Electronic Supplementary Information

Efficient visible-light-driven selective oxygen reduction to hydrogen peroxide by oxygen-enriched graphitic carbon nitride polymers

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Experimental section

Synthesis

50 mmol of dicyandiamide and 0.5 mmol of ammonium paratungstate were thoroughly ground in a mortar and mixed well, then transferred to a lidded crucible, then they were calcined in a corundum crucible at 400, 450, 475, 500, 525, 550°C for 4 h. After cooling to room temperature, the product was obtained. Marked as **OCN-400, 450, 475, 500, 525, 550,** respectively.

g-C_3N_4: Dicyandiamide calcined alone at 500 for 4 h, labelled as **g-C_3N_4**, as a reference sample.

WO_3: Ammonium paratungstate calcined alone at 500 for 4 h, labelled as **WO_3**, as a tungsten oxide reference sample.

Samples characterizations

The morphologies and structures of materials were measured by TEM operated on Hitachi HT 7700 at 100 kV. Details morphologies were observed by HAADF-STEM-EDX on the JEM-2100F field emission high-resolution transmission electron microscope at 200 kV with high angle annular dark-field STEM. Field emission scanning electron microscopy (FESEM) was observed on a Hitachi SU-8010 at 10 kV. Atomic force microscopy (AFM) measurements were carried out by using a SPM-9700 scanning probe microscope (Shimadzu Corporation). The samples for AFM measurements were prepared by spraying a diluted suspension of the sample on a freshly cleaved mica surface and then dried in air. Powder X-ray diffraction (XRD) was measured on Rigaku D/max-2400 with Cu Kα1 (λ= 1.5418 Å) radiation at 40 kV and 200 mA. The Brunauer–Emmett–Teller (BET) surface area measurements were performed by using a micromeritics (ASAP 2010 V5.02H) surface area analyzer. The nitrogen adsorption and desorption isotherms were measured at 77 K after degassing the samples on a Sorptomatic 1900 Carlo Erba Instrument. The UV–visible diffuse reflectance spectroscopy (DRS) of materials were carried out on Hitachi U-3010 spectrophotometer using $BaSO_4$ as a reference. Fourier transform infrared spectra (FT-IR) were taken on Bruker VERTEX-70 spectrometer from 4000 cm^{-1} to 600 cm^{-1} with the resolution of 1 cm^{-1}. The room temperature photoluminescence (PL) spectra of materials were recorded on Perkin-Elmer LS55 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was measured on a PHI Quantera SXM spectrometer using Al Ka radiation. In situ electron paramagnetic resonance (EPR) measurement was taken on an Endor spectrometer (JEOL ES-ED3X) at 103 K in liquid nitrogen. The g factor was obtained by taking the signal of manganese as a standard. Solid state NMR for ^{13}C magic angle spinning (MAS) measurements were carried out on JNM-ECZ600R solid-state NMR with the probe diameter 3.2 mm, 12kHz rotating speed and 2s relaxation time.

Electrochemical and photoelectrochemical measurements

The photoelectrochemical properties were evaluated in a conventional three-electrode cell system on CHI 660E (Shanghai, Chenhua) electrochemical workstation. ITO/product sample as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt wire used as the counter electrode. 0.1M Na_2SO_4 aqueous solution was used as the electrolyte. To remove the dissolved oxygen, N_2 was bubbled into the Na_2SO_4 aqueous solution for 30 minutes before measurement. The working electrode was irradiated by a 300 W Xe lamp (Institute for Electric Light Sources, Beijing) and the light intensity was about 100 $mW\cdot cm^{-2}$.

Rotating disk electrode (RDE) measurements

The measurements were performed on a Pine AFMSRXE 1523 advanced electrochemical system with a three-electrode cell using an Ag/AgCl electrode and a Pt wire electrode as the reference and counter electrode, respectively[1]. The working electrode was prepared as follows: catalysts (50 mg) were dispersed in EtOH (2 ml) containing Nafion (50 mg) by ultrasonication. The slurry (20 μl) was put onto a Pt disk electrode and dried at room temperature. The linear sweep voltammogram (LSV) were obtained in an O_2-saturated 0.1 M phosphate buffer solution (pH 7) with a scan rate 10 mV s^{-1} after O_2 bubbling for 5 min. The average number of electrons (n) involved in the overall O_2 reduction was determined by the slopes of the Koutecky–Levich plots with the following equation:

$$j^{-1} = j_k^{-1} + B^{-1}\omega^{-1/2}$$

$$B = 0.2nF\nu^{-1/6}CD^{2/3}$$

j is the current density, j_k is the kinetic current density, ω is the rotating speed (rpm), F is the Faraday constant (96485 C mol^{-1}), ν is the kinetic viscosity of water (0.01 cm^2 s^{-1}), C is the bulk concentration of O_2 in water (1.26×10^{-3} mol cm^{-3}), and D is the diffusion coefficient of O_2 (2.7×10^{-5} cm^2 s^{-1}), respectively.

Transient photovoltage (TPV) measurements

TPV measurements were carried out to study the kinetic features of the photogenerated charges with a 355 nm laser pulse from a third-harmonic Nd:YAG laser.[2, 3] TPV measurements were carried out on a home-made system in air atmosphere at room temperature. The samples were excited with a laser radiation pulse with the wavelength of 355 nm and pulse width of 5 ns from a third-harmonic Nd:YAG laser (Polaris II, New Wave Research, Inc.). Moreover, The TPV signal was recorded with a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix).

Photocatalytic reduction of oxygen to hydrogen peroxide

The photocatalytic reduction of O_2 to H_2O_2 was analyzed according to the literature with a slight modification [4, 5]. 50 mg of photocatalyst suspended in 50 mL of water (or isopropanol: 5mL and water: 45 mL) was placed Pyrex test tube. The suspension solutions were first ultrasonically dispersed for 30 min in the dark and then stirred for 30 min before irradiation to reach the absorption–desorption equilibrium. The light source was provided by a Xe lamp at 300 W with 420 nm cutoff filter. The average light intensity was 35.2 $mW \cdot cm^{-2}$. At certain time intervals, 3 mL solution was sampled and centrifuged to remove the photocatalysts, and then filtrated with a 0.45 μm Millipore filter to remove the photocatalyst. The reactions were carried out in the air atmosphere without special instructions. If compare the different atmospheres, it need to bubble N_2 or O_2 into the suspension solutions for 30 min before measurement. Keep the temperature at 298 K during all reactions.

The apparent quantum yields for H_2O_2 formation was determined using the equation: AQY (%) = ([H_2O_2 formed (mol)] × 2)/[photon number entered into the reaction vessel (mol)] × 100.

The amount of H_2O_2 was analyzed by iodometry. [6] 1 mL of 0.1 mol·L^{-1} potassium hydrogen phthalate ($C_8H_5KO_4$) aqueous solution and 1 mL of 0.4 mol·L^{-1} potassium iodide (KI) aqueous solution were added to obtained solution, which was then kept for 30 min. The H_2O_2 molecules reacted with iodide anions (I^-) under acidic conditions ($H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$) to produce triiodide anions (I_3^-) possessing a strong absorption at around 350 nm. The amount of I_3^- was determined by means of UV–vis spectroscopy on the basis of the absorbance at 350 nm, from which the amount of H_2O_2 produced during each reaction was estimated.

Photocatalytic H_2 evaluation

The photocatalytic activities of the as-prepared samples were evaluated by using a Perfect Light agitated reactor (LabSolar-III AG). A visible light source was obtained by using a 300 W Xe lamp with a 420 nm cut-off filter. 50 mg photocatalyst was added into 100 mL solution (90 mL deionized water and 10 mL triethanolamine as sacrificial agent). Before light irradiation, the suspensions were first ultrasonically dispersed in the dark for 30 min. At given time intervals (1 h), a certain amount of gas was taken from the reactor for gas concentration analysis using an online gas chromatograph (GC-7800) with a thermal conductivity detector (TCD) and using N_2 as carrier gas. Product gases were calibrated with standard H_2 gas and their identities were determined according to the retention time.

Photocatalytic degradation evaluation

The photocatalytic activity of the samples were evaluated by the photodegradation efficiency of phenol and 2,4-DCP solution under the irradiation of visible light. The light source was provided by a Xe lamp at 300 W with 420 nm cutoff filter. The average light intensity was 22 $mW \cdot cm^{-2}$. The photodegradation reactions were measured in the quartz tube reactors with 20mg as-prepared photocatalysts powders and 50 mL phenol or 2,4-DCP solution with a concentration of 5 ppm. The suspension solutions were first ultrasonically dispersed for 30 min in the dark and then stirred for 30 min before irradiation to reach the absorption–desorption equilibrium. At certain time intervals, 3 mL solution was sampled and centrifuged to remove the photocatalysts, and then filtrated with a 0.45 μm Millipore filter to remove the photocatalyst. The concentration of phenol and 2,4-DCP was analyzed by using the HPLC system (Shimadzu LC-20AT) with a C18 reversed phase column and an UV absorbance detector (K 2501). The determination wavelength was 270 nm (phenol) or 284 nm (2,4-DCP). The mobile phase was CH_3OH and H_2O (volume ratio: 60:40 (phenol) or 75/25 (2,4-DCP)) with a flow rate of 1 mL/min.

Theoretical calculations

Geometry optimizations for all structures were carried out by using the DFT functional B3LYP with 6-31G (d) basis sets. Frequence calculations were done to confirm the stationary points at the same level. High accuary energies were calculated by using the PBE0 functional with 6-311G(d) basis sets. All calculations were performed using the

Gaussian09 program. For the species C, all the possible spin states were canvassed and computational results shows that the triplet spin state with anti-parallel spin density on the C1 and N4 atoms is the ground spin state.

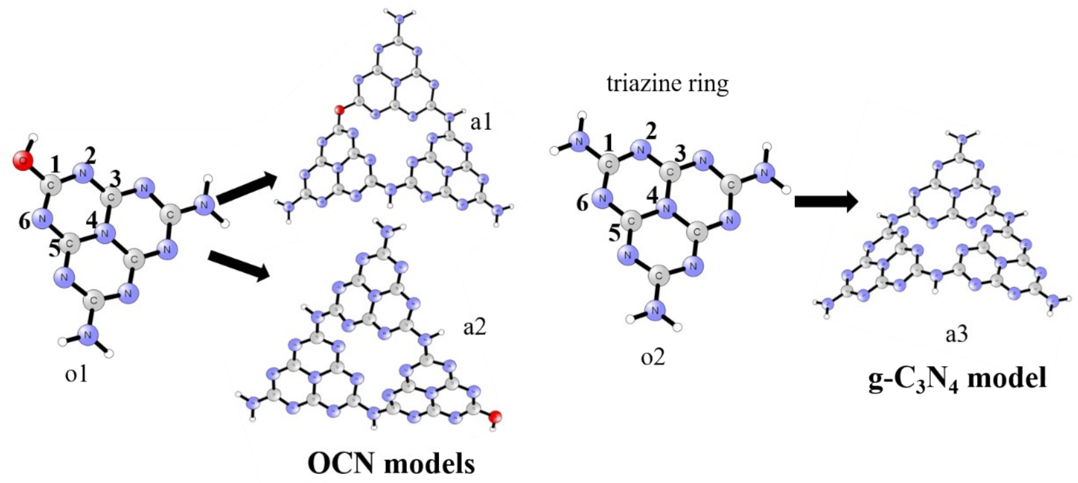


Fig. S1 The structure of OCN models (-OH and C-O-C) and g-C_3N_4 model.

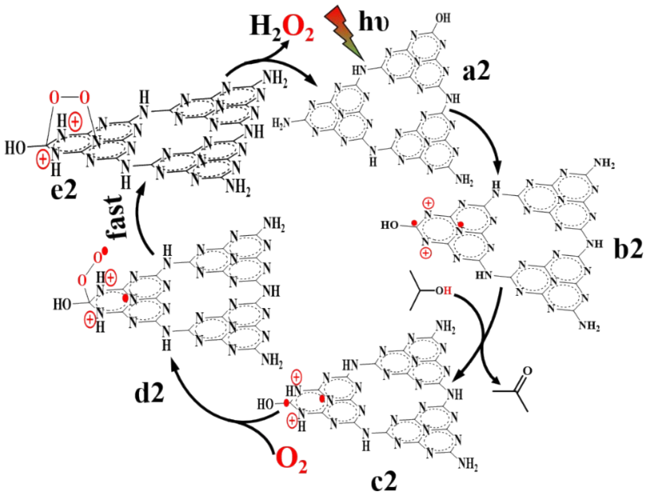


Fig. S2 The mechanism of OCN model (-OH) photocatalytic O_2 reduction to synthesis H_2O_2.

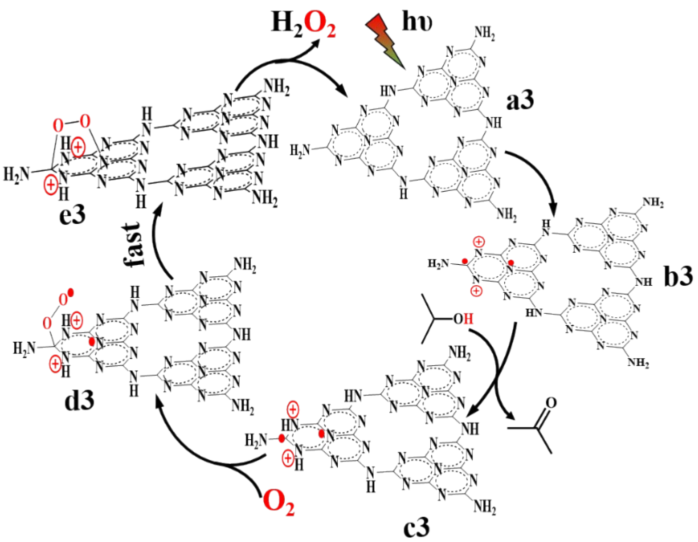


Fig. S3 The mechanism of g-C_3N_4 (-NH_2) photocatalytic O_2 reduction to synthesis H_2O_2.

Table S1. The energy of b→c

	b	c	acetone	isopropanol	ΔE (kcal/mol)
1(C-O-C)	2187.6877	2188.8810	192.9783	194.1782	4.2
2(-OH)	2187.7019	2188.8772			15.5
3($-NH_2$)	2167.8512	2169.0256			16.0

ΔE(b→c)=E(c)+E(acetone)-E(b)-E(isopropanol)

Table S2. The energy of e→a

	e	a	H_2O_2	ΔE (kcal/mol)
1(C-O-C)	-2339.1981	-2187.8003	-151.4270	-18.3
2(-OH)	-2339.2344	-2187.8117		-2.7
3($-NH_2$)	-2319.3767	-2167.9620		-7.8

ΔE(e→a)=E(a)+E(H_2O_2)-E(e)

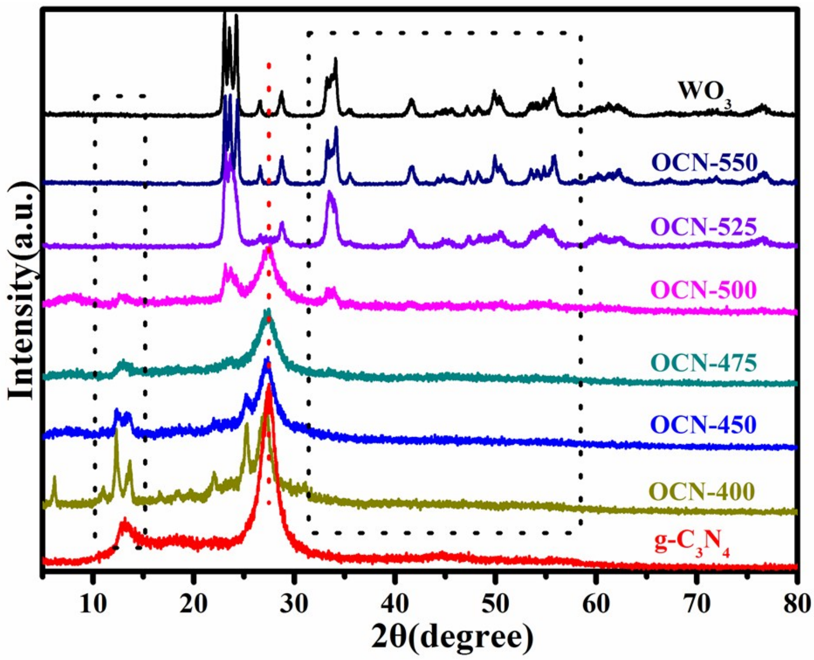


Fig. S4 XRD patterns (a) of the samples.

Table S3. The BET surface and product weight of $g-C_3N_4$ and OCN samples

Number	$g-C_3N_4$	OCN-400	OCN-450	OCN-475	OCN-500	OCN-525	OCN-550
BET/ $m^2 \cdot g^{-1}$	5.4201	8.3905	24.4578	25.4737	30.9021	29.8451	12.6376
Product weight/g	2.5560	2.8876	1.9255	1.7742	0.9891	0.4451	0.1149

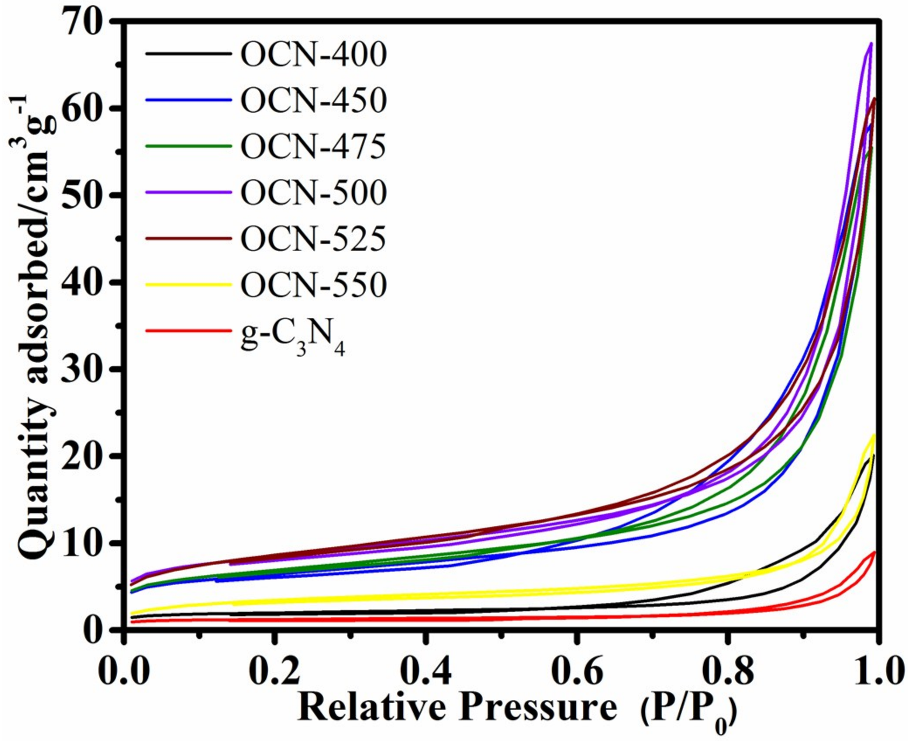


Fig. S5 N_2 adsorption–desorption isotherms of different samples.

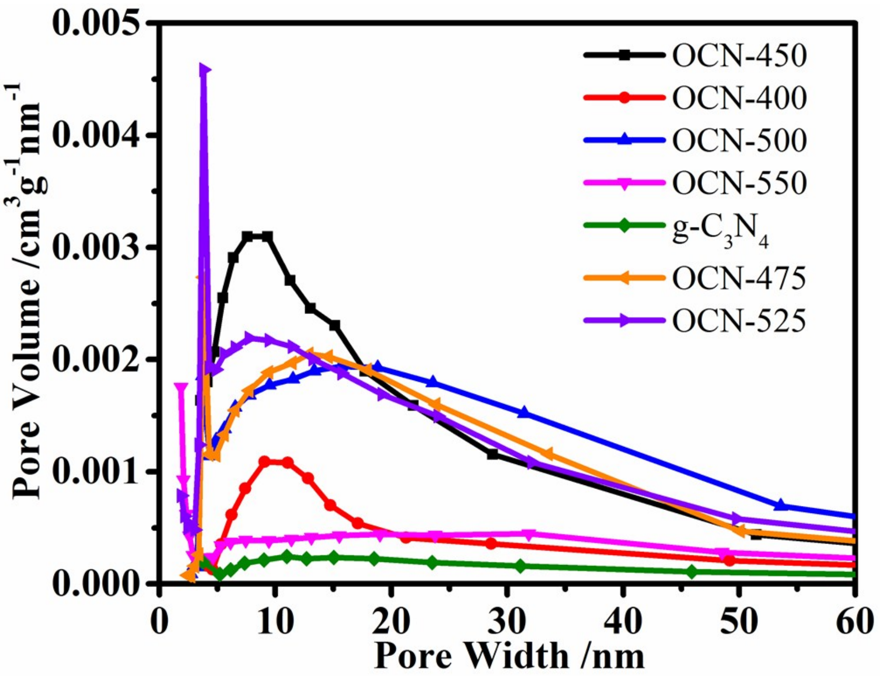


Fig. S6 BJH pore-size distribution of different samples.

Nitrogen adsorption−desorption isotherms (Figure S5) show that CW-500 exhibits a high Brunauer−Emmett−Teller (BET) surface area of 30.9021 m^2 g^{-1}. The average pore diameter is about 15.64 nm (Figure S6).

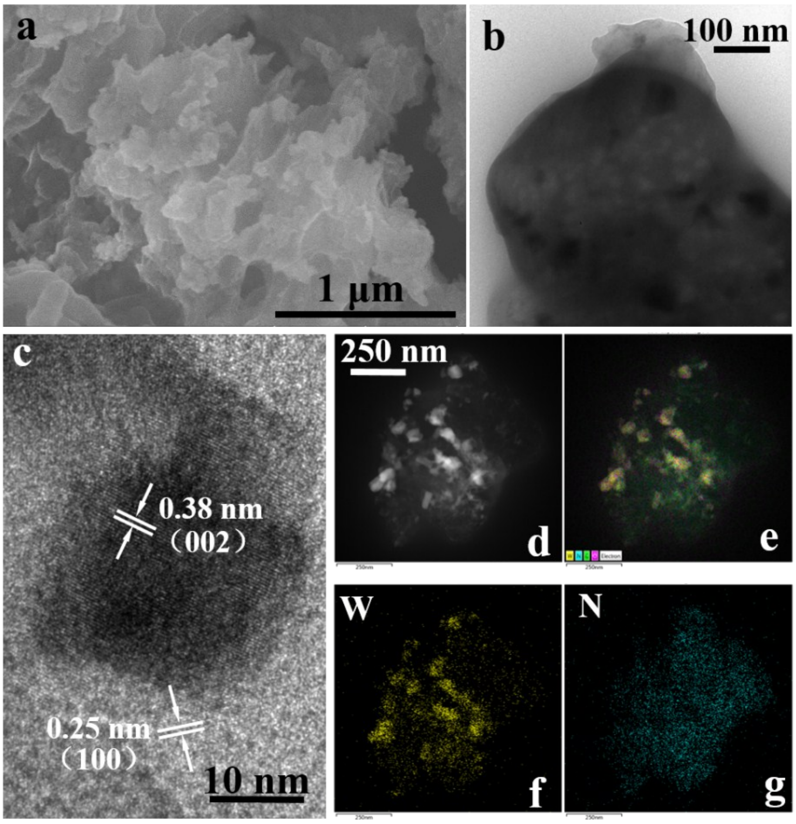


Fig. S7 (a) FE-SEM images of OCN-500; (b) TEM images of OCN-500; (c) HR-TEM images of OCN-500; (d)HAADF-STEM images of OCN-500, EDS mapping results W (f) and N (g) and overlay of HAADF-STEM of W (yellow) and N (blue) elements of OCN-500 (e).

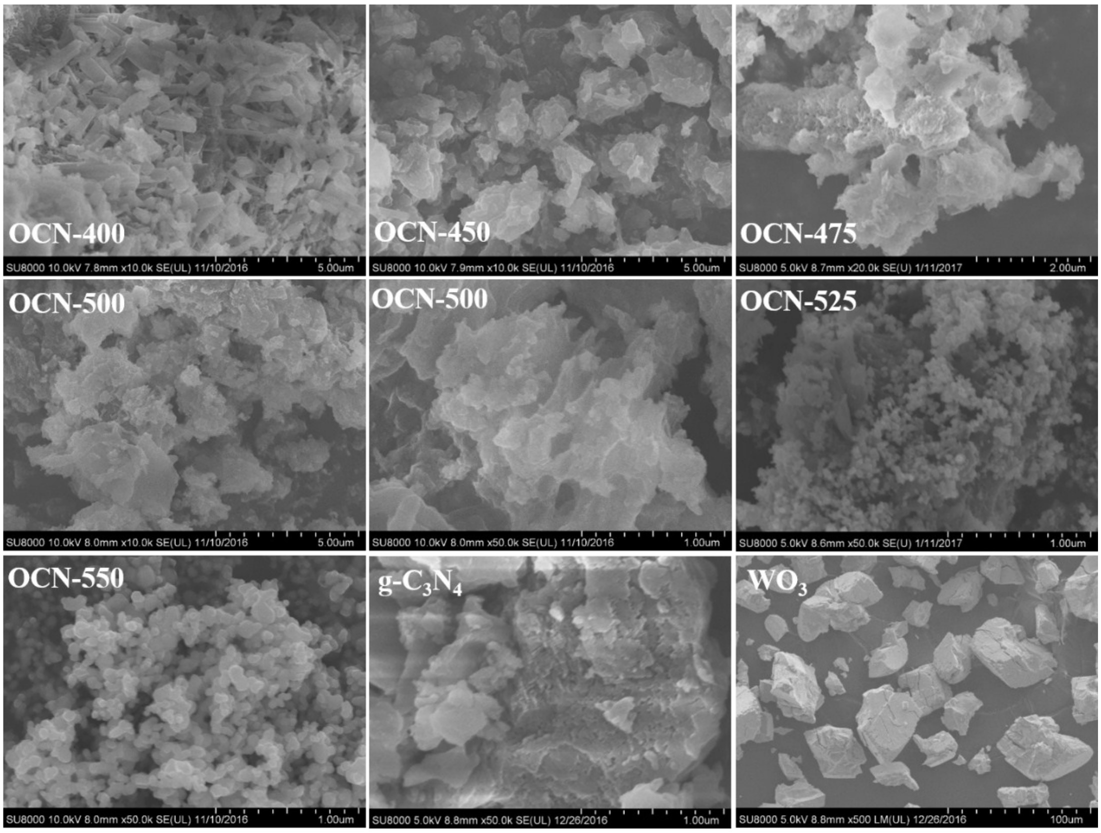


Fig. S8 FE-SEM images of different samples.

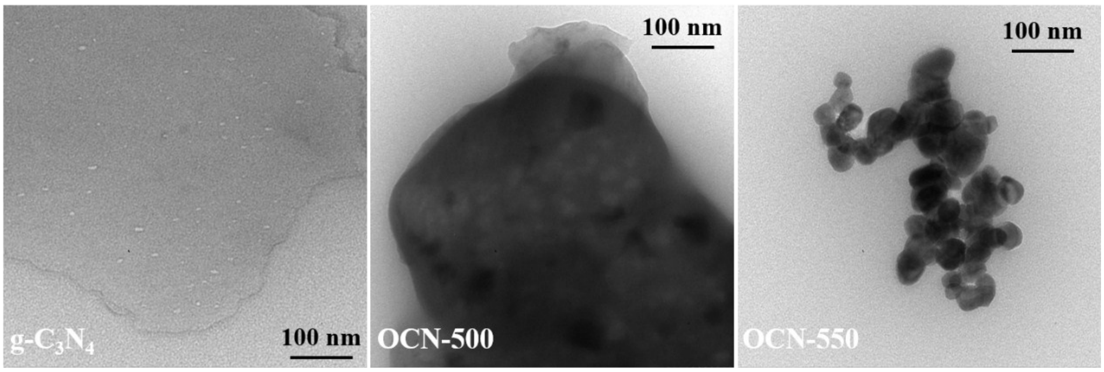


Fig. S9 TEM images of g-C_3N_4, OCN-500 and OCN-550.

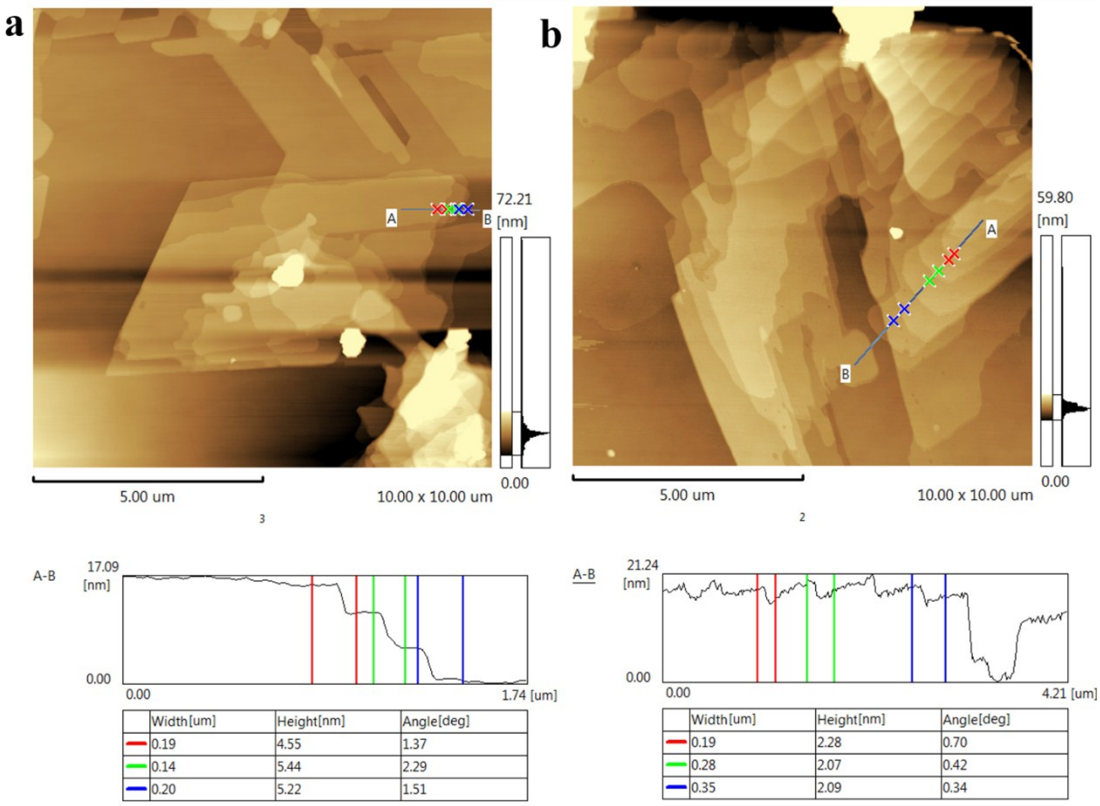


Fig. S10 AFM images of $g\text{-}C_3N_4$ (a) and OCN-500 (b).

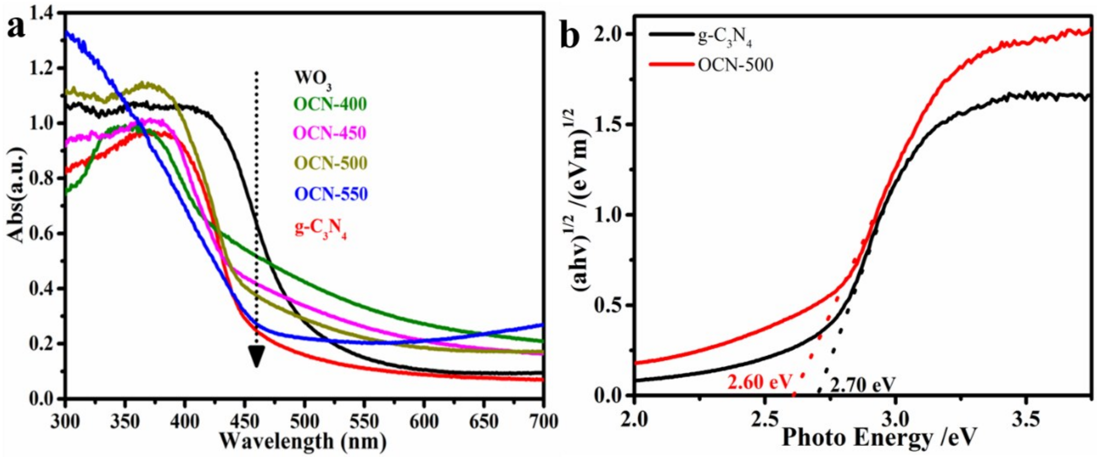


Fig. S11 (a) Diffuse reflectance absorption spectra of the samples; (b) gap energies of $g\text{-}C_3N_4$ and OCN-500.

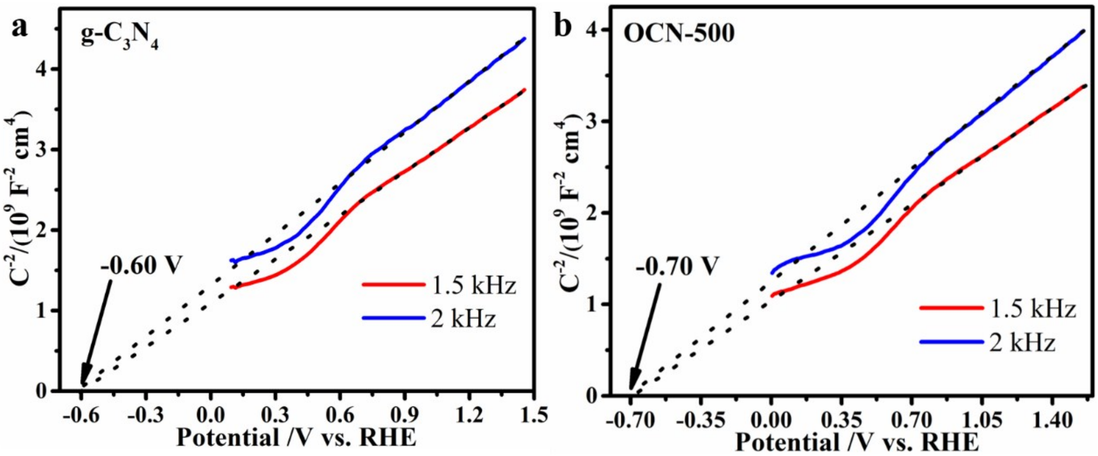


Fig. S12 Electrochemical Mott–Schottky curves of g-C_3N_4 (a) and OCN-500 (b).

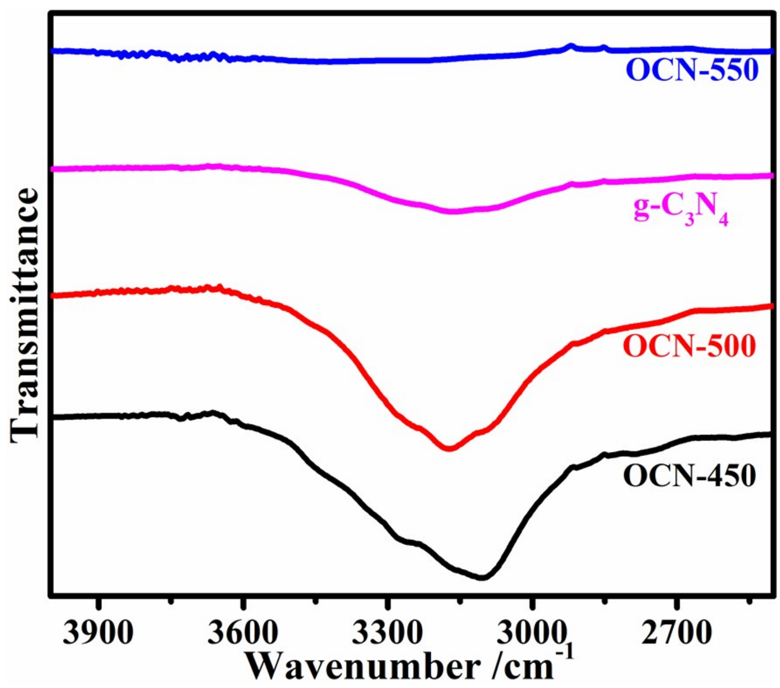


Fig. S13 FT-IR spectra of samples.

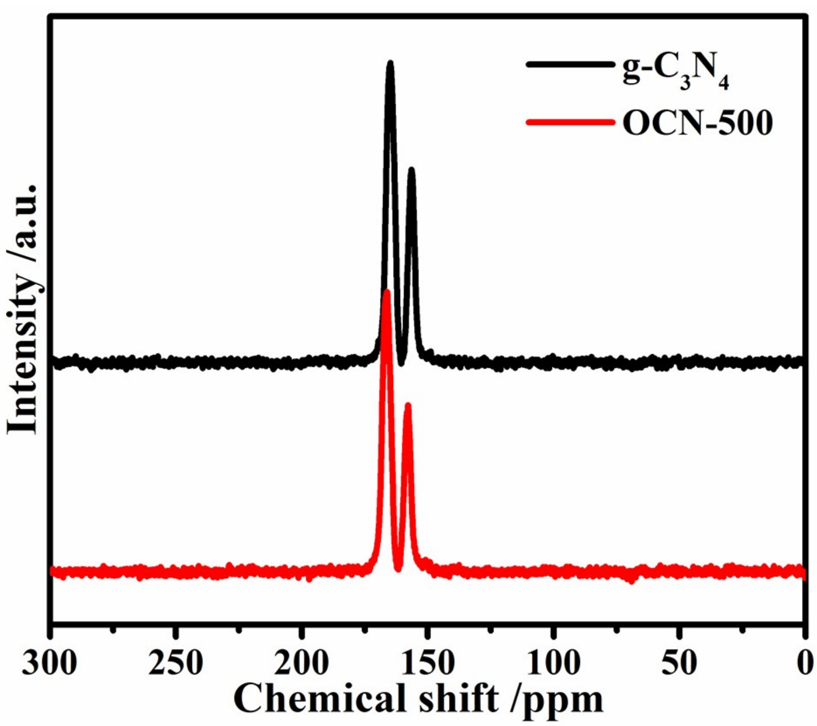


Fig. S14 Solid-state ^{13}C CP-MAS NMR of $g\text{-}C_3N_4$ and OCN-500.

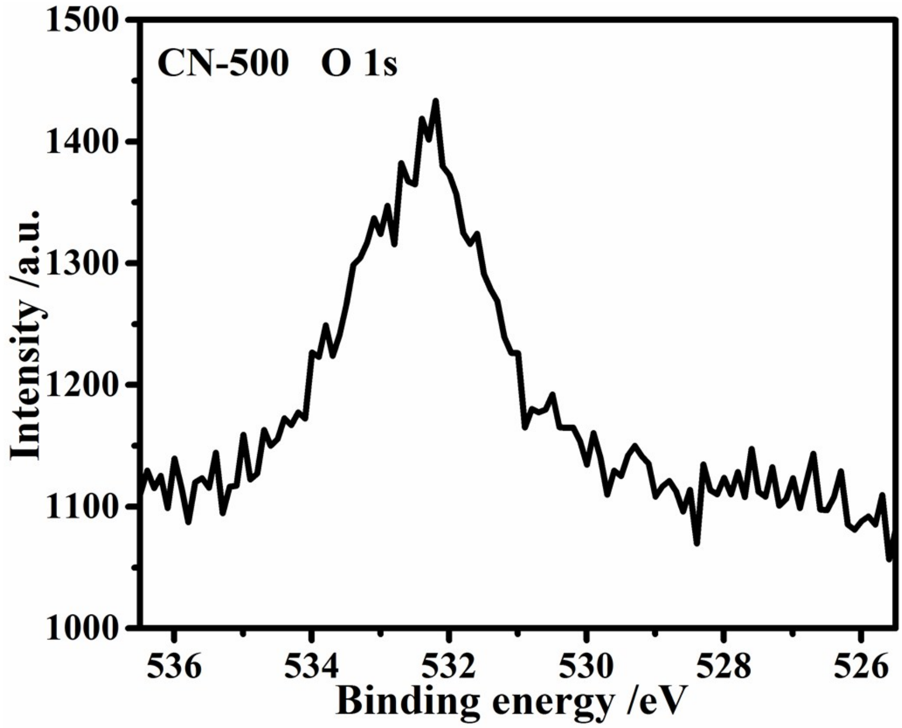


Fig. S15 O 1s high-resolution XPS spectra of g-C_3N_4.

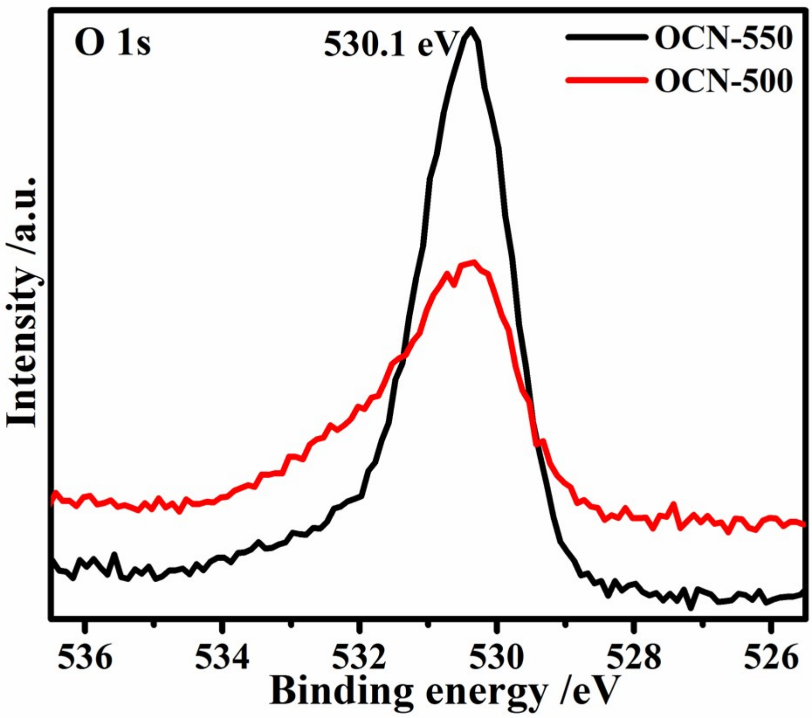


Fig. S16 O 1s high-resolution XPS spectra of OCN-500 and OCN-550.

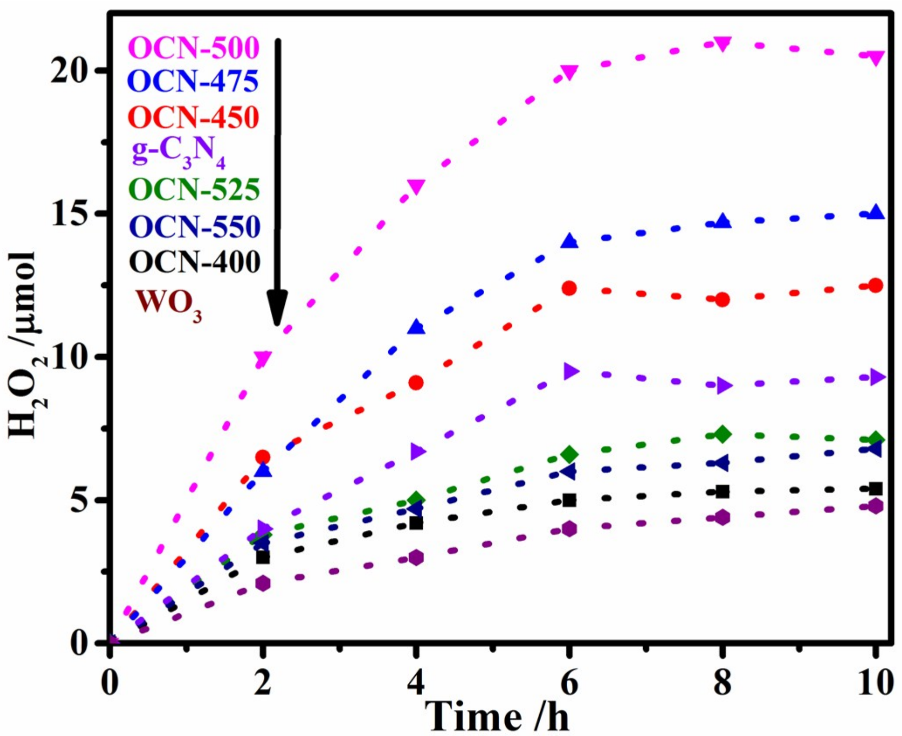


Fig. S17 The photocatalytic generation of H_2O_2 in pure water under visible light irradiation with air atmosphere.

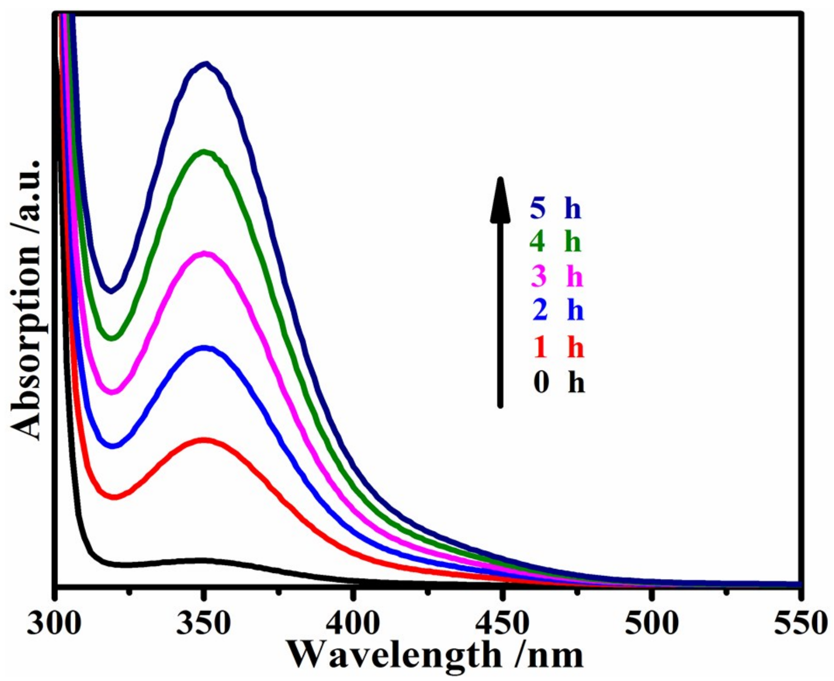
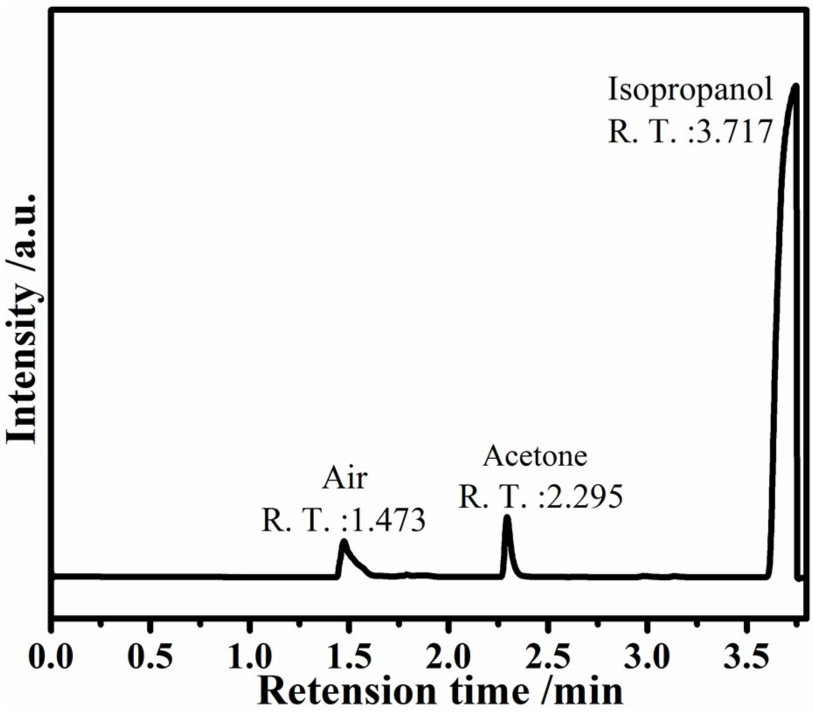
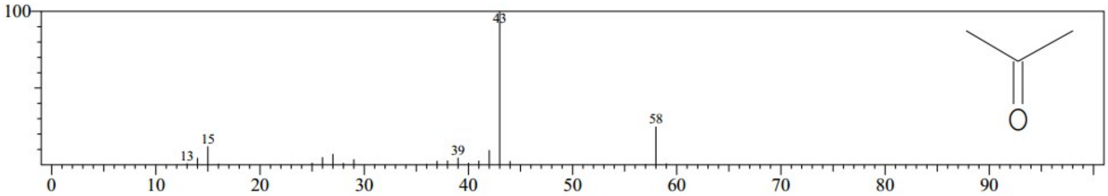
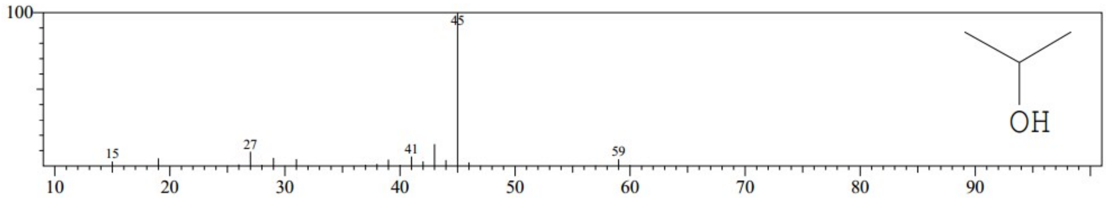


Fig. S18 UV-vis absorption spectrum changes of H_2O_2 generation of OCN-500 in isopropyl alcohol under visible light irradiation.





The MS spectrum of R.T. was 2.295 min.



The MS spectrum of R.T. was 3.717 min.

Fig. S19 Gas Chromatography–Mass Spectrometry (GC-MS) analysis for OCN-500 photocatalytic generation of H_2O_2 with 10% isopropyl alcohol under visible light irradiation.

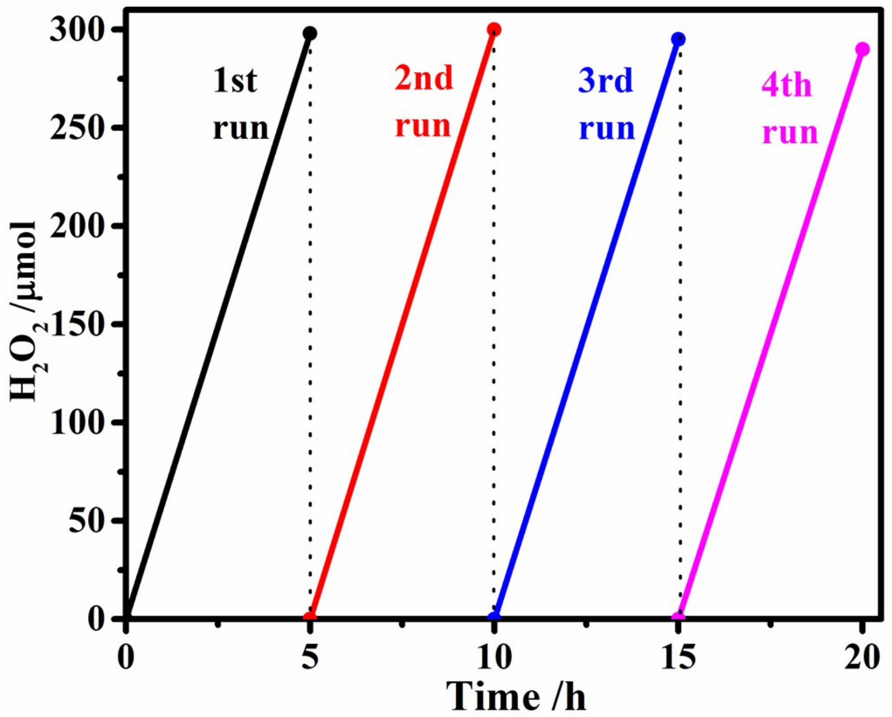


Fig. S20 The photocatalytic generation of H_2O_2 by OCN-500 for four times with 10% isopropyl alcohol under visible light irradiation.

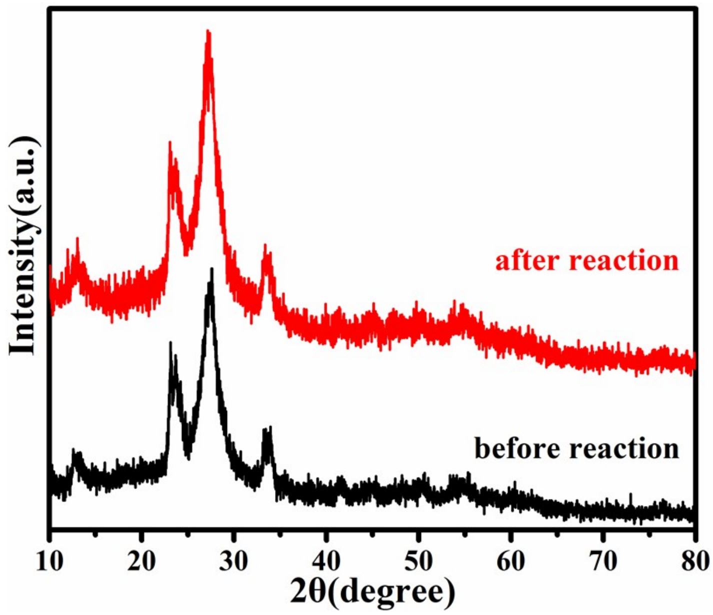


Fig. S21 XRD patterns of OCN-500 after 4 cycles of the photocatalytic generation of H_2O_2 with 10% isopropyl alcohol under visible light irradiation.

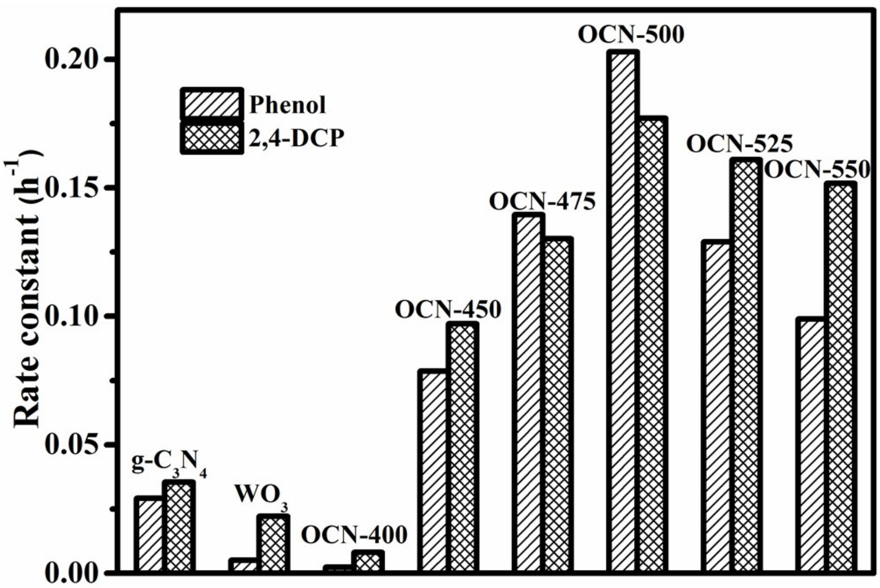


Fig. S22 Photocatalytic degradation of phenol and 2,4-DCP by different samples under visible light irradiation.

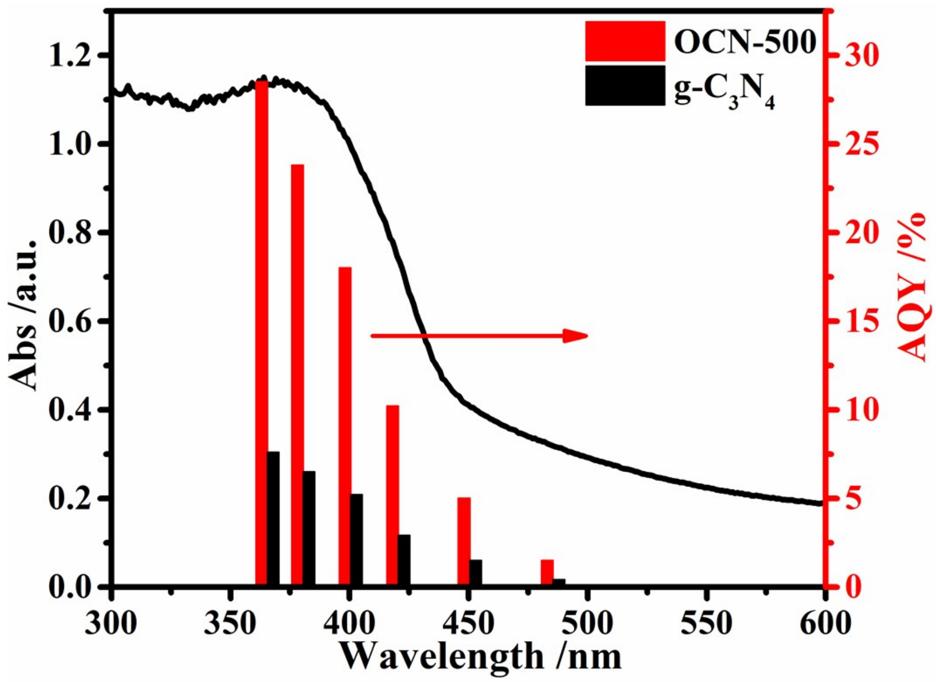


Fig. S23 Diffuse reflectance absorption spectra (left axis) of OCN-500 and apparent quantum yield (AQY, right axis) of g-C_3N_4 and OCN-500 photocatalytic H_2O_2 production with monochromatic light irradiation. The experimental conditions were as follows: 1 g/L of photocatalyst, 10 vol % of isopropyl alcohol, and O_2-saturated.

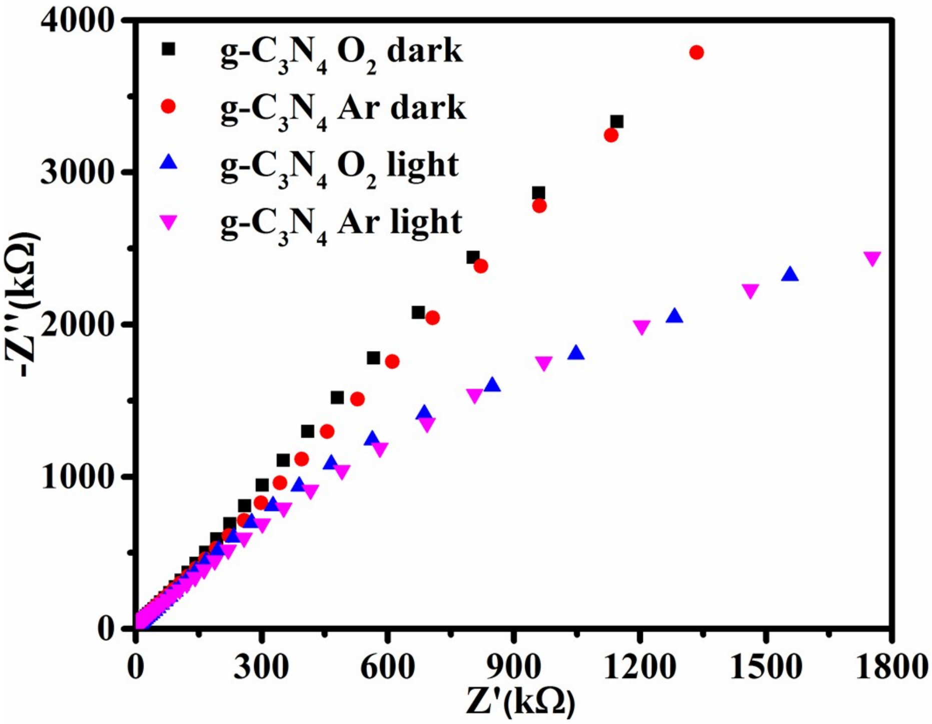


Fig. S24 Electrochemical impedance spectroscopy Nyquist plots of g-C_3N_4 with saturated Ar or O_2 atmosphere.

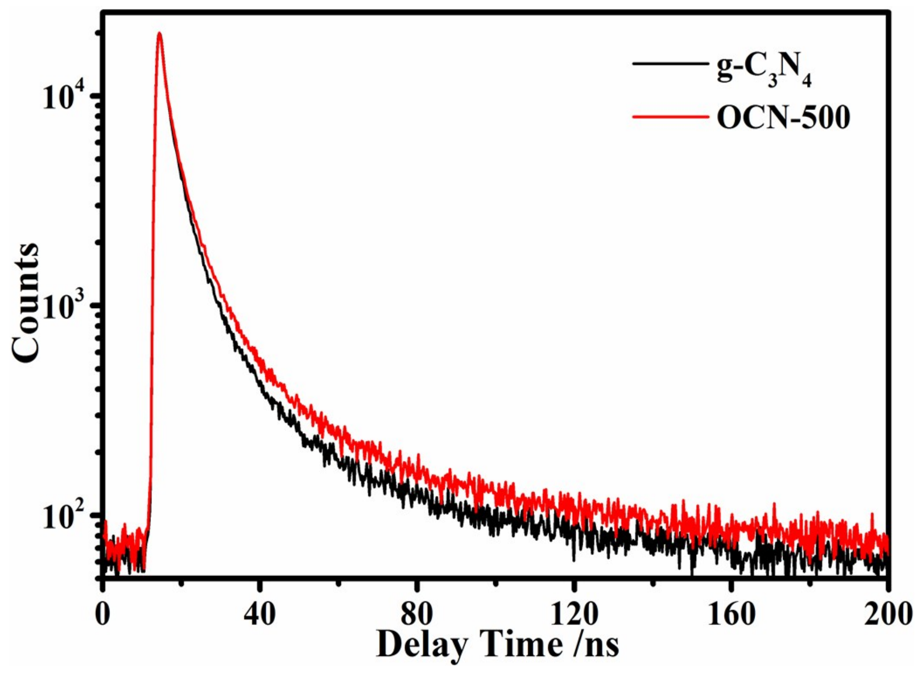


Fig. S25. Room temperature time-resolved transient photoluminescence decays spectroscopy for OCN-500 and g-C_3N_4, excited at 360 nm.

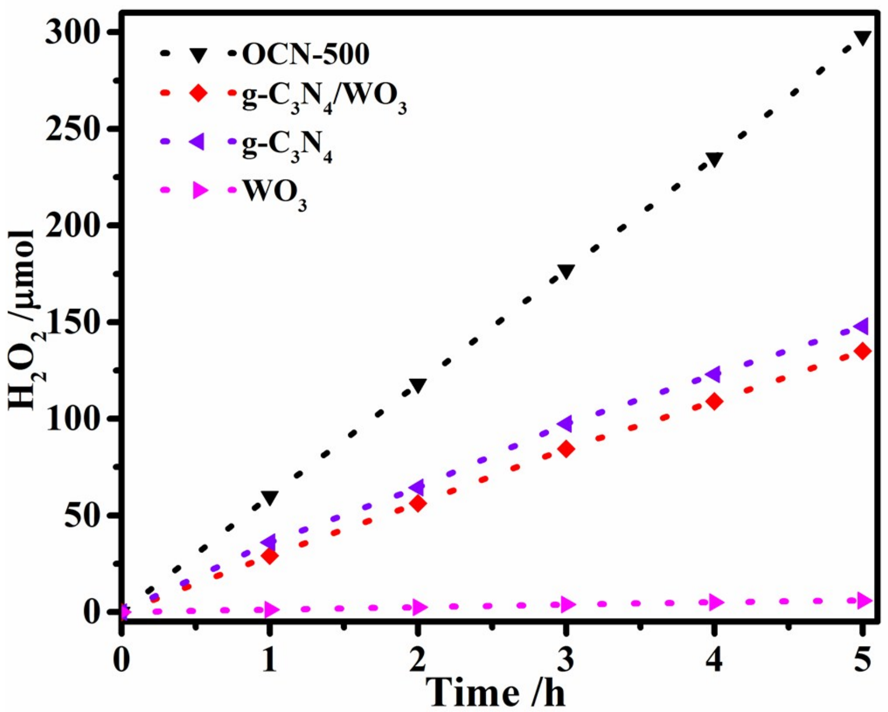


Fig. S26. The photocatalytic generation of H_2O_2 with 10% isopropyl alcohol under visible light irradiation. (g-C_3N_4/WO_3: g-C_3N_4 and WO_3 are ground and mixed according to the ratio of carbon nitride and tungsten in OCN-500)

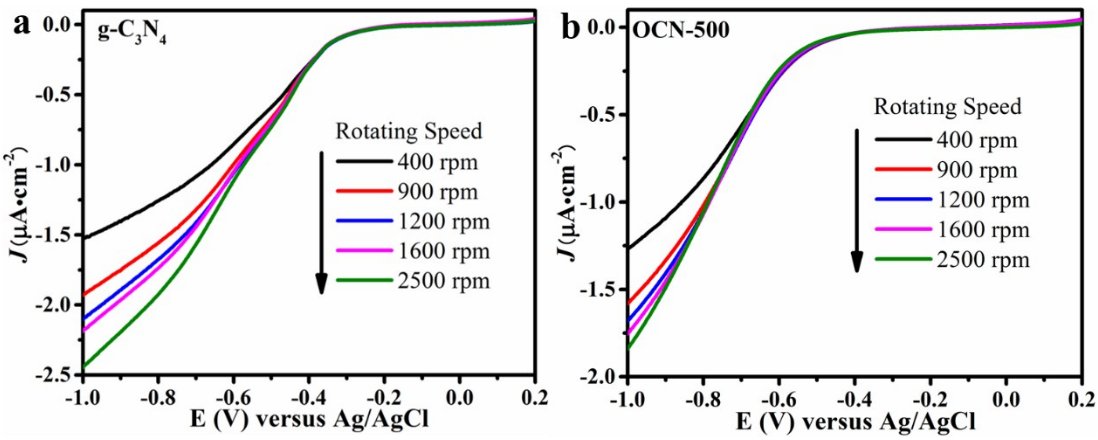


Fig. S27. LSV curves of g-C_3N_4 (a) and OCN-500 (b) measured on RDE analysis at different rotating speeds.

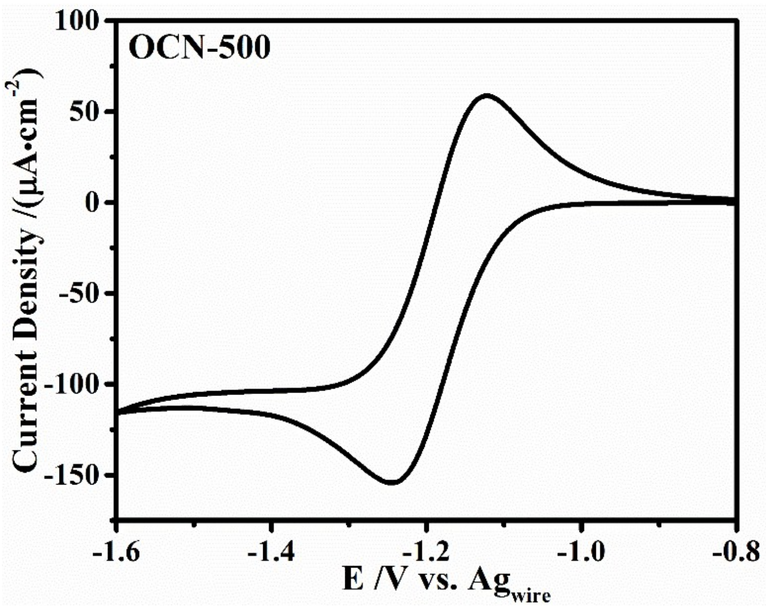


Fig. 28 Cyclic voltammetry for OCN-500 in acetonitrile solution. Experiment conditions: 0.1 M TBAP (tetra-n-butylammonium perchlorate), scan rates 10 mV/s, A silver wire was used as a reference electrode. All solutions were thoroughly degassed with N_2 before each experiment, and an inert atmosphere was maintained during the experiments.

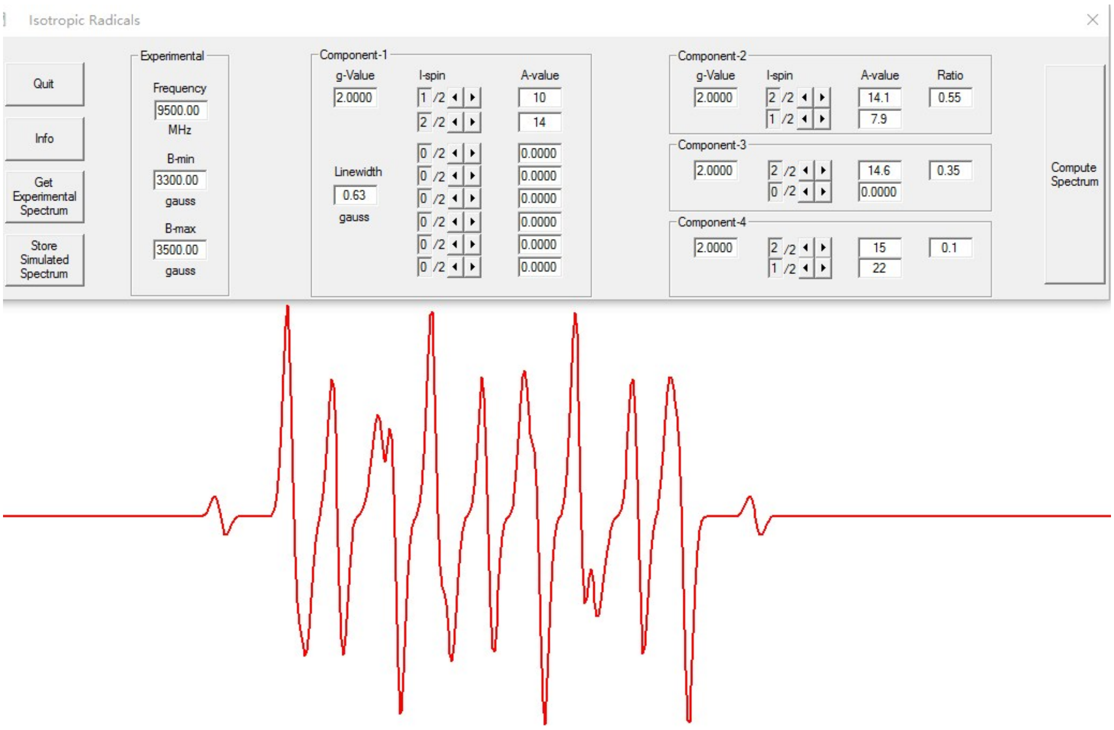


Fig. S29. The simulation ESR spectra of OCN-500 under visible light irradiation by the “Isotropic Radicals” software.

The simulation were performed by “Isotropic Radicals” software. In Fig. S29， A-value represents hyperfine splitting constants. The type of free radicals were judged from the A-value.

In component-1, A_N=14, A_H=10 attributed to ROO·;

In component-2, A_N=14.1 A_H=7.9 attributed to RO·;

In component-3, A_N=14.6, A_H=10 attributed to RN·;

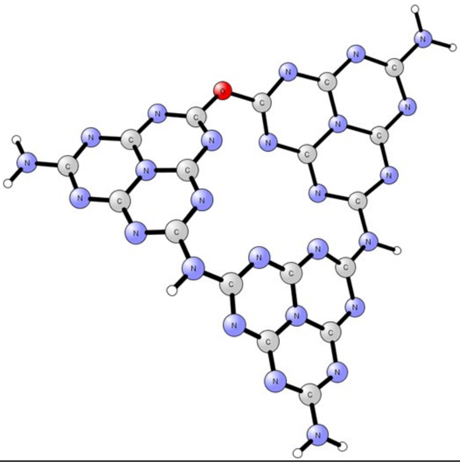
In component-4, A_N=15, A_H=22 attributed to R·.

Table S4. A detailed comparison of photocatalytic H_2O_2 production by different photocatalysts

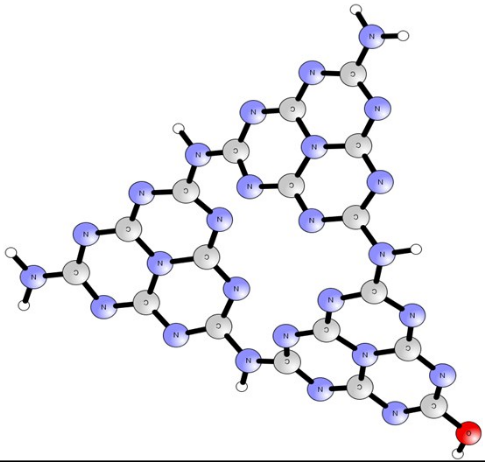
Catalyst	Conditions	Formed H_2O_2	Ref.
OCN-500	O_2; 1 g/L (catalyst), 10 vol % of 2-propanol, in water (pH=7); Xe-lamp λ≥420nm, 35.2 mW/cm^2; 298K	730 μmol for 5h	This work
OCN-500	O_2; 1 g/L, in the pure water; Xe-lamp λ≥420nm, 35.2 mW/cm^2; 298K	53 μmol for 10h	This work
g-C_3N_4/PDI	O_2; 1.67g/L; in the pure water; 420−500 nm, 43.3 W/m^2; 298K	14 μmol for 24h	1
g-C_3N_4/PDI/rGO0.05	O_2; 1.67g/L; in the pure water; Xe-lamp 420−500 nm, 43.3 W/m^2; 298K	29 μmol for 24h	1
g-C_3N_4/PDI/rGO0.05	O_2; 1.67g/L; 90 vol % of 2-propanol; Xe-lamp 420−500 nm, 43.3 W/m^2; 298K	400 μmol for 6h	1
g-C_3N_4/PDI51	O_2; 1.67g/L,;in the pure water; Xe-lamp 420−500 nm, 26.9 W/m^2; 298K	50.6 μmol for 48h	7
g-C_3N_4	O_2; 1.67g/L; 90 vol % of 2-propanol, Xe-lamp 420−500 nm, 26.9 W/m^2; 298K	148 μmol for 6h	7
g-C_3N_4/PDI51	O_2; 1.67g/L; 90 vol % of 2-propanol, 420−500 nm, 26.9 W/m^2; 298K	210 μmol for 6h	7
g-C_3N_4	O2; 4g/L, 90 vol % of ethanol, Xe-lamp 420−500 nm, 26.9 W/m^2; 298K	30 μmol for 12h	8
Mesoporous g-C_3N_4	O_2; 4g/L, 90 vol % of ethanol, Xe-lamp 420−500 nm, 26.9 W/m^2; 298K	92 μmol for 24h	9
CdS-graphene oxide	O_2-saturated; 0.5 g/L; 5 vol % of methanol, pH = 4.0; λ_{Ex} = 635 nm, 23 mW/cm^2	95 μM for 1h ,without longer reaction	10
reduced graphene oxide–TiO_2	O_2-saturated；0.5 g/L, 0.1 M phosphate buffer, 5 vol% 2-propanol, pH=3.0, **λ ≥320 nm**	4.8 mM for 3h	11
CoP decorated g-C_3N_4 (50Co/CN)	O_2-saturated;1g/L; 10 vol % of ethanol; Xe-lamp λ≥420nm	140 μM for 2h	12
g-C_3N_4	O_2-saturated;1g/L; 10 vol % of ethanol; Xe-lamp λ≥420nm	30 μM for 2h	12
CoP decorated g-C_3N_4 (50Co/CN)	Air;1g/L; 10 vol % of ethanol; Xe-lamp λ≥420nm	38 μM for 2h	12
g-C_3N_4	Air;1g/L catalyst; 10 vol % of ethanol; Xe-lamp λ≥420nm	10 μM for 2h	12
3DOM g-C_3N_4-PW_{11}	O_2-saturated; 1 g/L; in the pure water; λ ≥ 320 nm;298K	35 μmol for 1h; 144 μmol for 6h	13
3DOM g-C_3N_4	O_2-saturated; 1 g/L; in the pure water; λ ≥	13 μmol for 1h;	13

	320 nm;298K	23 μmol for 6h	
melam/WO_3	Air; 1g/L; in the pure water; 435 nm LED; 3.0 mW/cm^2	19 μM for 6h	5
Pt−WO_3	Air; 1.30 g/L; 0.43 mM phenol aqueous solution；Xe-lamp λ≥420nm, 25.2 mW/cm^2;	23 μM for 1h, without longer reaction	14
Bi_2WO_6	Air; 1.30 g/L; 0.43 mM phenol aqueous solution；Xe-lamp λ≥420nm, 25.2 mW/cm^2;	8 μM for 1h, without longer reaction	14
$Au_{0.1}Ag_{0.4}/TiO_2$	O_2; 1g/L, 4 vol % of ethanol; Hg lamp, **λ >280 nm**, 13.8 mW/cm^2; 298K	3.6 mM for 12 h	15

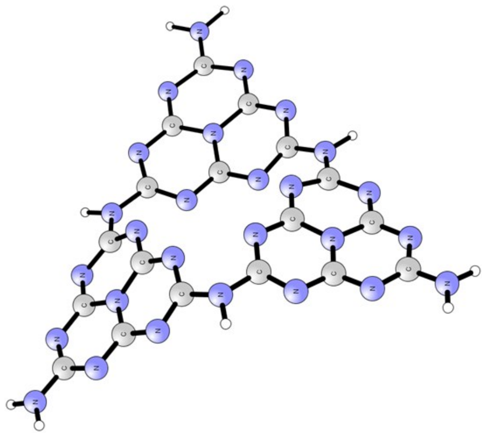
Cartesian Coordinates (in Å)



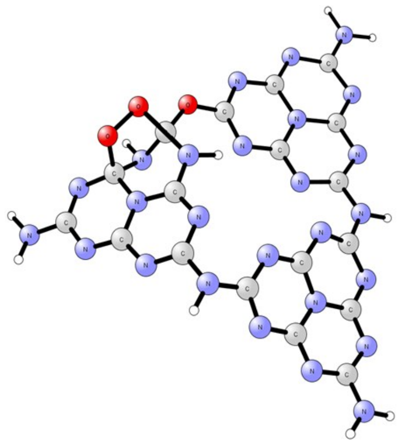
1. (C-O-C) a1 (53 atoms)							
N	-3.329219	3.018381	0.587859	C	6.331421	-1.488857	0.436987
C	-2.732063	1.916256	1.066905	H	1.410164	-4.656782	-0.834511
N	-3.596848	0.839842	1.246896	N	-5.006632	-3.391977	0.028079
N	-1.441257	1.743478	1.345957	C	-4.598503	-4.593913	-0.43176
C	-0.60971	2.626805	0.8104	N	-3.338545	-5.00466	-0.695048
N	0.707809	2.435971	0.827007	C	-2.37063	-4.141674	-0.428823
N	-1.127251	3.759244	0.161299	N	-1.08749	-4.409896	-0.700154
C	-2.519819	3.990851	0.164401	N	-2.705544	-2.886061	0.122673
N	-2.984907	5.141937	-0.298096	C	-4.055138	-2.512684	0.304492
C	-2.071654	6.003178	-0.791428	N	-4.333838	-1.273049	0.718393
N	-0.73962	5.815848	-0.926307	C	-3.279491	-0.494258	1.014951
C	-0.256098	4.681411	-0.451881	N	-1.997969	-0.838401	1.057835
N	1.040275	4.361521	-0.563594	C	-1.688012	-2.016993	0.538941
C	1.411925	3.245894	0.04569	N	-0.423633	-2.366671	0.372508
N	1.726886	-1.475564	-0.948018	C	-0.201692	-3.475537	-0.332496
C	2.107201	-2.723214	-0.656831	H	-4.569786	1.062545	1.06529
N	1.11692	-3.69772	-0.696411	N	7.610302	-1.804738	0.702866
N	3.333203	-3.158945	-0.351421	H	7.892178	-2.772892	0.706498
C	4.256926	-2.215878	-0.138942	H	8.258811	-1.074214	0.953489
N	5.511316	-2.522153	0.152125	N	-5.570028	-5.49302	-0.669312
N	3.866783	-0.860143	-0.177463	H	-5.32764	-6.398484	-1.040778
C	2.585145	-0.515472	-0.639802	H	-6.532705	-5.23435	-0.517739
N	2.254257	0.771875	-0.733521	N	-2.543119	7.187518	-1.217294
C	3.117701	1.628428	-0.201491	H	-3.533531	7.372095	-1.17487
N	4.352217	1.419107	0.231821	H	-1.907511	7.855332	-1.62597
C	4.778869	0.150859	0.187926	O	2.732516	2.938007	-0.131208
N	6.021876	-0.175794	0.497725				



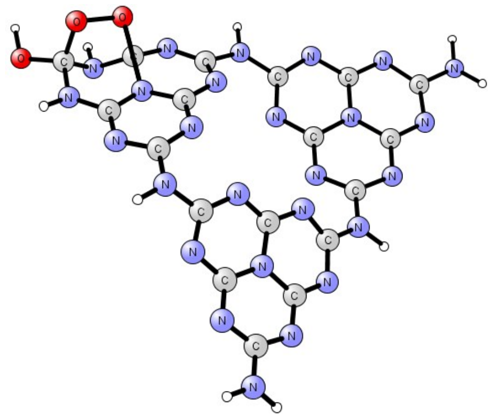
2. (-OH) a2 (53 atoms)							
N	-3.829114	2.507837	0.413546	N	4.167587	2.078623	-0.044956
C	-3.087247	1.465547	0.836836	C	4.781323	0.88943	-0.025493
N	-3.7905	0.274528	0.949285	N	6.092248	0.78467	0.124814
N	-1.787763	1.456806	1.113116	C	6.593345	-0.468483	0.173872
C	-1.086969	2.493537	0.677493	H	2.159153	-4.463724	-0.324401
N	0.237317	2.479761	0.701501	N	-4.419629	-4.141272	-0.267488
N	-1.753867	3.604425	0.135777	C	-3.789488	-5.286769	-0.604316
C	-3.16529	3.618741	0.104279	N	-2.460429	-5.520563	-0.67099
N	-3.788981	4.735177	-0.267215	C	-1.669369	-4.521844	-0.311463
C	-3.002119	5.754596	-0.607332	N	-0.336448	-4.604198	-0.401119
N	-1.663117	5.810318	-0.676315	N	-2.247835	-3.315316	0.136604
C	-1.007487	4.709827	-0.312596	C	-3.646903	-3.130363	0.100736
N	0.318538	4.612232	-0.399429	N	-4.146419	-1.928796	0.404834
C	0.852267	3.461716	0.045136	C	-3.264124	-1.010786	0.833667
N	2.205082	3.288809	-0.187482	N	-1.977708	-1.183774	1.112546
O	-3.644775	6.873706	-0.93941	C	-1.430987	-2.311681	0.677566
H	-2.957623	7.525086	-1.17198	N	-0.118612	-2.483354	0.703535
N	1.916633	-1.291893	-0.564945	C	0.349142	-3.544842	0.046266
C	2.525511	-2.43818	-0.257343	H	2.765966	4.116308	-0.346861
N	1.718447	-3.564093	-0.179133	H	-4.768668	0.345301	0.689943
N	3.832269	-2.645549	-0.049516	N	7.929067	-0.562719	0.297751
C	4.607182	-1.555963	-0.028728	H	8.35679	-1.472672	0.373763
N	5.920679	-1.637316	0.120466	H	8.48001	0.278112	0.376467
N	4.004423	-0.283781	-0.134175	N	-4.58447	-6.322147	-0.92771
C	2.635265	-0.187253	-0.432948	H	-4.169469	-7.193383	-1.219864
N	2.081437	1.010524	-0.567756	H	-5.58508	-6.197755	-0.927238
C	2.84683	2.056187	-0.259531				



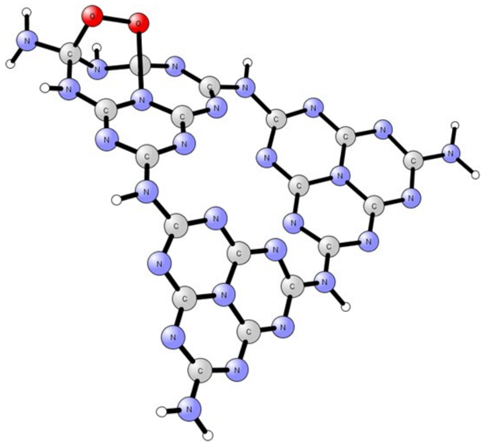
3.	(-NH$_2$)	a3 (54 atoms)					
N	-3.994298	2.223066	0.408662	C	6.614694	-0.002419	0.162702
C	-3.180347	1.243277	0.840132	H	2.472354	-4.300826	-0.325076
N	-3.796963	0.001396	0.957276	N	-4.112037	-4.444068	-0.270866
N	-1.884751	1.326722	1.121169	C	-3.402131	-5.540021	-0.611665
C	-1.259199	2.411406	0.683955	N	-2.060011	-5.679787	-0.677919
N	0.062481	2.490809	0.712592	C	-1.341451	-4.628749	-0.313763
N	-2.001587	3.469325	0.137947	N	-0.006303	-4.616931	-0.402337
C	-3.410168	3.383793	0.101213	N	-2.004058	-3.46791	0.137769
N	-4.108759	4.446793	-0.271774	C	-3.412595	-3.381454	0.101683
C	-3.397982	5.542182	-0.612595	N	-3.995901	-2.220313	0.40916
N	-2.055792	5.680881	-0.678811	C	-3.18107	-1.240741	0.839517
C	-1.338059	4.62946	-0.314028	N	-1.885279	-1.324703	1.11939
N	-0.002945	4.616699	-0.402234	C	-1.260745	-2.410202	0.682908
C	0.605258	3.5129	0.051397	N	0.060832	-2.490473	0.71115
N	2.005453	-1.154611	-0.55833	C	0.602761	-3.513278	0.050393
C	2.694802	-2.254274	-0.25377	H	-4.775911	0.00176	0.692267
N	1.969783	-3.435193	-0.174824	N	7.954897	-0.002908	0.281122
N	4.013875	-2.369376	-0.049424	H	8.444784	-0.880603	0.359672
C	4.709719	-1.227704	-0.031294	H	8.445352	0.874403	0.360425
N	6.026528	-1.216217	0.112657	N	-4.121641	-6.628371	-0.940427
N	4.018389	-0.001411	-0.134076	H	-3.645382	-7.466681	-1.235123
C	2.644178	-0.000847	-0.427124	H	-5.128457	-6.57555	-0.939964
N	2.006222	1.15349	-0.557599	N	-4.116653	6.631176	-0.941201
C	2.696426	2.252441	-0.252544	H	-5.123445	6.577872	-0.944523
N	4.015568	2.366492	-0.047711	H	-3.639737	7.467831	-1.239544
C	4.710556	1.224316	-0.030218	N	1.972325	3.43392	-0.173406
N	6.027335	1.211803	0.114034	H	2.475582	4.299179	-0.323454



(4) (C-O-C) e1 (57 atoms)							
N	0.229881	-4.383577	-0.163192	N	-5.939324	-1.995851	0.316686
C	-0.339168	-3.344253	-0.759176	C	-6.65933	-0.907281	0.656297
N	-1.72834	-3.450054	-0.89222	N	-6.254239	0.383391	0.697814
N	0.247934	-2.215252	-1.194608	C	-5.021016	0.62222	0.285919
C	1.51247	-2.095111	-0.853508	N	-4.469102	1.841802	0.35157
N	2.183775	-0.956348	-1.156101	N	-4.234432	-0.447303	-0.188883
N	2.188289	-3.066327	-0.181746	C	-4.698774	-1.777367	-0.097168
C	1.537487	-4.255625	0.170619	N	-3.859409	-2.771013	-0.389806
N	2.172578	-5.173336	0.85296	C	-2.644938	-2.414964	-0.84613
C	3.428106	-4.832005	1.298464	N	-2.241614	-1.196148	-1.208617
N	4.089844	-3.699984	1.143171	C	-3.000686	-0.190892	-0.803088
C	3.561545	-2.761793	0.291082	N	-2.578498	1.065088	-0.90668
N	3.505945	-1.380973	0.768315	C	-3.251104	1.958292	-0.188358
C	3.463874	-0.685778	-0.49872	H	-2.091911	-4.326116	-0.531667
N	-0.478002	2.267295	0.135149	N	2.850452	7.382966	0.507231
C	-1.245489	3.365368	0.120855	H	2.228827	8.17113	0.605753
N	-2.60922	3.177035	0.037882	H	3.850873	7.510479	0.486153
N	-0.84106	4.639238	0.215509	N	-7.934986	-1.131436	1.016943
C	0.479054	4.84679	0.254313	H	-8.508132	-0.358744	1.318831
N	0.992283	6.05979	0.379171	H	-8.283522	-2.077329	1.043265
N	1.354248	3.742294	0.133911	N	4.012074	-5.796475	2.051615
C	0.822016	2.452618	0.082846	H	3.567262	-6.699557	2.097724
N	1.65361	1.412766	-0.04193	H	4.983993	-5.697572	2.299852
C	2.946178	1.690465	-0.154684	O	3.805877	0.672174	-0.422137
N	3.552344	2.867043	-0.070745	O	4.515893	-1.243056	-1.275367
C	2.75456	3.931535	0.09463	O	4.40832	-2.672504	-0.937343
N	3.24012	5.152445	0.212942	H	4.400942	-1.181807	1.218756
C	2.338929	6.150484	0.362975	H	1.562161	-0.158066	-1.264389
H	-3.189573	3.958927	0.317073				



(5) (-OH) e2 (57 atoms)							
N	3.366491	-2.674282	-0.312543	N	-1.839536	5.939716	-0.084954
C	2.126577	-2.351076	-0.795668	C	-3.186275	5.946351	-0.138959
N	1.286287	-3.449518	-0.931632	H	-5.286783	0.359243	0.327744
N	1.67549	-1.154288	-1.091553	N	-2.602722	-5.649503	0.255719
C	2.398186	-0.104788	-0.662955	C	-3.902129	-5.479662	0.580339
N	1.920203	1.112283	-0.713219	N	-4.605111	-4.328338	0.640172
N	3.655268	-0.343758	-0.101775	C	-3.960443	-3.226646	0.285252
C	4.115035	-1.634734	-0.014706	N	-4.522338	-2.016441	0.37255
N	5.389494	-1.775066	0.421146	N	-2.623107	-3.326733	-0.153976
C	6.196328	-0.589828	0.641741	C	-1.940689	-4.561038	-0.109323
N	5.359045	0.363474	1.336928	N	-0.637434	-4.587333	-0.401279
C	4.523749	0.817673	0.244459	C	-0.103325	-3.430746	-0.831453
N	3.821882	1.996949	0.475842	N	-0.730788	-2.299094	-1.122686
C	2.607067	2.05217	-0.020081	C	-1.983917	-2.200189	-0.693918
N	1.910569	3.247489	0.183167	N	-2.621013	-1.042017	-0.724252
O	7.355344	-0.98293	1.254925	C	-3.781421	-0.990205	-0.068021
H	8.041545	-0.340763	1.004128	H	2.455679	4.091694	0.300104
N	-2.243532	1.284016	0.545923	H	1.702103	-4.330802	-0.652182
C	-3.531285	1.437736	0.245219	N	-3.766522	7.156294	-0.248185
N	-4.291267	0.275359	0.165482	H	-4.768836	7.217914	-0.336754
N	-4.203747	2.578418	0.045071	H	-3.186905	7.977454	-0.32601
C	-3.471806	3.698131	0.03532	N	-4.579492	-6.598066	0.89832
N	-4.029102	4.891701	-0.100793	H	-5.543573	-6.528432	1.184941
N	-2.068082	3.600419	0.139553	H	-4.09791	-7.483728	0.906203
C	-1.473281	2.358349	0.421275	O	6.548018	0.044392	-0.614747
N	-0.158499	2.275526	0.550974	O	5.464746	1.01769	-0.864551
C	0.53971	3.377188	0.261807	H	5.839615	-2.67621	0.335995
N	0.067634	4.620537	0.072597	H	5.912634	1.158962	1.655328
C	-1.259233	4.754189	0.049553				



6. (-NH_2) e3 (58 atoms)							
N	3.381945	-2.645948	-0.336582	H	-5.285144	0.32079	0.350869
C	2.137278	-2.331625	-0.814012	N	-2.559977	-5.669237	0.248531
N	1.306758	-3.437707	-0.95559	C	-3.858121	-5.508752	0.58249
N	1.672652	-1.137947	-1.098995	N	-4.568362	-4.362376	0.650619
C	2.385487	-0.084487	-0.662559	C	-3.933397	-3.255289	0.294541
N	1.903043	1.129952	-0.717089	N	-4.502955	-2.049278	0.388618
N	3.639148	-0.317462	-0.091465	N	-2.598366	-3.345358	-0.153657
C	4.116526	-1.600758	-0.021945	C	-1.907317	-4.575206	-0.117463
N	5.393565	-1.735391	0.420664	N	-0.605851	-4.591999	-0.41744
C	6.21169	-0.543142	0.632719	C	-0.082014	-3.430486	-0.84775
N	5.355125	0.408423	1.324597	N	-0.719766	-2.302752	-1.132486
C	4.512364	0.84531	0.230288	C	-1.970057	-2.212945	-0.69423
N	3.808553	2.028527	0.455022	N	-2.614449	-1.058482	-0.715826
C	2.590418	2.075302	-0.030217	C	-3.771586	-1.016541	-0.053317
N	1.886783	3.267618	0.173965	H	2.426214	4.117164	0.277513
N	-2.249116	1.271323	0.557927	H	1.731834	-4.316676	-0.682965
C	-3.538652	1.41349	0.259641	N	-3.823498	7.128051	-0.253537
N	-4.289546	0.244562	0.185485	H	-4.826403	7.180582	-0.341046
N	-4.221267	2.547786	0.057485	H	-3.251045	7.953681	-0.336712
C	-3.498757	3.673552	0.041897	N	-4.525879	-6.632528	0.902339
N	-4.066506	4.86188	-0.097103	H	-4.039848	-7.515748	0.899465
N	-2.094097	3.587931	0.142873	O	6.554934	0.08937	-0.621079
C	-1.487958	2.35199	0.428095	O	5.442587	1.026997	-0.884133
N	-0.172558	2.281096	0.555976	H	5.874274	-2.596128	0.190511
C	0.516249	3.387156	0.258813	H	5.903681	1.218313	1.615672
N	0.032682	4.625895	0.066605	N	7.435753	-0.942589	1.230823
C	-1.295067	4.748156	0.046919	H	8.100828	-0.174892	1.231702
N	-1.885903	5.928433	-0.09008	H	7.282937	-1.27915	2.177698
C	-3.232591	5.923415	-0.141194	H	-5.489865	-6.570698	1.190951

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