

Supporting information

Simultaneously improving O₂ adsorption and activation for H₂O₂ photogeneration on K-doped-carbon nitride

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Experimental Section

Synthesis of modified PCN

5 g of DCDA and KSCN (x g) were added into 30 mL distilled water, transferred into a 50 mL Teflon-lined stainless steel autoclave and subsequently heated at 180°C for 10 h. After natural cooling to room temperature, the sample was dried at 80°C for 10 h. The obtained sample was calcinated at 550°C (2°C/min) for 4 h in a muffle furnace. After cooling down to room temperature, the sample was ground and filtered three times with boiling water, and then dried at 80°C overnight. After that, a yellow powder was obtained and named as HCNSK- x . In order to investigate the effect of the amount of KSCN, the amount of KSCN was set at 0.3, 0.4, 0.5, or 0.6 g. Meanwhile, HCN sample was prepared by the same method without KSCN.

For comparison, BCN, a pristine PCN sample, was synthesized by directly thermal condensation DCDA at 550°C (2°C/min) for 4 h in a muffle furnace.

Characterization

The crystal phase of obtained PCN was determined by X-ray diffraction (XRD, Rigaku Corporation Ultima III). The chemical composition was performed by Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific Nicolet iS50ATR), X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha⁺), and solid-state ¹³C nuclear magnetic resonance spectroscopy (NMR, Bruker Advance III 500 spectrometer). The micromorphology of the obtained PCN was observed by scanning electron microscopy (SEM, Hitachi SU8010). The specific surface area was characterized *via* and the Brunauer–Emmett–Teller (BET) (Micrometrics Gemini VII

2390) analyses. The optical absorption properties and charge recombination of obtained PCN were measured via ultraviolet–visible (UV–Vis, Shimadzu UV-2550 UV-vis spectrophotometer) and photoluminescence (PL, Edinburgh FLS980 spectrometer) spectroscopies, respectively. The BCN, HCN and HCNSK-0.4 carrier lifetimes were determined at room temperature employing time-resolved PL (Edinburgh FLS980 spectrometer). The adsorptions of NH₃, CO₂ and O₂ on catalysts were measured via temperature-programmed desorption (TPD) using a chemisorption analyzer (Chembet TPR/TPD Micromeritics 2920).

Photoelectrochemical measurement

The measurement of the rotating disk electrode (RDE, Pine Co., Ltd) was conducted employing a three-electrode cell on a CHI 660E system. The linear sweep voltammetry (LSV) was detected in 0.1 M phosphate buffer solution (PBS, pH=7, O₂-saturated) with the scan rate of 5 mV/s. And the rotating speed of the working electrode was 400 rpm, 900 rpm, 1600 rpm and 2500 rpm, respectively. The transfer electron number (n) of O₂ reduction was calculated by the slopes of Koutecky-Levich plots with following equation:

$$j^{-1} = j_k^{-1} + B^{-1}\omega^{-1/2} \quad (1)$$

$$B = 0.2nFC_0D_0^{2/3}\nu^{-1/6} \quad (2)$$

j is current density (mA/cm²); j_k is the kinetic current density; ω is the angular velocity (rpm); F is Faraday constant (96485 C/mol); C_0 and D_0 are bulk concentration of O₂ (1.1×10⁻³ mol/cm³) and diffusion coefficient of O₂ (1.93×10⁻⁵ cm²/s), respectively; ν is dynamic viscosity of H₂O (0.01 cm²/s).

Electrochemical impedance spectroscopy (EIS), the periodic on/off photocurrent response, and the Mott–Schottky plots were tested on an electrochemical workstation (Chenhua CHI 660E, Shanghai) employing a conventional three-electrode system.

Photocatalytic H₂O₂ production

First, the photocatalytic H₂O₂-production properties of the obtained samples were screened on a multipass light catalytic reaction system (Perfectlight PCX50C Discover, Beijing) under white LED irradiation. Briefly, 0.01 g of the photocatalyst was adequately dispersed in 50 mL of ethanol solution (10 vol%), after which the solution was irradiated under white LED light (30.69 mW/cm²). The photocatalytic reaction was performed for 1 h with a 15-min interval for sample collection. The H₂O₂ concentration was determined with the colorimetric method, which is based on the peroxides (POD)-catalyzed oxidation of N, N-diethyl-*p*-phenylenediamine (DPD) by hydrogen peroxide¹.

The photogeneration H₂O₂ activities of HCNSK-0.4 in different reaction systems were explored. First, 0.01 g of HCNSK-0.4 was adequately dispersed in 50 mL of ethanol solution (10 vol%), after which the solution was irradiated under white LED light (30.69 mW/cm²). The results were named HCNSK-0.4 + ethanol. And then, 0.01 g of HCNSK-0.4 was ultrasonically dispersed in 50 mL of 10 vol% ethanol solution and then stirred in the dark for 10 min with a continuous injection of O₂ or air to ensure full saturation. Following that, O₂ or air was passed through the solution at a constant 300 mL/min flow, while the solution was continuously exposed to white LED light. The results were named HCNSK-0.4 + ethanol + O₂ or HCNSK-0.4 + ethanol + Air.

Furthermore, 0.01 g of HCNSK-0.4 was adequately dispersed in 50 mL of ethanol solution (10 vol%), and then stirred in the dark for 10 min with a continuous injection of N₂ to remove the dissolved oxygen. Following that, the solution was irradiated under white LED light in atmosphere. The results were named HCNSK-0.4 + ethanol without O₂. 0.01 g of HCNSK-0.4 was ultrasonically dispersed in 50 mL pure water without ethanol and then stirred in the dark for 10 min with a continuous injection of O₂ to ensure full saturation. Following that, O₂ was passed through the solution at a constant 300 mL/min flow, while the solution was continuously exposed to white LED light. The results were named HCNSK-0.4 + without alcohol + O₂. In the end, 0.01 g of HCNSK-0.4 was ultrasonically dispersed in 50 mL of 10 vol% ethanol solution and then stirred in the dark. The results were named HCNSK-0.4 + ethanol + dark.

The apparent quantum yield (AQY) of H₂O₂ formed on HCNSK-0.4 under conditions of pure water and sacrificial agent were tested separately. The AQY test used a LED light with different wavelengths of 385 nm, 420 nm, 450 nm, 485 nm, and 520 nm (FWHM=15 nm). The AQY was calculated by the following formula:

$$AQY = \frac{2 \times H_2O_2 \text{ formed (mol)}}{\text{the number of incident photons (mol)}} \times 100\% \quad (3)$$

The solar-to-chemical conversion (SCC) efficiency test was carried out with HCNSK-0.4 in pure water and sacrificial agent under LED white light. The solar-to-chemical conversion efficiency is determined by the following formula:

$$SCC = \frac{[\Delta G_{H_2O_2}] \times [n_{H_2O_2}]}{I \times S \times T} \times 100\% \quad (4)$$

Where $\Delta G_{H_2O_2}$, $n_{H_2O_2}$, I , S , and T represent the free energy for H₂O₂ generation

(117 KJ/mol), the molar amount of H₂O₂ generated, the energy intensity of LED white light (30.69 mW/cm²), the irradiated sample area and the irradiation time (s).

Density functional theory (DFT) calculations

The DFT calculations of BCN and HCNSK, as well as the adsorption energy of O₂ on the catalysts, were conducted by the generalized gradient approximation (GGA) in the form of PBE. The energy cutoff was set to 571.4 eV, and the atomic positions were allowed to relax until the energy and force were less than 10⁻⁵ eV and 0.03 eV/Å, respectively.

Results Section

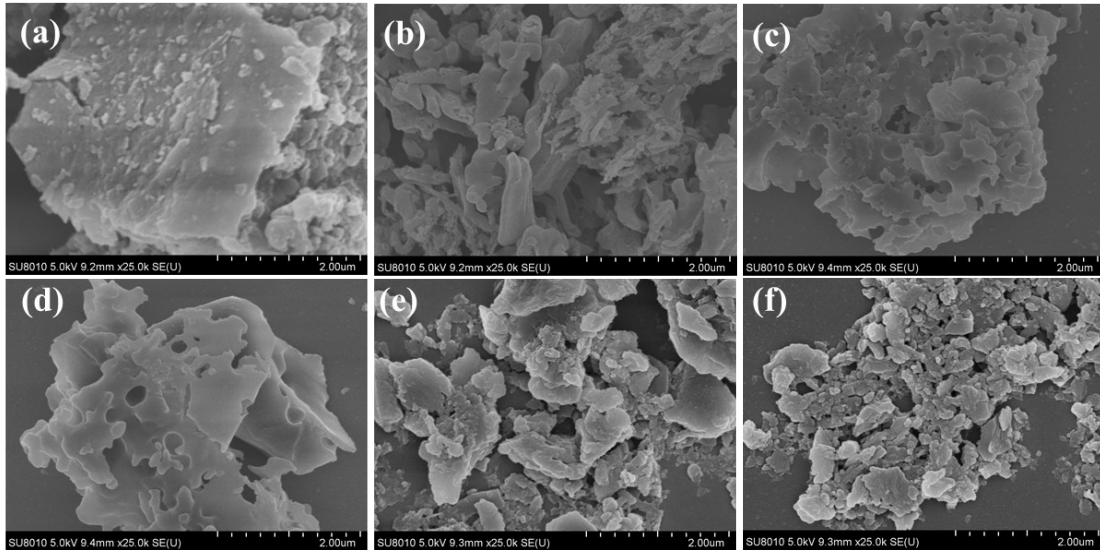


Fig. S1 SEM images of the obtained samples: (a) BCN, (b) HCN, (c) HCNSK-0.3, (d) HCNSK-0.4, (e) HCNSK-0.5, and (f) HCNSK-0.6

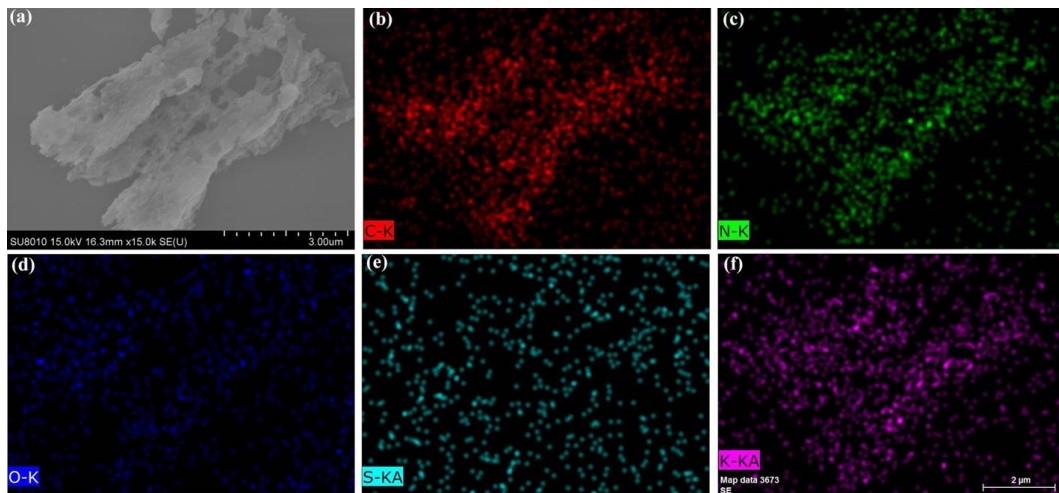


Fig. S2 The element mapping analysis of HCNSK-0.4: (a) SEM, (b) C, (c) N, (d) O, (e) S, and (f) K.

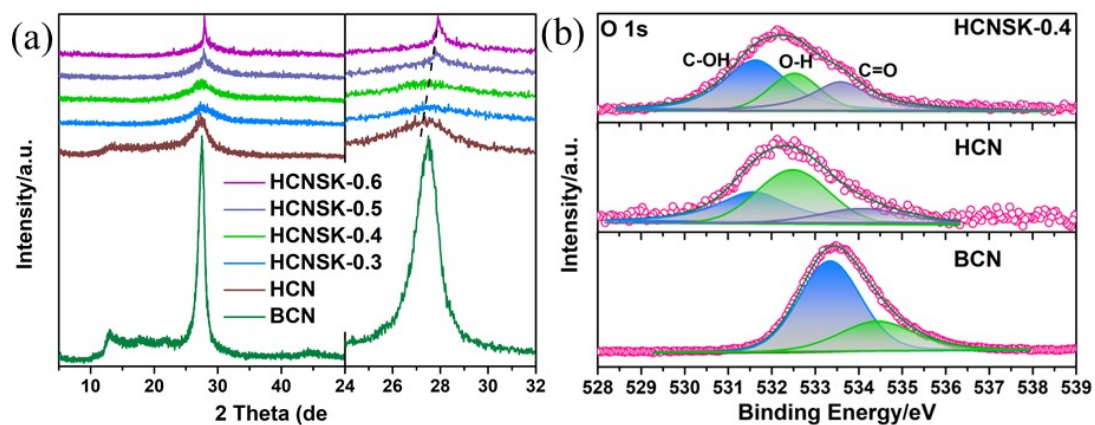


Fig. S3 (a) XRD patterns and (b) O 1s spectra of the PCN samples. The diffraction peak of HCNSK- x at 12.95° disappeared, indicating the destruction of the periodic array of the interlayer tri- s -triazine stacking.

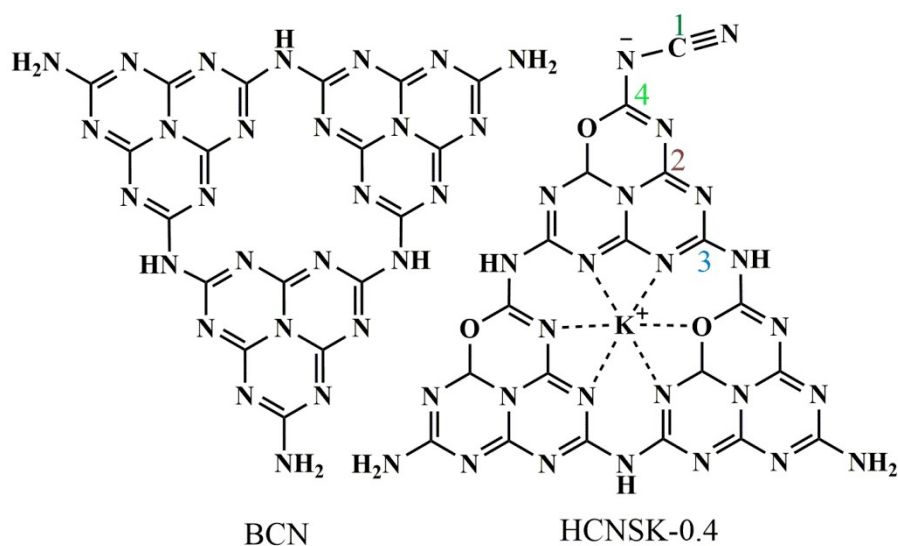


Fig. S4 Chemical structure of BCN and HCNSK-0.4.

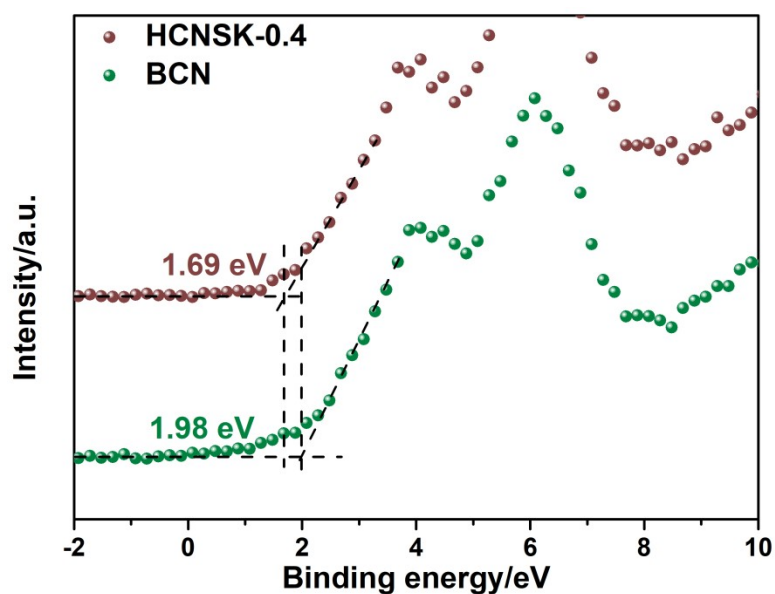


Fig. S5 XPS valence band spectra of BCN and HCNSK-0.4.

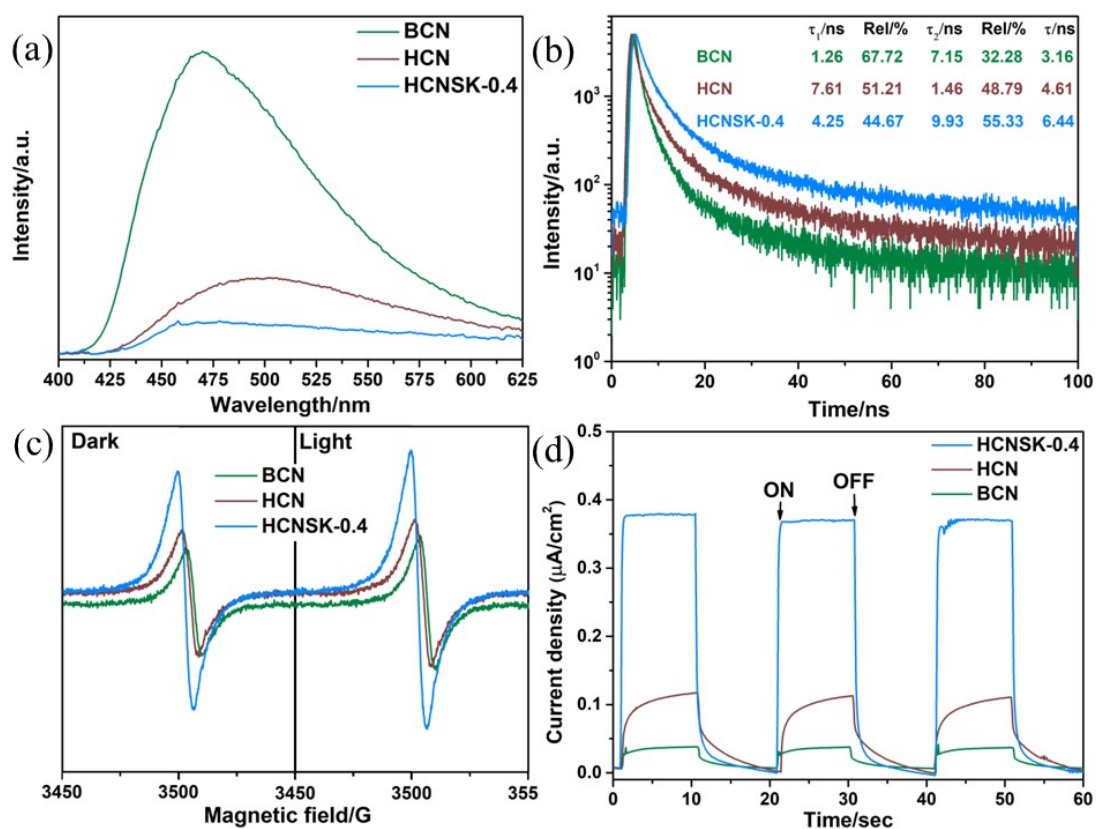


Fig. S6 (a) PL emission spectra and (b) Fluorescence lifetime decay curves of BCN, HCN, and HCNSK-0.4. (c) Room-temperature solid-state EPR spectra. (d) Periodic on/off photocurrent responses in a 0.5 M Na_2SO_4 electrolyte under visible-light irradiation ($\lambda > 420$ nm) at 0.5 V vs. Ag/AgCl electrode. The double-exponential

function was used to fit the fluorescence lifetime decay curves. The function is according to Eq. (5). And the weighted mean lifetime is according to Eq. (6). The τ_1 and τ_2 are short lifetime and long lifetime, respectively. The short lifetimes of charge carriers for HCNSK-0.4 and HCN are 4.25 ns (44.67%) and 7.61 ns (51.21%), respectively, compared to 1.26 ns (67.72%) for BCN. While the long lifetime increase from 7.15 ns with 32.28% for BCN to 9.93 ns with 55.33% for HCNSK-0.4.

$$I(t) = f_1 e^{-t/\tau_1} + f_2 e^{-t/\tau_2} + I(0) \quad (5)$$

$$\tau = (f_1 \tau_1^2 + f_2 \tau_2^2) / (f_1 \tau_1 + f_2 \tau_2) \quad (6)$$

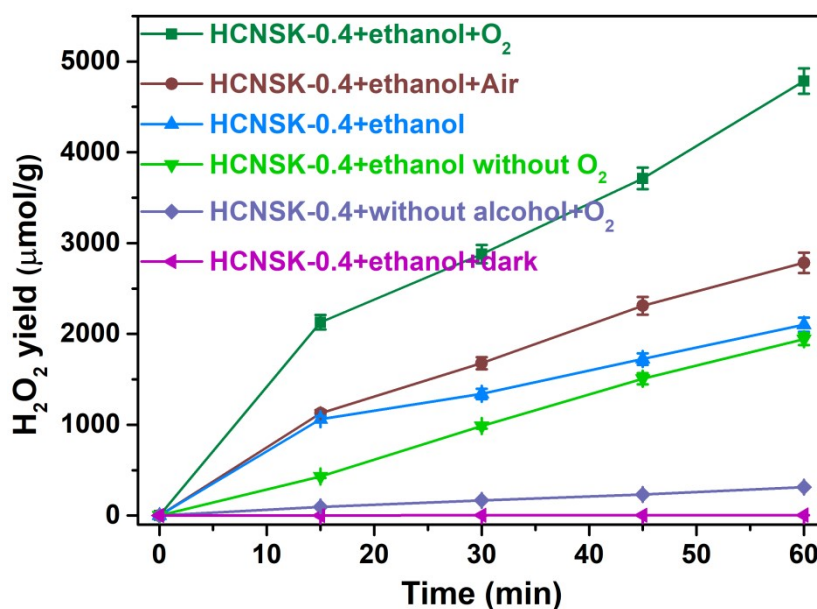


Fig. S7 Comparative H₂O₂ production activity of HCNSK-0.4 in pure water and ethanol, respectively. Firstly, the H₂O₂ production of HCNSK-0.4 in dark condition can be ignored. Moreover, after pumped N₂ into the reaction solution to remove the dissolved oxygen, the H₂O₂ production is much lower than that of without any operation at first 15 min. And then, with the progress of the reaction, its yield gradually increased and finally approached HCNSK-0.4+ethanol. The results means that the reaction solution of HCNSK-0.4 can quickly absorb oxygen from the air.

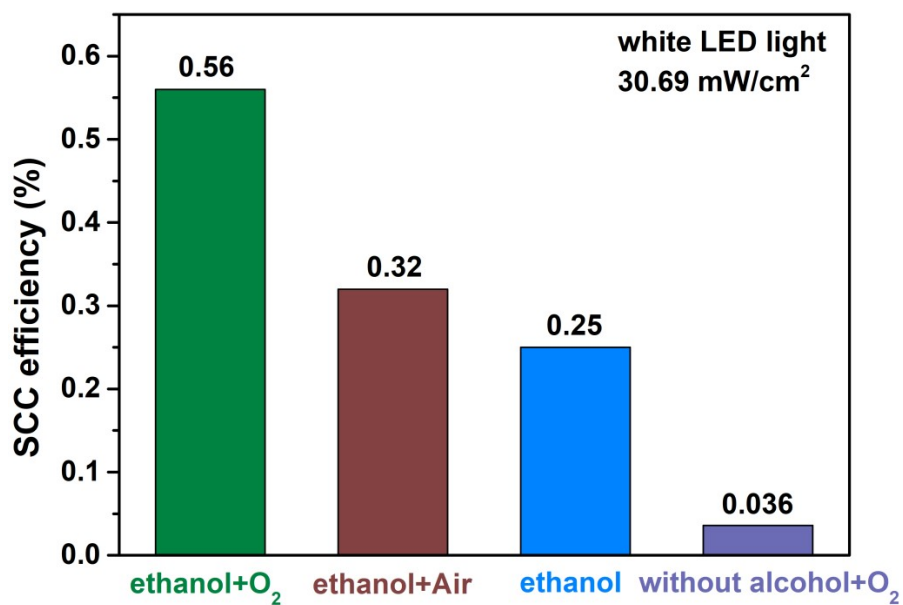


Fig. S8 The SCC efficiency of HCNSK-0.4.

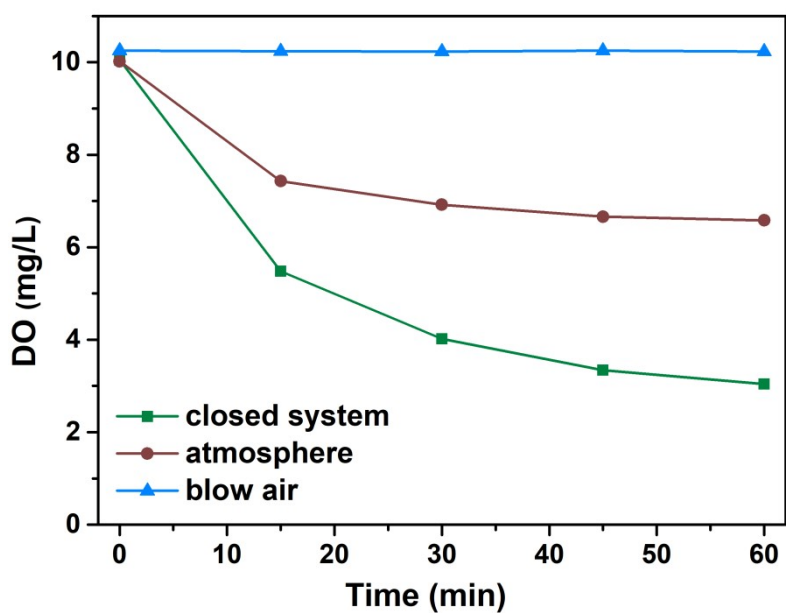


Fig. S9 The dissolved oxygen (DO) concentrations of reaction solution for HCNSK-0.4.

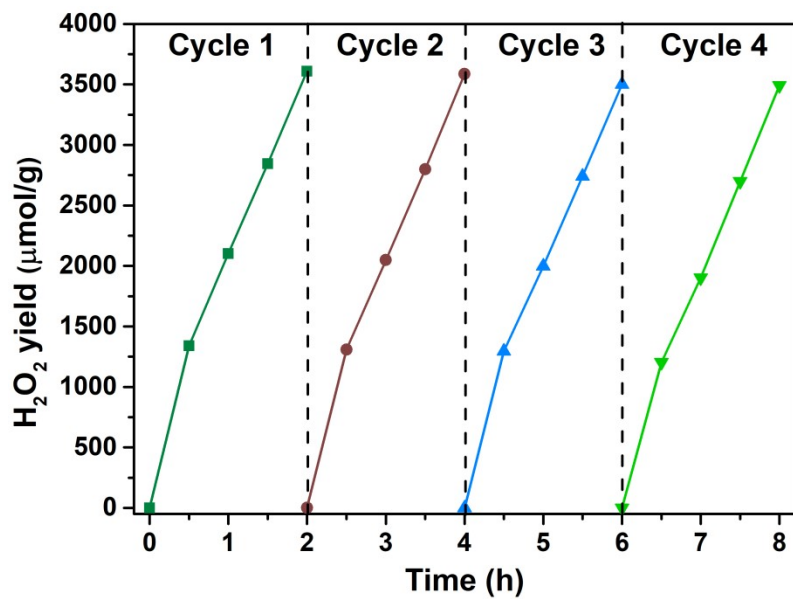


Fig. S10 Time course of the production of H₂O₂ employing HCNSK-0.4 under white LED light.

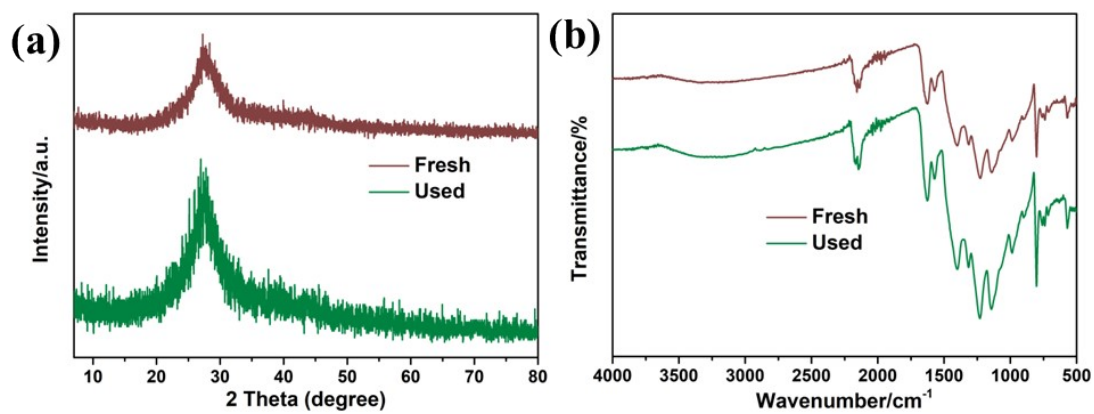


Fig. S11 (a) XRD patterns and (b) FTIR spectra of the fresh and used HCNSK-0.4.

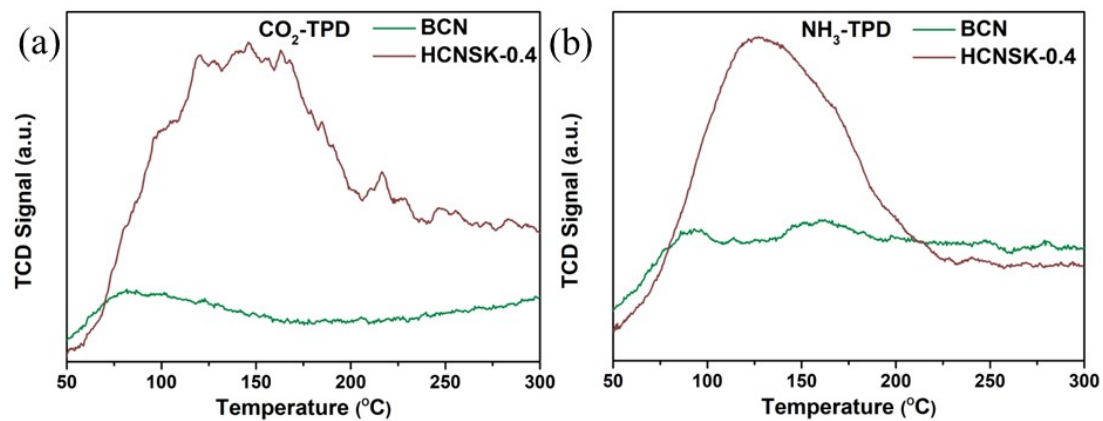


Fig. S12 (a) CO₂-TPD on BCN and HCNSK-0.4. (b) NH₃-TPD on BCN and HCNSK-0.4.

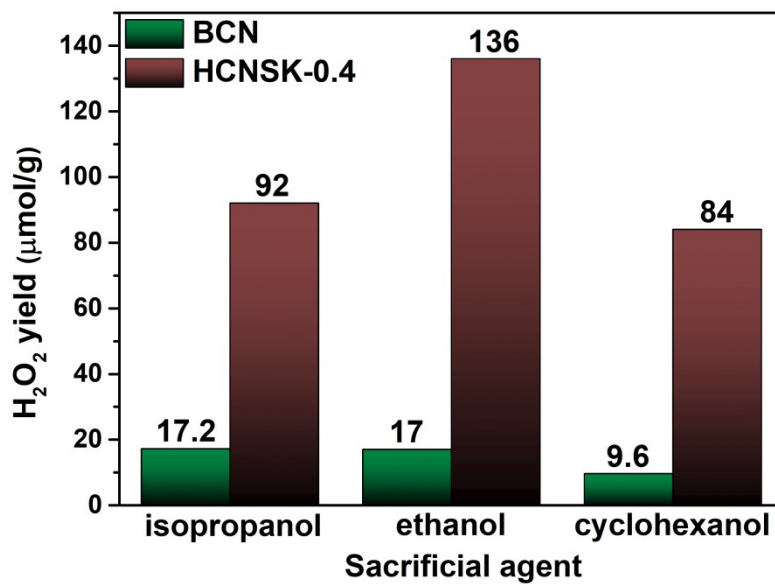


Fig. S13 Photocatalytic productions of H₂O₂ by BCN and HCNSK-0.4 in different alcohols under white LED light.

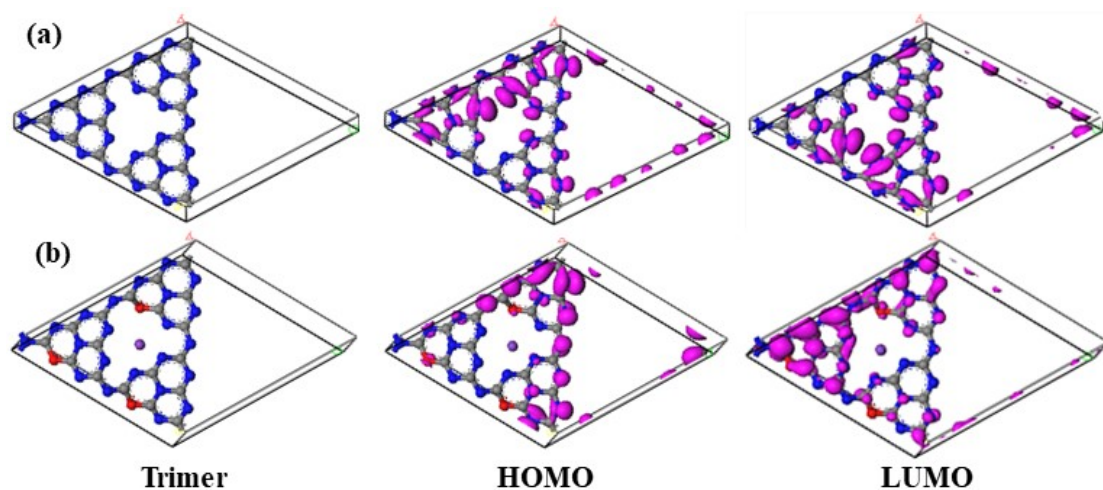


Fig. S14 Electronic structures of polymeric models for (a) BCN and (b) HCNSK-0.4 together with their optimized HOMO and LUMO.

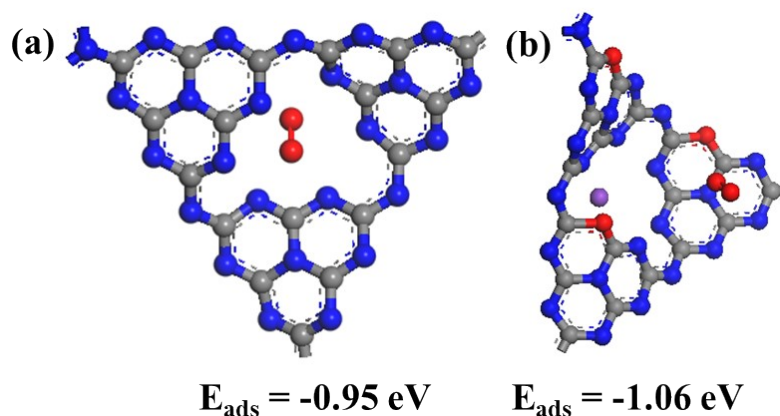


Fig. S15 Top views of the optimized geometries for the adsorbed molecular O_2 on (a) BCN and (b) HCNSK-0.4 (violet: K, blue: N, gray: C, red: O).

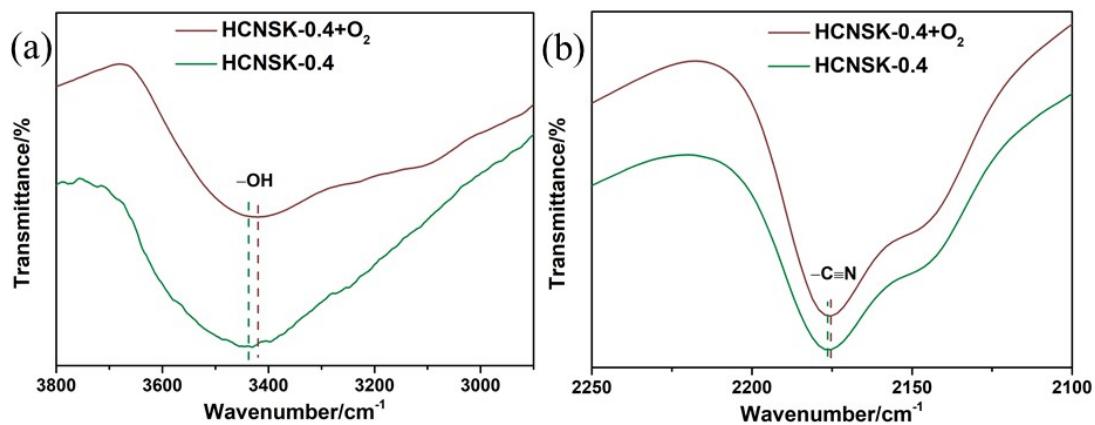


Fig. S16 The FTIR-ATR (attenuated total reflection) spectroscopic study of HCNSK-

0.4 before and after O₂ adsorption. (a) –C≡N group; (b) –OH group. Namely, HCNSK-0.4 is placed in a vacuum drying oven for dehydration and degassing. Take a part of the sample into a 5 mL centrifuge tube and continuously inject oxygen for 5 min. And then, the FTIR-ATR spectra of them are measured quickly. From the results, after O₂ adsorption, the peaks of the –C≡N group and –OH group show a right-shift slightly, which may be caused by O₂ adsorption of –C≡N/–OH groups.

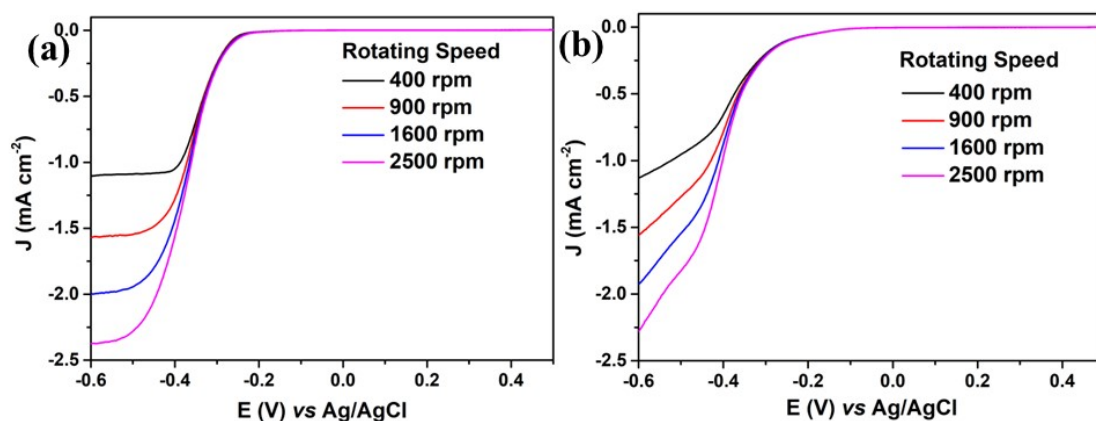


Fig. S17 LSV curves of (a) HCNSK-0.4 and (b) BCN were measured on an RDE at different rotating speeds.

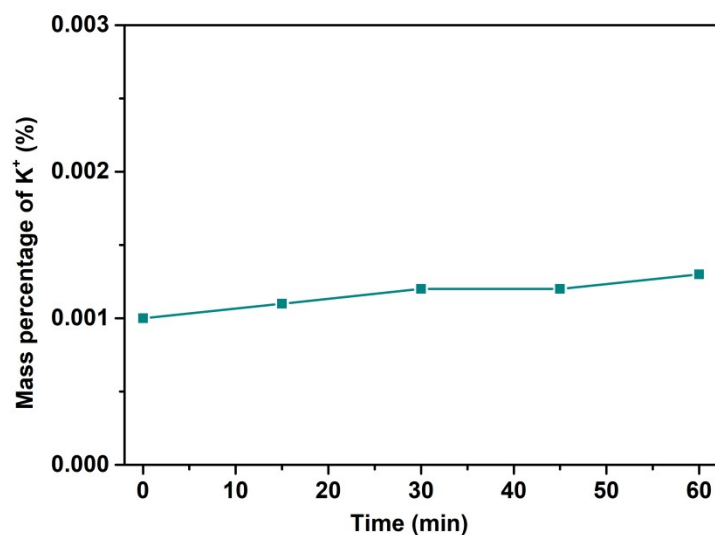


Fig. S18 The mass percentage of K⁺ in the reaction solution from inductively coupled plasma (ICP). The leakage of K⁺ for HCNSK-0.4 in the reaction solution during the reaction process can be ignored. Furthermore, the mass percentage of K⁺ for HCNSK-0.4 is 13.07%.

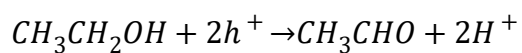


Fig. S19 The reaction process of ethanol as the sacrificial reagent during photocatalytic H₂O₂ production reaction.

Table S1 XPS peak area ratio of the as-prepared samples.

Sample	N 1s			C 1s
	C–N=C	N–(C) ₃	C–N–H	C–C
BCN	52.39%	30.39%	17.22%	28.08%
HCN	52.87%	29.91%	17.22%	13.47%
HCNSK-0.4	52.15%	33.97%	13.88%	31.39%

Reference:

1. Y. Zhao, P. Zhang, Z. Yang, L. Li, J. Gao, S. Chen, T. Xie, C. Diao, S. Xi, B. Xiao, C. Hu and W. Choi, *Nat. Commun.*, 2021, **12**, 3701-3711.