Electronic Supplementary Material

Multiscale structural engineering of carbon nitride for enhanced photocatalytic H_2O_2 production

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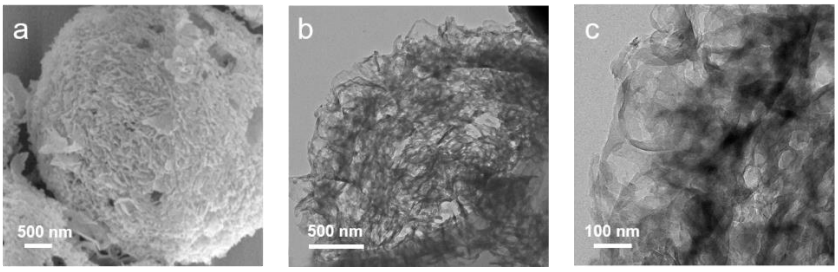

Figure S1 (a) SEM and ((b) and (c)) TEM images of CNS.

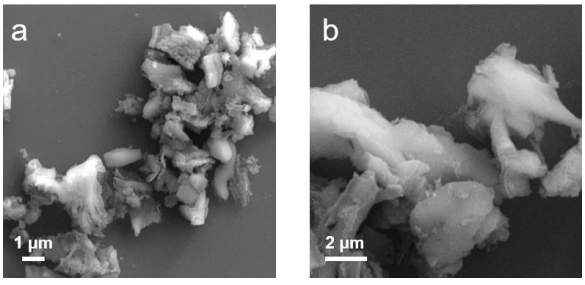

Figure S2 SEM images of bulk C_3N_4.

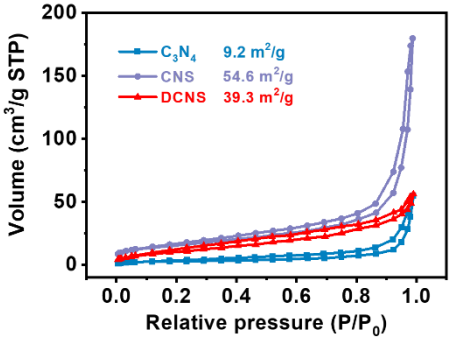

Figure S3 Nitrogen sorption isotherms of DCNS, CNS and bulk C_3N_4.

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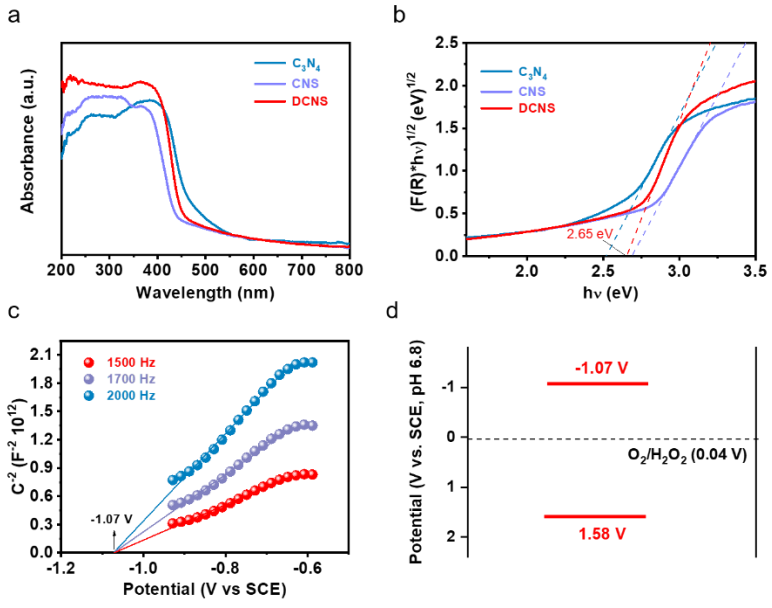

Figure S4 (a) UV-Vis absorption spectra and (b) corresponding Kubelka-Munk-transformed reflectance spectra of DCNS, CNS and bulk C_3N_4; (c) Mott-Schottky plots of DCNS to determine its flat band; (d) calculated band structure of DCNS.
Note: For Mott-Schottky analysis, a standard three-electrode system was used which consists of a catalyst-deposited FTO electrode as the working electrode, a Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte was 0.2 M Na_2SO_4 aqueous solution. The data was collected in the dark at the frequency of 1500, 1700 and 2000 Hz using a Gamry Reference 600 potentiostat.

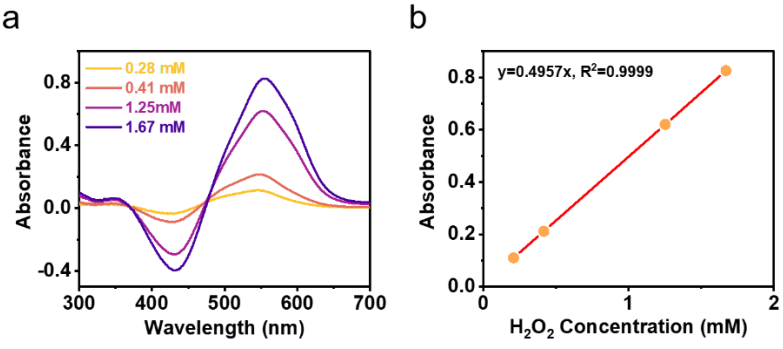

Figure S5 (a) UV-Vis absorption spectra of the FOX solution mixed with the standard H_2O_2 solution of different concentrations; (b) calibration curve by plotting the absorption intensity at 553 nm with respect to the H_2O_2 concentration.
Note: If the concentration of produced H_2O_2 is higher beyond the calibration range, the reaction should be diluted before quantified with the FOX solution.

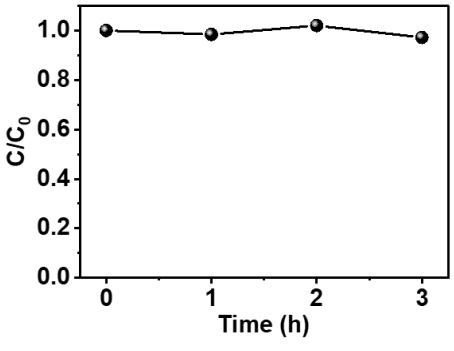

Figure S6 H_2O_2 decomposition on DCNS under visible light irradiation. Reaction conditions: 1 mg mL^{-1} catalyst, 10 vol% EtOH, 9.5 mM H_2O_2, Ar atmosphere, $\lambda > 400$ nm, Xe lamp, light intensity: 100 mW cm^{-2}.

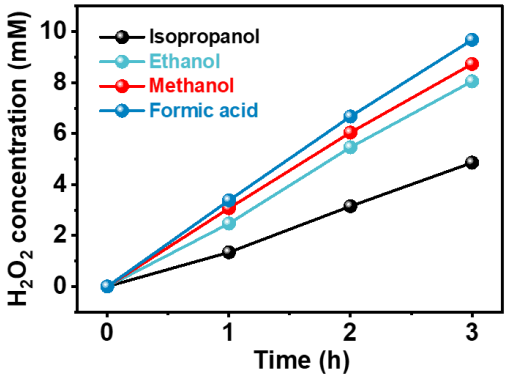

Figure S7 Increasing H_2O_2 concentration of DCNS using different sacrificial electron donors.

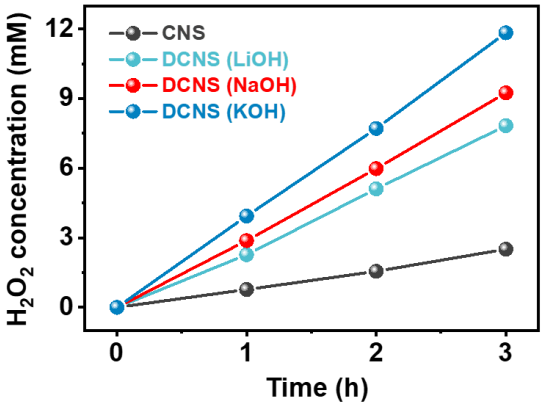

Figure S8 Increasing H_2O_2 concentration of DCNS treated by different alkali hydroxides as the etchant.

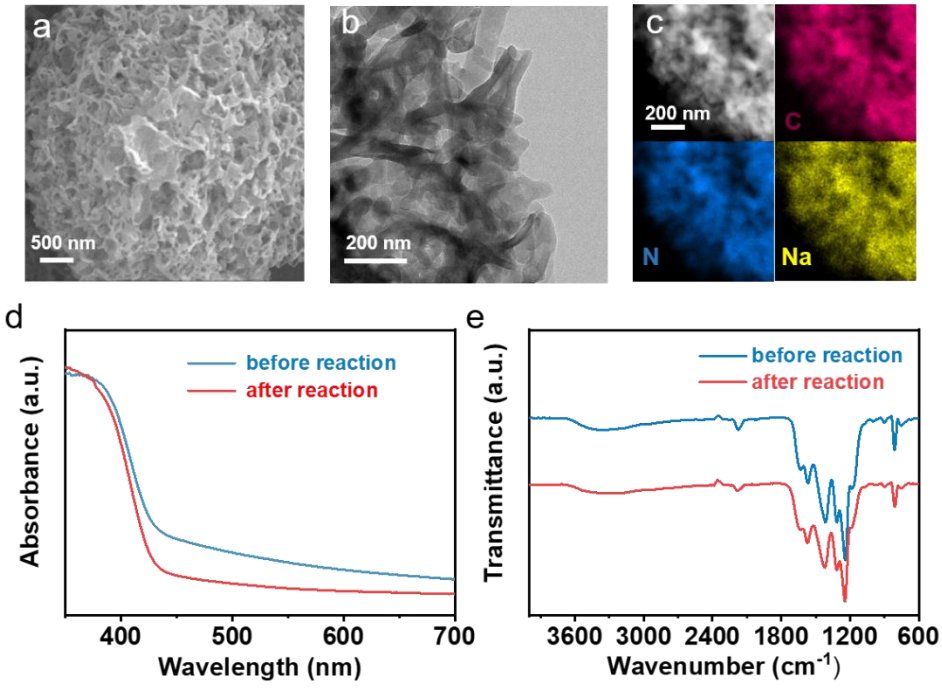

Figure S9 (a) SEM image, (b) TEM image and (c) corresponding EDX mapping of DCNS after the recycling experiment; (d) UV-Vis absorption spectra and (e) FT-IR spectra of DCNS before and after the recycling experiment

Table S1 Chemical compositions of three different samples estimated from XPS.

Samples	C (at. %)	N (at. %)	O (at. %)	Na (at. %)
C_3N_4	49.00	49.28	1.62	-
CNS	48.71	50.05	0.04	-
DCNS	51.26	44.94	1.56	2.2

Table S2 Elemental analysis results of three different samples.

Samples	N (wt%)	C (wt%)	H (wt%)	N/C molar ratio
C_3N_4	60.12	34.62	1.74	1.488
CNS	58.13	34.05	1.92	1.463
DCNS	51.04	31.77	1.81	1.377

Table S3 Contents of different N species derived from the deconvolution of N 1s XPS spectra.

Samples	N_{2C} (%)	N_{3C} (%)	NH_x (%)	N_{2C}/N_{3C}
C_3N_4	72.3	16.1	11.6	4.5
CNS	74.1	14.9	11.0	4.9
DCNS	58.6	23.0	16.4	2.5

Table S4 Fitting results of the PL decay curves.

Samples	τ_1 (ns)	Intensity (%)	τ_2 (ns)	Intensity (%)	τ_3 (ns)	Intensity (%)	$\tau_{average}$ (ns)	χ^2
C_3N_4	0.843	70.5	3.673	24.1	17.336	5.4	8.280	0.998
CNS	0.718	77.7	3.330	19.3	15.571	2.96	5.846	0.997
DCNS	0.378	82.8	1.691	16.1	7.215	1.1	1.713	0.999

Note: The above results are derived by using following fitting equation:

$$I(t) = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2} + A_3 e^{-t/\tau 3}$$

where, A_1, A_2 and A_3 represent the normalized amplitudes of each decay component and τ_1, τ_2 and τ_3 are values of the lifetime components, respectively.

Table S5 Performance comparison of DCNS with other photocatalysts for the H_2O_2 production.

Photocatalysts	Conditions	H_2O_2 production rate		References
		mM h^{-1}	μmol g^{-1} h^{-1}	
DCNS	**λ>400 nm; H_2O:EtOH (9:1)**	**3.08**	**3080**	**This work**
DCA-15A	λ>420 nm; H_2O:IPA (8:2)	0.08	96.8	*Small* **2018**, *14*, 1703142
KPD-CN-7.5	λ>420 nm; H_2O:EtOH (9:1)	0.24	485.7	*ACS Catal*. **2017**, *7*, 2886−2895
B doped CN	λ>420 nm; H_2O:IPA (9:1)	0.287	574	*Adv. Funct. Mater*. **2020**, *30*, 2001922
10% BP/CN	λ>420 nm; H_2O:IPA (9:1)	0.9	540	*Adv. Funct. Mater*. **2018**, *28*, 1705407
ACNN	λ>420 nm; H_2O:IPA (9:1)	5.1	10200	*ACS Catal*. **2020**, *10*, 14380−14389
OCN-500	λ>420 nm; H_2O:IPA (9:1)	2.8	2800	*Energy Environ. Sci*., **2018**, *11*, 2581-2589
C_v-g-C_3N_4	λ>420 nm; Pure water	0.09	92	*Appl. Catal. B* **2016**, *190*, 26–35
AKMT	λ>420 nm; H_2O:EtOH (9:1)	1.37	-	*Angew. Chem. Int. Ed*. **2020**,*59*, 16209-1621
g-C_3N_4/AQ-COOH	AM 1.5; H_2O:IPA (9:1)	-	361	*Appl. Catal. B* **2018**, *229*, 121–129
g-C_3N_4-CNT	λ>400 nm; H_2O:HCOOH (95:5)	0.32	326	*Appl. Catal. B* **2018**, *224*, 725–732
TAPD-$(Me)_2$ COF	λ>420 nm; H_2O:EtOH (1:9)	0.938	234.5	*J. Am. Chem. Soc*. **2020**, *142*, 47, 20107–20116
$Pd/BiVO_4$	λ>420 nm; H_2O:MeOH (9:1)	0.6	-	*Appl. Catal. B* **2020**, *272*, 119003

Note: EtOH, MeOH and IPA refer to ethanol, methanol and isopropanol, respectively.