Supporting Information

Enzyme-mimic single atoms enable selectivity control in visible-light-driven oxidation/ammoxidation to access bio-based nitriles

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1. Experimental section

Preparation of CN: 5 g melamine was added to a ceramic crucible at 550 ℃ for 4 h with a heating rate of 5 ℃/min, then the solid sample was washed with deionized water and ethanol absolute 3 times, and dried at 80 ℃ for 12 h in the oven to obtain CN.

Preparation of CNS: 5 g melamine and 0.1 g L-cysteine were ground uniformly and then transferred to a ceramic crucible for reaction at 550 ℃ for 4 h with a heating rate of 5 ℃/min. After the reaction, the obtained sample was washed with deionized water and ethanol solution 3 times and dried at 80 ℃ for 12 h in the oven to furnish CNS.

2. Characterization of photocatalysts

The sample crystal structures and phase compositions were performed using powder X-ray diffraction (XRD, Rigaku Ulitma IV) fitted with an optical source Cu Kα radiation (λ = 1.54178 Å) in the 2θ angle range of 5°-90° at 36 kV and 20 mA. Raman spectrum was tested using Invia Reflex (Renishaw). To observe the external morphology and microstructure of the photocatalysts, scanning electron microscope (SEM, JSM-7800F) and transmission electron microscope (TEM, JEM-2800F) were operated at the acceleration voltage of 15 kV and 200 kV, respectively. The elemental composition and chemical state of the samples were analyzed by X-ray photoelectron spectrometer (XPS, Thermo Scientific ESCALAB 250Xi) with Al anode target X-ray source. The XPS test was run under a voltage of 16 kV and a current of 15 mA. X-ray absorption fine structure spectroscopy (XAFS) data reduction and analysis were processed by the Athena software. The iron content in the catalyst was determined by ICP-AES on an Agilent 720ES instrument. The catalyst functional groups were determined by KBr compression using Nicolet 360 FT-IR (Fourier-transform infrared) apparatus. The specific surface areas and pore size distribution of the samples were carried out by Brunauer-Emmett-Teller (BET, TriStar II 3020). The ultraviolet-visible diffuse reflectance spectrum (UV-Vis DRS) was measured using PERKIN-ELMER Lambda 950 using $BaSO_4$ as a reference object in the detection range of 200-800 nm. The recombination rate of photogenerated electrons and holes was explored by

photoluminescence (PL, Edinburgh FLS1000) with an excitation light resource of 270 nm at room temperature. Electro spin-resonance (ESR) spectra of all samples were detected by a Bruker A300 spectrometer.

3. Photoelectrochemical measurements

The photoelectric properties were tested by electrochemical impedance spectroscopy (EIS) at the electrochemical workstation CHI760E. A 300 W Xe lamp was used as the light source. The conventional standard three-electrode system was utilized. The 1 × 1 cm Pt sheet was applied as the counter electrode and the saturated calomel electrode as the reference electrode. The electrolyte was obtained by deoxidizing 0.5 M Na_2SO_4 solution in a high-purity N_2 atmosphere for 1 h. The working electrode was prepared by coating the surface of the conductive glass with the prepared catalyst suspension. Firstly, 5 mg of the catalyst was dispersed in 350 μL of isopropanol solution. Secondly, 50 μL of 10% Nafion was added to the dispersion as a flocculant, followed by ultrasonic treatment for 30 min. Finally, 10 μL of suspension was dropped onto the surface of the glassy carbon electrode. The EIS was conducted in the frequency range of $0.01\text{-}10^5$ Hz.

4. Computational methods

The density of states, charge density difference and adsorption energy: The density functional theory (DFT) calculations were conducted by the CASTEP module implemented in Material Studio. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation function was used to describe the exchange-correlation effects. Interaction between the valence electrons and the ion core was substituted by an ultrasoft pseudopotential. We used the plane wave basis with a cut-off energy of 400 eV, self-consistent field (SCF) tolerance of 1×10^{-5} eV, maximum force 0.002 Hartree per Å, maximum displacement 0.005 Å, and Gaussian electron smearing width 0.005 eV for the geometry optimization, respectively.

ESP mapping, Hirshfield charge and Fukui index: The DFT calculations were performed on a Gaussian 16C. 01 program package.[S1-S3] The geometry optimization

was performed first according to B3LYP theoretical method on a standard 6-31+G(d, p) basis set, and then single-point energy calculations were obtained.

5. Product analysis

For the liquid products, quantitative and qualitative analyses were performed by gas chromatography (GC, Agilent 7890B) with an HP-5 capillary column (30 m × 0.320 mm × 0.25 μm) and flame ionization detector (FID) detector, and gas chromatography-mass spectrometry (GC-MS, Agilent 6890N GC/5973 MS, Santa Clara, CA), respectively. Naphthalene (15 mg) was used as the internal standard by referring to the standard curves prepared by commercial samples (containing $R^2 > 0.9996$). The substrate conversion and product yield were calculated by the following equations:

$$\text{Conversion (\%)} = 1 - \frac{\text{mole of residual substrate}}{\text{mole of initial substrate}} \times 100\%$$

$$\text{Yield (\%)} = \frac{\text{mole of product}}{\text{mole of initial substrate}} \times 100\%$$

6. Supplementary Tables and Figures

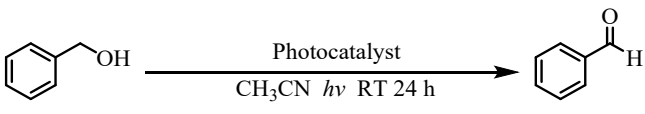**Table S1.** ICP-OES results for Fe/CNS.

Sample	Weight (g)	Constant volume (mL)	Element	Element content (mg/L)	Dilution times	Element content (mg/kg)	Element content (wt%)
Fe/CNS	0.0234	25	Fe	1.6720	10	17863.7	1.7864%

**Table S2.** EXAFS fitting parameters at the Fe K-edge of various samples（S_0^2=0.96）

Sample	Path	C. N.[a]	R (Å) [b]	σ^2 (× 10^{-3} Å^2)[c]	ΔE (eV) [d]	R factor[e]
Fe foil	Fe-Fe	8*	2.48*	6.2±1.1	7.2±2.3	0.01
	Fe-Fe	6*	2.87*	8.3±3.2		
Fe$_2$O$_3$	Fe-O	3*	1.98*	6.2±3.1	-3.6±2.8	0.03
	Fe-O	3*	2.13*	11.6±5.3		
	Fe-O-Fe	3*	3.00*	5.3±3.3		
	Fe-O-Fe	3*	3.42*	8.3±2.1		
Fe/CN	Fe-N	4.2±0.5	1.98±0.01	9.2±1.1	-3.4±1.2	0.01
	Fe-N-C	0.7±0.5	2.93±0.02	5.4±1.0		
Fe/CNS	Fe-N	4.1±0.8	2.00±0.01	9.4±1.9	-0.8±2.0	0.01
	Fe-N-C	2.7±2.4	3.00±0.03	13.2±2.1		

[a] C. N.: coordination numbers; [b]R: bond distance; [c]σ^2: Debye-Waller factors; [d]ΔE_0: the inner potential correction. [e]R factor: goodness of fit. *The experimental EXAFS fit by fixing C. N. as the known crystallographic value.

Table S3. Screening of different catalytic systems for the synthesis of benzaldehyde from benzyl alcohol

Entry	Photocatalyst	Oxidant	Conversion (%)	Yield (%)
1	CN	O_2	13	13
2	CNS	O_2	21	21
4	Fe/CN	O_2	58	58
5	Fe/CNS	O_2	>99	>99

Reaction conditions: 0.3 mmol substrate, 3.4 mol% photocatalyst, 1 bar O_2 balloon, 2 mL CH_3CN, 300 W Xe lamp (Perfectlight Co., CEL-HXF300-T3, $\lambda > 400$ nm), 25 °C, 24 h. Yields were determined by GC using naphthalene as the internal standard.
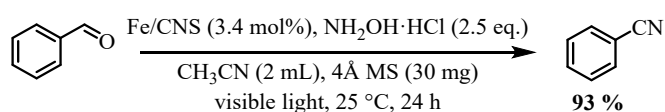
Scheme S1. Synthesis of benzonitrile from benzaldehyde. Reaction conditions: 0.3 mmol benzaldehyde, 3.4 mol% Fe/CNS, 2.5 eq. $NH_2OH \cdot HCl$, 30 mg 4 Å MS, 2 mL CH_3CN, $\lambda > 400$ nm, 25 °C, 24 h. Yields were determined by GC using naphthalene as the internal standard.
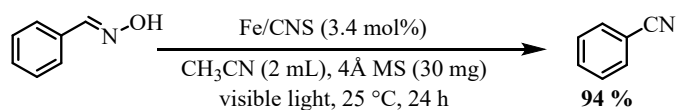
Scheme S2. Synthesis of benzonitrile from oxime. Reaction conditions: 0.3 mmol substrate, 3.4 mol% Fe/CNS, 30 mg 4 Å MS, 2 mL CH_3CN, $\lambda > 400$ nm, 25 °C, 24 h. Yields were determined by GC using naphthalene as the internal standard.
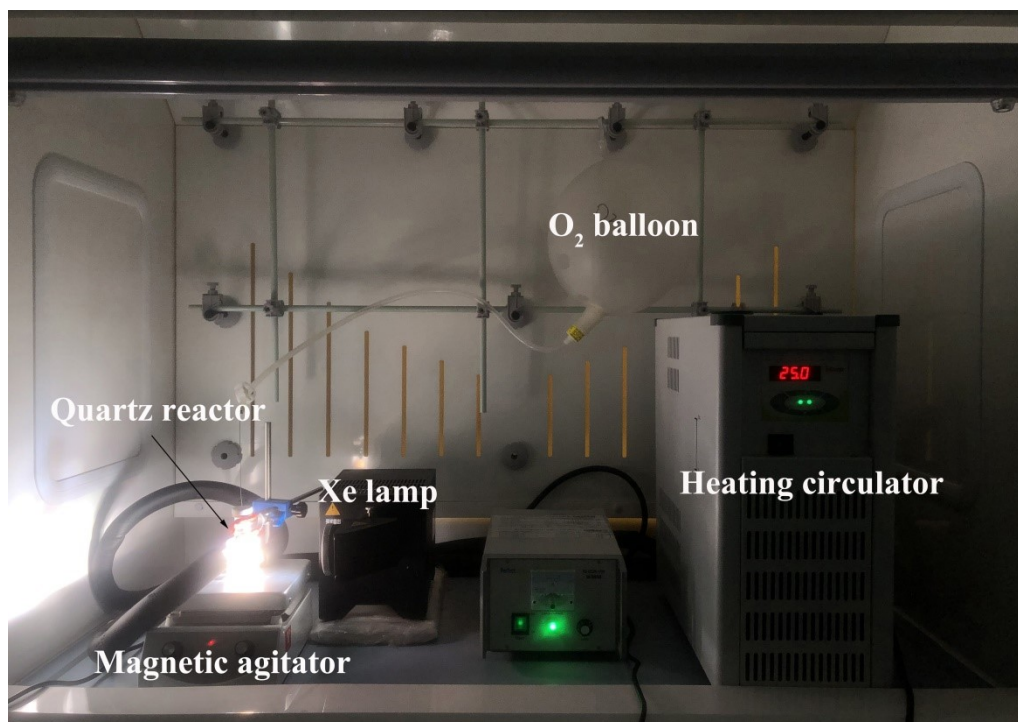
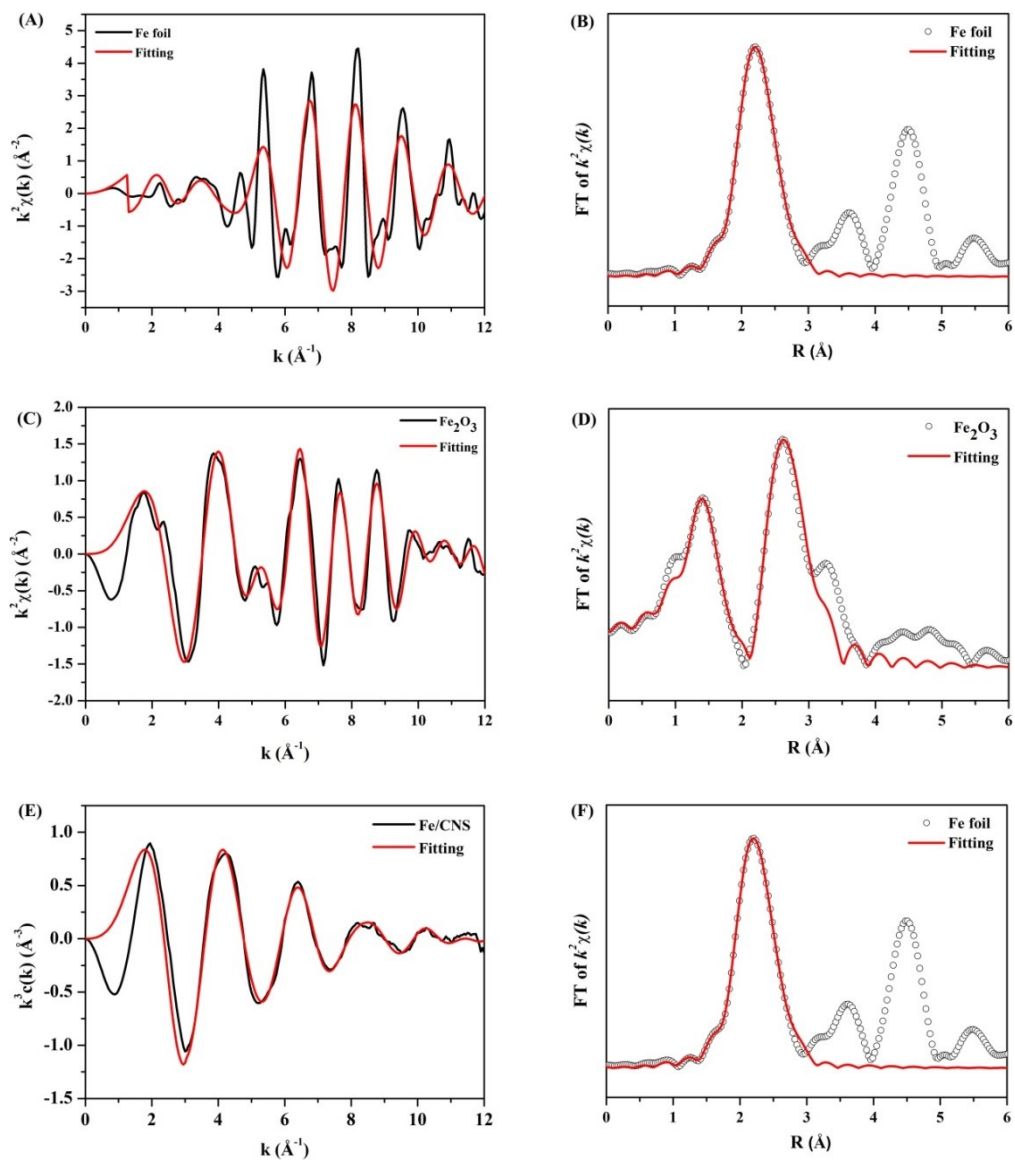**Fig. S1** Temperature-controlled photocatalytic reaction system in the lab

Fig. S2 XAFS fitting curves of CN, CNS, and Fe/CN at k space and R space.
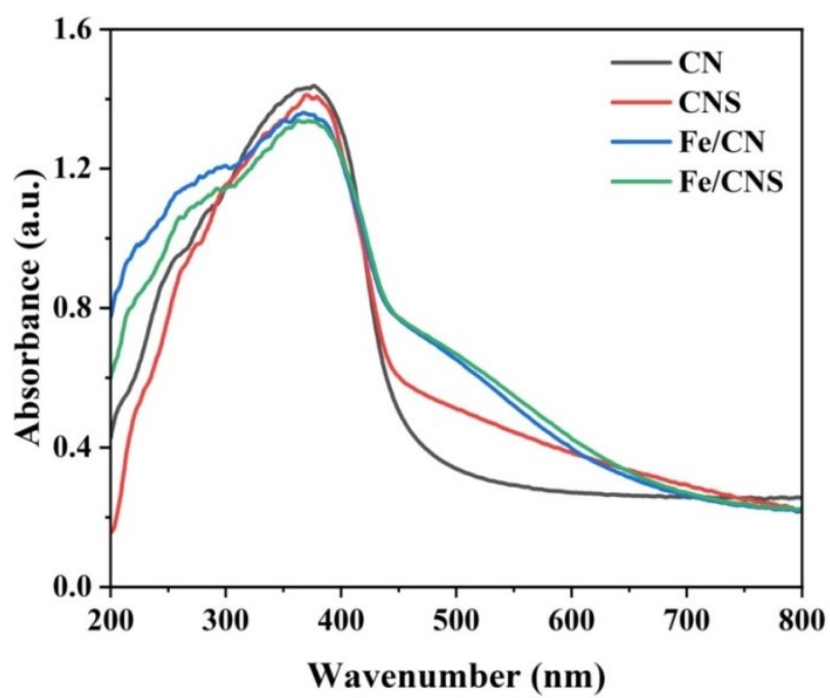
Fig. S3 UV–vis spectra of CN, CNS, Fe/CN, and Fe/CNS

To further clarify the reaction pathway of oxime **V**, DFT calculations were introduced to predict the feasibility of nucleophilic and radical attack to oxime **V**. Electrostatic potential (ESP) mapping showed that the N and O terminals presented strong negative potential (S4B), and it was speculated that electrons were easily stolen by photogenerated holes to promote the reaction. Fig. S4C depicts the calculated results on the Fukui index, in which the sites with higher f values are easier to be attacked by h^+, and the sites with higher f^0 values are easier to be attacked by $\cdot O_2^-$. It is obvious that the N8 atom on the oxime **V** is the most active site, with high f^- and f^0 values of 0.1360 and 0.1216, respectively.

(A)

(B)

(C)

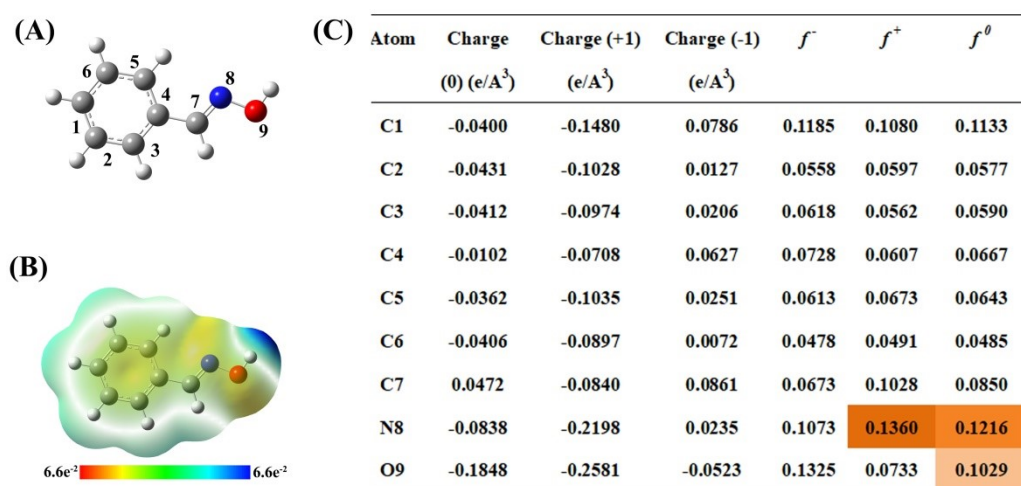| Atom	Charge (0) (e/A^3)	Charge (+1) (e/A^3)	Charge (-1) (e/A^3)	f^-	f^+	f^0
C1	-0.0400	-0.1480	0.0786	0.1185	0.1080	0.1133
C2	-0.0431	-0.1028	0.0127	0.0558	0.0597	0.0577
C3	-0.0412	-0.0974	0.0206	0.0618	0.0562	0.0590
C4	-0.0102	-0.0708	0.0627	0.0728	0.0607	0.0667
C5	-0.0362	-0.1035	0.0251	0.0613	0.0673	0.0643
C6	-0.0406	-0.0897	0.0072	0.0478	0.0491	0.0485
C7	0.0472	-0.0840	0.0861	0.0673	0.1028	0.0850
N8	-0.0838	-0.2198	0.0235	0.1073	0.1360	0.1216
O9	-0.1848	-0.2581	-0.0523	0.1325	0.0733	0.1029

Fig. S4 Chemical structure (A), ESP mapping (B), and Hirshfield charge and Fukui index (C) of oxime **V**.

The reusability of Fe/CNS was studied by catalyst cycle test in the photocatalytic conversion of benzylamine to *N*-benzylidenebenzylamine at a relatively lower conversion (less than 80%). It was found that the conversion of benzylamine and the yield of *N*-benzylidenebenzylamine decreased slightly by 7% (from 77% to 70%) and 6% (from 75% to 69%) after 5 times of recycling, respectively (Fig. S5).
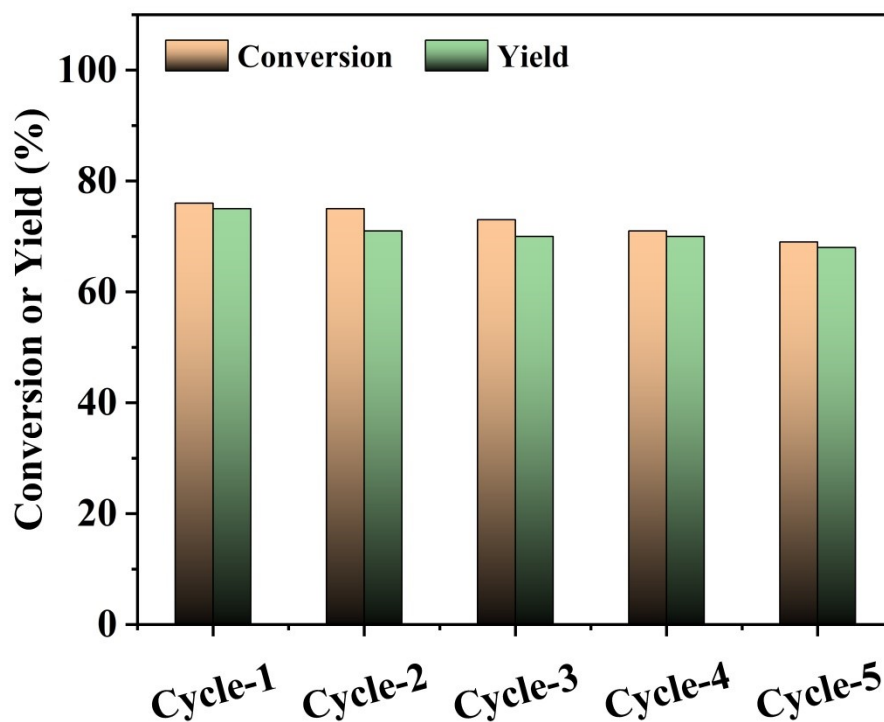

Fig. S5 Catalyst recycling study of Fe/CNS at a low conversion of <80% (Reaction conditions: 0.3 mmol benzylamine, 3.4 mol% Fe/CNS, 1 bar O_2 balloon, 2 mL CH_3CN, visible light, 25 ºC, 6 h).
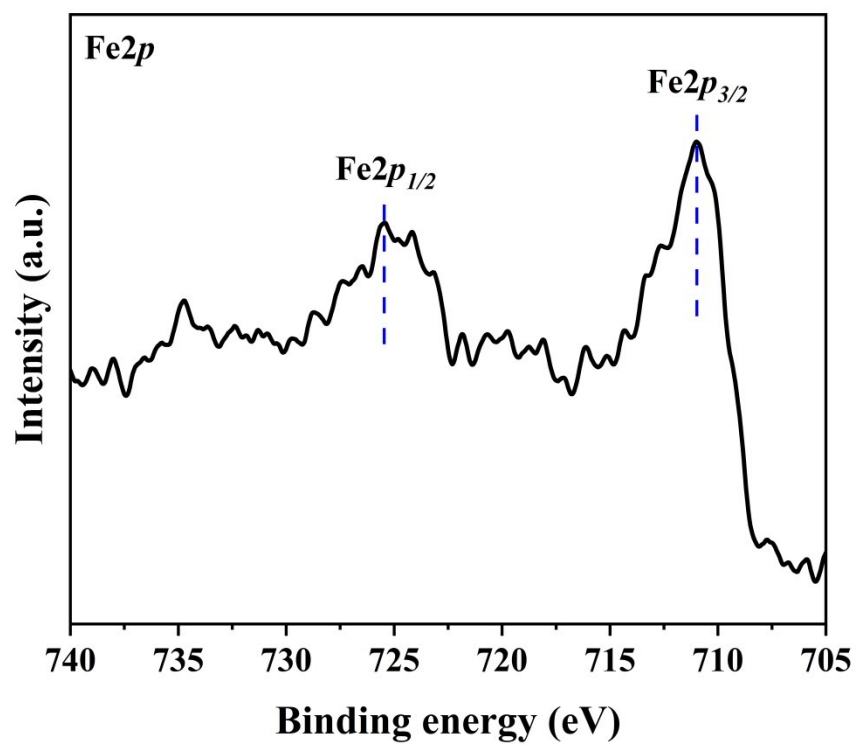
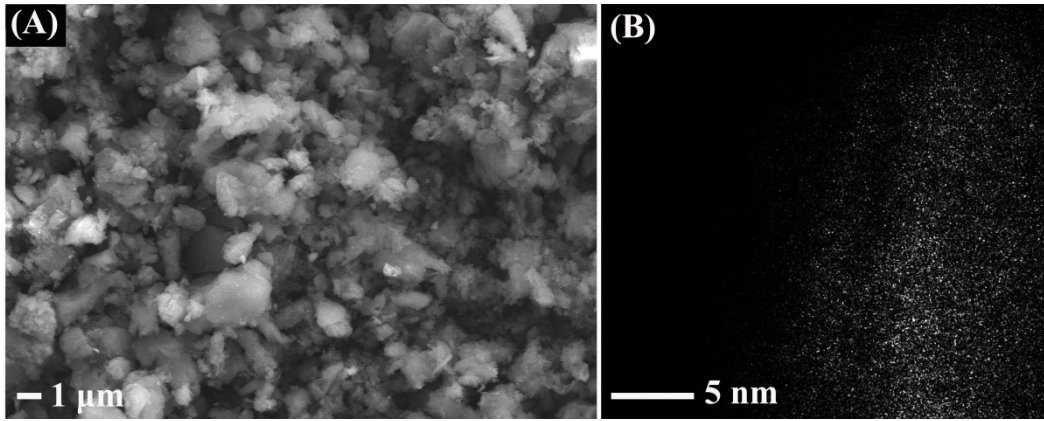**Fig. S6** Fe 2p XPS spectrum of reused Fe/CNS (R-Fe/CNS).

Fig. S7 SEM image (A) and AC-HAADF-STEM image (B) of reused Fe/CNS (R-Fe/CNS).

A 10 mL quartz reaction tube fitted with a magnetic stirrer was loaded with photocatalyst (3.4 mol%, Fe molar content relative to the substrate), 4 Å MS (30 mg), the corresponding alcohol (0.3 mmol), NH_2OH HCl (0.75 mmol, 2.5 eq.), and dry CH_3CN (2 mL). The resulting mixture was stirred with O_2 bubbling in the dark for 0.5 h to obtain adsorption equilibrium, then the container was sealed off, and the reaction pressure was kept at 1 bar of O_2 using an O_2-filled balloon. The reaction was carried out under normal sunlight for 8 h (from 9:00 a.m. to 17:00) at 25 °C (controlled by cooling water), and the experimental procedures with obtained results are also provided (Fig S8). Under otherwise identical conditions, the yield of benzonitrile was 29% at normal sunlight irradiation, which is comparable to that (ca. 32%) conducted under visible light irradiation. The experimental results demonstrated that the reaction can be run under normal sunlight.

Fig. S8 Photocatalytic reaction conducted under normal sunlight

Notes and references

[S1] S.A. Jenekhe, S. Yi, *Appl. Phys. Lett.*, 2000, **77**, 2635-2637.

[S2] X. Zhao, P. Du, Z. Cai, T. Wang, J. Fu, W. Liu, *Environ. Pollut.*, 2018, **232**, 580e590.

[S3] D. Zhang, J. Qi, H. Ji, S. Li, L. Chen, T, Huang, C. Xu, X. Chen, W. Liu, *Chem. Eng. J.,* 2020, **400**,125918.