54*, 724–728. [\[CrossRef\]](#)
55. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592. [\[CrossRef\]](#) [\[PubMed\]](#)
56. Lu, T.; Chen, F.-W. Comparison of computational methods for atomic charges. *Acta Phys. Chim. Sin.* **2012**, *28*, 1–18.
57. Zhu, L.; Zhang, J.; Guo, Y.; Yang, C.; Yi, Y.; Wei, Z. Small exciton binding energies enabling direct charge photogeneration towards low-driving-force organic solar cells. *Angew. Chem. Int. Ed.* **2021**, *60*, 15348–15353. [\[CrossRef\]](#) [\[PubMed\]](#)
58. Lu, T.; Chen, F.-W. Quantitative analysis of molecular surface based on improved Marching Tetrahedra algorithm. *J. Mol. Graph.* **2012**, *38*, 314–323. [\[CrossRef\]](#) [\[PubMed\]](#)
59. Zhang, J.; Lu, T. Efficient evaluation of electrostatic potential with computerized optimized code. *Phys. Chem. Chem. Phys.* **2021**, *23*, 20323–20328. [\[CrossRef\]](#) [\[PubMed\]](#)
60. Liu, Z.; Lu, T.; Chen, Q. Intermolecular interaction characteristics of the all-carboatomic ring, cyclo[18]carbon: Focusing on molecular adsorption and stacking. *Carbon* **2021**, *171*, 514–523. [\[CrossRef\]](#)
61. Liu, L.J.; Gao, M.-Y.; Yang, H.F.; Wang, X.Y.; Li, X.B.; Cooper, A.I. Linear conjugated polymers for solar-driven hydrogen peroxide production: The importance of catalyst stability. *J. Am. Chem. Soc.* **2021**, *143*, 19287–19293. [\[CrossRef\]](#)
62. Cheng, J.Z.; Wan, S.J.; Cao, S.W. Promoting solar-driven hydrogen peroxide production over thiazole-based conjugated polymers via generating and converting singlet oxygen. *Angew. Chem. Int. Ed.* **2023**, *62*, e202310476. [\[CrossRef\]](#)
63. Xu, X.H.; Sa, R.J.; Huang, W.; Sui, Y.; Chen, W.T.; Zhou, G.Y.; Li, X.D.; Li, Y.T.; Zhong, H. Conjugated organic polymers with anthraquinone redox centers for efficient photocatalytic hydrogen peroxide production from water and oxygen under visible light irradiation without any additives. *ACS Catal.* **2022**, *12*, 12954–12963. [\[CrossRef\]](#)
64. Chen, D.; Chen, W.; Wu, Y.; Wang, L.; Wu, X.; Xu, H.; Chen, L. Covalent organic frameworks containing dual O₂ reduction centers for overall photosynthetic hydrogen peroxide production. *Angew. Chem. Int. Ed.* **2023**, *62*, e202217479. [\[CrossRef\]](#) [\[PubMed\]](#)
65. Zhao, W.; Yan, P.Y.; Li, B.Y.; Bahri, M.; Liu, L.J.; Zhou, X.; Clowes, R.; Browning, N.D.; Wu, Y.; Ward, J.W.; et al. Accelerated synthesis and discovery of covalent organic framework photocatalysts for hydrogen peroxide production. *J. Am. Chem. Soc.* **2022**, *144*, 9902–9909. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Qin, C.C.; Wu, X.D.; Tang, L.; Chen, X.H.; Li, M.; Mou, Y.; Su, B.; Wang, S.B.; Feng, C.Y.; Liu, J.W.; et al. Dual donor-acceptor covalent organic frameworks for hydrogen peroxide photosynthesis. *Nat. Commun.* **2023**, *14*, 5238. [\[CrossRef\]](#)
67. Das, P.; Chakraborty, G.; Roeser, J.; Vogl, S.; Rabeah, J.; Thomas, A. Integrating bifunctionality and chemical stability in covalent organic frameworks via one-pot multicomponent reactions for solar-driven H₂O₂ production. *J. Am. Chem. Soc.* **2023**, *145*, 2975–2984. [\[CrossRef\]](#)

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