Supporting Information

Photocatalytic Selective Oxidation of HMF Coupled with H₂ Evolution on Flexible Ultrathin g-C₃N₄ Nanosheets with Enhanced N-H Interaction

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1. Chemicals and Reagents

Melamine (99%), 5-Hydroxymethylfurfural (HMF, 99%), and D₂O (99.8 atom% D) were purchased from Aladdin Chemicals. Urea (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water (18 m Ω) was used in all experiments.

2. Material characterizations

X-ray diffraction patterns (XRD) of the as-prepared samples were recorded on a Bruker AXS D8 diffractometer equipped with Cu Ka radiation. Diffuse reflectance UV-vis absorption spectra of obtained samples were measured on a Shimadzu UV-2550 UV/visible spectrophotometer, with $BaSO_4$ as the reference. Scanning electron microscopy (SEM, Hitachi S-4800) and Transmission electron microscopy (TEM, JEOL JEM-2100F) were applied to observe microstructures of the samples. Fourier-transform infrared (FTIR) spectra were conducted on a Nexus 670 infrared spectrophotometer. The specific surface areas were measured by using a Micromeritics ASAP 2020 apparatus. Photoelectron Spectroscopy (XPS) spectra were conducted on a Thermo Fisher Scientific ESCALAB 250 XI, and the C 1s peak at 284.6 eV was used to calibrate the peak positions. Photoluminescence (PL) spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer at room temperature with excitation wavelength at 365 nm. Timeresolved transient PL decay curves were measured at about 450 nm using same excitation wavelength by Edinburgh FLS920. Photoluminescence quantum yield was measured by Edinburgh Instrument FLS1000 spectrometer at an excitation wavelength of 365 nm with an integrating sphere. The ESR tests were carried out at room temperature using a JES-

FA200 (JEOL) ESR spectrometer performed at X-band frequency. The configuration parameter were set as follows: microwave power 20 mW, modulation frequency 100 kHz, attenuator 10 dB, microwave frequency 9.43 GZ. The TG-DSC test was performed on a simultaneous thermal analyzer (NETZSCH STA 449F3, Germany).

3. Apparent quantum yield (AQY) test

In order to assess the apparent quantum yield (AQY) of the as-prepared catalysts, the Xe lamp with different wavelengths band-pass filter (365, 420, 530, 600 nm) was applied to stimulate the photocatalytic activity after 2 h irradiation at 15 °C. The AQY can be calculated from the formula:

$$AQY(\%) = \left(\frac{2 * number of evolved hydrogen molecules}{number of incident photons}\right) * 100$$

The number of incident photons (N) can be calculated from the formula:

$$N = \frac{t * E * \lambda}{h * c} = \frac{t * S * P * \lambda}{h * c}$$

Where, *t* was the radiation time, *S* was the radiation coverage area, λ was the wavelength of the monochromatic light, *P* was the incident light intensity, *h* was Plank constant, and *c* was the velocity of light. Monochromatic light intensity was measured as follows: 365nm: 5.73mW cm⁻²; 420nm: 66.85mW cm⁻²; 530nm: 84.67mW cm⁻²; 600nm: 79.58mW cm⁻².

4. Theoretical calculation

DFT calculations were performed by using the Vienna Ab-initio simulation package (VASP).^{1, 2} A spin-polarized GGA PBE functional, all-electron plane-wave basis sets with

520 eV energy cutoff, and adopted a projector augmented wave (PAW) method.³ g-C₃N₄ is simulated using a surface model of p (3 × 3) unit cell periodicity with a single layer. A $(3 \times 3 \times 1)$ Monkhorst-Pack mesh was applied for sampling the Brillouin-zone integrations. In the optimization, the conjugate gradient algorithm was applied.⁴ The convergence threshold was set 1*10⁻⁴ eV in total energy and 0.05 eV/ Å in force on each atom. The adsorption energy change (ΔE_{abs}) can be calculated as follows:

$$\Delta E_{abs} = E_{total} - E_{sur} - E_{mol}$$

where E_{total} is the total energy for the adsorption state, E_{sur} is the energy of pure surface, E_{mol} is the energy of molecule, respectively.

The fracture energy change (ΔE_{fra}) can be calculated as follows:

$$\Delta E_{\rm fra} = E_{\rm after} - E_{\rm befor}$$

where E_{after} is the total energy after the fracture of O-H or α -C-H, E_{befor} is the total energy befor the fracture of O-H or α -C-H, respectively.

Supplementary Figures



Figure S1. Partial enlarged TG curves for g-C₃N₄ and g-C₃N₄+HMF.



Figure S2. PL spectra and absolute quantum yields of (a) $g-C_3N_4$ and (b) $g-C_3N_4$ +HMF.



Figure S3. (a) FTIR spectra of $g-C_3N_4$, HMF and $g-C_3N_4$ +HMF. (b) Partial enlarged FTIR

spectra.



Figure S4. (a) ¹³C NMR and (b) ¹H NMR spectra of 5-Hydroxymethylfurfural (HMF). ¹³C NMR (100 MHz, CDCl₃, 30 °C): δ = 177.8, 160.8, 152.3, 123.2, 110.1, 57.6;

¹**H NMR (400 MHz, CDCl₃, 30 °C)**: 9.57 (s, 1H), 7.23 (d, J = 3.6 Hz, 1H), 6.53 (s, J = 3.6 Hz, 1H), 4.72 (s, 2H), 2.98 (s, 1H).



Figure S5. FTIR spectra of pristine HMF and absorbed HMF.



Figure S6. Changes in the bond angle of α -C-H and O-H bonds before and after HMF was adsorbed on g-C₃N₄ surface.



Figure S7. Top-down irradiation photoreactor (500 mL) (a) front view and (b) top view. (c) Photocatalytic test system. The photos were taken by Bao, Xiaolei.



Figure S8. (a) H_2 evolution rate on different wavelength over UCNT. (b) Wavelength dependent AQY of H_2 evolution over UCNT. (c) The AQY of the as-prepared catalysts at 420 nm.

Table S1. Photocatalytic conversion of HMF to DFF coupled with H_2 evolution under overdifferent photocatalysts.

0	O HMF	H visible light photocatalyst	- o DFF	$O + H_2$
entry	catalyst	H ₂ (umol)	DFF (umol)	selectivity (%)
1a	TiO ₂	22.5	10.6	71
2 ^a	P25	48.9	26.3	75
3	Bi ₂ WO ₆	0.2	0.5	83
4	MCN	4.1	3.9	85
5	UCN	11.5	14.9	90
6	UCNT	46.0	47.5	95
7 ^a	UCNT	61.5	63.5	93

Reaction conditions: 100 mg of catalyst, 3 wt% Pt as the co-catalyst, 100 mL HMF aqueous solution (10 mM), a 300 W Xe lamp ($\lambda \ge 420$ nm), 5 h. ^a UV-vis light.



Figure S9. SEM images of (a) MCN, (b) UCN, and (c, d) UCNT.



Figure S10. TEM images of (a) MCN, (b) UCN, and (c, d) UCNT.



Figure S11. (a) N_2 adsorption-desorption isotherms and (b) pore size distributions.

Samples	Pore volume (cm ³ g ⁻¹)	$S_{\rm BET} ({ m m}^2~{ m g}^{-1})$
MCN	0.105	12.786
UCN	0.320	47.478
UCNT	0.853	155.915

Table S2. Physical properties of the three samples



Figure S12. The H₂ evolution rate for as-prepared catalysts after mass normalization and specific surface area normalization.



Figure S13. (a) Plots of transformed Kubelka-Munk function versus photon energy for MCN, UCN and UCNT. (b) VB-XPS spectra and (c) Band structure alignments for MCN, UCN and UCNT.



Figure S14. (a) C 1s XPS spectra, (b) N 1s XPS spectra and (c) O 1s XPS spectra for MCN, UCN and UCNT.

Table S3. The element components of three samples according to XPS results

Samples	C (wt%)	N (wt%)	O (wt%)	C/N (atomic ratio)
MCN	33.6	63.8	2.6	0.61
UCN	30.5	68.3	1.2	0.52
UCNT	30.5	68.3	1.2	0.52



Figure S15. (a) Long-time test over UCNT; (b) HPLC traces of reaction solution over reaction time; (c) XRD patterns and (d) FTIR spectra after cycling tests.

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