Supplementary Information

Na-doped g-C_3N_4/NiO 2D/2D laminate p-n heterojunctions nanosheets toward optimized photocatalytic performance

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Experimental section

Materials

Urea and sodium chloride (NaCl) were purchased from Tianjin Fengchuan Chemical Reagent Co, Ltd. Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) are purchased from Tianjin Guangfu Technology Development Co, Ltd. Deionized water (DI) was used during the experiment. All chemicals were analytically pure and did not require further purification.

Characterizations

The powder X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Advance diffractometer by using Cu Kα radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) images were obtained with a Philips XL-30-ESEM-FEG instrument operating at 20 kV. Transmission electron microscope (TEM) JEOL JEM-2010 at an accelerating voltage of 200 kV was also used to record the electron micrographs of the samples. X-ray photoelectron spectroscopy (XPS) was measured on a PHI-5700 ESCA instrument with Al-Kα X-ray source. UV-vis diffuse reflection spectra (DRS) were recorded on a UV-vis spectrophotometer (UV-2550, Shimadzu) with an integrating sphere attachment, and $BaSO_4$ was used as the reference material. Fourier transform infrared spectra (FT-IR) were detected with a PerkinElmer spectrum one system. The N_2 adsorption-desorption isotherms at 77 K were collected on an AUTOSORB-1 (Quantachrome Instruments) nitrogen adsorption apparatus. Surface area was estimated by BET method and pore-size distribution was measured from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

The steady-state photoluminescence (PL) spectra were measured with a PE LS 55 spectrofluoro-photometer at excitation wavelength of 325 nm. Transient-state photoluminescence (TS-PL) spectra were recorded on a single photon counting spectrometer from (Edinburgh Instrument, FLS 920). Scanning Kelvin probe (SKP) measurements (SKP5050 system, Scotland) were performed at normal laboratory conditions. LC-MS (Shimadzu, Japan) was used to determinate the intermediate products produced during the photodegradation process. The mobile phase was methanol and deionized water in the ratio of 70:30 (v/v), and the flow rate was 1 mL/min. The injection volume was 1 μL.

Photocatalytic degradation of CIP

The photocatalytic degradation of CIP and other fluoroquinolones were carried out in a XPA-7 rotary photochemical reactor. The simulated sunlight source was provided by a 350 W xenon lamp with a 290 nm cut-off filter. For each experiment, 50 mL of a 4 mg/L FQs aqueous solution that contained 1.0 g/L catalysts were introduced into a quartz tube. The pH of the reaction solution was adjusted by adding a 0.1% NaOH or H_2SO_4 solution. Prior to irradiation, the reaction solution was magnetically stirred in the dark for 30 min in order to obtain an adsorption-desorption equilibrium of FQs on the photocatalyst. During irradiation, aliquots of samples (1 mL) were withdrawn at predetermined time intervals and filtered through 0.22 μm Millipore filters to remove the photocatalyst. The residual CIP in the solution were analyzed through high performance liquid chromatography (HPLC).

Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution was tested in an online photocatalytic hydrogen evolution system (Au Light, Beijing, CEL-SPH2N) at room temperature. In a typical process, 50 mg of photocatalysts were suspended in 100 mL aqueous closed gas circulation reaction cell which include 80 mL deionized water and 20 mL of methanol used as the sacrificial reagent. Afterward, the suspension was purged with N_2 for several times to remove O_2 and CO_2. After that, the suspension solution was irradiated by a 300 W Xeon-lamp equipped with an AM 1.5 G filter (Oriel, USA), and use an on-line gas chromatography (SP7800, TCD, molecular sieve 5 Å, N_2 carrier, Beijing Keruida, Ltd) to analyze the hydrogen periodically with the interval of every 1 h.

Photoelectrochemical measurements

Photoelectrochemical measurements of photocatalysts were detected in a three-electrode system with the CHI760E electrochemical workstation. The electrolyte selected KOH solution (1 M), the reference electrode selected Ag/AgCl and the opposite electrode selected Pt. Then, 0.1 g of photocatalysts were mixed with 3 mL of ethanol at stirring for 10 min, and sprayed on the FTO-glass of 1×2 cm^2 further heating and drying. The photocurrent test was extra monitored under AM 1.5G light exposure.

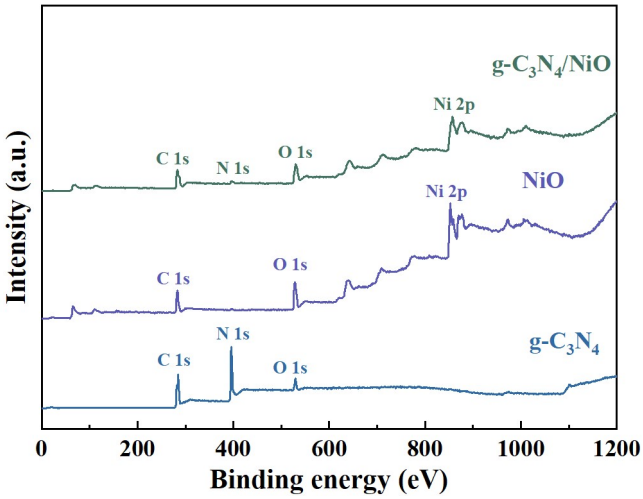

Fig. S1. The XPS survey scans of g-C_3N_4, NiO, g-C_3N_4/NiO.

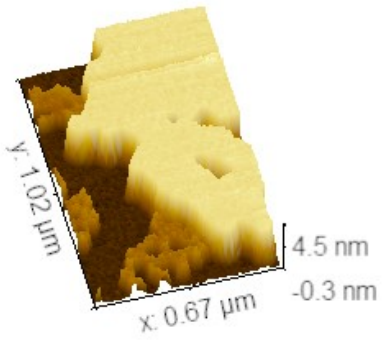

Fig. S2. The 3D AMF structure of the measured ultrathin g-C_3N_4.

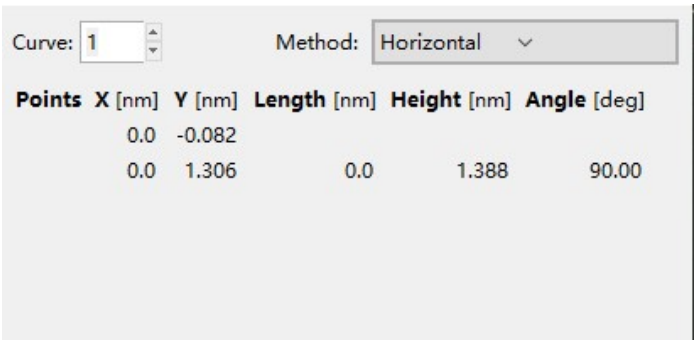

Fig. S3. Thickness of ultra-thin g-C_3N_4.

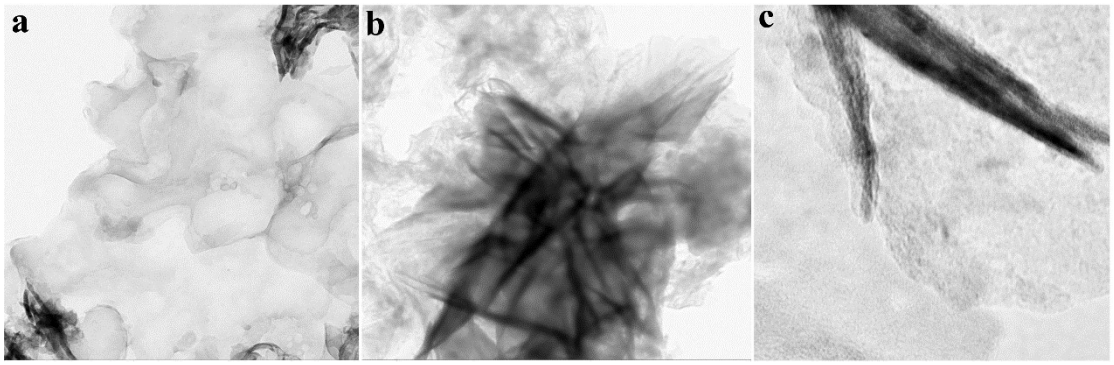

Fig. S4. TEM images of g-C_3N_4 (a) NiO (b), and Na-g-C_3N_4/NiO (c).

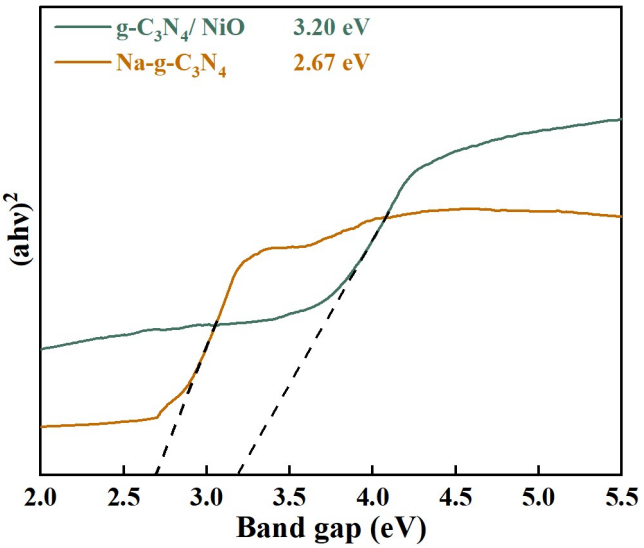

Fig. S5. The band gaps of Na-g-C_3N_4, and g-C_3N_4/NiO.

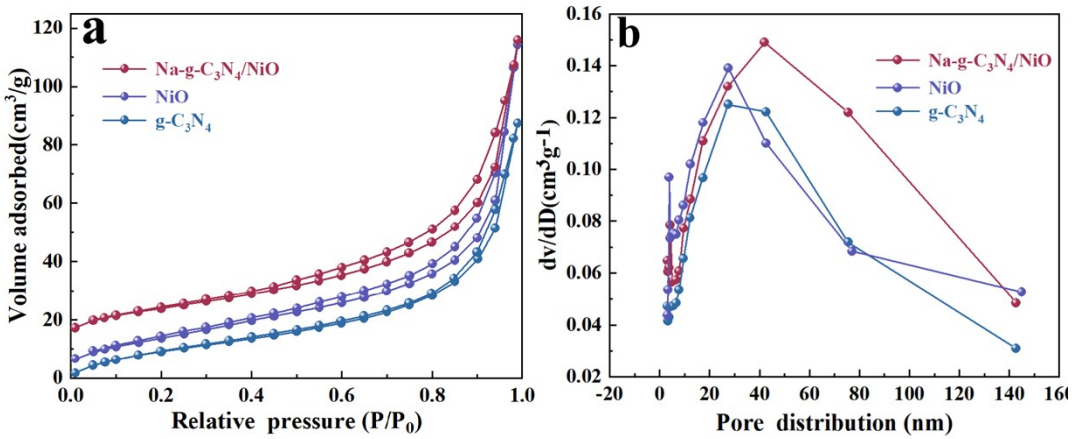

Fig. S6. The N_2 adsorption-desorption isotherms of g-C_3N_4, NiO and Na-g-C_3N_4/NiO (a) and the corresponding pore size distributions (b), respectively.

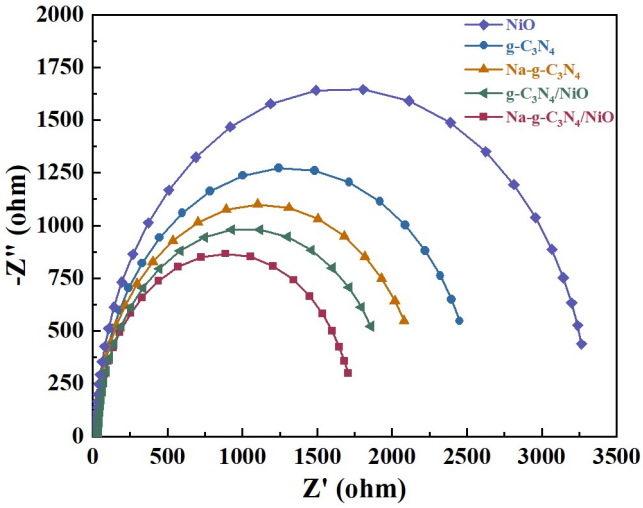

Fig. S7. Electrochemical impedance spectra of g-C_3N_4, Na-g-C_3N_4, NiO, g-C_3N_4/NiO and Na-g-C_3N_4/NiO, respectively.

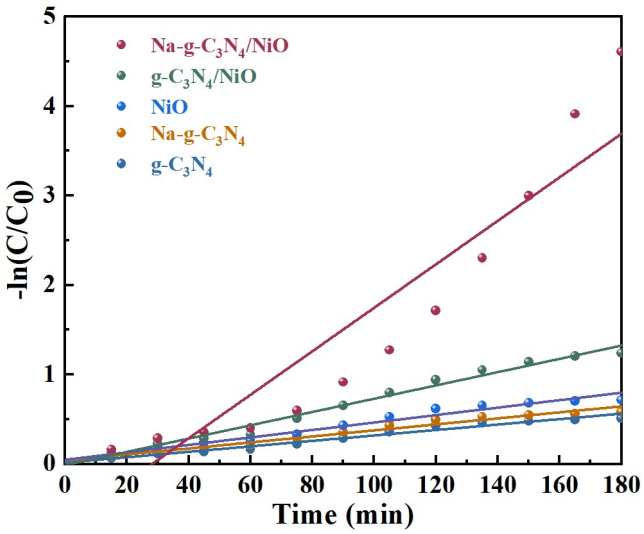

Fig. S8. The first order kinetic curves of CIP degradation for different photocatalysts.

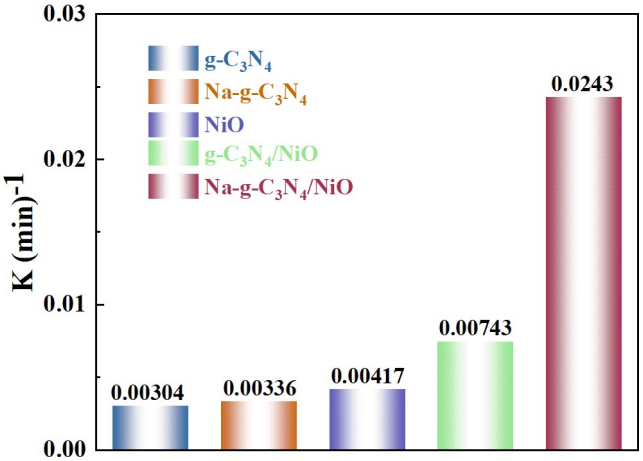

Fig. S9. The first-order reaction rate constants for photocatalytic reduction and degradation of CIP for different photocatalysts.

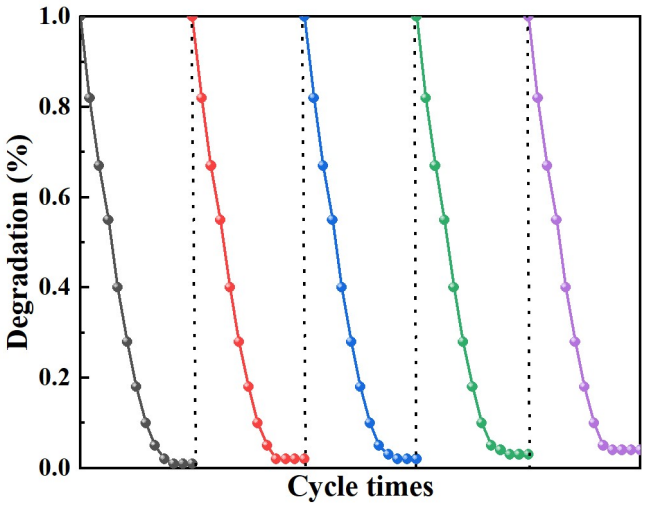

Fig. S10. Degradation cycle experiments of CIP degradation for Na-g-C_3N_4/NiO.

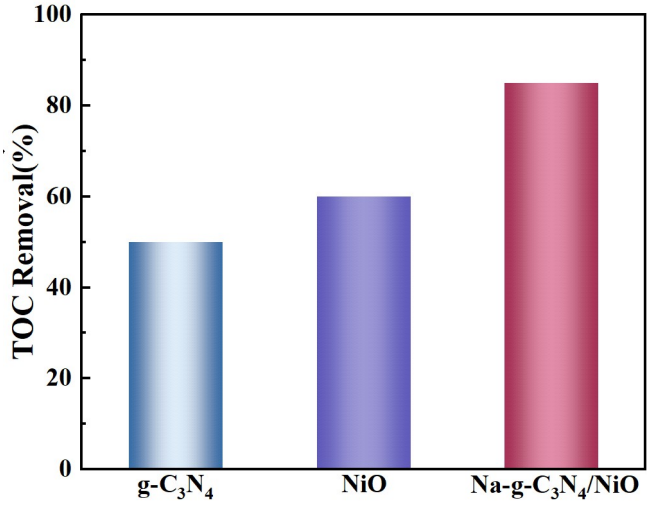

Fig. S11. The TOC removal rates of different samples for photocatalytic degrading CIP.

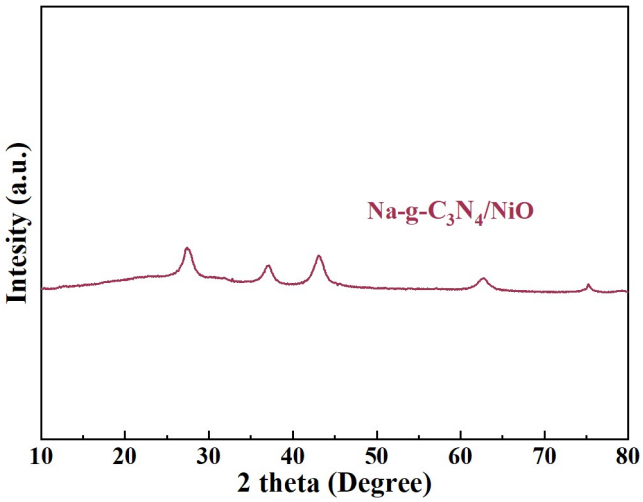

Fig. S12. XRD pattern of Na-g-C_3N_4/NiO after photocatalytic degradation.

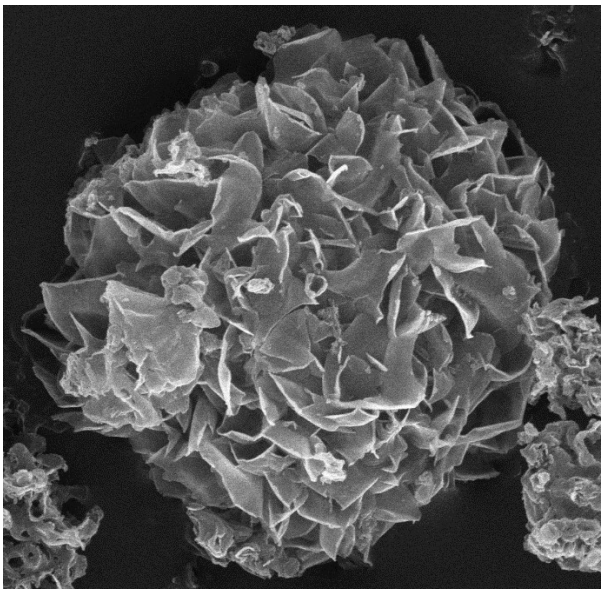

Fig. S13. SEM image of Na-g-C_3N_4/NiO after photocatalytic degradation.

Table S1. Comparison of photocatalytic H_2 evolution rates between Na-g-C_3N_4/NiO and other different photocatalysts under visible light irradiation.

Photocatalysts	Light source	H_2 evolution rate	Ref.
g-C_3N_4(P)	300 W Xe lamp (λ>420 nm)	916.2 μmol h^{-1} g^{-1}	[1]
N-defects g-C_3N_4	300 W Xe lamp (λ>420 nm)	1160 μmol h^{-1} g^{-1}	[2]
P-Na codoped g-C_3N_4	300 W Xe lamp (λ>400 nm)	2032 μmol h^{-1} g^{-1}	[3]
Na-g-C_3N_4	350 W Xe lamp (λ>400 nm)	18.7 μmol h^{-1}	[4]
NiO/Ni_2P/g-C_3N_4	300 W Xe lamp (λ>420 nm)	5.04 μmol h^{-1}	[5]
NiO QDs-g-C_3N_4	300 W Xe lamp (λ>400 nm)	260.2 μmol h^{-1} g^{-1}	[6]
Na-g-C_3N_4/NiO	**300 W Xe lamp (λ>420 nm)**	**2299.32 μmol h^{-1} g^{-1}**	**This work**

References

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