

Supporting Information for.

Sustainable Photocatalytic Synthesis of Hydrogen Peroxide from Catechol-Formaldehyde Resin Microspheres Modulated by Nitrogen-Doped Carbon Dots

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Preparation of CA CDs: CA CDs were synthesized from “bottom to top” method.¹ The round-bottomed flask containing citric acid (2 g) into 200 °C oil bath was put. After heating for 30 min, citric acid turned into orange liquid, indicating that CA CDs were formed. Then the product was added in NaOH solution (0.2 M) to obtain a neutral solution. Finally, CA CDs were purified by filtration and dialysis with a cellulose ester membrane bag (MW 3500 Da) for 3 days and the product in the dialysis membrane was dried by a freezing dryer.

Preparation of CA-Tris CDs: CA-Tris CDs were prepared by hydrothermal synthesis.² First, 0.21 g citric acid and 0.12 g Tris were dissolved in 10 mL ultrapure water thoroughly to form a clear solution. Then, the solution was transferred into a poly(tetrafluoroethylene) (Teflon)-lined autoclave (30 mL) and heated at a specific temperature (250 °C) for 6 h. After the reaction, the reactors were cooled down at room temperature. The deep-brown aqueous dispersion formed was centrifuged at high speed (12,000 rpm/min) for 15 min in order to remove any insoluble particulates. Then the upper brown solution was dialyzed against ultrapure water through a dialysis membrane (MW 3500 Da) for 3 days.

At last, the product in the dialysis membrane was dried by a freezing dryer.

Synthesis of CFR/CA CDs: CFR/CA CDs composite was synthesized by freeze-drying method. 95 wt % CFR microspheres and 5 wt % CA CDs (total mass 50 mg) dissolved in 30 mL deionized water, ultrasonic until completely dissolved. Finally, the composite was prepared by 24 h freeze-drying method.

Synthesis of CFR/CA-Tris CDs: CFR/CA-Tris CDs composite was synthesized by freeze-drying method. 95 wt % CFR microspheres and 5 wt % CA-Tris CDs (total mass 50 mg) dissolved in 30 mL deionized water, ultrasonic until completely dissolved. Finally, the product in the dialysis membrane was dried by a freezing dryer.

Instrument characterization

Scanning electron microscopy (SEM)(Hitachi SU8010) and field emission transmission electron microscopy (TEM) (JEM-2100F) were used to detect the size and morphology of the samples. The XRD pattern was determined with X-ray powder diffractometer (Dmax2200PC). The surface functional groups and chemical bonds of the samples were determined by Fourier Transform infrared (FT-IR) spectrometer (Magna 560), diffuse infrared Fourier transform spectroscopy (DRIFTS) (Magna 560 FTIR spectrometer) and X-ray photoelectron spectroscopy (XPS)(X-TOOL, ULVAC-PHI). The light absorption of materials was measured by SHIMADZU UV-2550 UV-vis spectrophotometer. The photoluminescence (PL) spectra were collected by the Varian Cary 5000 spectrophotometer. A three-electrode CHI 660D electrochemical workstation was used for the photoelectrochemical test. Saturated calomel electrode (SCE) and Pt sheet electrode (1 cm × 1 cm) were used as reference electrode and the opposite electrode, respectively.

The rotating ring-

disk electrode (RRDE) measurements were performed on BAS Inc setup with CHI 760E workstation. Electron spin resonance (ESR) spectra of $\cdot\text{O}_2^-$ in water were collected by Bruker EMXplus system using 5, 5-dimethyl-1-pyrroline n-oxide (DMPO) as spin catcher.

Determination of apparent quantum efficiency (AQE)

The catalyst (50 mg) and water (30 mL) were added to the three-hole reaction bottle, and the O_2 was bubbled in the solution for 15 min. Magnetically stirred in a 25 °C water bath and illuminated by 300 W xenon lamps with bandpass filters (420, 475, 520, 600 and 700 nm). For the action spectrum analysis, the reactions were carried out for 6 h at 25 °C using the monochromated light, where Φ_{AQY} was determined using the following equation³:

$$\Phi_{\text{AQY}} (\%) = ((\text{number of H}_2\text{O}_2 \text{ molecules}) \times 2) / (\text{number of incident photons}) \times 100 \quad \text{S1}$$

Determination of SCC efficiency

The solar-to-chemical conversion (SCC) efficiency of photocatalytic H_2O_2 production by CFR-140 or CFR/NCDs-220 was determined by the photoreaction under simulated solar light irradiation. The irradiance of solar simulator was adjusted to the AM1.5 global spectrum. The SCC efficiency was calculated by the following equation [3]:

$$\text{SCC efficiency} = [\Delta G^\circ \times n(\text{H}_2\text{O}_2)] / [(\text{total input energy}) \times (\text{reaction time})] \quad \text{S2}$$

Where ΔG° is the free energy for H_2O_2 generation ($117 \text{ kJ} \cdot \text{mol}^{-1}$), $n(\text{H}_2\text{O}_2)$ is the molar of the formed H_2O_2 (mol), the overall irradiance of the AM1.5 global spectrum (300-2500 nm) is $410 \text{ W} \cdot \text{m}^{-2}$, and the irradiation area is $8.2 \times 10^{-3} \text{ m}^2$. The total input power over the irradiation area is calculated to be 300 W.

Photoelectrochemical measurements

For electrochemical analysis, 0.1M Na₂SO₄ (pH 6.6) was used as electrolyte, and Pt wire and Ag/AgCl electrodes were used as counting electrodes and reference electrodes, respectively. The working electrode was prepared by the following method: 20 mg catalyst and 60 μL Nafion solution (5 wt %) were dispersed in 4 mL ethanol, and after ultrasound for 30 min, the mixture was uniformly dropped on FTO glass (1.0 cm × 1.0 cm) and dried at room temperature.⁴ 300 W Xenon light source with 420 nm cutoff filter (Beijing PerfectLight, China) was used to irradiate the working electrode.

The rotating ringdisk electrode (RRDE) measurements were performed on BAS Inc setup with CHI 760E workstation. Ag/AgCl used as a reference and Pt wire as a counter in an electrolyte composed of phosphate buffer (pH = 7, 0.1 M). The RRDE that was composed of a glassy carbon disk and a Pt ring was used as a working electrode. Prior to measurements, the catalyst ink was dropped on the glassy carbon disk and dried at room temperature.

Superoxide radical ($\cdot\text{O}_2^-$) examination : $\cdot\text{O}_2^-$ was examined by a Bruker model electron spin resonance (ESR) A300-10/12 spectrometer equipped with a quanta-Ray Nd: YAG laser system employing DMPO as the spin trapper. Typically, catalyst (0.10 g) was added to a aqueous solution containing DMPO (0.13 mmol). After O₂ bubbling for 10 min, the container was irradiated for 3 minutes. The catalyst was recovered by filtration, and the solution was subjected to analysis at 25 °C.

Table S1 | Properties of CFR spheres prepared under different conditions and their chem-catalytic activity for H₂O₂ production.

Sample	Temp. (°C)	Time (h)	Catechol/HCHO//NH ₃ (mmol/mmol/mmol)	Water/ethanol (mL/mL)	CFR diameter (µm)	H ₂ O ₂ ^a (µmol)
1	120	12	3.6/7.2/3.0	40/0	2-3	0.73
2	140	6	3.6/7.2/3.0	40/0	2-3	31
3	140	12	3.6/7.2/3.0	40/0	2-3	25
4	140	24	3.6/7.2/3.0	40/0	3-4	20.6
5	160	12	3.6/7.2/3.0	40/0	3-4	23.3
6	200	12	3.6/7.2/3.0	40/0	3-4	5
7	140	6	1.8/2.7/3	40/0	0.2-0.3	51
8	140	6	1.8/3.6/3	20/20	0.4-1	36.8
9	140	6	1.8/5.4/3	40/0	0.4-1	25

^a Reaction conditions: water (30 mL), catalyst (50 mg), O₂ (1 atm), temperature (298 K), catalytic time (6 h).

Table S2 | XPS analysis of CFR, NCDs-220 and CFR/NCDs-220.

Sample	Elemental Analysis (Atom conc %)		
	C	O	N
CFR	82.67	17.33	0
NCDs-220	79.31	15.13	5.56
CFR/NCDs-220	81.39	16.51	2.1

Table S3 | Performance summary of reported photocatalysts for H₂O₂ production.

Catalyst	Condition	Light source	H ₂ O ₂ yield [$\mu\text{mol g}^{-1} \text{h}^{-1}$]	SCC efficiency [%]	Φ_{AQY} (%)	Ref.
CFR/NCDs	O ₂ -saturated; 1.67 g·L ⁻¹ catalyst	Xe lamp ($\lambda > 420 \text{ nm}$)	213	≈ 1.06	7(420 nm)	This work
CFR	O ₂ -saturated; 1.67 g·L ⁻¹ catalyst	Xe lamp ($\lambda > 420 \text{ nm}$)	126.7	≈ 0.1	5.8 (420 nm)	This work
RF523	O ₂ -saturated; 1.67 g·L ⁻¹ catalyst	Xe lamp ($\lambda > 420 \text{ nm}$)	50	≈ 0.5	7.8 (420 nm)	[5]
RF-acid resins	O ₂ -saturated; 1.67 g·L ⁻¹ catalyst	Xe lamp ($\lambda > 420 \text{ nm}$)	65.8	≈ 0.7	8.5 (420 nm)	[6]
RF/P ₃ HT-1.0	O ₂ -saturated; 1.67 g·L ⁻¹ catalyst	Xe lamp ($\lambda > 420 \text{ nm}$)	233.3	≈ 1.0	11 (420 nm)	[7]
PDA	25.1 mg L ⁻¹	Xe lamp ($\lambda > 420 \text{ nm}$)	250	-	2 (280 nm)	[8]
RF-GQDs-0.4	O ₂ -saturated; 0.2 g·L ⁻¹ catalyst	Xe lamp ($\lambda > 420 \text{ nm}$)	4083.3	≈ 1.1	-	[9]
TiO ₂ @RF	O ₂ -saturated; 0.67g L ⁻¹ catalyst	Xe lamp (AM 1.5)	1000	≈ 0.21	-	[10]

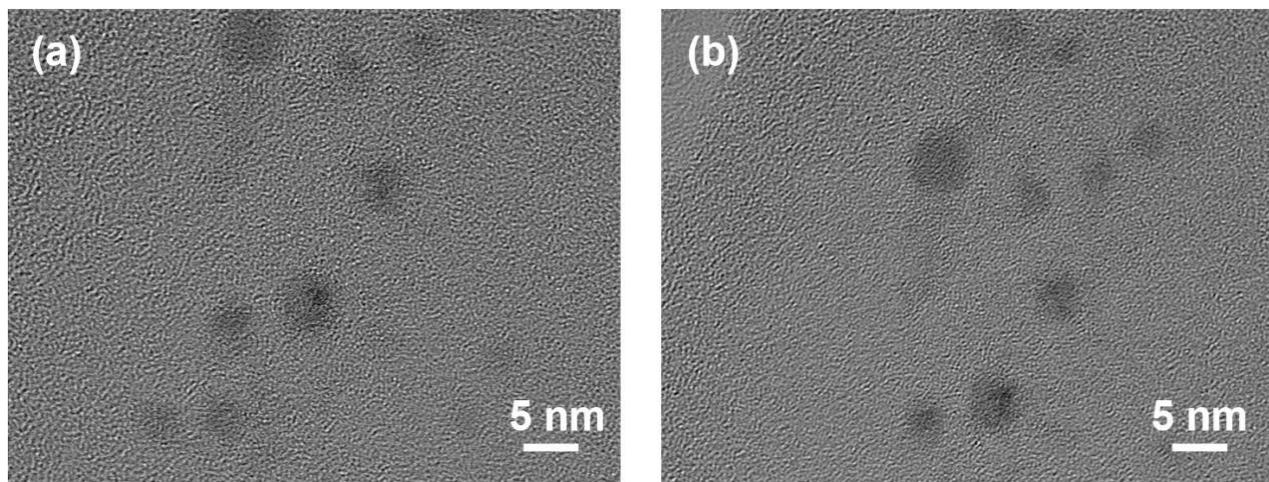


Fig.S1. TEM images of NCDs-200 (a) and NCDs-250 (b).

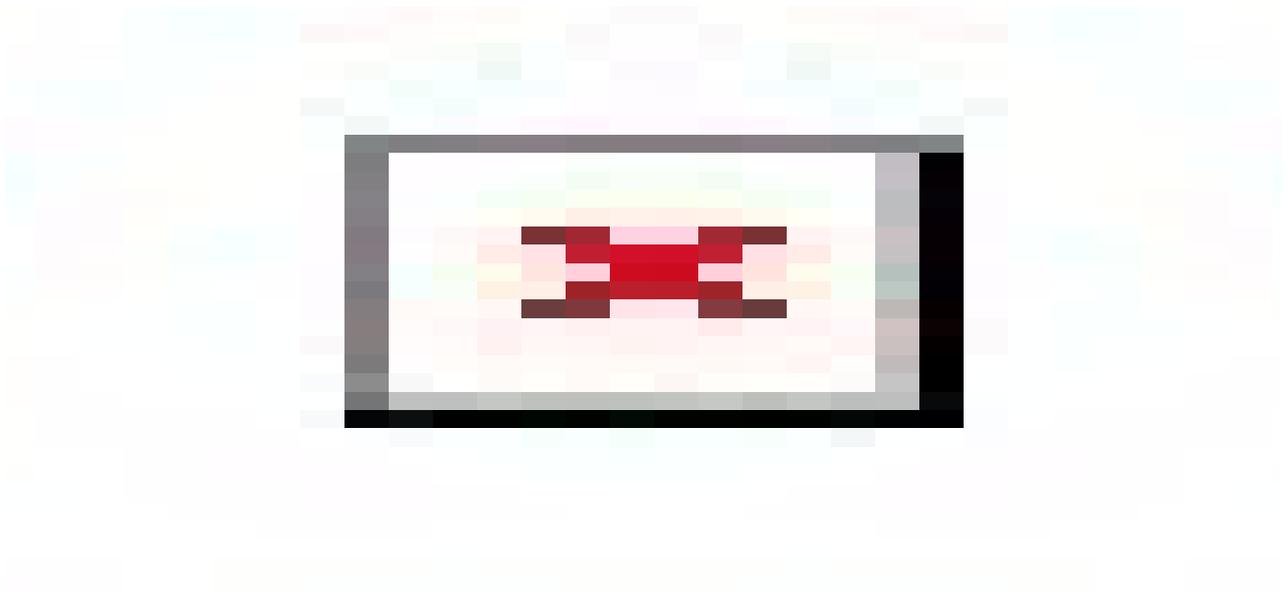


Fig.S2. (a) PL spectra of the NCDs-220 at different excitation wavelengths, (b) PL spectra of the NCDs synthesized at different temperatures.

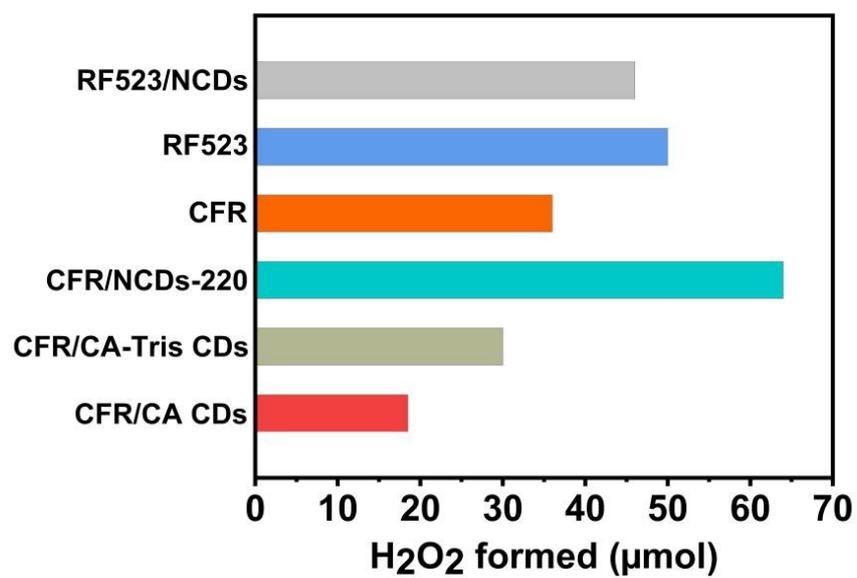


Fig.S3. Photocatalytic H₂O₂ production by different photocatalysts (The CFR_s in the figure are all CFR-140, sample 7 in Table S1).

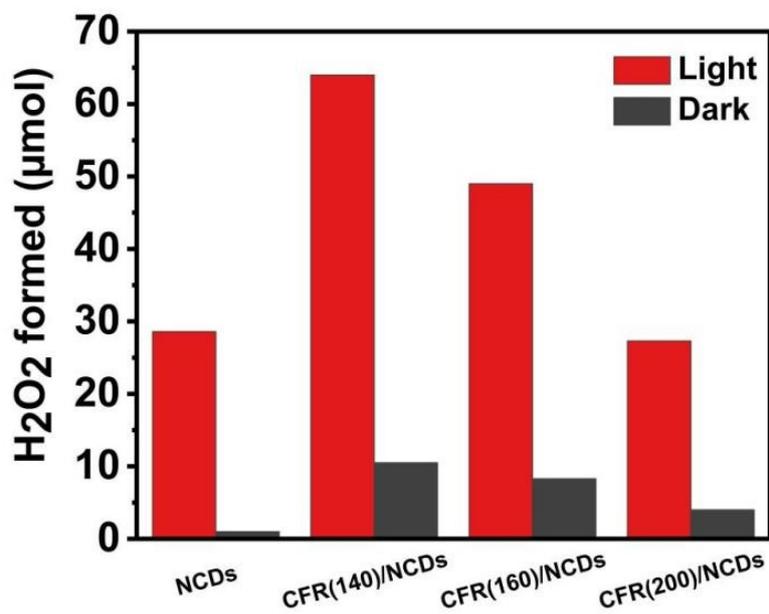


Fig.S4. H₂O₂ production catalyzed by respective photocatalysts under light/darkness for 6 h.(The carbon dots in the figure are all NCDs-220;The CFR microspheres from left to right in the figure are samples 7, 5 and 6 in Table S1.)

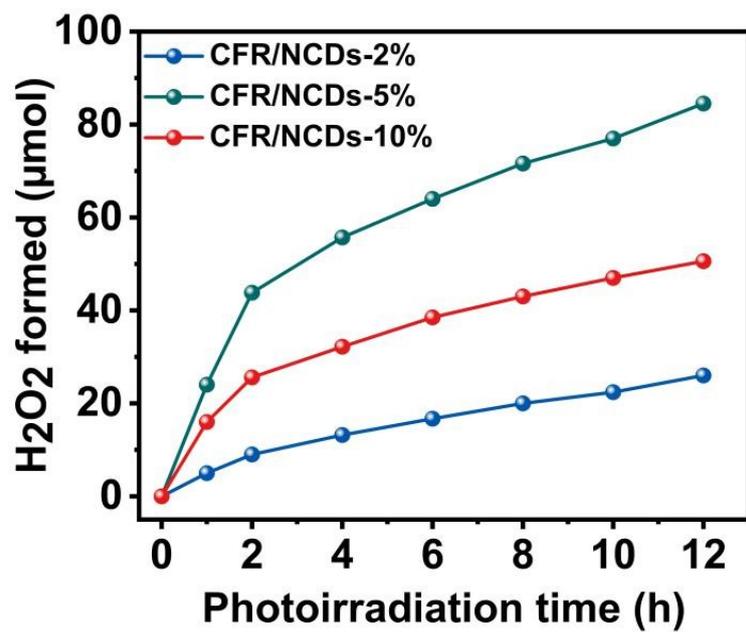


Fig.S5. Photocatalytic H₂O₂ production by CFR/NCDs-220 with different contents of NCDs-220.

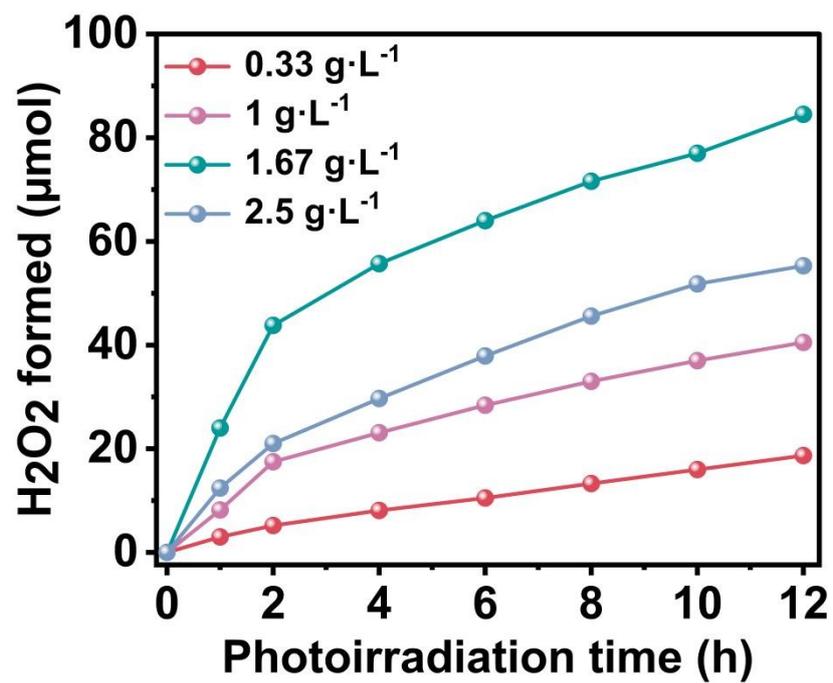


Fig.S6. Photocatalytic production of H₂O₂ with different CFR/NCDs-220 concentrations in the catalytic system.

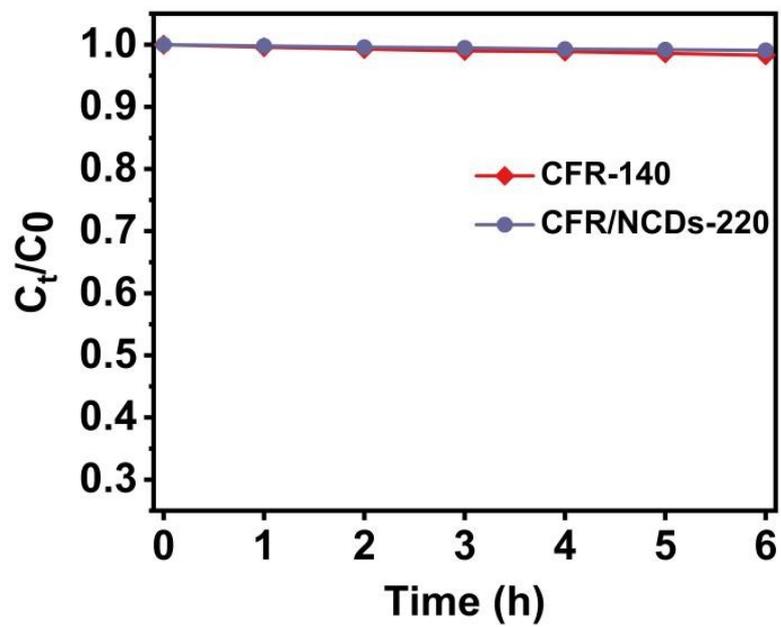


Fig.S7. Photocatalytic H₂O₂ decomposition of CFR and CFR/NCDs-220.

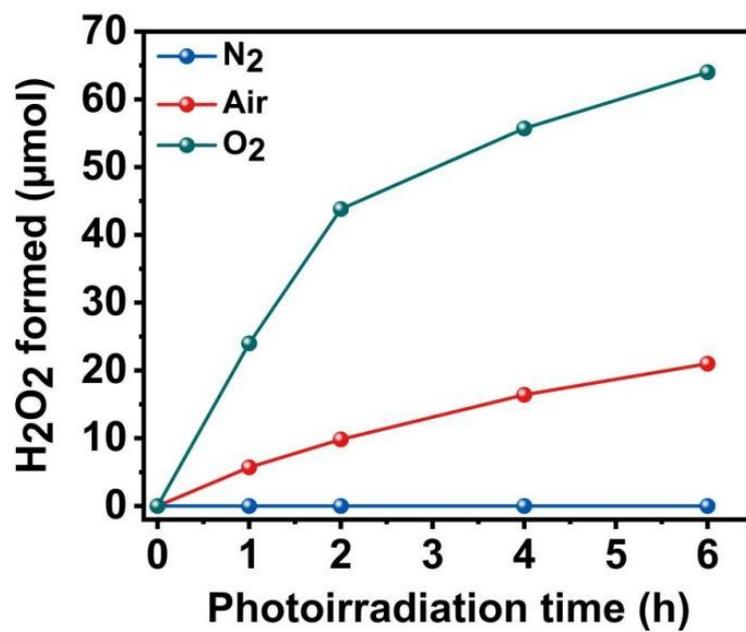


Fig.S8. Photocatalytic H₂O₂ production by CFR/NCDs-220 under a Xe lamp ($\lambda > 420$ nm) in O₂-, air-, or N₂-saturated atmospheres.

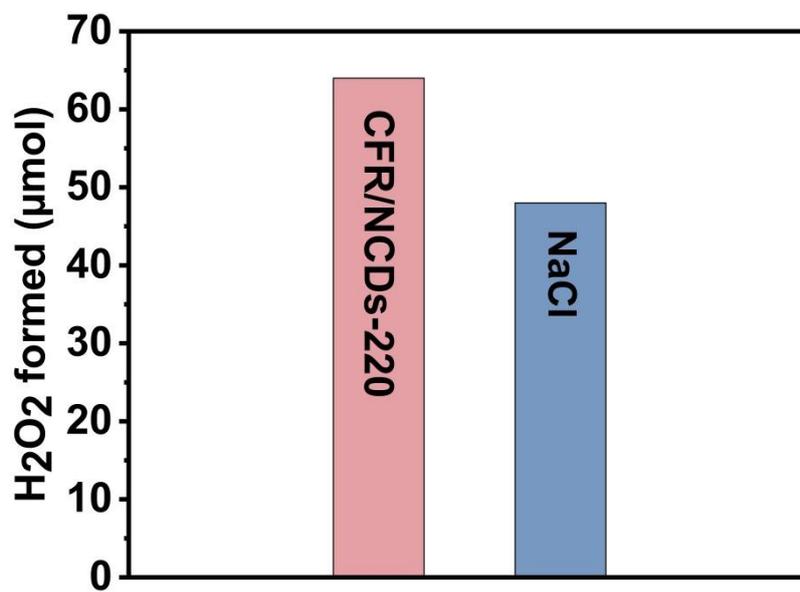


Fig.S9.CFR/NCDS-220 photocatalyzes H₂O₂ production in NaCl solution within 6 hours.

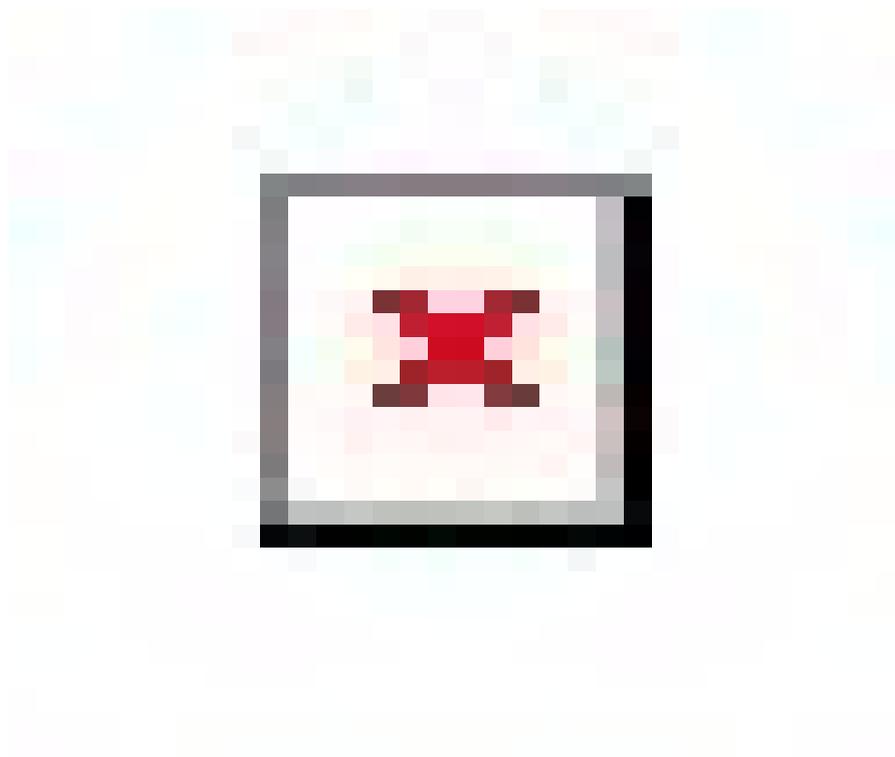


Fig.S10. The ratio ($I_{C=O}/I_{C-OH}$) of 1,2-benzoquinone groups to catechol groups in CFR/NCDs-220 and CFR-140 over time.

References

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