

Supporting information

Tuning Pt Surface Adsorption Energy with a Cr₂O₃ Thin Layer for Efficient Photocatalytic Overall Water Splitting

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Experimental Methods

Materials.

No further purification was conducted on any of the chemical reagents, all of which were of analytical grade (AR) and used as supplied. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Xilong Science Co., Ltd., AR, $\geq 99.0\%$); melamine ($\text{C}_3\text{H}_6\text{N}_6$, Macklin Biochemical Co., Ltd., AR, $\geq 99.0\%$); urea ($\text{CH}_4\text{N}_2\text{O}$, Macklin Biochemical Co., Ltd., AR, $\geq 99.0\%$); sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$, Xilong Science Co., Ltd., AR, $\geq 99.5\%$); anhydrous sodium sulfate (Na_2SO_4 , Macklin Biochemical Co., Ltd., AR, $\geq 99\%$); anhydrous ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Xilong Science Co., Ltd., AR, $\geq 99.7\%$); chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Macklin Biochemical Co., Ltd., AR, $\geq 99.7\%$).

Characterizations

The crystal structure of the catalysts was analyzed using X-ray diffraction (XRD, D8-FOCUS, BrukerAXS, Panalytical). The morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The chemical composition and chemical states of the catalyst were characterized using an ESCALAB 210 X-ray photoelectron spectrometer (XPS, VG Scientific, UK) with an Al target. UV-visible diffuse reflectance spectroscopy measurements were conducted using a Hewlett-Packard 8453 spectrophotometer with BaSO_4 powder as the background reference for baseline correction. Steady-state fluorescence spectra were recorded using a FluoroMax-4 fluorescence spectrometer (Horiba Scientific, France).

Preparation Method

Preparation of C_3N_4

C_3N_4 was synthesized via a conventional thermal polymerization method. A typical procedure is as follows: 25 g urea in a 60mm crucible subjected to the calcination at 550°C for 4 h, with a heating rate of $2.5^\circ\text{C min}^{-1}$. After holding, allow to cool naturally to 25°C . The obtained bulk solid was ground thoroughly into a fine powder using a mortar. The as-prepared powder was then placed again in a 100 mL

crucible heated at 510°C for 2 hours, then allow to cool naturally to 25 °C. The resulting product was denoted as C₃N₄.

Preparation of Pt/C₃N₄

The loading of Pt nanoparticles on the C₃N₄ surface was achieved by an in-situ photodeposition method. The detailed procedure is described as follows: 400 mg of C₃N₄ catalyst was weighed into a quartz reactor, followed by the addition of 180 mL of distilled water and a corresponding amount of H₂PtCl₆ solution with different Pt mass fractions (0.2%, 0.5%, 0.8%, 1%, 1.5%). The mixture was subjected to photodeposition under ultraviolet (UV) light for 24 h. The product was filtered, washed with distilled water three times, and dried at 60 °C. The resulting composite was labeled as Pt/C₃N₄.

Synthesis of Cr₂O₃/Pt/C₃N₄

Cr₂O₃/Pt/C₃N₄ was fabricated using an in-situ photodeposition method. A typical synthesis process is as follows: 120 mg of Pt/C₃N₄ catalyst was weighed into a quartz reactor, mixed with 180 mL of distilled water, and then an appropriate amount of Cr(NO₃)₃ solution was added. The mixture was irradiated under UV light for 24 h for photodeposition. After the reaction finished, the obtained product underwent filtration, was rinsed three times using 100 mL of distilled water every time, and finally dried at 60 °C. The final composite was designated as Cr₂O₃/Pt/C₃N₄.

Experiment on Photocatalytic OWS

The photocatalytic OWS performance of all catalysts was evaluated at room temperature and atmospheric pressure using a 197 mL quartz reactor. The detailed test procedure is as follows: 50 mg of catalyst and 100 mL of deionized water were transferred into the reactor, followed by ultrasonication to disperse the catalyst in the deionized water. Air in the reactor was replaced with argon. A xenon lamp was used as the light source, and the optical power of the xenon lamp was adjusted for each test. The gases generated from photocatalytic overall water splitting were analyzed by gas chromatography.

Isotope Labeling Experiment

10 mg of catalyst was dispersed in a sealed glass bottle containing 10 mL of D₂O

or 1 mL of H₂¹⁸O. After ultrasonic dispersion for 30 minutes, argon (Ar) was bubbled through to displace oxygen in the reaction bottle for 10 minutes. Following 6 h of full light irradiation, 0.5 mL of gas was extracted from the silicone pad on the reaction bottle and injected into a GC-MS system. The gas phase components were analyzed by referring to the NIST mass spectral database, and the origin of the gas was typically determined by analyzing the m/z signals.

Hydrogen-oxygen recombination test

The hydrogen-oxygen recombination performance of the catalyst was tested in a 197 mL quartz reactor wrapped with aluminum foil. In a typical measurement: 100 mL of deionized water and 100 mg of catalyst were added into the reactor, and the catalyst was fully dispersed via ultrasonication. The reactor was purged with argon to remove residual air. Then, 3 mL of oxygen and 6 mL of hydrogen were injected into the reactor, followed by continuous stirring. The gas composition in the reaction system was analyzed by gas chromatography every 10 min.

Photoelectrochemical performance experiment

Photoelectrochemical tests and analysis were accomplished on a CHI 660E electrochemical workstation. A typical three-electrode system was employed, in which a platinum sheet and a saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. The working electrode was prepared by directly drop-casting the as-prepared sample suspension onto a pre-cleaned FTO glass substrate with an effective area of 1.5 cm × 1.5 cm. A 300 W xenon lamp with full-spectrum output was used as the light source to simulate sunlight for photocurrent tests. Both electrochemical impedance spectroscopy and photocurrent measurements were carried out at room temperature in a 0.2 mol L⁻¹ Na₂SO₄ aqueous solution.

AQY experiments

Under identical photocatalytic reaction conditions, the apparent quantum yield (AQY) of the catalyst was determined by regulating the incident wavelength using band-pass filters centered at 375, 405, 430, 460 and 520 nm, respectively.

The AQY were tested at 25 °C in a 236 mL reactor. In a typical process, a

mixture of 250 mg of fresh-catalyst and 100 mL of distilled water was ultrasonically dispersed for 20 minutes. The liquid mixture in the quartz reactor is bubbled by argon gas for 15 minutes to replace the air with argon. The distance between the light source (NBeT, HSX-F/UV 300 Xe-lamp) and the quartz photocatalytic reactor is 10cm. The irradiation area is 1 cm².

AQY was calculated as follow:

$$AQY = \frac{N_e}{N_p} \times 100\% = \frac{2 \times n(H_2)}{t \times Q \times A} \times 100\%$$

Where, $n(H_2)$ is the amount of H₂ molecules (umol), Q is Total number of incident photons (umol m⁻² s⁻¹), A is the irradiation area (cm²), t is the photoreaction time (s).

Fluorescence property measurements

Photoluminescence spectra (PL) were obtained by FluoroMax-4 fluorescence spectrometer (Horiba Scientific, Japan). Time-resolved Photoluminescence spectra (TRPL) were measured on Horiba Jobin Yvon HUB workstation. The workstation was equipped with a time-dependent single-photon counting method with a time resolution of 200 ps, and the excitation source was 371 nm nanodiode exciter (pulse frequency: 1 MHz). The experimental results were fitted with Horiba Jobin Yvon DAS6 fluorescence lifetime analysis software.

DFT calculation

We used the DFT as implemented in the Vienna Ab initio simulation package (VASP) in all calculations. The exchange-correlation potential is described by using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE). The projector augmented-wave (PAW) method is employed to treat interactions between ion cores and valence electrons. The plane-wave cutoff energy was fixed to 450 eV. Given structural models were relaxed until the Hellmann-Feynman forces smaller

than -0.02 eV/\AA and the change in energy smaller than 10^{-5} eV was attained. The long-range van der Waals interaction is described by the DFT-D3 approach.

The adsorption energy (E_{ads}) of species is calculated by:

$$E_{\text{ads}} = E(\text{system}) - E(\text{catalyst}) - E(\text{species})$$

where $E(\text{system})$, $E(\text{catalyst})$, and $E(\text{species})$ are the total energy of the optimized system with adsorbed species, the isolated catalyst, and species, respectively.

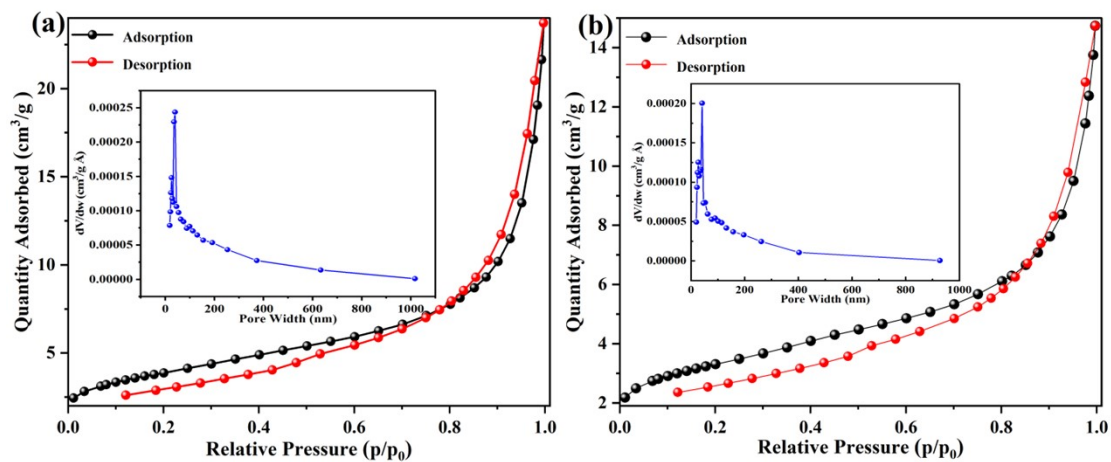


Figure S1. N₂ adsorption–desorption isotherms of (a) Cr₂O₃/Pt/C₃N₄, (b) C₃N₄

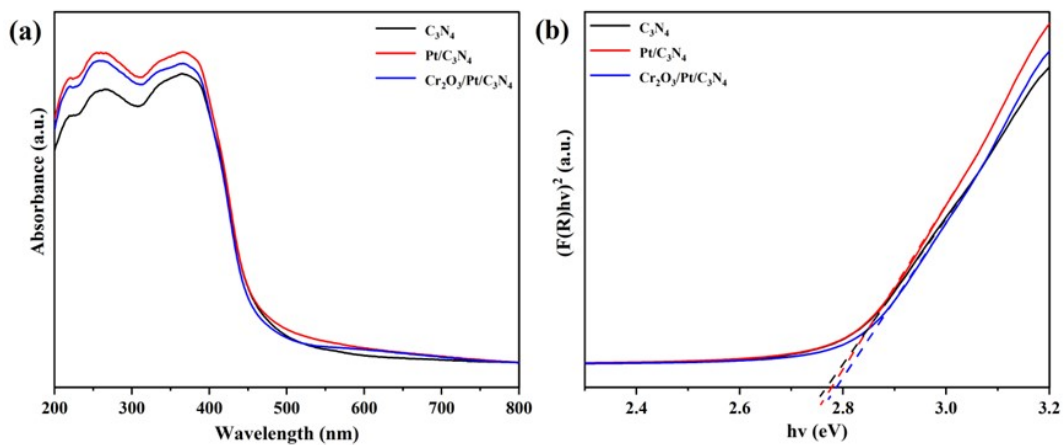


Figure S2 (a) UV-visible diffuse reflection spectra, (b) band gap energies of C₃N₄, Pt/C₃N₄, and Cr₂O₃/Pt/C₃N₄

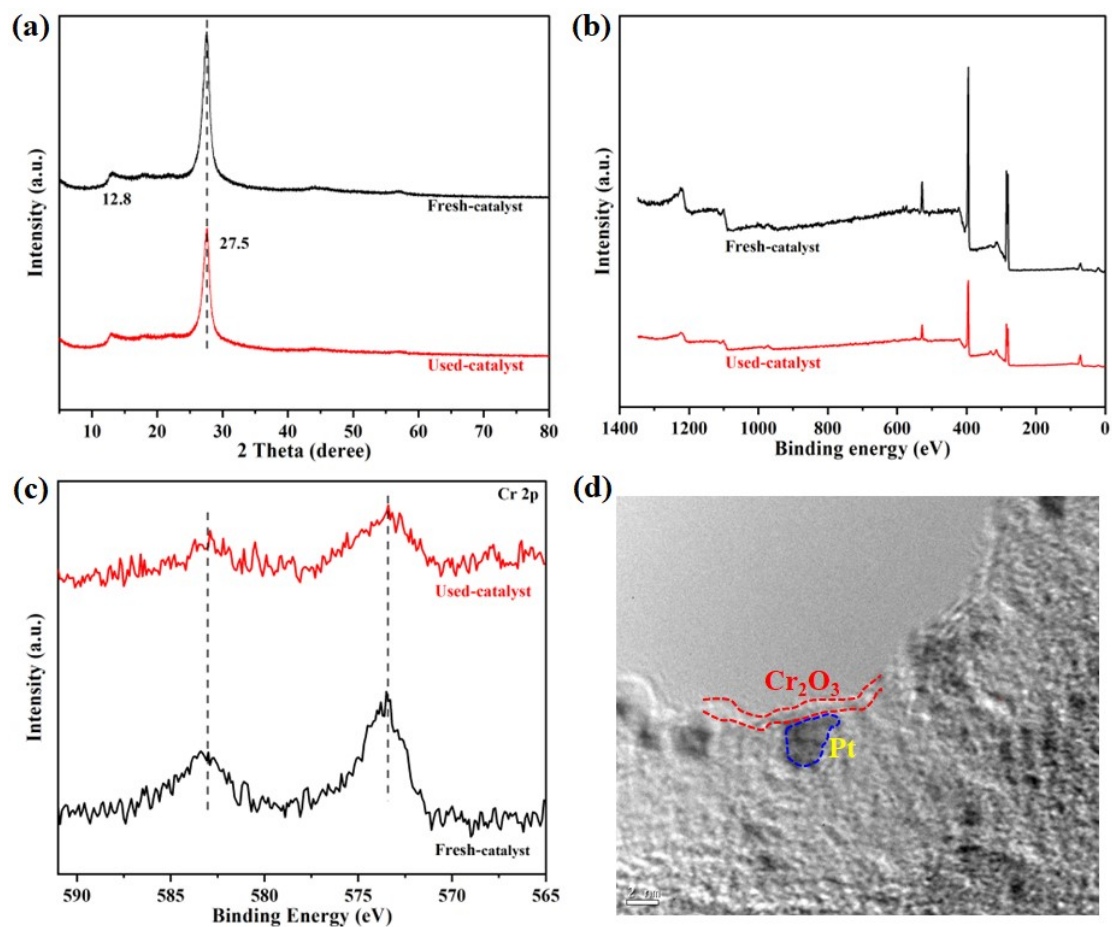


Figure S3 Comparison of (a) XRD patterns, (b) XPS survey spectra and (c) Cr 2p XPS survey spectra of used and fresh $\text{Cr}_2\text{O}_3/\text{Pt}/\text{C}_3\text{N}_4$ sample, (d) TEM images of the used $\text{Cr}_2\text{O}_3/\text{Pt}/\text{C}_3\text{N}_4$ sample

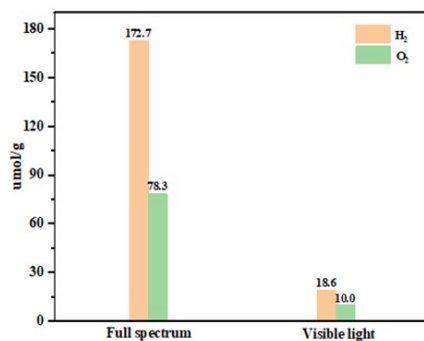


Figure S4 Overall water splitting performance of $\text{Cr}_2\text{O}_3/\text{Pt}/\text{C}_3\text{N}_4$ under visible light and full-spectrum conditions;

Table S1. S_{BET} , average pore size, and pore volumes of as-prepared catalysts

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Average pore size (nm)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
C_3N_4	11.69	7.27	0.021
$\text{Cr}_2\text{O}_3/\text{Pt}/\text{C}_3\text{N}_4$	13.90	9.63	0.033

Table S2 Overview of key research on C₃N₄-derived photocatalysts for photocatalytic overall-water-splitting processes

Catalysts	Test Conditions	H ₂ evolution rate of OWS ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	AQY	References
C ₃ N ₄	under ambient temperature and atmospheric pressure; 300 W Xe lamp	34.5	0.63% at 375 nm	This work
TiO ₂ /C ₃ N ₄	5 mM NaI or 2 mM FeCl ₂ ; 150W Xe lamp	502	4.94% and 4.01% under 365 and 405 nm, respectively.	1
CoO/g-C ₃ N ₄	Water ; 300 W xenon lamp	25.1	-	2
phosphorus doped g-C ₃ N ₄ /Ti ₃ C ₂	under ambient temperature and atmospheric pressure; 300 W Xe lamp	627.1	4.9% at 420 nm.	3
boron phosphide/graphitic carbon nitride (BP@g-C ₃ N ₄)	under ambient temperature and atmospheric pressure; 300 W Xe lamp with a 420 nm cutoff filter	31.5	0.03% at 400 nm	4
CoP/CoO@g-C ₃ N ₄	300 W Xenon lamp	133.2	0.53% at 420 nm	5
Pt/g-C ₃ N ₄ -D2/5%Co ₃ O ₄	300 W Xenon lamp	49.60	11.94 % at 400 nm	6
WC1-x/g-C ₃ N ₄	300 W Xenon lamp	84.1	11.24% at 420 nm	7
g-C ₃ N ₄ /rGO/PDIP	300 W Xe lamp	632	AQY 4.94% at 420 nm and STH 0.30%	8
3D g-C ₃ N ₄ NS	300 W Xe lamp under visible light	101.4	1.4% at 420 nm	9
MOC/g-C ₃ N ₄	300 W Xe lamp	80.1	31.6% at 425 nm	10

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