Supporting Information

Sodium/Potassium Poly(heptazine imide) with Electron Sink

Effect for Hydrogen Peroxide Photosynthesis

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Materials and Methods

Materials

All solvents and reagents obtained from commercial sources were used without further purification. Melamine, cyanuric acid, lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), N, N-Dimethylformamide (DMF), Sodium Sulfate (Na₂SO₄), potassium ferricyanide (K₃[Fe(CN)₆]), potassium hexacyanoferrate (II) (K₄ [Fe(CN)₆]), 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-tetramethylpiperidine (TEMP), oxygen (O₂), nitrogen (N₂), potassium hydrogen phthalate (C₈H₅KO₄), potassium iodide (KI), hydrogen peroxide(H₂O₂) were purchased from Sinopharm Chemical Reagent Co., Ltd. F-doped tin oxide (FTO) conductive glass was purchased from Wuhan Jinge-Solar Energy Technology Co., Ltd. Ultrapure water was used to prepare all solutions.

Synthesis of polymeric carbon nitride (PCN)

PCN was prepared by thermal polymerization of melamine and cyanuric acid. Specifically, 2 g of melamine and 2 g of cyanuric acid were dissolved in 50 mL of water. The solution was heated at 100 °C under stirring until the solvent was evaporated. The obtained powder was dried overnight in an oven at 60 °C, and then was heated to 500 °C at 2.5 °C·min⁻¹ and kept for 2 h in a muffle furnace under an air atmosphere. The product was washed with deionized water, filtered, and dried at 60 °C. The obtained sample was denoted as PCN.

Synthesis of sodium poly(heptazine imide) (Na-PHI)

NaK-PHI was prepared using the molten salt method. Typically, 0.6 g of PCN was ground in a mortar with LiCI (3 g) and NaCI (3 g). The mixture was heated to 550 °C at 2.5 °C min⁻¹ and kept for 2 h in a muffle furnace under an air atmosphere. The product was washed with boiling deionized water several times. Finally, the sample was dried overnight at 60 °C and ground to powder. The obtained sample was denoted as Na-PHI.

Synthesis of potassium poly(heptazine imide) (K-PHI)

NaK-PHI was prepared using the molten salt method. Typically, 0.6 g of PCN was ground in a mortar with LiCI (2.7 g) and KCI (3.3 g). The mixture was heated to 550 °C at 2.5 °C min⁻¹ and kept for 2 h in a muffle furnace under an air atmosphere. The product was washed with boiling deionized water several times. Finally, the sample was dried overnight at 60 °C and ground to powder. The obtained sample was denoted as K-PHI.

Synthesis of sodium/potassium poly(heptazine imide) (NaK-PHI)

NaK-PHI was prepared using the molten salt method. Typically, 0.6 g of PCN was ground in a mortar with LiCl (1.2 g), NaCl (2.4 g) and KCl (2.4 g). The mixture was heated to 550 °C at 2.5 °C min⁻¹ and kept for 2 h in a muffle furnace under an air atmosphere. The product was washed with boiling deionized water several times. Finally, the sample was dried overnight at 60 °C and ground to powder. According to the molar ratio of NaCl to KCl (0.2:1, 0.5:1, 1:1, 1.3:1, 1.5:1, 2:1 or 5:1), the NaK-PHI samples are denoted as NaK-PHI-x (x = 0.2, 0.5, 1, 1.3, 1.5, 2 or 5) (**Table S1**). The NaK-PHI-1.3 with the optimal catalytic performance was referred to as NaK-PHI.

Synthesis of protonated poly(heptazine) imide (H-PHI)

NaK-PHI (0.5 g) was stirred in 1 M HCI (100 mL) overnight at room temperature. The material was washed with pure water six times by centrifugation until the supernatant was neutral. The sample was dried at 60 °C in vacuum overnight. The obtained sample was denoted as H-PHI.

Characterizations and Instruments

The morphology and microstructure were investigated by scanning electron microscopy (SEM, JSM-6701F) and transmission electron microscopy (TEM, FEI Talos F200X). X-ray diffraction (XRD) measurements were performed on an Ultima IV diffractometer with Cu Ka radiation. The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS50 spectrometer. The potassium content was determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Plasma Quant PQ9000). The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were recorded on a UV-vis spectrometer (SHIMADZU UV-2600i) with BaSO₄ as the reference. The photoluminescence (PL) spectra were measured on an FLS920 spectrophotometer under the excitation of 350 nm, and the fluorescent lifetimes were obtained using a microsecond pulse lamp as the exciting source (405 nm). The Zeta potential of samples was detected by zeta potential and particle size analyzer spectrometer (Bruker 90Plus Pals). The specific surface area and pore volume were determined by the Brunauer-Emmett-Teller (BET) method based on N₂ adsorption/desorption measurements (Micromeritics ASAP 2460) at 77 K, all samples were outgassed under vacuum at 200 °C for 12 h. The temperature-programmed oxygen desorption (O2-TPD) measurement was performed on a fully automated chemisorption analyzer (Micromeritics AutoChem II 2920). The transient-state surface photovoltage (TPV) spectrum was obtained through the CEL-SPS1000 system (Tektronix MSO46).

Photoelectrochemical test

Electrochemical measurement was carried out with an electrochemical workstation (CHI760E) in a traditional three-electrode cell. Pt and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. The working electrode was prepared on FTO glass, which had been cleaned via sonication in 10 mL of glass cleaner and 150 mL of ultrapure water for 1 h and dried at 60 °C. 10 mg of the sample was dispersed in 5 mL of DMF under ultrasound for 30 minutes to obtain a homogeneous mixture. 20 µL of the sample was dropped onto the clean FTO glass and dried at room temperature. For Mott–Schottky (M–S) measurements, the plots were recorded at frequencies of 1000, 1500, and 2000 Hz in 0.5 M Na₂SO₄ aqueous solution (pH = 6.3). The photocurrent with on/off response was measured by a 300 W Xenon lamp at an applied potential of 0.5 V in 0.5 M Na₂SO₄ aqueous solution. Electrochemical impedance spectroscopy (EIS) was measured using 0.01 M K₃[Fe(CN)₆]/K₄[Fe(CN)₆] aqueous solution as the electrolyte.

A rotating ring-disk electrode (RRDE) was used to measure the number of transferred electrons (*n*) and H_2O_2 selectivity of the samples in the oxygen reduction reaction (ORR) reaction by Chenhua CHI 760D electrochemical workstation with standard three electrodes. The Ag/AgCl electrode and graphite rod were used as the reference and counter electrodes, respectively. The rotating disk electrode (ALS RRDE-3A) was employed as the working electrode. The typical catalyst ink was prepared was prepared as follows. Firstly, 2 mg of the catalysts and 10 µL of Nafion (5 wt%) were added into the 1 mL of IPA and then dispersed by sonication for 1 h to form a homogeneous ink. Lastly, 20 µL of the ink was dropped on the polished RRDE and dried at room temperature. Before the ORR, cyclic voltammetry (CV) measurement at the scan rate of 100 mV s⁻¹ for 30 cycles was conducted on RRDE to electrochemically clean until stable CV curves could be achieved. The linear sweep voltammetry (LSV) was detected in 0.1 M phosphate buffer solution with the scan rate of 10 mV s⁻¹ at 1600 rpm. The potential vs. the Ag/AgCl reference electrode was converted to the potential vs. RHE according to the Nernst equation:

E (vs. RHE) = E (vs. Ag/AgCl) + 0.059 × pH + 0.197

The *n* was calculated with the equation:

$$n = 4 \times \frac{I_{\rm D}}{I_{\rm D} + I_{\rm R}/N}$$

The selectivity of H_2O_2 was determined by the equation:

$$H_2O_2\% = 2 \times \frac{I_R/N}{I_D + I_R/N} \times 100\%$$

 $I_{\rm D}$ is the disc current, $I_{\rm R}$ is the ring current and *N* is the collection efficiency. The value of *N* was experimentally determined to be 0.37 by a standard ferricyanide system. In detail, the bare RRDE was examined in 0.1 M KCl electrolyte solution containing 0.01 M K₃Fe(CN)₆ under different rotation rates from 400 to 2500 rpm. The average ratio of $I_{\rm R}/I_{\rm D}$ at different rotation rates was measured for *N*.

Photocatalytic activity test

The photocatalytic conversion of O_2 into H_2O_2 was evaluated under visible-light irradiation. The experimental condition is to add 10 mg photocatalyst to 50 mL water without a sacrificial agent under stirring. 10 mg photocatalyst and 5 mL isopropanol (IPA) as a sacrificial electron donor were added to 45 mL water under stirring. The photoreaction tests were performed under irradiation from a 300 W Xenon Lamp Source (PLS-SXE300+, Beijing Perfectlight) filtered with a cutoff filter ($\lambda > 420$ nm). The solution was continuously filled with O_2 or N_2 for 30 min in the dark before measurement. All photocatalytic reactions were carried out with a recirculating water system. During the photocatalytic reaction, 2 mL of suspension was collected at 15-minute intervals and filtrated with a 0.45 µm filtration membrane to remove the catalysts.

H₂O₂ detection methods

The amount of H_2O_2 was analyzed by iodometry. 1 mL 0.1 mol L⁻¹ C₈H₅KO₄ aqueous solution and 1 mL of 0.4 mol L⁻¹ KI aqueous solution were added to 2 mL obtained solution, which was then kept for 30 min. H_2O_2 reacted with iodine ions (I⁻) under acidic conditions to generate triiodide ions (I₃⁻) ($H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$), which has a strong absorption at about 350 nm. The absorbance of I_3^- at 350 nm was measured by UV–vis spectrophotometer, and then the amount of H_2O_2 generated during the reaction can be calculated.

The amount of H₂O₂ was analyzed by the Ce(SO₄)₂ titration method. In brief, the reaction solution was filtered with a 0.45 µm filtration membrane to remove the catalysts and mixed with the prepared solution containing 0.5 mM of Ce(SO₄)₂ and 0.25 M of H₂SO₄. H₂O₂ can reduce the yellow solution of Ce⁴⁺ to a colorless Ce³⁺ (2Ce⁴⁺ + H₂O₂ \rightarrow 2Ce³⁺ + 2H⁺ + O₂). The concentration of H₂O₂ generated in the reaction was estimated by measuring the absorbance at 316 nm using a UV–vis spectrophotometer.

The apparent quantum yield (AQY) measurement

AQY for H_2O_2 evolution was measured using bandpass filters (420 ± 2.0 nm). The irradiation area was approximately 1 cm². Based on the amounts of H_2O_2 produced during the photocatalytic reaction for 1 h, the AQY was calculated as follows:

AQY (%) =
$$\frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\%$$

= $\frac{(\text{Number of evolved H}_2\text{O}_2 \text{ molecules}) \times 2}{\text{Number of incident photons}} \times 100\%$
= $\frac{(M_{\text{H}_2\text{O}_2} \times N_A \times h \times c) \times 2}{S \times P \times t \times \lambda} \times 100\%$

M = yield of H₂O₂ (mol); *N*_A (Avogadro constant) = 6.02×10^{23} mol⁻¹; *h* (Planck constant) = 6.626×10^{-34} J s; *c* (Speed of light) = 3×10^8 m s⁻¹; *S* (Irradiation area) = 1 cm^2 ; *P* (the intensity of irradiation light) = 0.01 W cm^{-2} (420 nm); *t* (the photoreaction time) = 3600 s; λ (the wavelength of the monochromatic light) = 420×10^{-9} m.

Solar-to-chemical conversion (SCC) efficiency measurement

The SCC efficiency was evaluated usin0g a 300 W Xe lamp (PLS-SXE300+, Beijing Perfectlight) with an AM 1.5 G filter as a simulated sunlight source. 250 mg of the catalyst was dispersed in 50 mL of pure water with sufficient O_2 for photoreaction. The irradiation area was approximately 1 cm², and the light intensity is set to 100 mW cm⁻² by the optical power meter (FZ-A, Beijing Shida Photoelectric Technology Co., Ltd). The SCC efficiency is calculated as follows:

SCC (%) =
$$\frac{\Delta G_{H_2O_2} \times n_{H_2O_2}}{S \times I \times t} \times 100\%$$

where $\Delta G_{H_2O_2}$ is the Gibbs free energy (117 KJ mol⁻¹) of forming H_2O_2 , $n_{H_2O_2}$ is the amount of H_2O_2 produced, *S* is the illuminated area (1 cm²), *I* is the light intensity of simulated sunlight (100 mW cm⁻²), and *t* is the illuminated time (s).

Free radical quenching experiment

Free radical quenching experiments were performed by introducing a series of specific scavengers into the reaction system. Typically, 1mM AgNO₃, benzoquinone, β -carotene and tert-butyl alcohol (TBA) are used as e⁻, •O₂⁻, ¹O₂ and •OH trapping reagents, respectively.

Electron paramagnetic resonance (EPR) test

EPR measurements were performed on an EPR spectrometer (Bruker ER200DSRC10/12). 20mg powder of samples was placed in a nuclear magnetic tube to detect the signal of unpaired electrons at room temperature. DMPO was used as the spin-trapping agent for $\cdot O_2^-$. 1 mg sample was added to 2 ml methanol and dispersed with ultrasonic sonication for 5 minutes, followed by adding 100 mM DMPO into the solution. After being irradiated for 3 min under visible light, the solution was analyzed at room temperature. DMPO was used as the spin-trapping agent for $\cdot OH$. 1 mg sample was added to 2 ml pure water and dispersed with ultrasonic sonication for 5 minutes, followed by adding 100 mM DMPO into the solution. After being irradiated for 3 min under visible light, the solution was analyzed at room temperature. TEMP was used as the spin-trapping agent for 1O_2 . 1 mg sample was added to 2 ml pure water and dispersed with ultrasonic sonication for 5 minutes, followed by adding 100 mM DMPO into the solution. After being irradiated for 3 min under visible light, the solution was analyzed at room temperature. TEMP was used as the spin-trapping agent for 1O_2 . 1 mg sample was added to 2 ml pure water and dispersed with ultrasonic sonication for 5 minutes, followed by adding 100 mM TEMP into the solution. After being irradiated for 3 min under visible light, the solution was analyzed at room temperature. TEMP was used as the spin-trapping agent for 1O_2 . 1 mg sample was added to 2 ml pure water and dispersed with ultrasonic sonication for 5 minutes, followed by adding 100 mM TEMP into the solution. After being irradiated for 3 min under visible light, the solution was analyzed at room temperature.

In-situ FTIR measurement

In-situ FTIR measurement was performed on an FTIR spectrometer (Bruker TENSOR 27). 10 mg photocatalyst was added to 50 mL water under stirring. The solution was continuously filled with O_2 for 30 min in the dark before measurement. The probe for collecting sample signals is directly inserted into the reaction solution. The spectra were collected under irradiation from a 300 W Xenon Lamp Source (PLS-SXE300+, Beijing Perfectlight) filtered with a cutoff filter ($\lambda > 420$ nm).

Computational method

DFT calculations were conducted through the Vienna ab initio Simulation Package (VASP) with the projector augment wave method.^{1, 2} Generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) functional was used as the exchange-correlation functional.³ The Brillouin zone was sampled with $2 \times 2 \times 1$ K points for surface calculation.⁴ The cutoff energy was set as 500 eV, and structure relaxation was performed until the convergence criteria of energy and force reached 1×10^{-5} eV and 0.02 eV Å⁻¹, respectively. A vacuum layer of 15 Å was constructed to eliminate interactions between periodic structures of surface models. The van der Waals (vdW) interaction was amended by the zero damping DFT-D3 method of Grimme.⁵ The Gibbs free energy was calculated as $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$, where the ΔE , ΔE_{ZPE} , and ΔS are electronic energy, zero-point energy, and entropy difference between products and reactants. The zero-point energies of isolated and absorbed intermediate products were calculated from the frequency analysis.⁵ The vibrational frequencies and entropies of molecules in the gas phase were obtained from the National Institute of Standards and Technology (NIST) database.^{6,7}

Quasi-in situ X-ray photoelectron spectroscopy (QIS-XPS) measurement

The XPS data were obtained on a spectrometer (Thermo ESCALAB 250Xi) equipped with a monochromatized AI K α X-ray source, and the binding energies were normalized with the signal of C 1s at 284.8 eV. The QIS-XPS instrument was fitted with a 300 W Xe lamp (nbet HSX-UV300) as an additional light source (λ > 300 nm). The prepared sample was transferred to the analysis chamber of the XPS instrument for QIS-XPS measurements. In the process of measurements. The changes in XPS spectra were recorded by controlling light on or off to detect the dynamic evolution process on the photocatalyst surface.

Kelvin probe force microscopy (KPFM) measurement

The surface potential of the samples was tested by KPFM (Bruker, Dimension Icon). 5 mg of the sample was dispersed in 5 mL ethanol under ultrasound for 30 minutes to obtain a homogeneous mixture. 20 µL of the sample was dropped onto the clean FTO glass and dried at room temperature. The silver conductive adhesive was used to stick the FTO glass of the sample onto the sample stage. The sample and the sample stage are conductive. KPFM was performed in lift mode. The sample morphology and surface potential signals were acquired in lift mode sequentially. The surface potential signals of the samples were collected under both dark and 420nm light irradiation conditions (PLS-SXE300+/UV, Beijing Perfectlight).

The steady-state surface photovoltage (SPV) measurement

The software for testing SPV (SPVM101) and the software for testing KPFM (Bruker, Dimension Icon) are interconnected. KPFM was performed in lift mode. The sample morphology and SPV signals were acquired in lift mode sequentially. The SPV magnitude is directly proportional to the number of separated charges and charge separation distance. The SPV sign reflects the types of surface photogenerated charge with positive SPV-denoted photogenerated holes and negative SPV-denoted photogenerated electrons. Wavelength-tunable monochromatic light was generated by a 300 W Xenon Lamp Source (PLS-SXE300+/UV, Beijing Perfectlight) using a Zolix Omni- λ 500 monochromator. The wavelength range of light irradiation is from 350 to 600 nm.

The transient photovoltage (TPV) measurement

The TPV (CEAuLight CEL-SPS1000) test was carried out under a 355 nm laser pulse illumination. The

internal structure of the sample pool, from top to bottom, consists of a platinum mesh electrode, mica sheet, tested sample, and FTO electrode.

Experimental support for the built-in electric field (BIEF) intensity

The BIEF magnitude of the obtained photocatalysts was calculated by using the following equation:

$$F_{\rm s} = \sqrt{\frac{-2V_{\rm s}\rho}{\mathcal{E}\mathcal{E}_0}}$$

Where F_s is the intensity of the built-in electric field, V_s is the surface potential detected via KPFM, ρ is the surface charge density, which is obtained by the integral value of the current density, \mathcal{E} is the low-frequency dielectric constant, and \mathcal{E}_0 is the vacuum dielectric constant. The above equation reveals that the BIEF magnitude is mainly determined by the surface voltage and the charge density because \mathcal{E} and \mathcal{E}_0 are two constants.

Supporting Figures



Fig. S1. Scanning electron microscopy images of (a) PCN, (b) Na-PHI, (c) K-PHI and (d) NaK-PHI.



Fig. S2. XPS results of the (a) survey scan and fine scan of (b) C 1s, (c) N 1s, and (d) O 1s for samples.



Fig. S3. The high-angle annular dark-field scanning TEM (HAADF-STEM) and the elemental (C, N, O, Na and K) mapping images of NaK-PHI.



Fig. S4. Plots of the converted Kubelka–Munk function versus photon energy for the prepared samples.

The obtained UV-vis diffuse reflectance spectra were first transformed into absorption spectra according to the Kubelka-Munk function:

 α and *R* were the absorbance index and the relative reflectance of samples with infinite thickness compared to the reference, respectively. Moreover, the band gaps of samples were estimated based on the Tauc equation:

$$\alpha hv = A \ (hv - E_g)^{n/2}$$

h, *v*, *A*, and *E*_g represent the Planck constant, light frequency, proportionality constant, and band gap, respectively, while n depends on the nature of transition in a semiconductor. Values of 1, 3, 4, and 6 for n correspond to allowed direct, forbidden direct, allowed indirect, and forbidden indirect transitions, respectively. The values of *E*_g were determined from the plot of $(\alpha h v)^{2/n}$ against *hv* and corresponded to the intercept of the extrapolated linear portion of the plot near the band edge with the *hv* axis. CN samples were treated as semiconductors with allowed indirect transition. The values of *E*_g were thus determined from the plot of $(\alpha h v)^{1/2}$ against *hv* (**Fig. S4**).



Fig. S5. VB-XPS spectra of (a) PCN, (b) Na-PHI, (c) K-PHI and (d) NaK-PHI.

According to the VB-XPS plots, *E*_{VB-XPS} of PCN, Na-PHI, K-PHI, and NaK-PHI are about 1.35, 1.28, 1.36 and 1.74 V, respectively.

The valence band potential (E_v) can be calculated with the equation:

 $E_{\rm v} = \Phi + E_{\rm VB-XPS} - 4.44$

 ϕ is the electron work function of the XPS analyzer and the ϕ value is 4.67. E_{VB-XPS} is the VB value and is tested by VB-XPS spectra. The E_v of PCN, Na-PHI, K-PHI, and NaK-PHI are calculated to be 1.58, 1.51, 1.59 and 1.97 V versus standard hydrogen electrodes (NHE).

The conduction band potential (E_c) can be calculated with the equation:

 $E_v = E_c + E_g$

The E_c of PCN, Na-PHI, K-PHI, and NaK-PHI are calculated to be -1.23, -1.22, -1.07 and -0.66 V.



Fig. S6. (a) Determination of UV-vis absorption intensity of different H_2O_2 concentrations by iodimetry. (b) The linear fitting formula of standard H_2O_2 concentration.



Fig. S7. (a) Determination of UV-vis absorption intensity of different H_2O_2 concentrations by $Ce(SO_4)_2$ titration method. (b) The linear fitting formula of standard H_2O_2 concentration.



Fig. S8. Comparison of H_2O_2 concentration during photocatalytic reaction over NaK-PHI measured using iodometry and cerium sulfate titration methods.



Fig. S9. Comparison of photocatalytic H₂O₂ production of NaK-PHI with different content of Na and K in O₂-saturated pure water. Reaction conditions: water (50 mL), catalyst (10 mg), λ > 420 nm.



Fig. S10. (a) FTIR, (b) XRD spectra, (c) UV-vis DRS and (d) Plots of the converted Kubelka– Munk function versus photon energy of NaK-PHI and H-PHI.

For a more detailed comparison, the properties of NaK-PHI and H-PHI are shown in **Fig. S8**. The NaK-PHI catalysts exhibit a peak at 993 cm⁻¹, which is assigned to the symmetric vibration of Na/K–NC₂ groups (**Fig. S8a**). Compared to NaK-PHI, the metal-NC₂ symmetric vibration of H-PHI has disappeared, confirming that the Na⁺ and K⁺ are replaced with H⁺. As shown in **Fig. S8b**, the (100) peak of H-PHI slightly shifts from 8.1° to 8.0° compared with the NaK-PHI. The position of the (002) peak of H-PHI shifts from 28.3° to 28.0° in comparison with the NaK-PHI, indicating that the interlayer space was slightly shortened by replacing Na⁺ and K⁺ ions, which has a larger ionic radius with H⁺ [Chem. Mater. 2023, 35, 1283–1294]. The optical properties present a blue shift of absorption edge from 480 nm (for NaK-PHI) to 444 nm (for H-PHI) (**Fig. S8c**). After acid treatment, the light absorption of H-PHI under visible light is significantly reduced. The converted Kubelka–Munk function shows that the band gap values (*E*_g) of NaK-PHI and H-PHI are 2.63 and 2.82 eV, respectively (**Fig. S8d**). Based on the comparison of photocatalytic performance and properties above, it is shown that alkali metal ions can not only enhance the light absorption capacity of catalysts but also provide effective active sites for catalysts.



Fig. S11. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution curves for samples.



Fig. S12. Cycling test of NaK-PHI for photocatalytic H₂O₂ production under O₂ atmosphere in pure water. Reaction conditions: water (50 mL), catalyst (10 mg), λ > 420 nm.



Fig. S13. (a) XRD patterns and (b) FTIR spectra of NaK-PHI before and after reaction.



Fig. S14. XPS results of the (a) survey scan and fine scan of (b) C 1s, (c) N 1s, (d) O 1s (e) Na 1s and (f) K 2p for NaK-PHI before and after the reaction.



Fig. S15. Comparison of photocatalytic H₂O₂ production by all samples under the different atmospheres (Air or O₂). Reaction conditions: water (45 mL), isopropanol (5 mL), catalyst (10 mg), $\lambda > 420$ nm.



Fig. S16. Comparison of photocatalytic O₂ production for 1h of PCN and NaK-PHI. Reaction conditions: 1 g L⁻¹ La₂O₃, 20 mM AgNO₃, 30 mg catalyst in 30 mL solution, $\lambda \ge 420$ nm.



Fig. S17. EPR spectra of all samples in the presence of DMPO.



Fig. S18. The linear sweep voltammetry curves in 0.1 M KCl electrolyte solution containing 10 mM K₃Fe(CN)₆ under different rotation rates (ω = 400, 800, 1200, 1600, and 2000 rpm).



Fig. S19. (a, b) High-resolution XPS spectra of C 1s and N 1s in the optimized NaK-PHI with and without light irradiated conditions.



Fig. S20. (a, b) High-resolution XPS spectra of Na 1s and K 2p in the NaK-PHI-0.2 with and without irradiated conditions. (c, d) High-resolution XPS spectra of Na 1s and K 2p in the NaK-PHI-5 with and without light irradiated conditions.



Fig. S21. (a, b) High-resolution XPS spectra of C 1s and N 1s in the NaK-PHI-0.2 with and without irradiated conditions. (c, d) High-resolution XPS spectra of C 1s and N 1s in the NaK-PHI-5 with and without light irradiated conditions.



Fig. S22. Top (top part) and side (bottom part) views of the structure models with three important adsorption states (*O₂, *OOH and *HOOH) of (a-c) BCN and (d-f) NaK-PHI.



Fig. S23. Surface morphologies (a), corresponding surface potential images in the absence (b) and presence (c) of light and \triangle CPD profiles before and after irradiation (d) for H-PHI.

Supporting Tables

Samples	LiCl (a)	NaCl (g)	KCl (a)	Na/K mole ratio
	(g)			
NaK-PHI-0.2	1.2	0.65	4.15	0.2:1
NaK-PHI-0.5	1.2	1.35	3.45	0.5:1
NaK-PHI-1	1.2	2.11	2.69	1:1
NaK-PHI-1.3	1.2	2.4	2.4	1.3:1
NaK-PHI-1.5	1.2	2.59	2.21	1.5:1
NaK-PHI-2	1.2	2.93	1.87	2:1
NaK-PHI-5	1.2	3.82	0.98	5:1

 Table S1. Synthesis of NaK-PHI with different ratios of NaCl to KCI.

Sample	Mass fraction of Na (%)	Mass fraction of K (%)
PCN	0	0
Na-PHI	2.69	0
K-PHI	0	6.07
NaK-PHI	1.07	8.25
H-PHI	0.02	0.02

Table S2. Analysis of Na and K components in PCN, Na-PHI, K-PHI and NaK-PHI obtained from ICP-OES.

The NaK-PHI-1.3 with the optimal catalytic performance was referred to as NaK-PHI.

Sample	Mass fraction of Na (%)	Mass fraction of K (%)
NaK-PHI-0.2	0.34	10.54
NaK-PHI-0.5	0.54	8.8
NaK-PHI-1	0.67	8.34
NaK-PHI-1.3	1.07	8.25
NaK-PHI-1.5	1.19	5.19
NaK-PHI-2	1.27	4.83
NaK-PHI-5	2.41	2.73

Table S3. Analysis of Na and K components in different NaK-PHI samples obtained from ICP-OES.

The NaK-PHI-1.3 with the optimal catalytic performance was referred to as NaK-PHI.

Element	Atomic fraction (%)	Mass fraction (%)
С	77.82	73.54
Ν	16.56	18.26
0	4.66	5.87
Na	0.49	0.88
К	0.47	1.45

Table S4. Element components analysis of the NaK-PHI obtained from the EDX mapping.

Reactions	φ^{Θ} (V vs. NHE, pH=0)
$O_2 + e^- \rightarrow \bullet O_2^-$	-0.33
$\bullet O_2^- + h^+ \rightarrow {}^1O_2$	+0.34
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	+0.68
$\mathrm{H_2O_2} + \mathrm{e^-} \rightarrow \mathrm{\bullet OH} + \mathrm{OH^-}$	+0.87
$2H_2O+4h^{\scriptscriptstyle +}\rightarrow O_2+4H^{\scriptscriptstyle +}$	+1.23
$\bullet O_2^- + 2H^+ + e^- \rightarrow H_2O_2$	+1.44
$2H_2O+2h^+\rightarrow H_2O_2+2H^+$	+1.76
$H_2O + h^+ \rightarrow \bullet OH + H^+$	+2.73

Table S5. The main reactions for the photocatalytic H_2O_2 production process.⁸⁻¹⁰

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S	Samples	A ₁	T1 (NS)	A ₂	т ₂ (ns)	T _{ave} (ns)
	PCN	4763.33157	1.48827	743.87665	8.26225	4.63
	Na-PHI	5468.78286	0.93106	193.19417	8.57953	2.81
	K-PHI	5692.97477	0.69227	34.12283	15.16068	2.37
1	NaK-PHI	5536.20366	0.76994	146.84351	7.79822	2.26

Table S6. Exponential decay-fitted parameters of fluorescence lifetime for as-obtained samples.

A double exponential function fitting was employed to analyze the time-resolved PL spectra, and the average PL lifetime (τ_{ave}) was calculated by the following equation:

$$\tau_{\text{ave}} = \frac{A_1 \times \tau_1^2 + A_2 \times \tau_2^2}{A_1 \times \tau_1 + A_2 \times \tau_2}$$

 r_i is the estimated lifetime value and A_i is the corresponding amplitude.

Material	Light source	Atmos	AQY	SCC	H ₂ O ₂ productivity	Reference
	(nm)	pnere	(%)	(%)	(µmol g ⁻¹ h ⁻¹)	
NaK-PHI	> 420	O ₂	13.9 (420 nm)	0.68	672.5	This work
		Air	NA	NA	308.1	
	400	0	2.6	N 1 A	04.4	Angew. Chem. Int. Ed.
g-C3N4/PDI	> 420	O_2	(420 nm)	NA	21.1	2014, 53 , 13454-13459
g-			0.4			J. Am. Chem. Soc.
C ₃ N ₄ /PDI/r	> 420	O ₂	6.1	0.2	24.3	2016, 138 , 10019-
GO			(420 nm)			10025
	100	0	4.6	0.40	47.4	ACS Catal. 2016, 6,
g-C3N4/BDI	> 420	02	(420 nm)	0.13	17.1	7021-7029
CN	100	•				Angew. Chem. Int. Ed.
aerogels	> 420	O ₂	NA	NA	28.8	2017, 56 , 10905-10910
						Energy Environ. Sci.
OCN-500	> 420	O2	NA	NA	2.1	2018, 11 , 2581-2589
Ag@U-g-	AM	-				Adv. Mater. 2019, 31 ,
C ₃ N₄-NS	1.5G	O ₂	NA	NA	118.5	1806314
						Proc. Natl. Acad. Sci. U.
Co ₁ /AQ/C ₃ N ₄	AM 1.5G	O2	NA	NA	124	S. A. 2020, 117 , 6376-
						6382
	AM	0	2.12		222.4	ACS Catal. 2020, 10,
PEI/C ₃ N ₄	1.5G	O ₂	(420 nm)	0.05	208.1	3697-3706
01 04 0045	100	0	17.6	0.04	500.4	Nat. Catal. 2021, 4,
SD-SAPC15	> 420	O ₂	(420 nm)	0.61	588.1	374-384
	AM	0	N1.4	N 1 A	0.40.00	Appl. Catal. B 2021,
ACNT-5	1.5G	O_2	NA	NA	240.36	288 , 119993
	. 100	0	15.4	0.55	455	Angew. Chem. Int. Ed.
C5IN2	> 400	O_2	(420 nm)	0.55	155	2022, 61 , e202210856
	> 420		4.0		137	
	AM	-	1.8	0.23	100	
	1.5G	0	(420 nm)		198	Energy Environ. Sci.
INV-C=IN-CIN	> 420	- U ₂			211	2022, 15 , 830-842
	AM	-	NA	NA	000	
	1.5G				323	
			0.43	NIA	055.4	J. Am. Chem. Soc.
IVIN/AD-	427	O2	(427 nm)	NA	200.4	2023, 145 , 16584-
C3IN4			NA	NA	176.8	16596
	AM	0	9.1	0.70	254 5	Nat. Commun. 2023,
	1.5G	U_2	(420 nm)	0.72	304.0	14 , 2493

Table S7. Summary of CN-based materials for photocatalytic H_2O_2 production in pure water.

Nisaps-	. 400	0	10.9	10.9	242.2	Nat. Commun. 2023,
PuCN	> 420	O_2	(420 nm)	0.82	342.2	14 , 4344
CoO _x -BCN-	AM	0	8.36	240	Nat. Commun. 2024,	
FeOOH	1.5G	O_2	(420 nm)	0.75	340	15 , 9224
	. 400	0	5.1	0.14	EE7 4	Angew. Chem. Int. Ed.
CN-PDA	> 400	02	(400 nm)	0.14	1.100	2024, 63 , e202319216
Tri-Phase	AM	۸:-	26.8	NIA	2062.2	Adv. Mater. 2024, 36 ,
system	1.5G	All	(400 nm)	NA	2063.2	2307967
CN-NH4-	× 420	0.	NA	ΝΙΔ	120	Adv. Mater. 2024, 36 ,
NaK	> 420	02	INA	INA	139	2307490
	. 420	0.	8.53	0.21	FFG	Energy Environ. Sci.
CINVUS	> 420	02	(420 nm)	0.31	556	2024, 17 , 1520-1530
K+/I⁻-	> 400	0.	NA	ΝΙΔ	2240.2	Adv. Funct. Mater.
CN/CdSe-D	> 400	02	INA	INA	2240.2	2024, 34 , 2315426
	> 120		5.73	0.47	244.9	
	> 420	0	(420 nm)	0.47	244.0	ACS Catal. 2024, 14,
	AM	02	NΙΔ	ΝΙΔ	267.9	10893-10903
	1.5G		INA	INA	307.0	
C-N- py	× 420	0.	1.9	ΝΙΔ	75.66	ACS Nano 2024, 18 ,
C3IN4-IIV	> 420	02	(420 nm)	NA	75.00	20435-20448
	> 100	0	NIA	0.01	122 / 9	Appl. Catal. B 2024,
ING-FUIN	> 400	02	INA	0.01	100.40	342 , 123340

AQY, apparent quantum yield; SCC, solar-to-chemical conversion; NA, not available.

Material	Salts	Sacrificial reagent	Light source (nm)	Atmos phere	AQY (%)	SCC (%)	H ₂ O ₂ productivity (µmol g ⁻¹ h ⁻¹)	Reference
		None		O ₂	13.9 (420 nm)	0.68	672.5	
NaK-PHI	NaCI/		> 120	Air	NA	NA	308.1	This work
Naixi Th	KCI	10 wt.%	2420	O ₂	62.13 (420 nm)	NA	27150	This work
		Isopioparior		Air	NA	NA	10160	
K,Na-PHI	NaOH/ KOH	0.1 mmol 4- methoxybe nzyl alcohol	365	Air	NA	NA	1083.3	Angew. Chem. Int. Ed. 2020, 59 , 487–495
ACNN	NaCl/ KCl	10 wt.% isopropanol	> 420	O ₂	30.7 (429 nm)	NA	10200	ACS Catal. 2020, 10 , 14380-14389
PCN- NaCA-2	NaSCN	3.5 wt.% glycerol	Solar simula tor	NA	11.8 (420 nm)	NA	18700	<i>Nat. Commun.</i> 2021, 12 , 3701
TP-PCN	Nal	10 wt.% isopropanol	> 420	O ₂	NA	NA	6530.8	Angew. Chem. Int. Ed. 2021, 60 , 25546-25550
FCv@a		10 wt 9/	> 420	_	0.59		7010	Adv. Funct.
C3N4	NaCl	ethanol	AM 1.5G	O ₂	9.58 (420 nm)	NA	16500	<i>Mater.</i> 2021, 31 , 2105731
ACNT-5	KCI/ NH₄CI	None	AM 1.5G	O ₂	NA	NA	240.36	Appl. Catal. B 2021, 288 , 119993
O/K-CN	LiCl/ KCl	10 wt.% isopropanol	> 420	O ₂	NA	NA	15472	Adv. Funct. Mater. 2022, 32 , 2205119
CN- KCI/KI	KCI/ KI	10 wt.% isopropanol	> 400	O ₂	13.7 (420 nm)	NA	13100	Proc. Natl. Acad. Sci. U.S.A. 2023, 120 , e2215305120
HTCN	LiCl/ KCl	1 wt.% isopropanol	400- 800	O ₂	21.5 (420 nm)	NA	22850	<i>Adv. Mater.</i> 2023, 35 , 2306831
KCN-0.5	KCI/ KOH	10 wt.% isopropanol	420	O ₂	11.27 (420 nm) NA	NA	26360	Appl. Catal. B 2023, 331 , 122716
Ox-KPHI	LiCl/ KCl	glycerol	410	O ₂	40.72 (410 nm)	NA	6772	Adv. Mater. 2024, 36 , 2412753

Table S8. Summary of PHI prepared by different alkali metal salts for photocatalytic H₂O₂ production.

		10 wt.%			28.4	0.0	40075	Adv Matar 2021	
CIN-INH4-	NaCi/	isopropanol	> 420	O ₂	(420 nm)	2.3	10075	Adv. Mater. 2024,	
Nak	KU	None			NA	NA	139	30 , 2307490	
		10 m/t 9/			100			ACS Nono 2024	
CNKLi		10 WL 76	> 420	O ₂	(360-	NA	9870	ACS Nano 2024,	
	KCI	isopropanol			450nm)			18 , 14583-14594	
		10 wt.%	100			N1.4	40040		
		ethanol	> 400		22.3	NA	16010	Appl. Catal. B	
Na-PCN	NaCl	10 wt.%	AM	O ₂	(420 nm)	NIA	00750	2024, 342 ,	
		ethanol	1.5G			NA	20756	123340	
		None	> 400		NA	0.01	133.48	_	
H-0.25								Appl Catal P	
PHI/PTI	LiCl/	20 wt.%	100	0	64	N1.0	4000	Appi. Calal. B	
heterojun	KCI	methanol	> 400	O_2	(420 nm)	NA	4000	2024, 357 ,	
ction								124323	
		10 m/t 9/			146			Appl. Catal. B	
Na-PHI	NaCl	TU WL 76	> 380	O ₂	(400)	NA	3480	2025, 361 ,	
		ethanol			(420 nm)			124586	
CN-	NaCI/	5 wt %			23.0			Appl. Catal. B	
		5 WL 70	> 400	O ₂	کې.خ (۱۹۵۵ مېچ	NA	17195	2025, 361 ,	
K/Na3	KU	isopropanol			(420 nm)			124599	

AQY, apparent quantum yield; SCC, solar-to-chemical conversion; NA, not available.

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