

Supporting Information:

**Photocatalytic selective oxidation of
biomass-derived 5-hydroxymethylfurfural to
2,5-diformylfuran under ambient conditions
over CdIn₂S₄/g-C₃N₄ heterojunctions**

Jifang Cui, Zhihao Yu, Linhao Sun, Ming Zhang, Mengyan Guo, Jian Xiong, Yina Qiao, Rui Zhang,
Xuebin Lu**

1. Experimental details

1.1 Characterization of the materials

The X-ray diffraction spectra of the samples were measured on a BRUCKER D8 ADVANCE X model X-ray powder diffractometer from Bruker, Germany, using a Cu target (wavelength $\lambda = 1.5406 \text{ \AA}$), a Co target (wavelength $\lambda = 1.79026 \text{ \AA}$), a scan rate of $5^\circ/\text{min}$ and a sample scan range of 5 to 80° at a current of 40 mA and a voltage of 40 kV . Afterwards, to further observe the sample structure, the specific internal morphology and microstructure of the samples were observed with a field emission scanning electron microscope (SEM) (Hitachi SU8020). After this, the specific internal morphology and microstructure of the samples were observed with a transmission electron microscope (TEM) (FEI Tecnai G2 F30) at an accelerating voltage of 200 kV and analyzed together with the SEM. X-ray photoelectron spectroscopy (XPS) spectral profiles were obtained with a Thermo escalab 250Xi and then analyzed. A QUANTAS EDS X-ray spectrometer from Bruker, Germany, was used to test the microscopic morphology and metal element distribution of the catalysts. Nitrogen adsorption and desorption isotherms were obtained using an ASAP 2460 model physisorption instrument at 77.3 K . Before nitrogen adsorption, the samples were degassed at 200°C for 12 h . After completion of the measurements, the specific surface area of the catalyst was calculated by the BET (Brunauer-Emmett-Teller) method, and the pore size of the catalyst was calculated by the BJH (Barrett-Joyner-Halenda) method. Photoluminescence Spectroscopy (PL) was carried out on an FLS1000/FS5 model steady-state transient fluorescence spectrometer with an excitation wavelength of 380 nm . The characteristic functional group identification of the catalysts was tested using a Nicolet IS10 model infrared spectrometer manufactured by Nicolet, USA. The resolution of the spectrometer was 4 cm^{-1} and the signal to mania ratio was $50000:1$ with 32 scans. The wave number range was $400\text{-}4000 \text{ cm}^{-1}$. Sample preparation was carried out using KBr compression (tableting method), where the sample and KBr were mixed and ground in an agate mortar body at a mass ratio of $120:1$, then compressed, and the resulting homogeneous tablets were used for analytical testing. Cyclic experiments were carried out to prepare DFF by photocatalytic oxidation of HMF using a composite catalyst under the same reaction conditions. At the end of each reaction, the catalyst was separated from the solution using high-speed centrifugation, followed by continued centrifugation with water washing three times and alcohol washing three times, and the final separated solids were recovered by drying them in a vacuum drying oven at 60°C for 12 h , and then the reaction was continued.

2. Supporting Figures and Tables

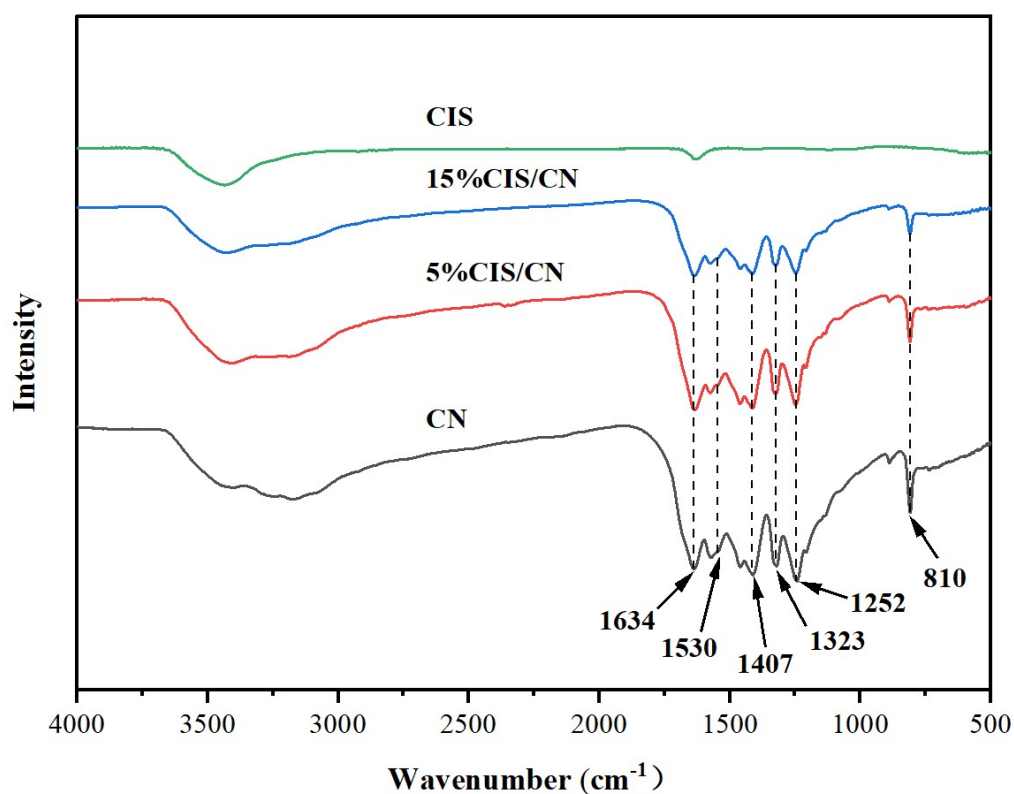


Figure S1. FT-IR spectra of catalysts $\text{g-C}_3\text{N}_4$ (CN), CdIn_2S_4 (CIS) and the composite catalysts 5%CIS/CN, 15%CIS/CN

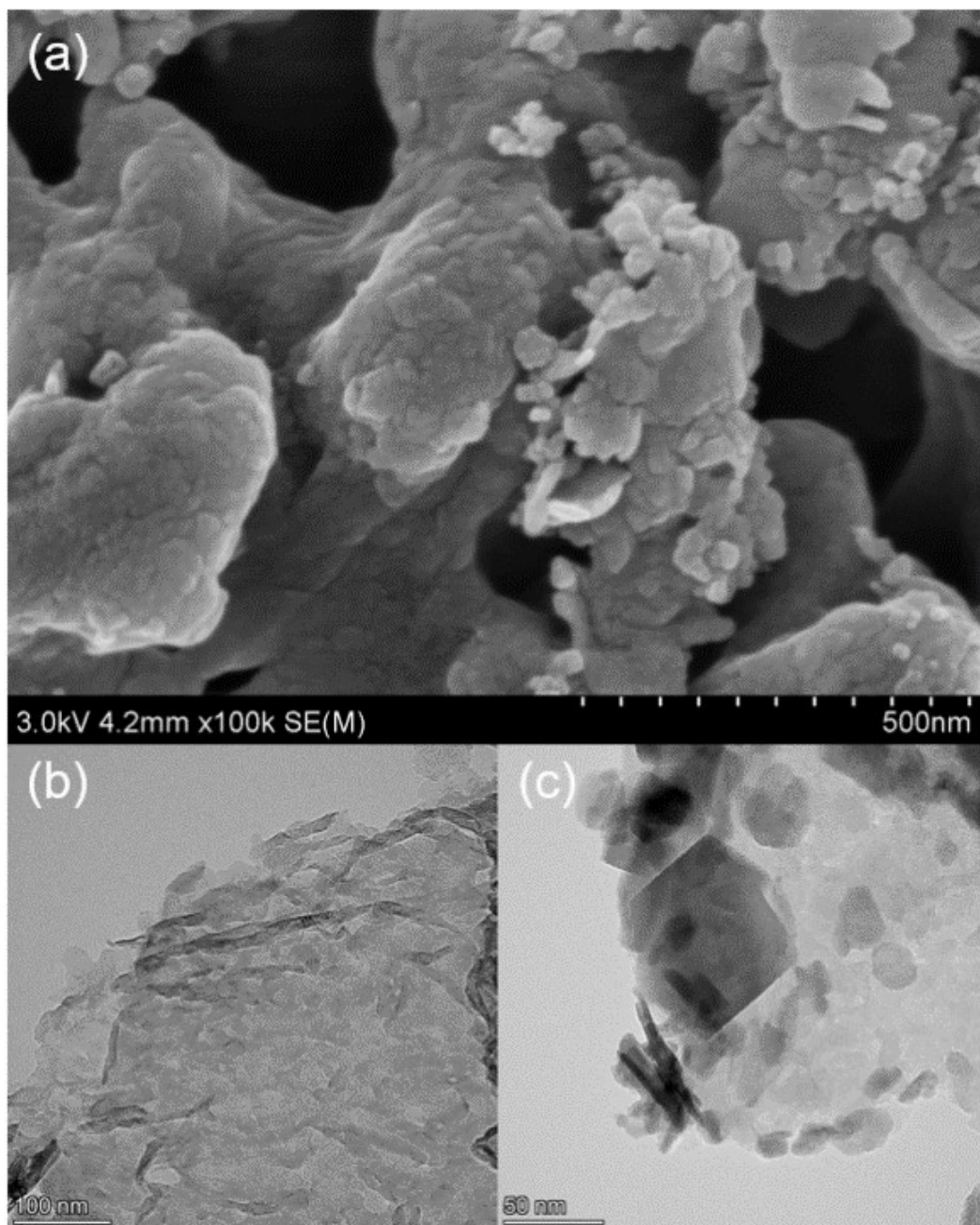


Figure S2. (a) SEM image of the mesoporous structure of g-C₃N₄ synthesized by secondary calcination. (b) SEM image of the microwave-synthesized sheet CdIn₂S₄. (c) TEM image of CdIn₂S₄/g-C₃N₄.

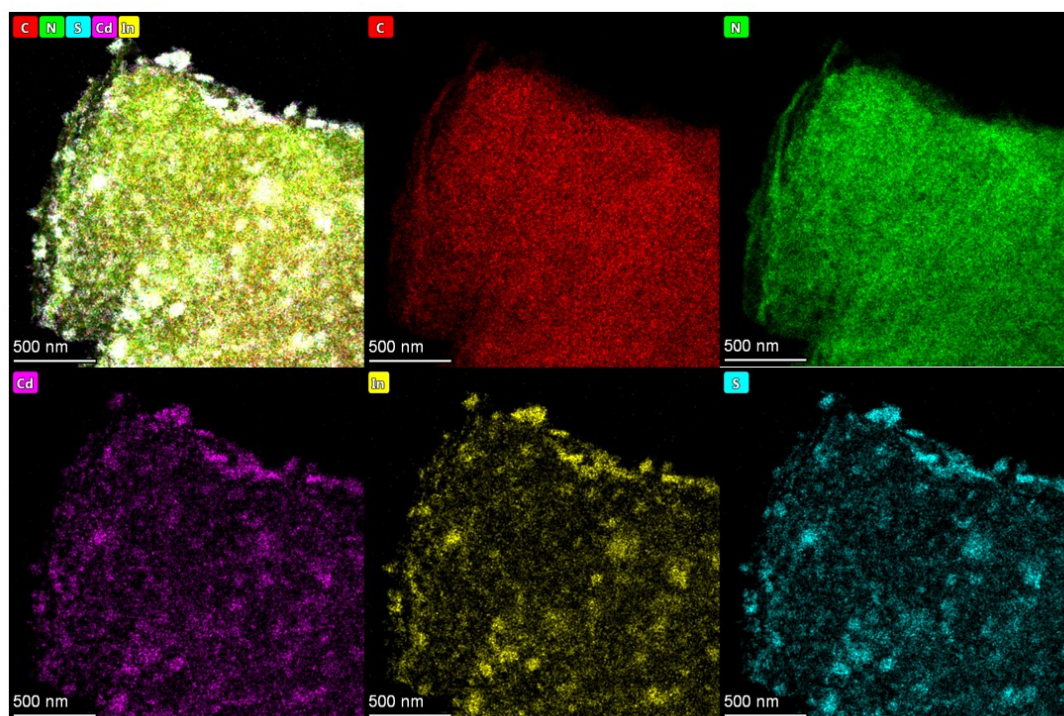


Figure S3. Elemental mapping images of N, C, In, Cd, and S in CdIn₂S₄/g-C₃N₄.

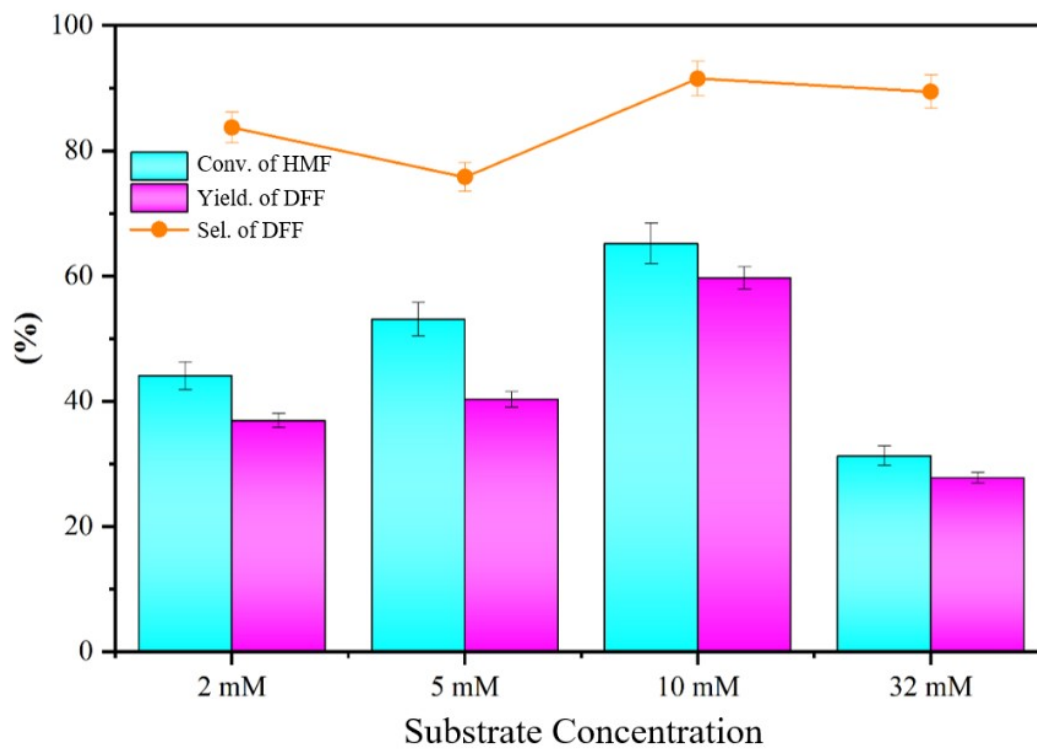


Figure S4. Effect of substrate concentration on reaction performance (reaction conditions: 40 mg of 15% CIS/CN as a catalyst, 5 mL of water as the solvent, 6 h reaction time)

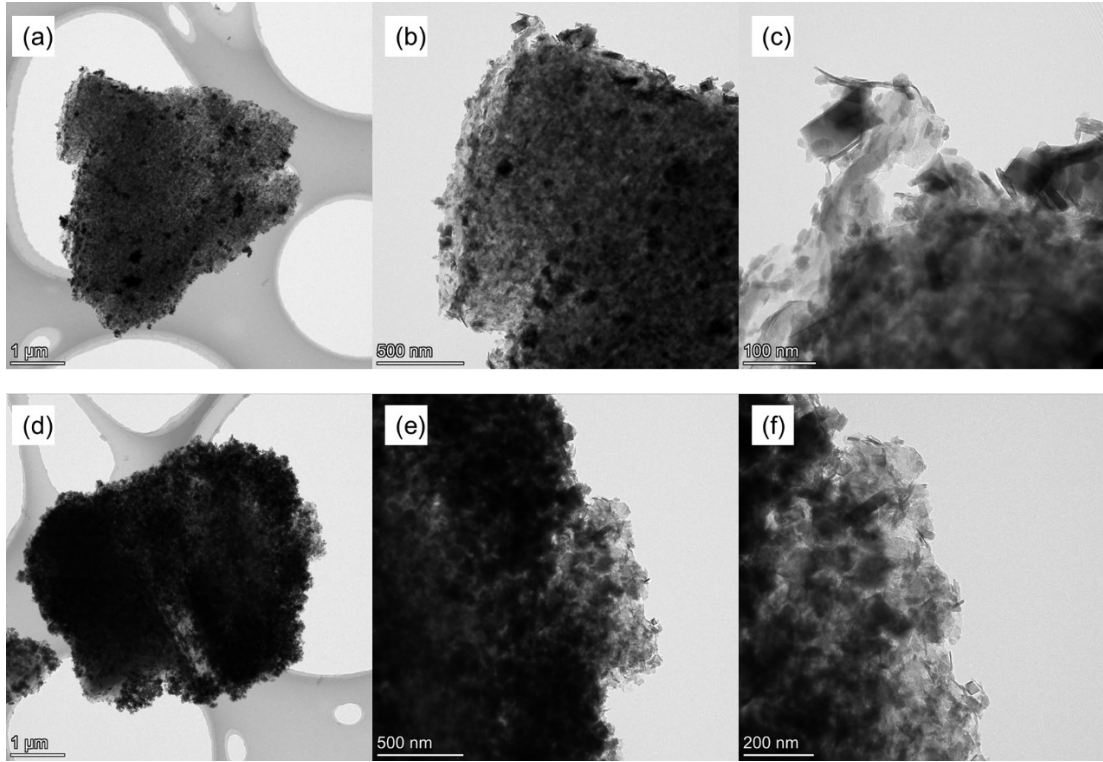


Figure S5. (a) (b) (c) and (a) (b) (c) are TEM images of 15% and 20% CIS/CN at different magnifications.

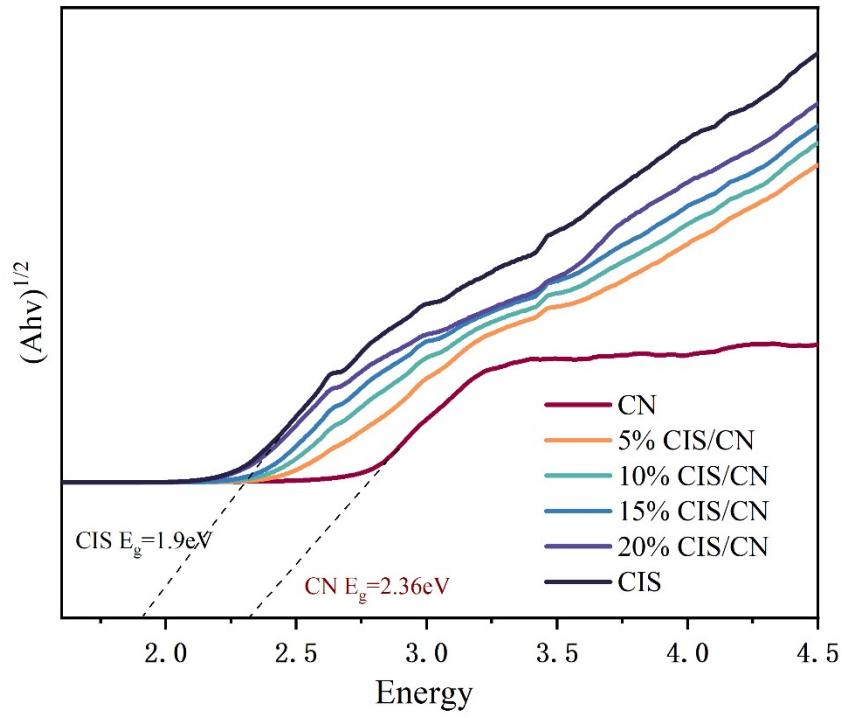


Figure S6. Plot of transferred Kubelka-Munk vs light absorbed energy of pure CdIn_2S_4 , $\text{g-C}_3\text{N}_4$ and 5%, 10%, 15% and 20% $\text{CdIn}_2\text{S}_4/\text{g-C}_3\text{N}_4$ heterojunction.

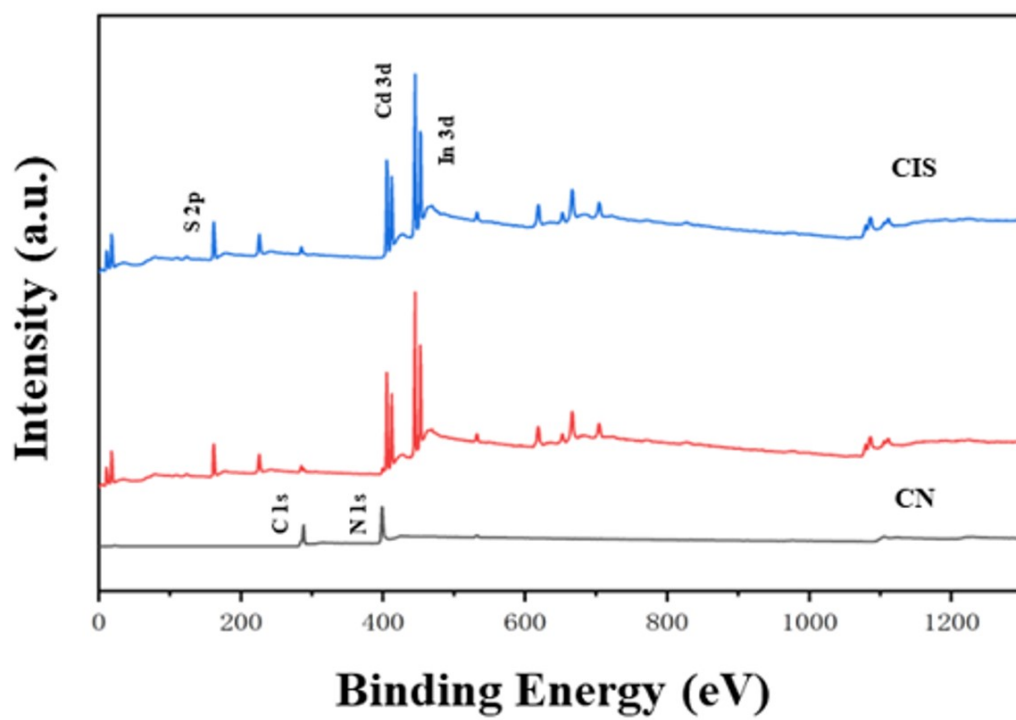


Figure S7. The survey scan spectra of XPS full spectrum.

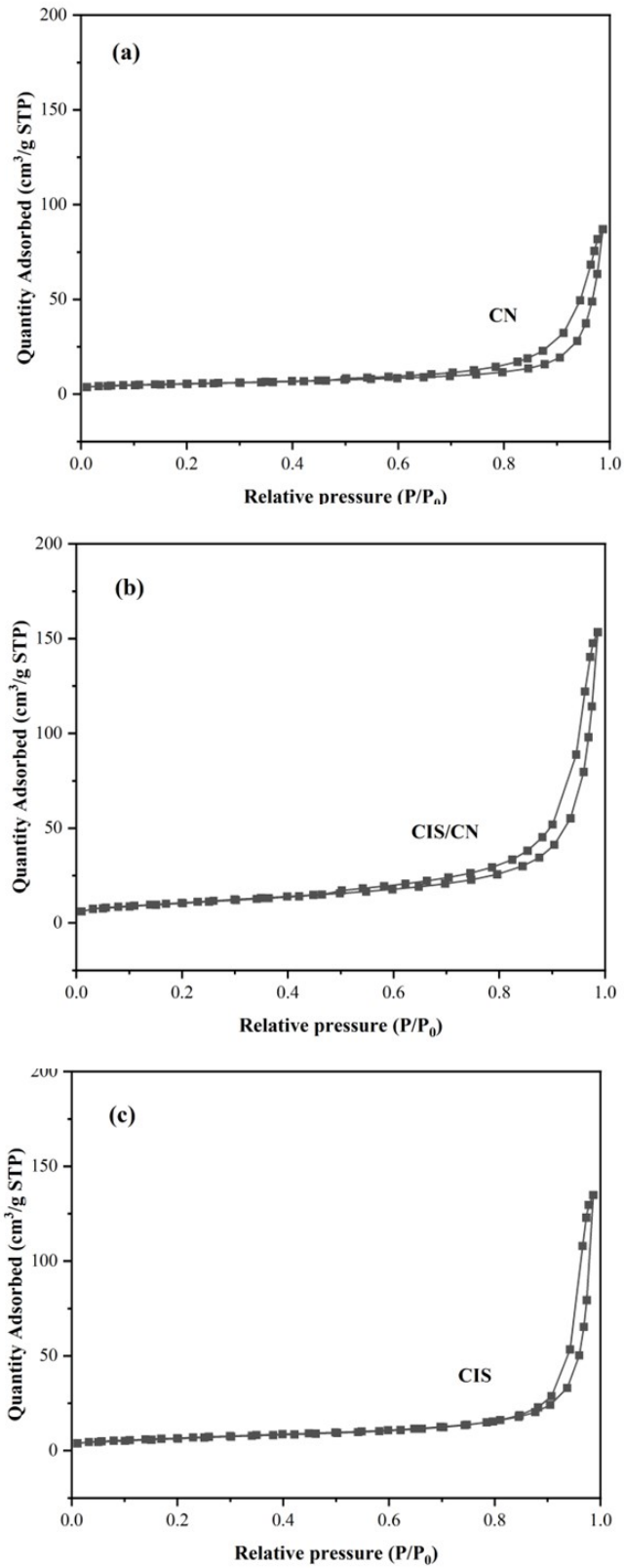


Figure S8. N_2 adsorption-desorption isotherms for catalyst CN (a), 15% CIS/CN (b), and CIS (c)

Table S1. Comparison of conditions and photocatalytic activity of different carbon nitride-based catalysts for oxidation of 5-HMF

Catalyst	Oxygen source	Solvent	Substrate concentration	Con. of HMF	Sel. of DFF	Ref.
15% CN/CIS	Air	H ₂ O	10 mM	65.2%	91.5%	This article
g-C ₃ N ₄	O ₂ 10mL·min ⁻¹	ACN+PhCF ₃	0.1 mM	31.2%	85.6%	1
Nb ₂ O ₅ /g-C ₃ N ₄	O ₂ 10mL·min ⁻¹	ACN+PhCF ₃	0.1 mM	25.1%	91.2%	2

Table S2. Structural parameters of the different catalysts

Catalysts	BET specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)
CN	19.28	0.129	26.75
15% CIS/CN	38.77	0.231	23.87
CIS	24.37	0.199	32.65

References:

1. Q. Wu, Y. He, H. Zhang, Z. Feng, Y. Wu and T. Wu, *Molecular Catalysis*, 2017, **436**, 10-18.
2. H. Zhang, Q. Wu, C. Guo, Y. Wu and T. Wu, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 3517-3523.