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Simultaneous photocatalytic hydrogen peroxide production and pollutant degradation via bipyridine-based polyimide covalent organic framework

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degradation and H₂O₂ production.

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<i>Keywords:</i> Covalent organic framework Polyimide Photocatalyst Hydrogen peroxide Bipyridine	Covalent organic framework (COF) photocatalysts for hydrogen peroxide (H_2O_2) production are receiving sig- nificant attention because of the ever-increasing demand for H_2O_2 . Despite the redox-active property and notable photophysical characteristics of polyimide (PI), the potential of PI-based COFs (PICs) for photocatalytic H_2O_2 production remains unexplored. Herein, we present a dual redox-active bipyridine-containing PIC (PIC-BPY) as an efficient photocatalyst for H_2O_2 production. PIC-BPY demonstrated exceptional performance by achieving an H_2O_2 production rate of 2772 µmol g_{cal}^{-1} , which is three times higher than its biphenyl-based counterpart. We elucidated the reaction pathway through a series of scavenger tests and electron spin resonance analysis, thereby confirming the additional active role of BPY along with that of PIC framework. Furthermore, we harnessed

1. Introduction

Hydrogen peroxide (H₂O₂) is a valuable chemical that plays a vital role in various industrial processes such as paper bleaching, wastewater treatment, and wafer cleaning, among others [1]. In particular, H2O2 has garnered attention as a potential energy carrier for fuel cells due to its comparable energy density to compressed H₂ coupled with the added convenience of its storage and transportation [2,3]. As a result, the demand for H₂O₂ is estimated to increase up to 2.7 million tons by 2027 [4]. Although more than 95% of H₂O₂ is currently produced via an indirect method in which anthraquinone is used as an intermediate, the process requires precious metals and a series of reactors [5]. Meanwhile, the direct reaction between H2 and O2 shows promise for manufacturing H₂O₂, as additives are not required. However, this process necessitates the use of precious metal catalysts, resulting in high production costs and the requirement for elevated pressure [6]. Alternatively, the electrochemical oxygen reduction reaction process, which relies on electrochemical cells in which metal catalysts and electrolytes are employed, produces H₂O₂ efficiently while eliminating the risk of explosion [7]. While challenges persist in the separation of H_2O_2 from the electrolyte, electrochemical methods for H_2O_2 production that eliminate the necessity for H_2 gas along with advancements in addressing the aforementioned issues have been reported [8].

hydroxyl radicals generated during photocatalysis to explore the potential of PIC-BPY for concurrent pollutant

The photocatalytic synthesis of H₂O₂ utilizes natural energy sources such as sunlight, thereby eliminating the need for artificial energy input and making it environmentally friendly. Since graphitic carbon nitride (g-C₃N₄) was first reported as a polymeric photocatalyst for H₂O₂ generation in 2014 [9], various photocatalysts have been investigated as alternatives to noble metals [3,10,11]. Among them, covalent organic frameworks (COFs) have been suggested as photocatalysts on the basis of utilizing their porosity, conjugated structure, high stability, crystallinity, and versatility [12-14]. For example, s-heptazine- and triazine-containing imine COFs [12], acetylene-containing triazine COFs [13], and anthraquinone-containing enamine COFs have been reported [14]. Furthermore, the introduction of functional groups such as fluorine or sulfone into the COF structure can enhance the adsorption of O₂, consequentially improving the catalytic performance [15,16]. Notably, Ma and coworkers reported that bipyridine-containing COFs exhibited excellent catalytic performance due to the dual active site of bipyridine moiety, which can facilitate both the water oxidation reaction (WOR)

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and the oxygen reduction reaction (ORR) [14]. However, since no catalytically active linkage other than using triazine has been reported, it is highly desirable to explore other redox-active linkages to further tailor COF photocatalysts and ultimately enhance the production of $\rm H_2O_2$.

As one of the most widely used high-performance polymers, polyimide (PI) is generally synthesized via an imidization reaction between anhydride and amine precursors. The presence of both electron-deficient and electron-rich moieties in PI enables the formation of charge-transfer complexes that promote efficient charge separation, thereby making PI suitable for photocatalytic applications. Furthermore, its band structure can be readily controlled by adjusting the conjugation length [17]. Based on these unique properties, PI-functionalized g-C₃N₄ derivatives have been investigated as photocatalysts for H₂O₂ production [18,19]. While the band structure of g-C₃N₄ can be modulated by using PI, there is no discernible influence of this on the photocatalytic reaction pathway. Consequently, despite the versatile redox-active property of PI in generating radical anions under UV irradiation [20,21], an investigation of utilizing PI in COFs to provide photocatalytic active sites for H₂O₂ production has not yet been undertaken.

Herein, we demonstrate for the first time the successful photocatalytic production of H₂O₂ using a bipyridine-containing PI-based COF (PIC-BPY) that possesses dual redox-active centers provided by both PI and BPY. In contrast to its single redox-active biphenyl-based PIC (PIC-DP) counterpart, the PIC-BPY exhibited additional absorption in the visible light range and delivered a performance approximately three times superior, achieving 1762 μ mol g_{cat.} in H₂O₂ production (vs. 630) μ mol g_{cat.} of PIC-DP) under the same conditions. More notably, a greater enhancement in H₂O₂ production by PIC-BPY (2772 μ mol g⁻¹_{cat}) was observed in the presence of a proton source such as ethanol. Furthermore, a detailed mechanistic study of the photocatalysis was performed by using electron spin resonance (ESR) and scavenger testing. These results confirmed the generation of H2O2 via the two-electron ORR and the generation of hydroxyl radicals (•OH) via the WOR. Finally, by employing the arsenic oxidation reaction as a model pollutant degradation process utilizing •OH, we demonstrated the significant potential of the bifunctional PIC-BPY photocatalyst for simultaneous H₂O₂ production and pollutant degradation.

2. Experimental method

2.1. Materials

2,2'-Bipyridine-5,5'-diamine (BPY) was purchased from AngeneChemical (China). N-methyl-1-pyrrolidone (NMP), mesitylene, monobasic sodium phosphate, dibasic sodium phosphate heptahydrate, sulfuric acid, N,N-diethyl-1,4-phenylenediamine sulfate (DPD), horseradish peroxidase (Type VI-A), ethanol (EtOH), sodium (meta)arsenite (As(III)), sodium arsenate dibasic heptahydrate (As(V)), molybdate reagent solution, L-ascorbic acid, titanium(IV) sulfate solution, hydrogen peroxide (H₂O₂) (34.5 %), Nafion[™] perfluorinated resin solution (5 wt %), 2-propanol, sodium sulfate, p-benzoquinone, tert-butanol, silver nitrate, and terephthalic acid were purchased from Sigma-Aldrich (USA). Isoquinoline was purchased from Tokyo Chemical Industries (Japan). Dimethyl sulfoxide (DMSO) was purchased from Alfa Aesar (USA). HPLC-grade tetrahydrofuran (THF), acetone, and methanol (MeOH) solvents were purchased from Duksan. All chemicals were used without further purification unless specified. 4,4'-diaminobiphenyl (DP) and triphenylene-2,3,6,7,10,11-hexacarboxylic acid (TPHCA) were synthesized following the methods in our previous study [22].

2.2. Characterizations

Scanning electron microscopy (SEM) was performed using an IT-500HR instrument (JEOL) at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was performed using a JEM-F200

(JEOL). Fourier-transform infrared (FT-IR) spectroscopy was conducted by using an FT-IR spectrophotometer (Cary 630, Agilent) equipped with an ATR module. Powder X-ray diffraction (PXRD) analysis was carried out using a SmartLab instrument (Rigaku) with Cu- K_{α} radiation. N2 isotherms were obtained using an Autosorb IQ instrument (Quantachrome). Solid-state ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE II+ 400 MHz NMR system at the Korean Basic Science Institute (KBSI) Seoul Western Center. Electron spin resonance (ESR) spectra were obtained using a Bruker EMX Plus 6/ 1 spectrometer at KBSI in Seoul Western Center. A UV/vis spectrophotometer (UV-2600, Shimadzu) was used to obtain absorbance profiles. Photoluminescence (PL) emission (excitation at 490 nm) and timecorrelated single photon counting (TCSPC) with an excitation wavelength of 375 nm from a laser were measured (λ_{em} 431 nm) with a spectrofluorometer (FS5, Edinburgh). Electrochemical analysis to determine Mott-Schottky plots was performed using a standard threeelectrode cell system connected to a computer-controlled potentiostat (PGSTAT302N, Autolab), where 0.1 M Na₂SO₄ solution (pH 6.6), catalyst-coated glassy carbon electrode (GCE), platinum wire, and Ag/ AgCl (KCl sat.) electrode were employed as the electrolyte and working, counter, and reference electrodes, respectively. Catalyst inks were prepared by dispersing a catalyst (2 g L^{-1}) in 2-propanol (50 vol%, 3 mL) with NafionTM perfluorinated resin solution (60 µL), followed by sonication for at least 15 min. 30 µL of the as-prepared catalyst ink was dropcasted on a GCE and dried at 60 °C overnight. Data for the Mott-Schottky plots were obtained at room temperature at a frequency of 1,2, and 3 kHz.

2.3. Synthesis of polyimide-based covalent organic framework (PIC-BPY)

BPY (28.9 mg, 0.15 mmol) and TPHCA (51 mg, 0.10 mmol) were added into a 25 mL screw cap tube and dissolved in a mixture of NMP (4 mL), mesitylene (4 mL), and isoquinoline (0.4 mL). The tube was locked with screw cap, and the aperture between them was sealed with a Teflon tape. The reaction mixture was heated at 200 °C for 48 h to obtain a brown precipitate, which was isolated by centrifugation and washed with MeOH, DI water, THF, DMSO, and acetone. The obtain product was dried at 80 °C to obtain a brown powder of PIC-BPY. Yield: 69.5 mg (87.0 %, isolated yield).

2.4. Synthesis of PIC-DP

Following our previous method [22], DP (28.5 mg, 0.15 mmol) was placed in a 25 mL screw cap tube and dissolved in 5.0 mL of deionized water at 100 °C. Subsequently, TPHCA (51 mg, 0.10 mmol) in 5.0 mL of deionized water was added to the solution. The tube was then locked with the screw cap and the aperture between them was sealed with Teflon tape. The reaction mixture was heated at 250 °C for 48 h to obtain a gray precipitate, which was isolated via centrifugation and sequentially washed with MeOH, DI water, THF, DMSO, and acetone. The product (PIC-DP) was dried at 80 °C to obtain a gray powder with a yield of 24.5 mg (30.8 %, isolated yield).

2.5. Photocatalytic H₂O₂ production

Photocatalytic H_2O_2 production experiments were carried out by irradiating simulated solar light (AM 1.5 G, 100 mW cm⁻²) from a 150 W Xe Arc lamp (LS 150, Abet Technologies) onto an aqueous suspension where the incident light intensity was determined using a Newport calibrated Si solar cell. The aqueous suspension was prepared by dispersing one of the photocatalysts in the presence or absence of 3 mL of 10 vol% ethanol as an electron donor in 30 mL of DI water. Subsequently, it was continuously stirred and purged with oxygen or argon for 15 min both before and during irradiation. A sample aliquot was collected from the aqueous suspension using a syringe, and the suspended solids were removed by filtering through a hydrophilic

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polytetrafluoroethylene (PTFE) filter $(0.2 \,\mu\text{m})$ ·H₂O₂ was quantitatively analyzed via the DPD colorimetric method ($\varepsilon_{551 \,\text{nm}} = 21,000 \,\text{M}^{-1} \,\text{cm}^{-1}$) [23] or titanium sulfate method ($\varepsilon_{240 \,\text{nm}} = 19.6 \,\text{M}^{-1} \,\text{cm}^{-1}$) [24]. Triplicate tests were conducted independently for each of the photocatalytic experiment. To evaluate the effect of radicals on photocatalytic H₂O₂ production, *p*-benzoquinone (100 μ M), *tert*-butanol (5 vol%), and silver nitrate (100 mM) were used as scavengers for superoxide radicals [15, 25], hydroxyl radicals [26], and electrons [27], respectively. Detection of hydroxyl radicals produced during photocatalysis was carried out by observing the PL intensity following excitation at 310 nm emitted from 2-hydroxyl radicals with terephthalic acid [28].

The apparent quantum yield (AQY) at 298 K was determined using a monochromator (Oriel CornerstoneTM 130 1/8 m Monochromator, Newport) and the following equation [29]:

$$AQY(\%) = \frac{[Amount of H_2O_2 generated(mol)] \times 2}{[Number of photons entering the reactor(mol)]} \times 100 \%.$$

The solar-to-chemical conversion (SCC) efficiency was calculated using the following equation [29]:

$$\begin{split} n &= 4*\frac{I_d}{I_d+\frac{I_r}{N}}\\ \mathrm{H}_2\mathrm{O}_2(\%) &= \frac{200\times \frac{I_r}{N}}{I_d+\frac{I_r}{N}} \end{split}$$

where I_d is the disk current, I_r is the ring current, and N is the collection efficiency (24.9 %).

2.7. Photocatalytic arsenic oxidation

 $[As(III)]_{time} = [As(III)]_{initial} - [As(V)]_{time}$

As(III) and As(V) are the main inorganic forms of arsenic in the aquatic environment. Since As(III) is predominantly oxidized to As(V) by hydroxyl radicals among the various reactive species, the remaining As(III) can be evaluated by subtracting the amount of As(V) from the initially injected amount of As(III). The concentration of As(V) was determined via the molybdenum blue method (ϵ_{870} nm = 26,000 M⁻¹

$$SCC(\%) = \frac{\left[\Delta G \text{ for } H_2O_2 \text{ generation}(J \text{ mol}^{-1}) \right] \times [\text{Amount of } H_2O_2 \text{ formed}(\text{mol})]}{[\text{total input energy}(W)] \times [\text{reaction time}(s)]} \times 100 \%,$$

where ΔG is the Gibb's free energy (117 kJ mol⁻¹ for H₂O₂ generation), the total input energy is 78.5 mW, and AM 1.5 G irradiance was applied at 0.1 W cm⁻² over an irradiated area of 0.78 cm².

2.6. Electrochemical analysis

Electrochemical experiments were conducted using a standard threeelectrode cell system, which was connected to a computer-controlled potentiostat (PGSTAT302N, Autolab). The reactor contained a GCE, a platinum wire, and a Ag/AgCl/KCl (sat.) electrode as a working, counter, and reference electrode, respectively, with an aqueous solution of 0.1 M Na₂SO₄ (pH 6.6) as an electrolyte. Catalyst inks were prepared by dispersing a 6 mg of catalyst in 1.5 mL of DI water, 1.5 mL of 2-propanol, and 60 µL of 5 wt% Nafion solution (Sigma-Aldrich) followed by sonication process for 15 min. The as-prepared catalyst ink was dropcasted on a glassy carbon electrode or disk electrode of rotating ring--disk electrode (RRDE, glassy carbon disk and Pt ring, AG) as 7.64 mg $\rm cm^{-2}$, and dried at room temperature overnight. Cyclic voltammetry (CV) was performed at 10 mV s^{-1} with a potential range between -1.0 V and 0.0 V vs. Ag/AgCl, with a GCE having a geometric diameter of 1 mm. To evaluate electrochemical impedance spectroscopy (EIS), a potential of -0.40 V vs. Ag/AgCl was applied across a frequency range from 10 mHz to 1000 kHz in either an O2- or Ar-saturated environment. The resulting Nyquist plots were then fitted and simulated using the equivalent circuit model represented as (R[Q[RW]]). The transient photocurrent response for H2O2 was recorded in an O2 -saturated electrolyte while alternating 1-Sun irradiation (AM 1.5 G, 100 mW cm⁻²) over a period of 30 seconds, with a potential applied at a bias of 1.2 V vs. RHE to the Pt-ring electrode, which was rotating at a speed of 1600 rpm. The RRDE analyses were carried out by sweeping the disk potential from -1.2 V to 0.0 V vs. Ag/AgCl at 10 mV s⁻¹ with rotation rates 1600 rpm, while holding the Pt ring at 0.6 V vs. Ag/AgCl to oxidize the in situ produced H2O2 formed on the disk electrode, in an O₂-saturated electrolyte. The number of transferred electrons (n) and H₂O₂ yields and were calculated using the following equations:

cm⁻¹).[30] Briefly, a sample aliquot was collected from the reaction suspension and filtered using a syringe filter (0.22 µm) to which the molybdate reagent with L-ascorbic acid was added, and the solution was then kept in the dark for 2 h at room temperature. The absorbance was monitored at 870 nm using a UV/vis spectrophotometer.

2.8. Computational calculation of the crystal structure

Density functional theory-based tight binding (DFTB) calculations were performed using the DFTB+ program. [31] The crystal structures of the PICs were investigated using the 3OB Slater–Koster atomic parameters suitable for organic materials.[32] Spin polarization and universal-forcefield-based Lennard–Jones dispersion correction were used in all calculations. The wavefunction was integrated using Monkhorst-Pack k-point grids:[33] $1 \times 1 \times 8$ k-point grid for unit cells consisting of one PI-COF layer and a $1 \times 1 \times 4$ k-point grid for unit cells consisting of two or more covalent organic framework (COF) layers. The convergence criterion for the self-consistent charge calculation was set to 1×10^{-8} . The convergence criteria for geometry optimization were set to 0.01 kcal mol⁻¹ for the maximum displacement were set at 0.05 kcal mol⁻¹ Å⁻¹, 0.02 GPa, and 5×10^4 , respectively. Periodic boundary conditions were applied in three dimensions.

A potential energy surface was constructed using single-point energy calculations for structures with different ab-plane displacements between the top and bottom layers. To account for the AA and AB packing modes, two- and three-layer bulk systems were modeled. In the three-layer bulk model, the bottom two layers were arranged in AB packing mode. In each model, various packing modes were sampled by shifting the top layer within the ab-plane, but the other layers were fixed. A 17 \times 17 grid of ab-plane displacements was used to sample 289 different unit cells. The potential energy surface was generated by interpolating the DFTB total energies over a 1000 \times 1000 fine grid using the bicubic spline method. The energy at the global minimum of the potential energy surface was set to zero.

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Fig. 1. A schematic illustration of the synthesis of polyimide-based COFs (PICs) by reacting triphenylene-2,3,6,7,10,11-hexacarboxylic acid (TPHCA) with 2,2'bipyridine-5,5'-diamine (BPY) and 4,4'-diaminobiphenyl (DP) for PIC-BPY and PIC-DP, respectively. Inset images represent the corresponding powders obtained.

3. Results and discussion

3.1. Synthesis and characterizations of PICs

PIC-BPY was synthesized via the solvothermal imidization reaction of triphenylene-2,3,6,7,10,11-hexacarboxylic acid (TPHCA) with BPY (Fig. 1). FT-IR spectra display characteristic peaks at 1593, 1561, and 734 cm⁻¹ that confirm the presence of the BPY moiety in PIC-BPY. Furthermore, the presence of imide bond peaks at 1717, 1778, and 1344 cm⁻¹ in the absence of the TPHCA precursor and amide intermediate peaks at 1693 and 1660 cm⁻¹ provide clear evidence for the fully imidized structure of PIC-BPY (Fig. 2a). In parallel, the solid-state crosspolarization magic-angle-spinning (CP-MAS) ¹³C NMR spectrum demonstrated the presence of the carbonyl carbon in the imide ring at 164.9 ppm, pyridinic carbons at 152.3 and 144.5 ppm, and aromatic carbons in overlapping peaks from 110 to 140 ppm (Fig. 2b). Taken together, these results suggest the successful formation of PIC-BPY free of amide and amic acid intermediates.

The crystal structure of PIC-BPY was determined by using powder Xray diffraction (PXRD) analysis (Fig. 2c). As the COF structure comprises not only 2D individual layers and linkages but also the 3D-stacking structure of the constituent 2D layers, the detailed structure of PIC-BPY was calculated using the density functional-based tight binding (DFTB) calculation. From the results, two types of possible 3D-stacking structures in 2D PIC-BPY were generated, including eclipsed AA stacking and staggered AB stacking. Based on the potential energy surfaces that are generated by scanning the potential energy with a shifting monolayer, AA-eclipsed stacking is the most thermodynamically stable structure in PIC-BPY (Fig. 2d), which is in good agreement with the peaks observed at 2.62°, 4.58°, and 25.26° in the PXRD pattern in Fig. 2c. As a control, we prepared PIC-DP using a biphenyl group in place of the BPY moiety to highlight the role of the latter, as detailed in our previous report (Fig. 1) [22]. The chemical structure and corresponding crystal-packing structure of PIC-DP were fully characterized by using FT-IR, solid-state CP-MAS ¹³C NMR, and PXRD (Fig. S1 in the Supplementary material).

To evaluate the morphology of PICs, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed (Fig. S2). Both PIC-BPY and PIC-DP exhibited distinct fibrous morphologies. Notably, PIC-BPY displayed fibers with a finer diameter of 40 nm, compared to PIC-DP, which had a larger diameter of 400 nm. Furthermore, thermal stability was determined by using thermogravimetric analysis (TGA). Significant weight losses were observed at 606 °C for PIC-BPY and 634 °C for PIC-DP, respectively, indicating the superior thermal stability of the PICs prepared in this study (Fig. S3).

In catalytic reactions, a porous structure enhances the diffusion kinetics, thereby improving the overall catalytic performance. The porosity of the prepared PICs was examined by generating N₂ sorption isotherms at 77 K; the resulting adsorption/desorption curves exhibit type-II isotherms for both PIC-BPY and PIC-DP, which indicates the presence of a macroporous structure without micropores (Fig. S4). The Brunauer–Emmett–Teller (BET) surface areas of PIC-BPY and PIC-DP were determined as 123 and 125 m² g⁻¹, respectively. It is of note that the effect of the functional moiety on catalytic performance could



Fig. 2. Characterization of PIC-BPY. (a)FT-IR and (b)solid-state CP-MAS ¹³C NMR spectra of PIC-BPY with the corresponding chemical structure of the repeating unit. (c) Synchrotron powder X-ray diffraction (PXRD) patterns of PIC-BPY (black) and calculated patterns of the AA-eclipsed (red), and AB-staggered (blue) structures. (d) A potential energy surface map of PIC-BPY with calculated stacking patterns labelled, along withtop and side views of the calculated AA-stacking structures in the PIC-BPY layers.

be compared more effectively by assuming that the diffusion kinetics of the two samples were similar.

3.2. Photocatalytic performance

To evaluate the optical properties of the PICs, UV/vis diffuse reflectance spectroscopy (DRS) was examined (Fig. 3a). Although both PIC-BPY and PIC-DP exhibit similar absorption characteristics in the UV range, PIC-BPY has a broader absorption spectrum in the visible range, thus indicating a wider window for effective photo-absorption compared to PIC-DP. In addition, the Mott-Schottky plots of PIC-BPY and PIC-DP possess positive slopes in the linear range, which is a common characteristic of *n*-type semiconductors (Figs. S5a and S5b) [34]. The flat band potentials determined from the Mott-Schottky plots for PIC-BPY and PIC-DP are associated with the conduction band (CB) and afford CB levels of 0.29 V and -0.41 V, respectively. Combined with the Tauc plots derived from the corresponding diffuse reflectance spectra, the energy band gap (E_g) values of PIC-BPY and PIC-DP were determined as 2.58 eV and 3.04 eV, respectively (Figs. S5c and S5d). Interestingly, both PICs displayed suitable CB levels for the reduction of oxygen to H₂O₂ (i.e., 0.68 V vs. RHE) (Fig. 3b). However, the valence band (VB) of PIC-BPY (2.87 V) is positioned appropriately for generating •OH through water oxidation (2.73 V vs. RHE), whereas the VB of PIC-DP (2.63 V) is more negative than the potential required [4]. Additionally, PIC-BPY displayed a significantly reduced electron-hole recombination capability, as evidenced by the markedly decreased photoluminescence around 600 nm when excited at 490 nm (Fig. S6a). Time-correlated single-photon counting (TCSPC) measurements ($\lambda_{ex} =$

375 nm and $\lambda_{em} = 431$ nm) were employed to estimate the excited-state lifetime of PICs (Fig. S6b and Table S1). Analysis revealed that when both samples were optimally characterized by using three distinct exponential decay functions, PIC-BPY exhibited a longer average excited-state lifetime (3.45 ns) than PIC-DP (2.35 ns). Notably, while all three components showed slightly faster rates for PIC-BPY, the relative contribution of the fast component (τ_1) , which is attributed to intrinsic emissions associated with the sp^2 domain [35–37], was significantly smaller for PIC-BPY (6.1 %) than PIC-DP (41.2 %). In contrast, the intermediate (τ_2) and slow (τ_3) components, which are attributed to various functional groups [38], were more pronounced in PIC-BPY (93.9 % for $\tau_2 + \tau_3$) than in PIC-DP (58.8 % for $\tau_2 + \tau_3$). In particular, the τ_3 component, which is assigned to more oxidized states [35,39], exhibited a higher relative contribution in PIC-BPY (84.9%) compared to PIC-DP (54.5 %). This difference can be attributed to the nitrogen in the BPY moiety, which is known for its easy of protonation and oxygen adsorption [14]. Moreover, PIC-BPY demonstrated significantly improved electrochemical kinetics over PIC-DP, characterized by an increased oxygen reduction current ($-18.4 \,\mu$ A vs. $-13.6 \,\mu$ A at $-0.4 \,$ V vs. Ag/AgCl) and a decreased charge transfer resistance (R_{ct}) (9.27 k Ω vs. 17.7 k Ω), as measured by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) (Fig. S7 and Table S2). This indicates that PIC-BPY facilitates more efficient charge transfer to oxygen. Collectively, these findings suggest that PIC-BPY offers a unique advantage in charge separation and electron transfer over PIC-DP for photocatalytic H₂O₂ production through the ORR.

To determine the optimal conditions for photocatalytic H_2O_2 production, we conducted photocatalytic ORR testing under solar-



Fig. 3. Photocatalytic H_2O_2 production. (a) UV/vis diffuse reflectance spectra and (b) energy band diagrams of PIC-BPY and PIC-DP. (c) Time-dependent profiles of photocatalytic H_2O_2 production over PIC-BPY and PIC-DP under various operating conditions in the presence or absence of ethanol (EtOH) as an electron donor under irradiation: [catalyst] = 0.15 g L⁻¹, 100 mW cm⁻² (AM 1.5 G), [EtOH]₀ = 0 or 10 vol%, and O₂-saturated. (d) Photocatalytic recycling testing of PIC-BPY and PIC-DP was normalized to that of PIC-DP as 1.0.

simulated light illumination using various concentrations of PIC-BPY (Fig. S8). An increase in the concentration of PIC-BPY from 0.05 to 0.15 mg mL⁻¹ resulted in a direct increase in the H₂O₂ production rate from 1.26 to 1.39 mmol $g_{cat.}^{-1}$ h⁻¹. This clearly demonstrates that the pathway for H₂O₂ production is influenced by the amount of PIC-BPY used in the process. However, when the dosage was further increased from 0.15 to 0.30 mg mL⁻¹, the H₂O₂ production rate decreased sharply from 1.39 to 0.90 mmol $g_{cat.}^{-1}$ h⁻¹, which is attributed to either catalyst agglomeration or light scattering, as similarly suggested in a previous study [40]. Based on the results, subsequent examinations for photocatalytic H₂O₂ production were performed using the optimal catalyst concentration of 0.15 mg mL⁻¹.

On the basis of the optimized catalyst concentration, the photocatalytic production of H₂O₂ was assessed under various reaction conditions (Fig. 3c). For example, PIC-BPY produced 2772 µmol $g_{cat.}^{-1}$ of H₂O₂ in the presence of ethanol as an electron donor under O₂-saturated conditions and irradiation for 2 h. Notably, H₂O₂ production was found to be negligible in the absence of light (5.8 µmol $g_{cat.}^{-1}$) or oxygen (119 µmol $g_{cat.}^{-1}$), indicating that both light and oxygen are essential for the photocatalytic H₂O₂ production on PIC-BPY. Moreover, PIC-BPY exhibited approximately 3.6 times higher H₂O₂ productivity than PIC-DP (2772 vs. 769 µmol $g_{cat.}^{-1}$) in the presence of ethanol and about 2.8 times higher productivity (1762 vs. 630 µmol $g_{cat.}^{-1}$) even in the absence of ethanol. In addition, using a rotating ring-disk electrode (RRDE) set in an oxygen-enriched atmosphere, transient photocurrent signals indicative of H₂O₂ production were recorded under alternating light exposure at a bias of 1.2 V vs. RHE (Fig. S9). Within this configuration, H₂O₂ photocatalytically formed on the surfaces of disk electrodes (no bias) coated with either PIC-BPY or PIC-DP could migrate to the Pt-ring electrode, rotating at 1600 rpm, where it was subsequently oxidized by the applied potential [41]. The activation of the Pt-ring electrode allowed for the detection of photocurrent responses directly related to the amounts of H₂O₂ generated instantaneously. Interestingly, the photocurrent density for PIC-DP was observed to be lower than that for PIC-BPY, consistent with the reduced photocatalytic H₂O₂ production rate depicted in Fig. 3c. This difference further validated by electrochemical evaluation highlights the excellent photocatalytic efficiency of PIC-BPY in generating H₂O₂. The superior photocatalytic performance of PIC-BPY for H₂O₂ production in comparison to PIC-DP is attributable to the presence of the nitrogen atom in the BPY moiety enhancing the charge-transfer processes and increasing photo-absorption, thereby improving the photocatalytic efficiency of PIC-BPY.

To assess the stability of PICs, FT-IR, XRD, and SEM were conducted after 2 h of photocatalysis without ethanol (Figs. S10 and S11). In the FT-IR and XRD spectra, both PICs maintained their chemical and crystal structures, still exhibiting characteristic peaks (Figs. S10a,b and S11a,b). However, a noticeable difference was observed in the morphology. While fibrous morphology was retained in PIC-BPY, significant aggregation was observed in PIC-DP (Figs. S10c,d and S11c,d). As a result, it was evident that the PIC-BPY was more stable compared to PIC-DP.

To objectively compare the samples under various reaction conditions, the apparent quantum yield (AQY) and the solar-to-chemical conversion (SCC) efficiency for H_2O_2 production are commonly used as unbiased parameters [42]. The AQY based on the photoabsorbance spectrum of PIC-BPY was determined as 10.2 % at 400 nm, which is superior to other metal-free photocatalysts (Fig. S12 and Table S3). In addition, time-dependent H_2O_2 production in the absence of ethanol was analyzed alongside the corresponding SCC efficiency, the latter accounting for the free energy of H_2O_2 formation relative to the total incident energy (Fig. S13) [42]. The SCC efficiency for PIC-BPY gradually decreased over time, eventually reaching 0.22 % (0.08 % for PIC-DP). This value is comparable to those of other organic materials and is attributed to the presence of the BPY moiety contributing to charge transfer (Table S3) [14]. In parallel, the decomposition of H_2O_2 was found to be negligible over 2 h (Fig. S14). Considering that the VB levels of both PICs are favorably positioned for H_2O oxidation by holes, it is plausible that those in these PICs could potentially engage in alternative pathways instead of degrading H_2O_2 . This observation strongly supports the suitability of these PIC-based materials as efficient photocatalysts for H_2O_2 production.

Finally, the results from photocatalytic recyclability tests provide compelling evidence that PIC-BPY demonstrates remarkable and consistent H_2O_2 production performance over five consecutive cycles, each lasting 2 h (Fig. 3d). In contrast, PIC-DP exhibited a gradual increase in performance with each cycle, achieving up to 1.8 times the productivity relative to the first cycle. This improvement is possibly due to a negative shift in the flat band potential of PIC-DP to -0.61 V after photocatalysis (Fig. S15), originated from aggregation of PIC-DP after post-photocatalysis [43,44], thereby enhancing the driving force for the



Fig. 4. (a) The effect of various radical scavengers on photocatalytic H_2O_2 production by PIC-BPY and PIC-DP over 1 h: [catalyst] = 0.15 g L⁻¹, 100 mW cm⁻² (AM 1.5 G), and O_2 -saturated. The following scavengers were used; [EtOH]₀ = 10 vol% as a hole scavenger, [AgNO₃]₀ = 100 mM as an electron scavenger, [*p*-BQ]₀ = 100 µM as a superoxide radical scavenger, and [*t*-butanol]₀ = 5 vol% as a hydroxyl radical scavenger. (b) Electron spin resonance (ESR) spectra of (square) PIC-BPY and (triangle) PIC-DP showing the time-dependent DMPO-OH adduct intensity at 342.8 mT. (c) A schematic of the proposed photocatalytic H_2O_2 production mechanism for PIC-BPY. Note that only active sites are presented for simplicity while product-related aspects are highlighted.

reduction potential. Nonetheless, it is important to note that the initial productivity of PIC-DP was significantly lower (only 21.5 μM h^ $^{-1}$) compared to that observed with PIC-BPY (159.0 μM h $^{-1}$). Furthermore, it became apparent that the increase in productivity of PIC-DP reached a plateau at around the 4th cycle. These findings indicate that PIC-DP exhibits comparatively lower stability for H_2O_2 production over multiple cycles, thereby highlighting the unique advantage of PIC-BPY for sustainable H_2O_2 production.

3.3. Photocatalytic mechanism study

To further investigate the mechanism of photocatalytic H_2O_2 production, the generation of H_2O_2 was evaluated in the presence of various scavengers for radical species. These included silver nitrate (AgNO₃) as an electron scavenger [45], ethanol as a hole scavenger [46], *p*-benzoquinone (*p*-BQ) as a superoxide radical (O_2^{\bullet}) scavenger [15,25], and *t*-butanol as an •OH scavenger (Fig. 4a) [47]. The photocatalytic H_2O_2 generation by both PICs notably diminished to negligible levels with the addition of the electron scavenger whereas the presence of •OH scavenger had only a minimal impact on the H_2O_2 production rate. This indicates that the H_2O_2 production pathway is predominantly driven by reduction reactions involving electrons rather than oxidation reactions involving holes. Furthermore, the presence of a hole scavenger (ethanol) promotes the consumption of holes, thus enhancing photoexcited electron generation and proton transfer and leading to enhanced H_2O_2 production through the ORR, as mentioned earlier.

Notably, the addition of p-BQ as an $O_2^{\bullet-}$ scavenger led to a drastic reduction in the photocatalytic H₂O₂ production by both PICs. Specifically, there was an approximately 86 % decrease in H₂O₂ production for PIC-BPY (from 972 µmol $g_{cat.}^{-1}$ to 134 µmol $g_{cat.}^{-1}$) and an almost complete diminishment for PIC-DP (from 305 μ mol g_{cat}^{-1} to an unmeasurable concentration). These results clearly suggest that H₂O₂ production by both PIC-BPY and PIC-DP is primarily governed by the ORR predominantly involving $O_2^{\bullet-}$ through a stepwise 2-electron transfer process [16, 48]. In addition, the presence of nitrogen in the BPY moiety in PIC-BPY plays an important role in the ORR process via a 2-electron-one-step redox reaction without forming $O_2^{\bullet-}$ [14], as evidenced by the fact that PIC-BPY still managed to produce a notable amount of H₂O₂. In other words, the core PIC unit with the PI moiety provides primary redox-active sites where the radical anions are generated under light irradiation and are eventually transferred into O2 molecules, leading to H₂O₂ production through the ORR [20,21]. Meanwhile, the BPY moiety serves as secondary redox-active sites that promote a one-step H₂O₂ production reaction [14]. Owing to the unique one-step H_2O_2 production reaction facilitated by the BPY moiety of PIC-BPY, its selectivity and electron transfer number for H₂O₂, as measured by a RRDE, improve to 69.7 % and 2.6, respectively, within the potential range of -0.8 to -0.4 V vs. Ag/AgCl (Fig. S16). In contrast, PIC-DP exhibits a selectivity of 55.1 % and an electron transfer number of 2.9.

Independently, ESR spectroscopy was employed for both PICs to conduct an in-depth study of the main reactive oxygen species involved in photocatalytic H₂O₂ production (Fig. S17). Here, 5,5-dimethyl-pyrroline N-oxide (DMPO) was used as a free-radical spin-trapping agent. When the PICs were irradiated, a characteristic ESR spectrum consisting of a quartet with a magnetic field peak separation of $\alpha_N = 1.46$ mT was observed; this is typical for the DMPO-OH adduct and indicates the generation of •OH during the photocatalytic process (Fig. S17) [49,50]. The absence of •OH peaks without light irradiation indicates that the generation of radical species is clearly associated with the photocatalytic activity of the PICs. Notably, the intensity of these peaks increased upon irradiation, further confirming the generation of •OH in the photocatalytic process involving the PICs (Fig. 4b and Fig. S17). However, the intensity observed with PIC-DP was lower than that with PIC-BPY, which strongly suggests that •OH is generated to a greater extent due to the high photoactivity of PIC-BPY. Furthermore, additional peaks distinct from DMPO-OH emerged in the case of PIC-DP (Fig. S17b).

Along with the DMPO-OH quartet signal, the ESR spectrum for PIC-DP also contains triplet signals ($\alpha_N = 1.50$ mT), closely resembling those of previously identified by-products reported in the literature (Figs. S17b and S17c) [47]. This implies that although PIC-DP can generate •OH under irradiation, its behavior differs from that of PIC-BPY, which efficiently consumes holes via water or ethanol oxidation reactions. Indeed, this difference can be attributed to the relatively slow utilization rate of holes in PIC-DP for •OH generation.

It is well-known that non-fluorescent terephthalic acid (TA) is converted to 2-hydroxyterephthalic acid (HTA) in the presence of •OH, which leads to fluorescence at 425 nm (Fig. S18) [51,52]. Interestingly, the fluorescence intensity at 425 nm increased upon irradiation of PIC-BPY under argon, demonstrating that PIC-BPY did not generate •OH from O₂ (Fig. S18a). Furthermore, considering the observed decrease in fluorescence intensity throughout the irradiation period when ethanol is introduced as a hole scavenger and the VB of PIC-BPY is located at an energy level that allows the effective water oxidation to •OH (2.73 V vs. RHE) [4], it is reasonable that •OH is originated from water oxidation (Fig. S18b and S18c). In accordance with the ESR data, the amount of HTA was considerably lower with PIC-DP than with PIC-BPY (Fig. S18d). This observation strongly suggests that •OH is generated in these COFs through the WOR facilitated by holes, and •OH generation exhibits a direct correlation with the photocatalytic H₂O₂ production process.

Taken together, we propose mechanistic reaction pathways for photocatalytic H_2O_2 production from PIC-BPY with dual redox-active centers and PIC-DP with a single redox-active center. In the case of PIC-BPY, water molecules are adsorbed by the BPY moiety and oxidized under light irradiation, resulting in protonated BPY and producing •OH. Subsequently, oxygen molecules are adsorbed by the protonated BPY and undergo reduction via photoexcited electrons, leading to the production of H_2O_2 . In addition, under light irradiation, radical anions are generated at the PI moiety and along with the oxygen molecules adhered to it, undergo reduction via photoexcited electrons, resulting in the production of H_2O_2 (Fig. 4c). In stark contrast, PIC-DP produces H_2O_2 exclusively by exploiting radical anions generated at the PI moiety (Fig. S19).

3.4. Pollutant degradation

Thus far, we established that the photocatalytic H₂O₂ production by PIC-BPY primarily occurs through the ORR, while generating •OH via water oxidation. This dual mechanism not only offers a unique opportunity to produce H2O2 but also to generate •OH for highly effective pollutant degradation [53,54]. In this context, we examined the capability of PIC-BPY for simultaneous photocatalytic H₂O₂ production and arsenic pollutant degradation. Since the allowable concentration of arsenic in drinking water has recently been revised to a lower threshold of 10 μ g L⁻¹ by regulatory agencies [55–57], there has been a growing need to develop efficient methods for arsenic removal from water sources. Arsenic is commonly present in groundwater in two oxidation states: As(III) and As(V). Since the former is known to be more toxic and mobile than the latter, the pre-oxidation of As(III) to As(V) before adsorption of the latter onto a solid surface is desirable for water treatment applications [58]. Especially, it is well-known that the major reactive species responsible for this transformation is •OH rather than other potential oxidizing species such as H_2O_2 , $O_2^{\bullet-}$, or holes (h_{vb}^+) (Table S4) [59-61], which makes arsenic an appropriate model pollutant for our study.

First, it was reported that some of the As(V) can be reduced back to As(III), similar to finding in a previous study where As(V) was shown to accept electrons from the inner layers of bimetallic particles under anoxic conditions [62]. To investigate whether As(V) can be reduced to other species by the excited electrons or adsorbed onto photocatalysts, we monitored the change in As(V) concentration under anaerobic photocatalytic conditions, as depicted in Fig. S20. The results indicated that



Fig. 5. (a) Time-dependent profiles of arsenic degradation (dashed lines) and photocatalytic H_2O_2 production (solid lines) by PIC-BPY and PIC-DP under the following conditions: [catalyst] = 0.5 g L⁻¹, [As(III)]_{initial} = 500 μ M, 100 mW cm⁻² (AM 1.5 G), [EtOH]₀ = 0 vol% and O₂-saturated. (b) A schematic of the proposed mechanism for simultaneous photocatalytic H_2O_2 production and arsenic pollutant degradation. (c) Photoluminescence intensity with 2-hydroxyterephthalic acid (HTA) excited at 310 nm for the PIC-BPY and PIC-DP over 90 min: [catalyst] = 0.15 g L⁻¹, [terephthalic acid]_{initial} = 17 mg L⁻¹ (saturated at 25 °C), and 100 mW cm⁻² (AM 1.5 G). (d) As(III) oxidation rate for the PIC-BPY and PIC-DP over 90 min under the following conditions: [catalyst] = 0.5 g L⁻¹, [As(III)]_{initial} = 500 μ M, 100 mW cm⁻² (AM 1.5 G), and O₂-saturated. The experiments were repeated three times for obtaining error bar.

only 8 % of As(V) decreased over 12 h, suggesting that the likelihood of a reverse reaction from oxidized As(III) to As(V), or the adsorption of As (V), is insubstantial. This result indirectly demonstrates that As(V) does not reduce back to As(III) under oxygen conditions. Over a period of 9 h, the concentration of As(III) gradually decreased from an initial concentration of 500 µM to 322.2 µM. Simultaneously, H₂O₂ was produced, reaching 562.1 µM via the photocatalytic activity of PIC-BPY (Fig. 5a). This successful outcome confirms the feasibility of simultaneous arsenic oxidation and H₂O₂ production using PIC-BPY as the photocatalyst. Furthermore, Figs. 5c and 5d display a consistent ratio between the fluorescence intensity from HTA, indicating •OH production, and the As (III) oxidation rate in both PIC-BPY and PIC-DP. This consistency supports the notion that As(III) enhances this process by showing a relatively higher reaction rate with •OH compared to other reactive oxygen species, as indicated by previous research [61,63]. Thus, considering that •OH is predominantly generated through the oxidation of water facilitated by the holes in the VB of photocatalysts, and given that •OH is likely the primary reactive species responsible for As(III) oxidation, it can be inferred that the conversion of As(III) to As(V) is primarily due to the oxidatively produced •OH in this photocatalytic system using PICs as photocatalysts. Furthermore, PIC-DP reduced the amount of As(III) to 419.4 μ M while generating 56.8 μ M of H₂O₂, thus demonstrating that both PICs possess this dual capability. However, it is evident that PIC-BPY is more suitable for the desired applications owing to its higher H₂O₂ productivity and faster rate of arsenic oxidation.

Furthermore, PIC-BPY demonstrated a consistent reduction in As(III) concentration from 500 µM to 396.6 µM, and produced only a minimal amount of H₂O₂, which reached 20.5 µM for 9 h under anaerobic condition (Fig. S21a). Although the rate of As(III) oxidation (103.4 µM over 9 h) is lower than that of observation under O2-saturated conditions (177.8 µM over 9 h), it shows that the As(III) oxidation is primarily mediated by •OH, which resulted from the hole oxidation pathway. This aligns with the results from PIC-DP, where a decrease of 34.6 μ M in As (III) was observed with negligible H₂O₂ production. A slower As(III) oxidation rate can be attributed to incomplete charge separation due to the absence of oxygen, which serves as an electron acceptor. Moreover, in the presence of the •OH scavenger (e.g. TA), the As(III) oxidation rate was insignificant for both PIC-BPY and PIC-DP with oxidation of As(III) only 1.6 µM for PIC-BPY and 3.7 µM for PIC-DP over 9 h, respectively (Fig. S21b). This clearly indicates that As(III) degradation relies on the •OH produced from WOR. In summary, photocatalytic H₂O₂ production by PIC-BPY predominantly occurs through the ORR without depleting •OH produced via the WOR (Fig. 5b). These findings suggest that PICs offer significant benefits for simultaneous photocatalytic H₂O₂ production and As(III) oxidation.

4. Conclusion

Herein, we present the novel design and synthesis of PIC-BPY for photocatalytic H₂O₂ production. Compared to its PIC-DP counterpart, PIC-BPY exhibited a remarkable three-fold improvement in performance, which can be attributed to its broader absorption range, extended exciton lifetime, and the presence of additional catalytic active sites. Notably, we unveiled the critical role of the PI moiety within the PICs, which provides efficient ORR and WOR active sites that further boost the photocatalytic performance. Furthermore, our investigation extended beyond H_2O_2 production by PIC-BPY to harness the •OH generated from the WOR for simultaneous arsenic pollutant degradation. We anticipate that this study will provide a platform for the construction of multifunctional photocatalysts, opening new avenues for eco-friendly energy generation and environmental remediation strategies.

CRediT authorship contribution statement

Taehyung Kim: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. Eunwoo Choi: Investigation, Data curation. Do-Yeon Lee: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. Byeong-Su Kim: Writing – review & editing, Writing – original draft, Visualization, Supervision, Funding acquisition, Formal analysis, Conceptualization. Hyoung-il Kim: Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2024.124264.

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