Supplementary Material

K/O co-doping and introduction of cyano groups in polymeric carbon nitride towards efficient simultaneous solar photocatalytic water splitting and biorefinery

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1. Experimental section

1.1 Materials

Xylose ($C_5H_{10}O_5$, ≥ 99%), glucose ($C_6H_{12}O_6$, 96%), fructose ($C_5H_{10}O_5$, ≥ 99%), mannose ($C_6H_{12}O_6$, 99%), rhamnose ($C_6H_{12}O_5 \cdot H_2O$, 99%), arabinose ($C_5H_{10}O_5$, 98%), benzoquinone (BQ), ethylenediaminetetraacetic acid (EDTA), isopropyl (IPA), tryptophan (TRP) and chloroplatinic acid hexahydrate (>99%, $H_2PtCl_6 \cdot 6H_2O$) were all purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Anhydrous ethanol was purchased from Tianjin Kermio Chemical Reagent Co., Ltd. Potassium hydroxide (KOH) was obtained from Sinopharm Chemical Reagent Co., Ltd. All solutions were prepared from ultrapure (Milli-Q) water. All the chemicals and solvents were analytical grade.

1.2 Characterization

The equipment used for characterization is introduced in detail, namely scanning electron microscope (SEM), transmission electron microscopes (TEM), Brunauer-Emmett-Teller (BET), powder x-ray diffraction (XRD), Fourier infrared (FT-IR), x-ray photoelectron energy spectrometer (XPS), ultraviolet-visible diffuse reflectance spectrometer (UV-vis DRS), Mott-Schottky (M-S), ultraviolet photoelectron spectroscopy (UPS), transient photocurrent responses, electrochemical impedance spectroscopy (EIS), photoluminescence (PL), electron spin-resonance (ESR), Same as previous reports [1,2].

2. Results and discussion

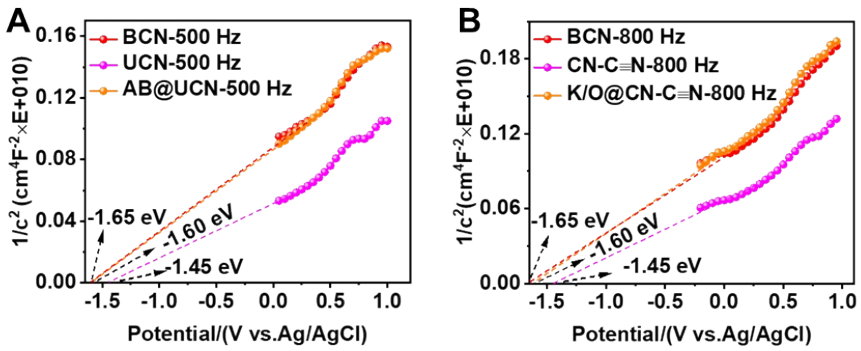

Fig. S1 Mott-Schottky plots of BCN, CN-C≡N and K/O@CN-C≡N at frequencies of

500 Hz (A) and 800 Hz (B) in 0.5 M Na_2SO_4.

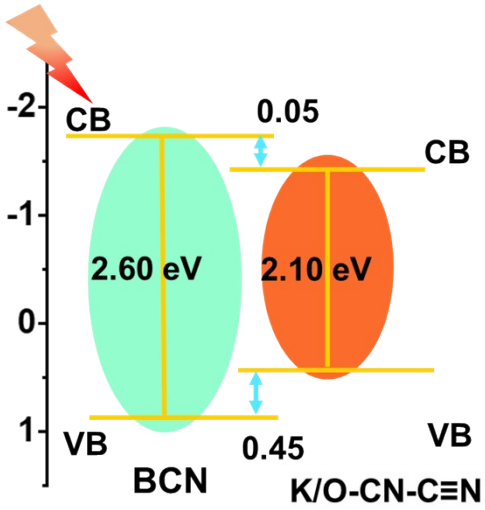

Fig. S2 Relative band alignment of BCN and K/O@CN-C≡N.

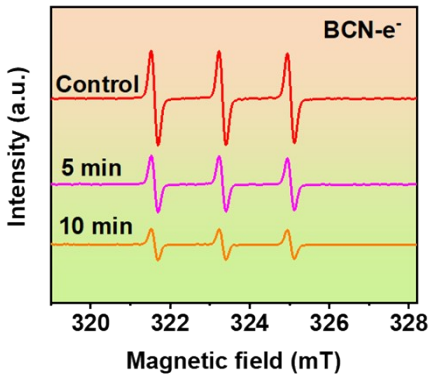

Fig. S3 TEMPO ESR spin-labeling for e^-.

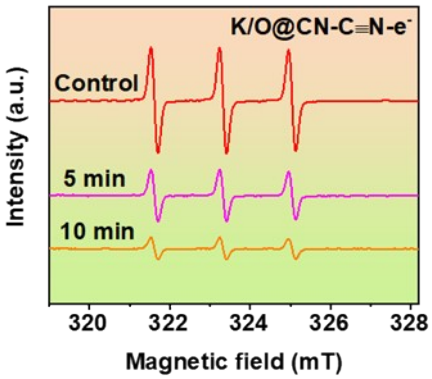

Fig. S4 TEMPO ESR spin-labeling for e^-.

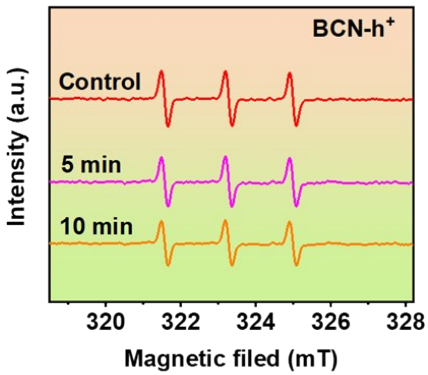

Fig. S5 TEMPO ESR spin-labeling for h^+.

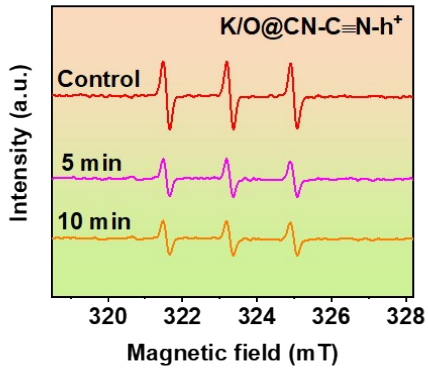

Fig. S6 TEMPO ESR spin-labeling for h^+.

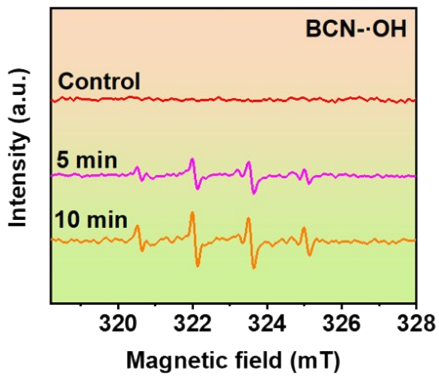

Fig. S7 DMPO ESR spin-labeling for ·OH.

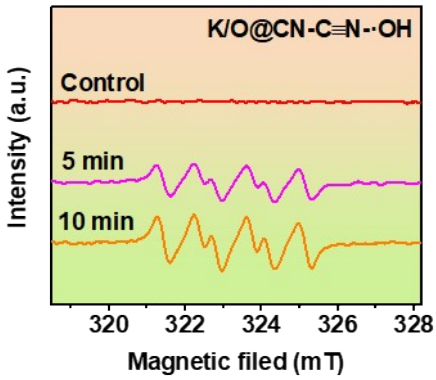

Fig. S8 DMPO ESR spin-labeling for ·OH.

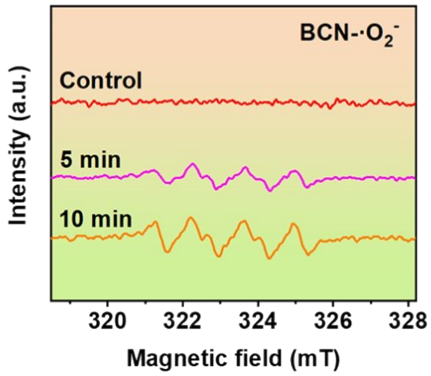

Fig. S9 DMPO ESR spin-labeling for $\cdot O_2^-$.

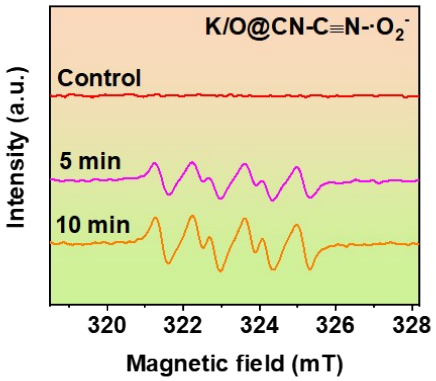

Fig. S10 DMPO ESR spin-labeling for $\cdot O_2^-$.

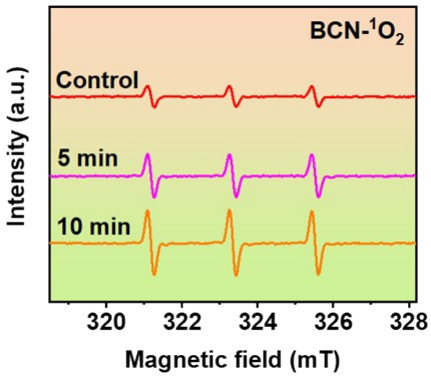

Fig. S11 TEMPONE ESR spin-labeling for $^1O_2$.

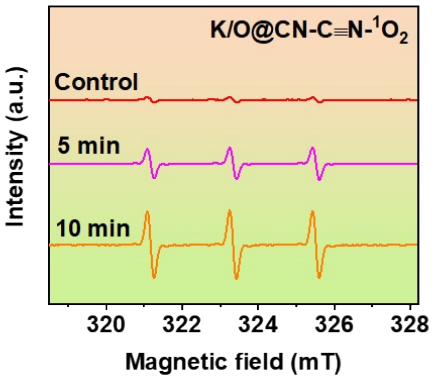

Fig. S12 TEMPONE ESR spin-labeling for $^1O_2$.

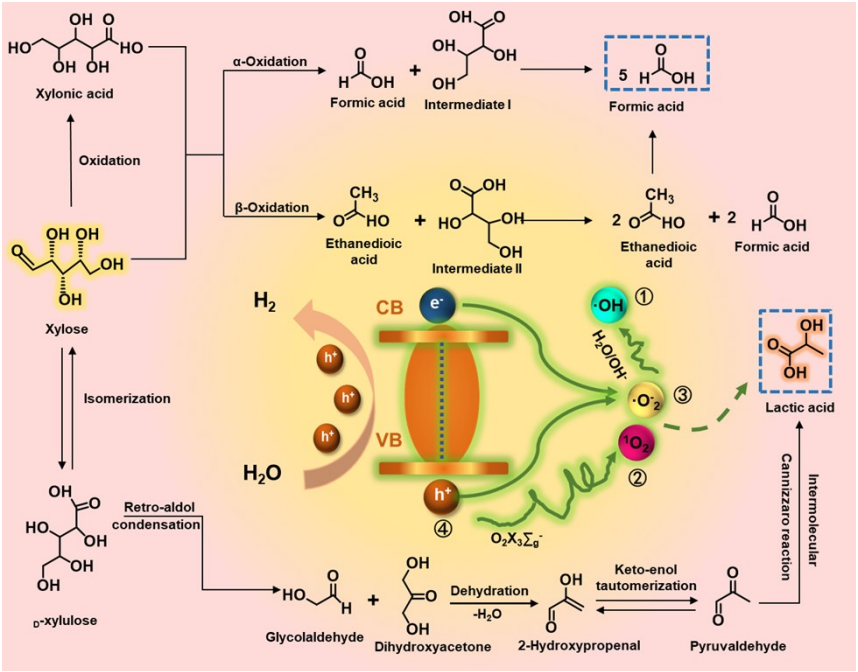

Fig. S13 Possible reaction pathway for the conversion of xylose photocatalyzed by K/O@CN-C≡N under visible-light irradiation.

Table S1 The effects of different catalysts on hydrogen production under different conditions were studied.

Entry	Photocatalysis	Hydrogen evolution rate ($\mu mol \cdot h^{-1} \cdot g^{-1}$)	References
1	K/O@CN-C≡N [a]	33380	This word
2	Nic-CN	6310	3
3	NMS/SCN	658.5	4
4	K-Na-CCN	1380.1	5
5	UCN	590	6

Reaction conditions: [a] 0.8 mL H_2PtCl_6, 6 h; [b] 1 wt% Pt, 1 h; [c] 10 mL triethanolamine, 4 h; [d] 3 wt%, 4 h; [f] 3 wt% Pt, 6 h.

Table S2 The effects of different catalysts on synthesis of lactic acid at various conditions.

Entry	Sample	Thermo-catalysis	Photocatalysis	Conversion (%)	Yield (%)	References
1	Xylose		K/O@CN-C≡N [a]	95.0	86.6	This work
2			CuO@CS-H [b]	100.0	81.6	7
3			B@*m*CN [c]	99.9	79.1	2
4		Sn-β [d]		-	70.0	8
5		ZrO_2 [e]		-	42.0	9
6		$LaCoO_3$ [f]		-	37.9	10
7	Glucose		K/O@CN-C≡N [a]	88.0	63.6	This work
8			CuO@CS-H [b]	98.2	54.2	7
9		Na_2O_5 Nanorod [g]		99.0	39.0	11
10		Sn-Beta-NH_2 [h]		99.9	56.0	12

Reaction conditions: [a] 30 °C, 6 h; [b] 60.0 °C, 90.0 min; [c] 60 °C, 90 min; [d] 200 °C, 60 min; [e] 200 °C, N_2: 24 MPa 40 min; [f] 200 °C, N_2: 200 psi, 1 h; [g] 250 °C, 4 h; [h] 190.0 °C, 120 min.

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