Electronic Supplementary Information (ESI)

In-situ Growth of Crystalline Carbon Nitride on LaOCl for Photocatalytic Overall Water Splitting

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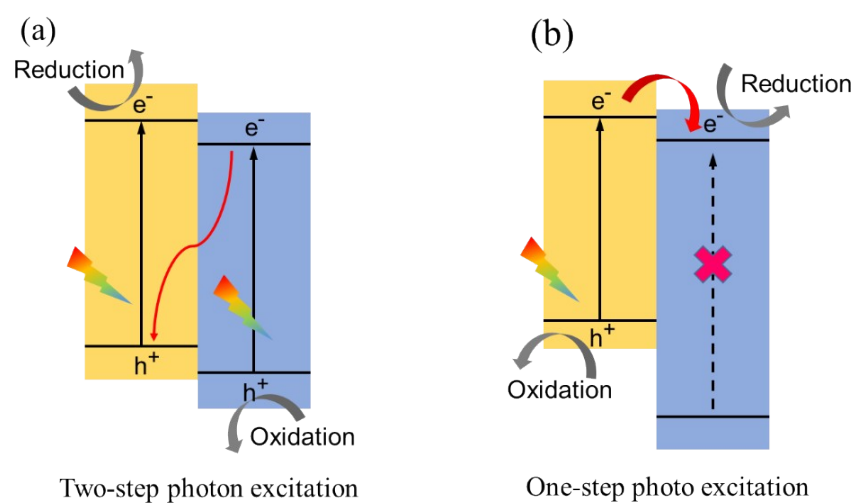
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Experimental Section

Characterization of materials: Scanning electron microscopy (SEM) images were collected using a Hitachi SU8010 field emission scanning electron microscope. Transmission electron microscopy (TEM) was performed using a Talos F200S microscope. The powder X-ray diffraction (XRD) was analyzed using a Bruker D8 Advance X-ray diffractometer. Solid-state ^{13}C NMR measurements were performed on a Bruker Advance 500 spectrometer. Electron paramagnetic resonance (EPR) spectra was recorded on a Bruker A300 spectrometer. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained using a Varian Cary 5000 Scan UV-vis-NIR spectrophotometer. The Brunauer–Emmett–Teller (BET) specific surface areas were measured with an ASAP 2020 (Micromeritics Instrument Corp.). The contents of C and N are determined by element analysis (Vario EL Cube). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 photoelectron spectroscope system with the C1s peak (284.6 eV) as a reference. Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted using an unfiltered He I (21.22 eV) gas discharge lamp. Femtosecond Transient Absorption (fsTA) measurements were performed through a femtosecond Ti:Sapphire regenerative amplified laser system (Spectra Physics, Spitfire-Pro) and the corresponding data acquisition system (Ultrafast Systems, Helios model), samples were irradiated with 400 nm laser light, and the data were collected by the acquisition system as the three-dimensional wavelength-time-absorbance matrices that were exported for further use with the fitting software. Photoluminescence (PL) spectra were obtained with an F-7000 FL spectrophotometer. The electrochemical impedance spectra (EIS) and photocurrent-time (I-t) profiles were conducted on a CHI660D electrochemical workstation using a Pt plate as the counter electrode and a saturated calomel electrode as the reference electrode, respectively. A 0.2 M Na_2SO_4 solution was used as the electrolyte. To fabricate the working electrode, 20 mg sample was dispersed in 1 mL dimethylformamide (DMF) solvent with 40 μL Nafion solution (5 wt.%, Du Pont) to form a homogeneous ink with ultra-sonication for 30 min. Next, 15 μL of the dispersion was loaded onto fluorine-doped tin oxide (FTO) glass with an area of 0.25 cm^2 as the working electrode. The work functions (WF) of CCN and LaOCl were determined by Kelvin probe system (SKP5050, KP Technology Ltd.) with a single-point measurement. The work function of the tip was corrected using a gold disk (gold, 5.1 eV). The relationship between the (work functions) WF and the contact potential difference (CPD) can be calculated on the followed formula:

$$WF_{sample} = WF_{tip} + CPD$$

(a)

Reduction

e⁻

e⁻

h⁺

h⁺

Oxidation

Two-step photon excitation

(b)

Reduction

e⁻

e⁻

h⁺

Oxidation

One-step photo excitation

Figure S1. Schematic of two-step photon excitation (a) and one-step photon excitation (b) pathway.
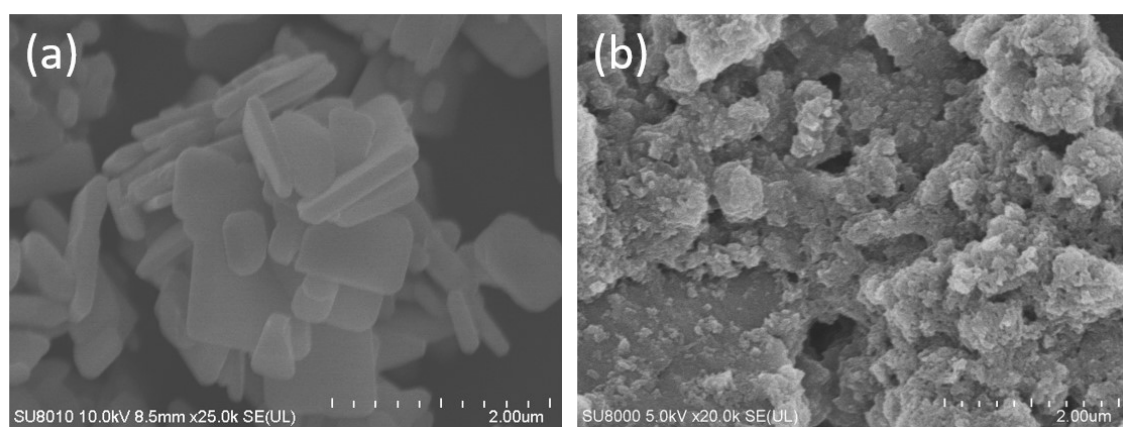
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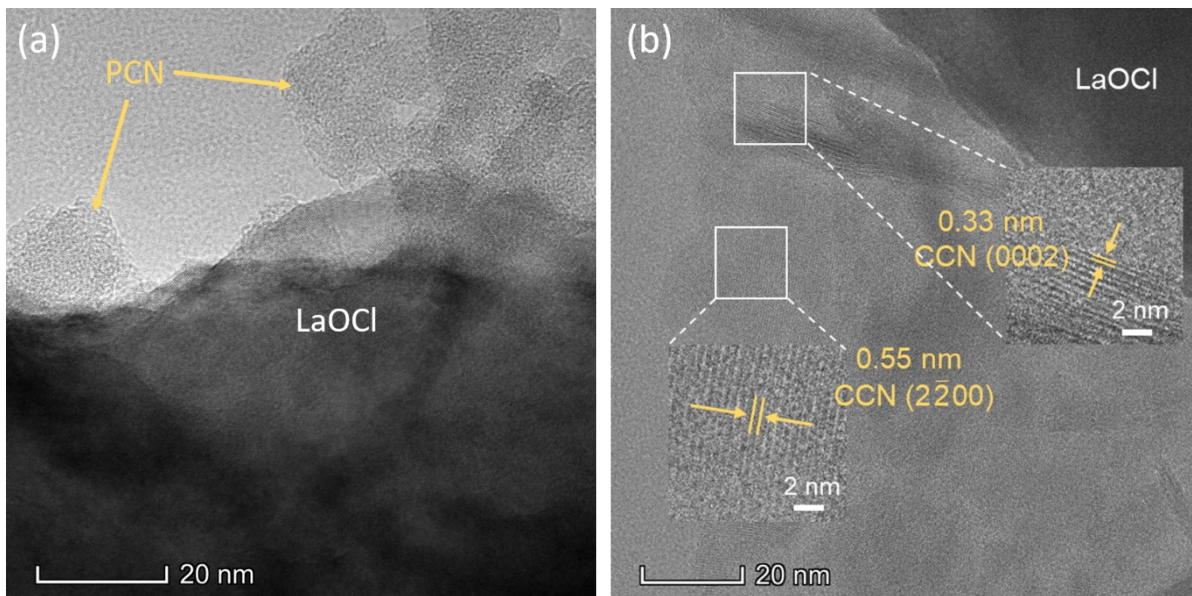
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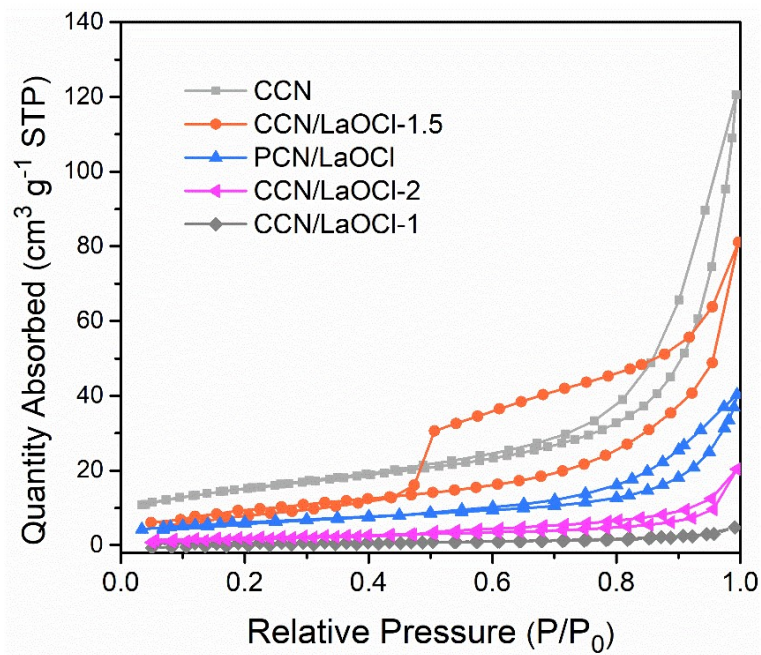
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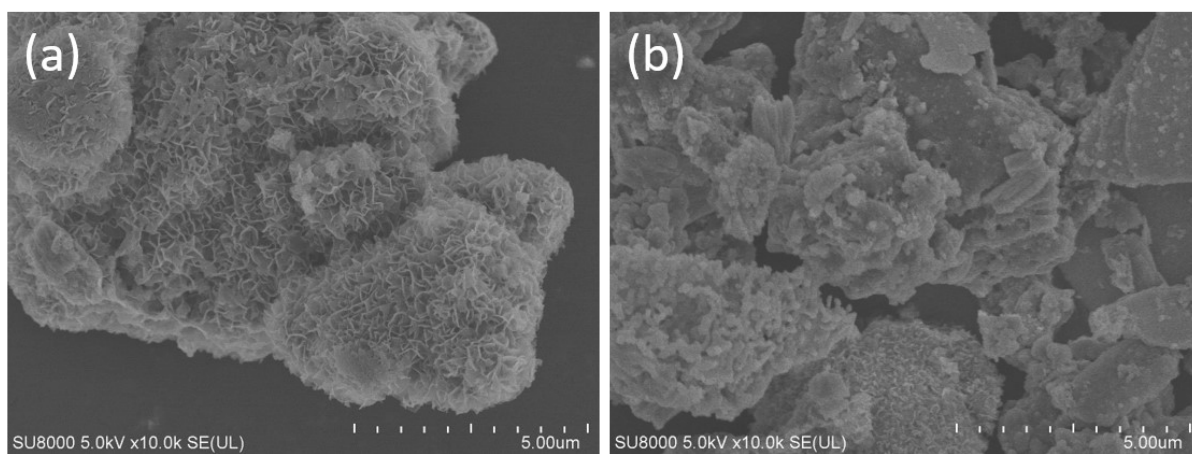
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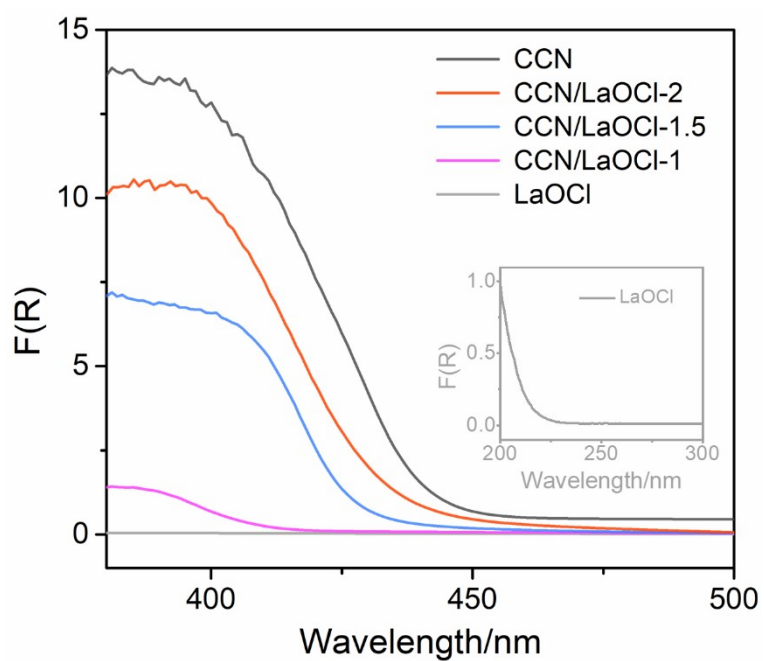
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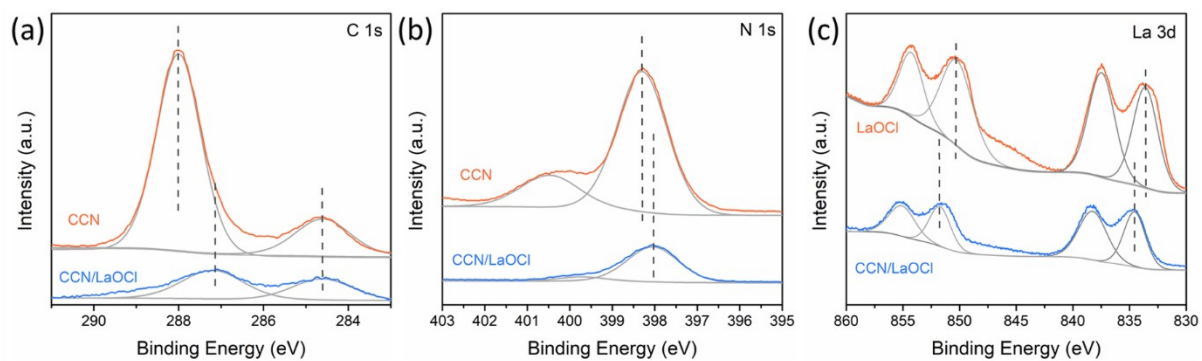
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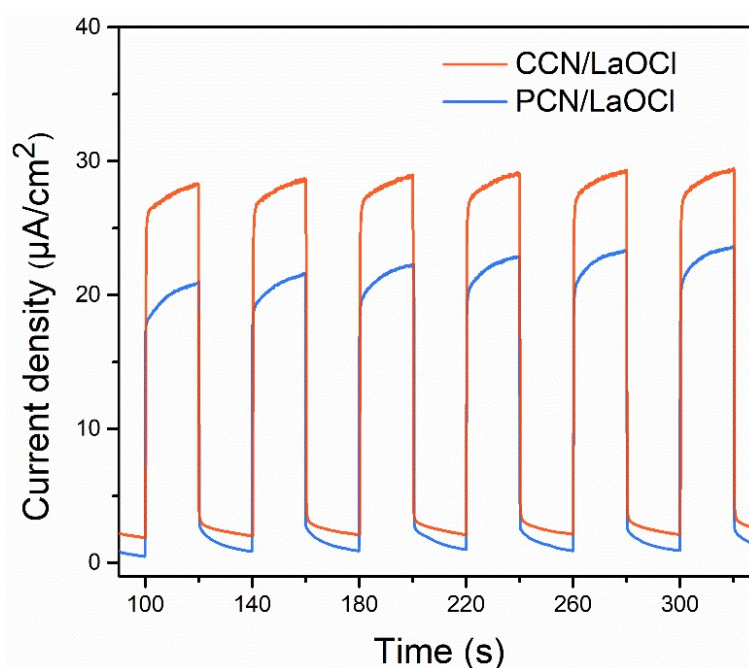
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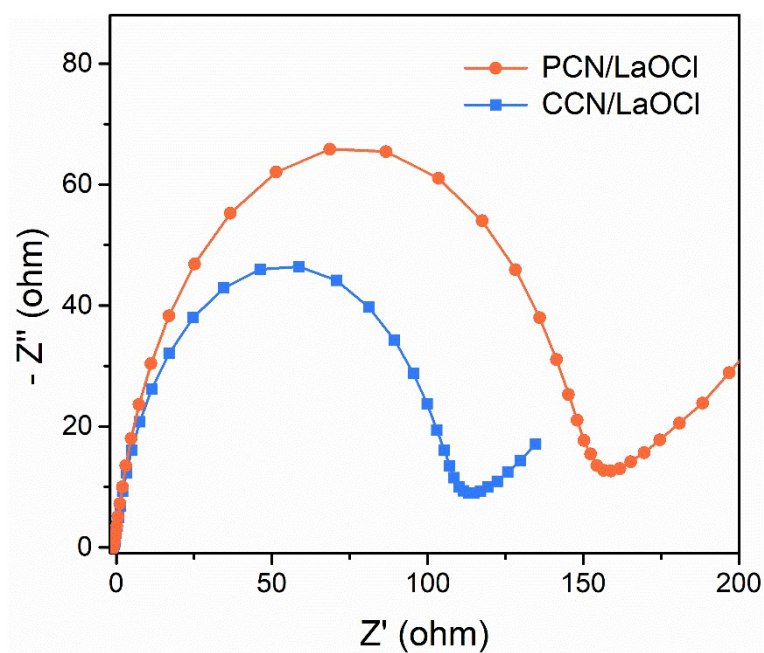
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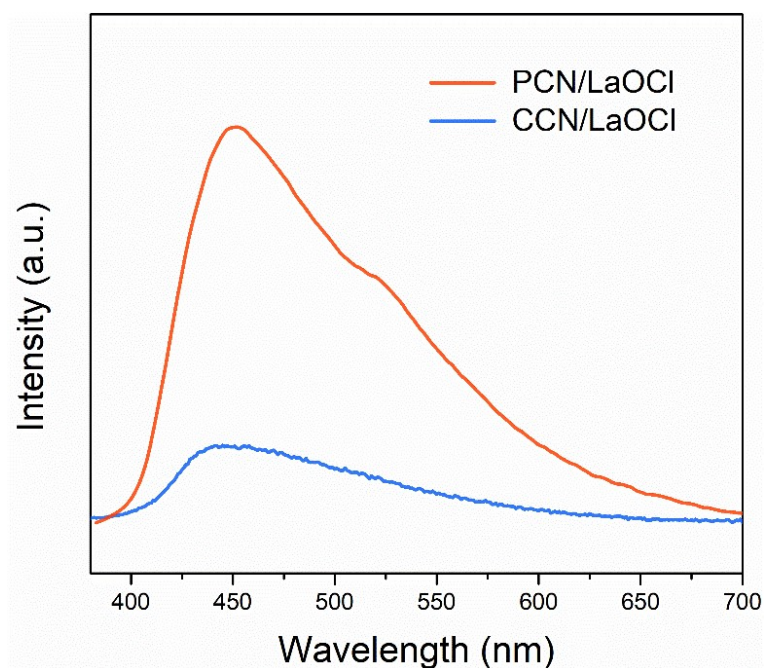
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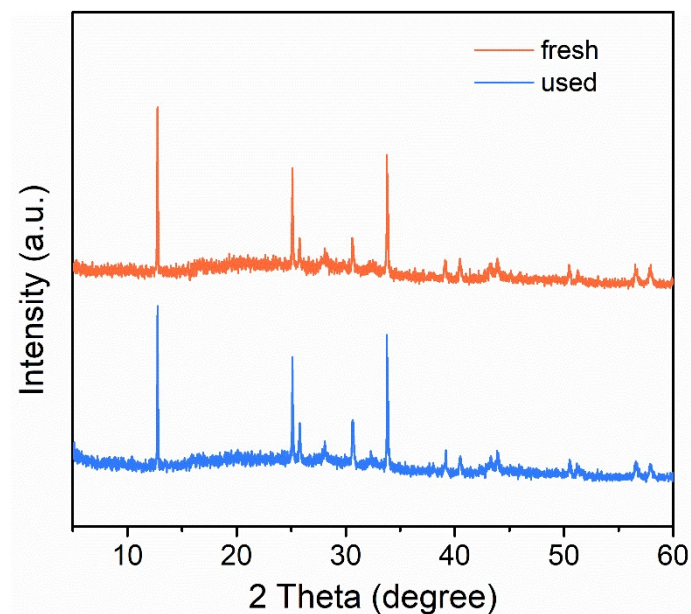
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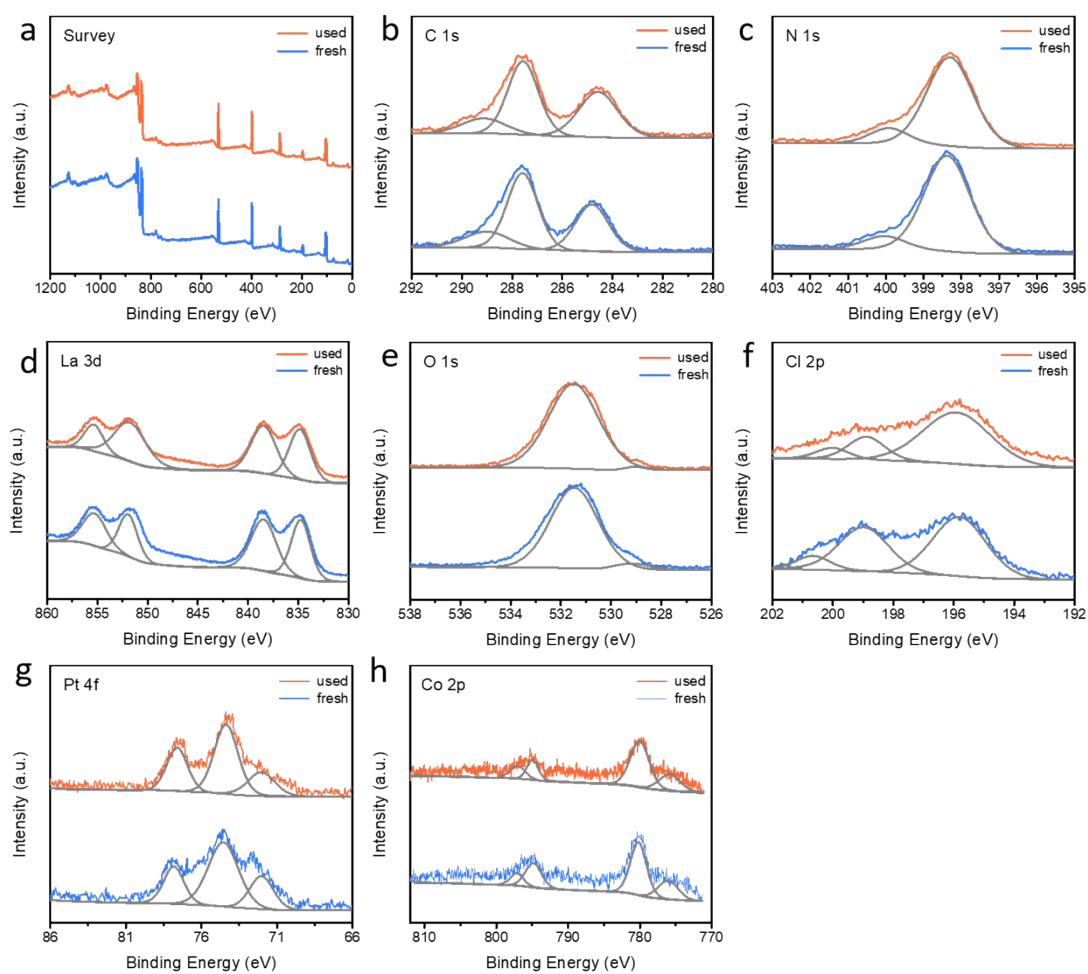
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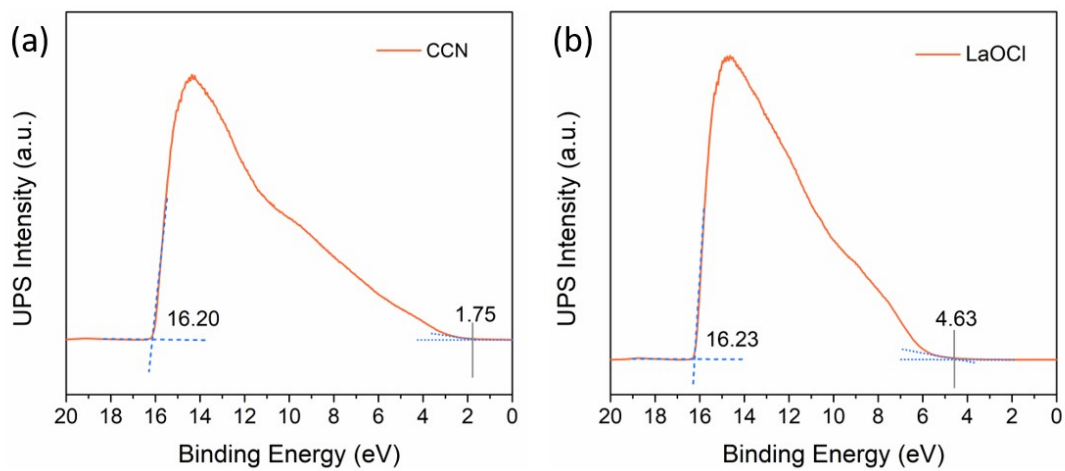
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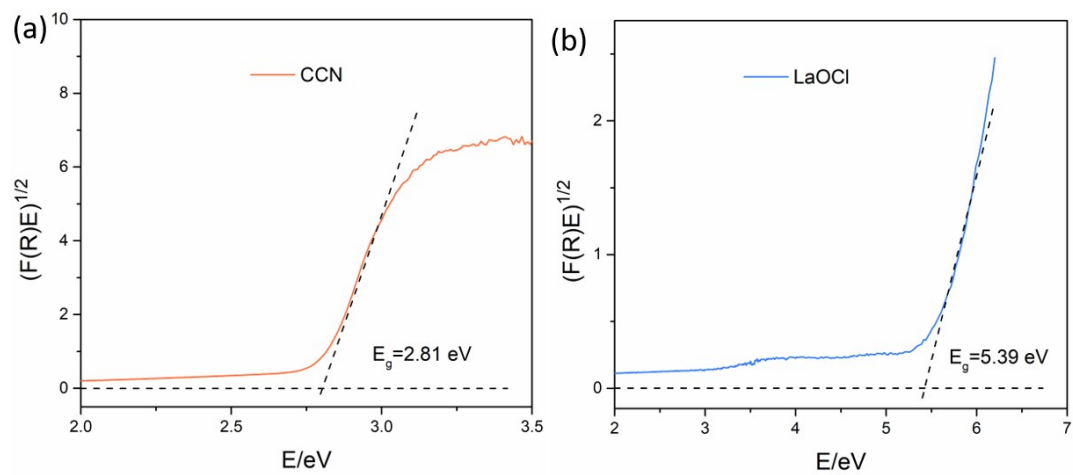
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Table S1. The BET specific surface area and the CCN amount of CCN/LaOCl-x samples.

Samples	Specific surface area (m²/g)	wt. % of CCN
LaOCl	3.8	-
CCN/LaOCl-0.5	4.0	5.7
CCN/LaOCl-1	4.3	13.1
CCN/LaOCl-1.5	34.3	30.9
CCN/LaOCl-2	8.6	40.4
CCN/LaOCl-3	8.1	45.7

Table S2. Fs-TA exponential function fitted parameters of absorption decay for PCN/LaOCl and CCN/LaOCl at 650 nm.

Materisla	τ_1 (ps)	A_1 (%)	τ_2 (ps)	A_2 (%)	Average τ (ps)
PCN/LaOCl	12.9	55.4	158	44.6	77.6
CCN/LaOCl	13.5	58.2	224	41.8	101.4

Table S3. Exponential function fitted parameters of the time-resolved PL decay spectra for the prepared samples.

Samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	Average τ (ns)
PCN/LaOCl	3.30	16	0.61	84	1.03
CCN/LaOCl	4.16	39	0.79	61	2.12

Table S4. Comparison of photocatalytic activity for overall water splitting over carbon nitride-based materials.

Materials	Reaction conditions	H_2 evolution rate ($\mu mol\ h^{-1}$)	O_2 evolution rate ($\mu mol\ h^{-1}$)	AQE (%)	Ref.
CCN/LaOCl	300 W Xe lamp, 50 mg catalyst, 0.5 wt.% Pt, 0.2 wt.% CoO_X cocatalyst	60.6 ($\lambda > 300$ nm) 20.2 ($\lambda > 400$ nm)	28.1 ($\lambda > 300$ nm) 9.1 ($\lambda > 400$ nm)	1.13 (400 nm)	**This work**
PCN/LaOCl	300 W Xe lamp, 50 mg catalyst, 0.5 wt.% Pt, 0.2 wt.% CoO_X cocatalyst	22.3 ($\lambda > 300$ nm) 8 ($\lambda > 400$ nm)	10.7 ($\lambda > 300$ nm) 3.8 ($\lambda > 400$ nm)	0.33 (400 nm)	[1]
g-C3N4/rGO/PDIP	300 W Xe lamp, 25 mg catalyst, Pt/Cr_2O_3, $Co(OH)_2$ cocatalyst	15.8 ($\lambda > 420$ nm)	7.8 ($\lambda > 420$ nm)	3.6 (420 nm)	[2]
CNN/BDCNN	300 W Xe lamp, 40 mg catalyst, 0.9 wt.% Pt and 3.0 wt.% $Co(OH)_2$ cocatalyst	32.9 ($\lambda > 300$ nm) 9.85 ($\lambda > 420$ nm)	16.4 ($\lambda > 300$ nm) 4.88 ($\lambda > 420$ nm)	11.90 (400 nm)	[3]
BDCNN350/BDCNN425	300 W Xe lamp, 100 mg catalyst, 0.9 wt.% Pt and 3.0 wt.% $Co(OH)_2$ cocatalyst	62.9 ($\lambda > 300$ nm)	31.3 ($\lambda > 300$ nm)	23.52 (420 nm)	[3]
PTI-550	300 W Xe lamp, 100 mg catalyst, 0.5 wt% Co and 1.0 wt% Pt cocatalyst	189 ($\lambda > 300$ nm)	91 ($\lambda > 300$ nm)	8 (365 nm)	[4]
3D g-C_3N_4 NS	300 W Xe lamp, 50 mg catalyst, 1 wt.% Pt, 3 wt.% IrO_2 cocatalyst	5.1 ($\lambda > 420$ nm)	2.5 ($\lambda > 420$ nm)	1.4 (420 nm)	[5]
Fe_2O_3/RGO/PCN	300 W Xe lamp, 40 mg catalyst, Pt cocatalyst	43.6 ($\lambda > 300$ nm) 6 ($\lambda > 400$ nm)	21.2 ($\lambda > 300$ nm) 3 ($\lambda > 400$ nm)	N/A	[6]
Pt/g-C_3N_4	300 W Xe lamp, 200 mg catalyst, 3 wt.% Pt, 1 wt.% CoO_X cocatalyst	12.2 ($\lambda > 300$ nm) 1.2 ($\lambda > 420$ nm)	6.3 ($\lambda > 400$ nm) 0.6 ($\lambda > 420$ nm)	0.3 (405 nm)	[7]
Co_3O_4/HCNS/Pt	300 W Xe lamp, 20 mg catalyst, 1 wt.% Pt, 3 wt.% Co_3O_4 cocatalyst	3.2 ($\lambda > 300$ nm)	1.7 ($\lambda > 300$ nm)	N/A	[8]
Pt/CoP/g-C_3N_4	300 W Xe lamp, 80 mg catalyst, pH = 3, 3 wt.% Pt, 3 wt.% CoP cocatalyst	21 ($\lambda > 300$ nm) 2.1 ($\lambda > 400$ nm)	10 ($\lambda > 300$ nm) 1.0 ($\lambda > 400$ nm)	N/A	[9]
α-Fe_2O_3 /2D-C_3N_4	300 W Xe lamp, 10 mg catalyst, 3 wt.% Pt, 0.1 wt.% RuO_2 cocatalyst	0.38 ($\lambda > 400$ nm)	0.19 ($\lambda > 400$ nm)	N/A	[10]
Na-CN	300 W Xe lamp, 100 mg catalyst, 1 wt.% Pt cocatalyst	31.5 ($\lambda > 420$ nm)	15.2 ($\lambda > 420$ nm)	1.45 (420 nm)	[11]
Co_1-phosphide/CN	300 W Xe lamp, 20 mg catalyst,	8.2 ($\lambda > 300$ nm) 2,5 ($\lambda > 420$ nm)	4.1 ($\lambda > 300$ nm) 1.3 ($\lambda > 420$ nm)	2.2 (500 nm)	[12]
(C_{ring})−C_3N_4	300 W Xe lamp, 30 mg catalyst, 3 wt.% of Pt cocatalyst	11.1 ($\lambda > 300$ nm) 4.5 ($\lambda > 420$ nm)	5.5 ($\lambda > 300$ nm) 2.2 ($\lambda > 420$ nm)	5 (420 nm)	[13]
C_{CO}-C_3N_4	300 W Xe lamp, 30 mg catalyst,	15.9 ($\lambda > 300$ nm)	7.7 ($\lambda > 300$ nm)	N/A	[14]
CQDs/ holey CN	300 W Xe lamp, 10 mg catalyst, 2 wt.% of Pt cocatalyst	9.3 ($\lambda > 420$ nm)	4.6 ($\lambda > 420$ nm)	N/A	[15]

CoO/g-C$_3$N$_4$	LED, 50 mg catalyst,	2.5 (λ > 400 nm)	1.4 (λ > 400 nm)	1.91 (420 nm)	[16]
C$_3$N$_4$/MnO$_2$	300 W Xe lamp, 100 mg catalyst,	5.5 (λ > 420 nm)	2.8 (λ > 420 nm)	~3.7 (420 nm)	[17]
g-C$_3$N$_4$-carbon dots	300 W Xe lamp, 100 mg catalyst,	0.5 (λ > 420 nm)	0.25 (λ > 420 nm)	N/A	[18]
MnO$_2$/g-C$_3$N$_4$	300 W Xe lamp, 100 mg catalyst, 3 wt.% of Pt cocatalyst	6.1 (λ > 400 nm)	2.9 (λ > 400 nm)	N/A	[19]
Mn–C$_3$N$_4$	300 W Xe lamp, 20 mg catalyst, 0.9 wt.% of Pt cocatalyst	13.9 (λ > 300 nm) 6.1 (λ > 420 nm)	6.6 (λ > 300 nm) 2.9 (λ > 420 nm)	4.0 (420 nm)	[20]
TH−CN	300 W Xe lamp, 50 mg catalyst, 1 wt. % CoP, 1.5 wt. % Pt, Ph=5.6	10.2 (λ > 400 nm)	5.7 (λ > 400 nm)	N/A	[21]
PTI-LiNa	300 W Xe lamp, 100 mg catalyst, 0.5 wt% Co and 1.0 wt% Pt cocatalyst	273 (λ > 300 nm)	135 (λ > 300 nm)	12% (365 nm)	[22]
NdCo$_3$/PCN	300 W Xe lamp, 40 mg catalyst	11.8 (λ > 300 nm) 0.7 (λ > 420 nm)	6.0 (λ > 300 nm) 0.35 (λ > 420 nm)	2.0 (350 nm)	[23]
C$_3$N$_4$−Cl4	20 mg catalyst, Pt cocatalyst	48.2 (λ > 300 nm)	21.8(λ > 300 nm)	6.9 (420 nm)	[24]

Table S5. AQE of CCN/LaOCl for overall water splitting.

Wavelengths (nm)	H$_2$ evolution (μmol/h)	Light power (mW/cm^2)	irradiated area (cm^2)	AQE(%)
380	31.4	13.42	32.15	1.27
400	37.6	17.16	32.15	1.13
420	11.2	12.53	32.15	0.44
450	2.1	17.06	32.15	0.05
475	0.6	16.11	32.15	0.02

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