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Hydroxyl-Modified C_3N_4 -Ni Nanosheets Enhance Photocatalytic CO_2 Methanation

XIAO Shi^{1,2}, ZHANG Zhiqiang^{1,2}, ZHENG Jingwen^{1,2}, XUE Jinbo³

(1. CRRC Qingdao Sifang Company LTD., Qingdao, Shandong, China; 2. State Key Laboratory of High-speed Maglev Transportation Technology, Qingdao, Shandong, China; 3. Key Laboratory of Interface Science and Engineering in Advanced Materials of Ministry of Education, Taiyuan University of Technology, Taiyuan, Shanxi, China)

Abstract: [Purposes] In photocatalytic CO_2 reduction reaction, since the electron transfer efficiencies of CH_4 and CO are close and their thermodynamic properties are similar, achieving high electron selectivity for CH_4 still faces significant challenges. **[Methods]** In this study, a single-atom Ni-doped C_3N_4 catalyst (CN-Ni) was first synthesized and then hydroxyl-modified to obtain hCN-Ni through the hydrothermal method. **[Results]** Experimental results show that the hydroxyl-modified hCN-Ni catalyst exhibits excellent CO_2 reduction performance, with CO and CH_4 generation rates of 22 and $3.3 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, respectively, and the CH_4 electron selectivity reaches 37.5%. The remarkable performance enhancement stems from the synergistic effect of hydroxyl modification and Ni monoatoms. On one hand, the introduction of hydroxyl groups enhances the hydrophilicity of the catalyst surface, and promotes the adsorption of water molecules as well as the formation of a local water-rich microenvironment, while its asymmetric steric hindrance effectively inhibits the recombination of photogenerated carriers; On the other hand, the dispersed Ni monoatoms on the surface of hCN-Ni serve as active centers for CO_2 adsorption and activation, and protons enriched on the hydroxyl-modified surface can be rapidly transferred to these Ni active sites, thus significantly facilitating the hydrogenation of CO_2 to CH_4 .

Keywords: CO_2 reduction; hydroxyl groups; electron selectivity of CH_4 ; H_2O adsorption

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Introduction

The reduction of CO_2 into high-value-added chemical fuels by using semiconductor photocatalytic technology can simultaneously alleviate the growing energy crisis and environmental problems, making this technology one of the most promising photoca-

lytic reactions^[1]. For the practical application of photocatalytic CO_2 reduction, the development of efficient and stable photocatalysts has become a core research objective in this field^[2].

Over the past few decades, graphitic carbon nitride ($g\text{-}C_3N_4$) has attracted widespread attention owing to its excellent physicochemical stability, facile

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第一作者: XIAO Shi, Senior Engineer, (E-mail)xiaoshi@cqsf.com

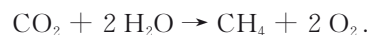
通信作者: XUE Jinbo, Ph. D., Associate Professor, Doctoral Supervisor, primarily engaged in research on the application of photocatalysis in energy and environmental fields, (E-mail)xuejinbo@tyut.edu.cn

synthesis, low cost, abundant reserves, and visible-light response^[3,4]. However, g-C₃N₄ still faces severe challenges in photocatalytic CO₂ methanation^[5]: its weak surface water adsorption severely restricts proton transport efficiency, and the high recombination rate of photogenerated charge carriers leads to insufficient electrons for the reduction reaction. These factors collectively result in unsatisfactory CH₄ electron selectivity and yield^[6,7].

To enhance the photocatalytic CO₂ reduction activity of g-C₃N₄, the rational design of unique nanostructures is crucial^[8]. Yan et al^[9] introduced electron donor or acceptor units into the g-C₃N₄ framework to construct donor-acceptor g-C₃N₄. Owing to its strong electron push-pull effect, this material shows enhanced light-harvesting capability and charge separation efficiency. Dong et al^[10] doped single-atom Ni into the unsaturated sites of g-C₃N₄; single-atom Ni acts as an electron trap to promote charge separation, and the impurity levels introduced by Ni narrow the catalyst band gap, broaden the light absorption range, and thus strengthen light absorption. Furthermore, single-atom Ni can serve as CO₂ adsorption sites, donate electrons to CO₂, and promote its activation and reduction.

Notably, in CO₂ methanation, the adsorption and activation of H₂O molecules (as proton sources) on the catalyst surface are equally critical for the CO₂ reduction reaction. Therefore, improving the water adsorption capacity of g-C₃N₄ remains an urgent key issue. Among current g-C₃N₄-based modified materials: cyano-modified g-C₃N₄ shows a CO production rate of 12 μmol·g⁻¹·h⁻¹ with a CH₄ electron selectivity of only 21%^[3]; g-C₃N₄ supported with Au nanoparticles gives a CH₄ production rate below 2 μmol·g⁻¹·h⁻¹^[6]; although ball-milled single-atom Ni-doped g-C₃N₄ increases the CO production rate to 18 μmol·g⁻¹·h⁻¹, its CH₄ electron selectivity remains below 26%^[7]. These materials generally suffer from the “difficulty in balancing high activity and high CH₄ electron selectivity”.

This study aims to realize photocatalytic CO₂ reduction to CH₄ with H₂O as the proton source. The overall reaction is:



This process involves simultaneous CO₂ reduction and H₂O oxidation, with the released oxygen atoms finally forming O₂. Thermodynamic analysis shows that the standard Gibbs free energy change (Δ*G*) of this reaction is +818.1 kJ/mol, indicating a strongly endothermic process. This theoretically requires sustained external energy input (e.g., light) to drive the reaction, highlighting the great challenge and importance of developing highly efficient catalytic systems.

To address the above challenges, a “hydroxyl modification” strategy is proposed on the basis of single-atom Ni-doped g-C₃N₄ nanosheets (CN-Ni) prepared by metal vapor exfoliation method^[11]. On one hand, the strong polarity of hydroxyl groups improves material hydrophilicity, promotes the adsorption of ambient water vapor to supply protons, and suppresses photogenerated charge recombination via asymmetric steric hindrance. On the other hand, combining the CO₂ adsorption/activation ability of single-atom Ni with the large specific surface area and short charge migration pathway of the nanosheet structure, efficient synergy among CO₂ adsorption, proton transfer, and catalytic reduction is achieved.

1 Experimental Section

1.1 Sample preparation

Preparation of bulk carbon nitride (CN) via thermal polymerization: 3 g of melamine was weighed and placed into a covered alumina crucible. The crucible was heated from 20 to 550 °C in 2 h and then held at 550 °C for 2 h in air. After cooling naturally to room temperature, the product was collected and ground into powder; the obtained sample was denoted as CN.

Preparation of Ni-loaded carbon nitride (CN-Ni) nanosheets via metal vapor exfoliation: Nickel foam was rinsed with absolute ethanol to remove surface impurities, dried, and cut into pieces of 3 cm × 1 cm. 20 mg of CN was weighed and uniformly filled into the pores of one piece of nickel foam. The sample was covered with another piece of nickel foam, tightly pressed, and transferred into an alu-

mina crucible. The crucible was placed in a tube furnace, and the furnace was purged with argon. The system was heated from 20 to 550 °C in 2 h and maintained at 550 °C for 2 h. After natural cooling, the nickel foam was peeled off, and the powder product was collected and denoted as CN-Ni.

Preparation of hydroxylated Ni-loaded carbon nitride (hCN-Ni) via hydrothermal treatment: 0.8 g of CN-Ni and 20 mL of ultrapure water were transferred into a 50 mL stainless steel autoclave with a polytetrafluoroethylene liner. The autoclave was placed in an oven and heated at 140 °C for 6 h. After cooling, the sample was collected, washed with ultrapure water, and dried in a vacuum oven for 12 h; the final product was denoted as hCN-Ni. For comparison, a reference sample (denoted as hCN) was prepared with the same procedure by using CN instead of CN-Ni.

1.2 Sample characterization

X-ray diffraction (XRD) patterns were recorded on a Smartlab SE diffractometer (Rigaku, Japan) with Cu K α radiation ($\lambda=1.541\ 78\ \text{\AA}$) at 40 kV and 40 mA. Data were collected in the 2θ range of 10° – 80° at a scanning rate of $3\ (^\circ)\cdot\text{min}^{-1}$. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet AVATAR 330 spectrometer using the KBr pellet technique. Thermogravimetric (TG) analysis was performed on a STA449F5 Jupiter thermal analyzer (Germany). The morphologies were observed by field-emission scanning electron microscopy (FESEM, JEOL JSM-6 700F, Japan), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, Japan), and aberration-corrected scanning transmission electron microscopy (AC-STEM, JEOL JEM-ARM300F, Japan). X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250Xi spectrometer (USA), with binding energies calibrated by using the standard C 1s peak at 284.8 eV. Photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were measured on an Edinburgh LFS-920 fluorescence spectrometer. UV-visible diffuse reflectance spectra (UV-vis DRS) were recorded on a PerkinElmer Lambda 950 spectropho-

tometer. Water contact angles were measured with a Drop Shape Analyzer DSA100S (Germany).

1.3 Photoelectrochemical tests

Photoelectrochemical measurements were performed on an AutoLab electrochemical workstation with a three-electrode system: a platinum counter electrode, a saturated calomel reference electrode (SCE), and a working electrode. The electrolyte was 0.5 mol/L Na₂SO₄ solution. The working electrode was prepared by mixing 8 mg of catalyst powder with 250 μL of anhydrous ethanol and 100 μL of PVDF binder, followed by sonication for 0.5 h. The slurry was coated onto a $3\ \text{cm} \times 1\ \text{cm}$ FTO glass and dried. Transient photocurrent responses were measured under intermittent irradiation from a 300 W xenon lamp (on/off every 20 s). Mott-Schottky (M-S) curves were recorded at 1 kHz with an AC amplitude of 10 mV. Electrochemical impedance spectroscopy (EIS) curves were tested in the frequency range of 0.01–100 kHz.

1.4 Photocatalytic CO₂ reduction

Photocatalytic CO₂ reduction was carried out in a sealed quartz reactor (RL2360-C, RUIDA). 10 mg of photocatalyst and 10 mL of deionized water were added into the reactor. The system was purged with argon for 0.5 h to remove air, and then 50 mL of high-purity CO₂ (99.999%) was introduced. The reaction was irradiated with a 300 W xenon lamp for 4 h. Gaseous products were analyzed by an Agilent 8890 gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).

2 Results and Discussion

2.1 Morphological and structural analyses of samples

The morphological and structural properties of the samples were systematically investigated by using XRD, TG analysis, FTIR spectroscopy, SEM, TEM, AC-STEM, and XPS. As shown in Fig. 1a, the XRD patterns of CN, hCN, CN-Ni, and hCN-Ni all exhibit two characteristic diffraction peaks centered at 13.0° and 27.3° . These peaks are assigned to the (100) crystal plane (corresponding to the in-

plane repeating triazine ring units of CN) and the (002) crystal plane (associated with the out-of-plane vertical stacking of aromatic layers in CN), respectively^[12]. Furthermore, no additional diffraction peaks (e.g., for Ni nanoparticles or impurity phases) are detected in any of the samples except for the peaks attributed to CN. This result indicates that the crystal structure and phase composition of CN remain unchanged after hydroxyl modification and Ni single-atom loading.

TG is a critical method for detecting surface-adsorbed functional groups on photocatalysts, as it reflects mass loss at different temperatures to infer the types of adsorbed functional groups. The TG curves of CN-Ni and hCN-Ni are shown in Fig. 1b. For both samples, the initial weight loss below 150 °C is attributed to the removal of physically adsorbed water molecules from the catalyst surface^[13]. Notably, in the temperature range of 150–500 °C, hCN-Ni ex-

hibits significantly increased mass loss compared to CN-Ni. This disparity is ascribed to the thermal decomposition of surface hydroxyl groups (—OH) introduced during the hydrothermal treatment^[14], confirming the successful hydroxylation of hCN-Ni. FT-IR spectroscopy further corroborates the presence of hydroxyl groups. As shown in Fig. 1c, all samples display a characteristic —OH bending vibration peak at 1 542 cm⁻¹^[15]. After hydrothermal treatment, the peak intensity at 1 542 cm⁻¹ increases (Fig. 1d) for both hCN and hCN-Ni. Additionally, hCN and hCN-Ni exhibit a broadened peak in the 3 000–3 600 cm⁻¹ region, the combination of thermogravimetry and XPS data can be attributed to the stretching vibration of adsorbed hydroxyl groups^[16]. This spectral feature is absent in the pristine CN and CN-Ni samples, providing direct evidence of hydroxyl functionalization.

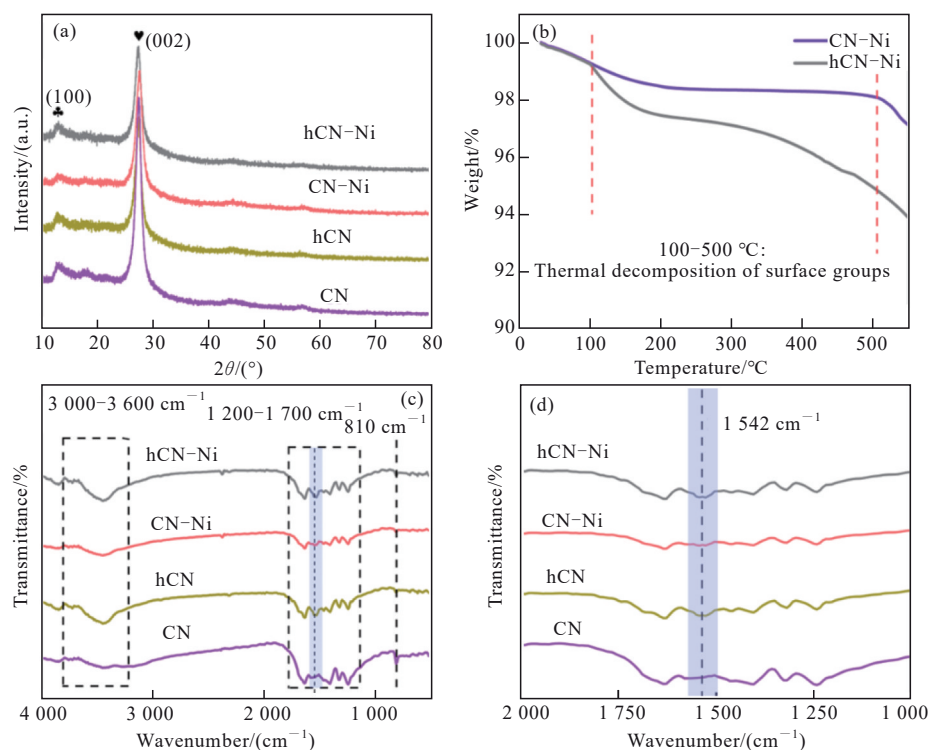


Fig.1 (a) XRD patterns of CN, hCN, CN-Ni, and hCN-Ni; (b) Thermogravimetric curves of CN-Ni and hCN-Ni; (c) FTIR spectra and (d) FTIR magnifications in the range of 1 000–2 000 cm⁻¹

SEM and TEM were employed to characterize the morphological changes induced by Ni doping and hydroxyl modification. The SEM images in Fig. 2a and 2b reveal that pristine CN and hydroxylated hCN

both exhibit a bulk stacked structure with minimal morphological alterations after hydroxyl treatment. In contrast, CN-Ni prepared via Ni-assisted thermal exfoliation (Fig. 2c) displays a distinct ultrathin

nanosheet structure, indicative of successful exfoliation of bulk CN into 2D nanosheets. Hydroxylated hCN-Ni (Fig. 2d) retains this nanosheet morphology, demonstrating that hydroxyl modification does not disrupt the Ni-doped CN nanostructure. The TEM images of CN-Ni and hCN-Ni (Fig. 2e and 2f) further confirm the preservation of nanosheet dimensions and crystallinity after hydrothermal treatment. The formation of ultrathin nanosheets introduces curled edges (Fig. 2c), which arise from surface

tension minimization during exfoliation^[17]. Hydroxylated CN-Ni significantly increases surface exposure area, providing more active sites for CO₂ adsorption and activation while offering additional modification sites for hydroxyl introduction. Additionally, the ultrathin nanosheet architecture of CN-Ni shortens the electron migration pathway from the bulk to the surface, accelerating charge separation and thereby boosting the CO₂ reduction reaction efficiency^[18].

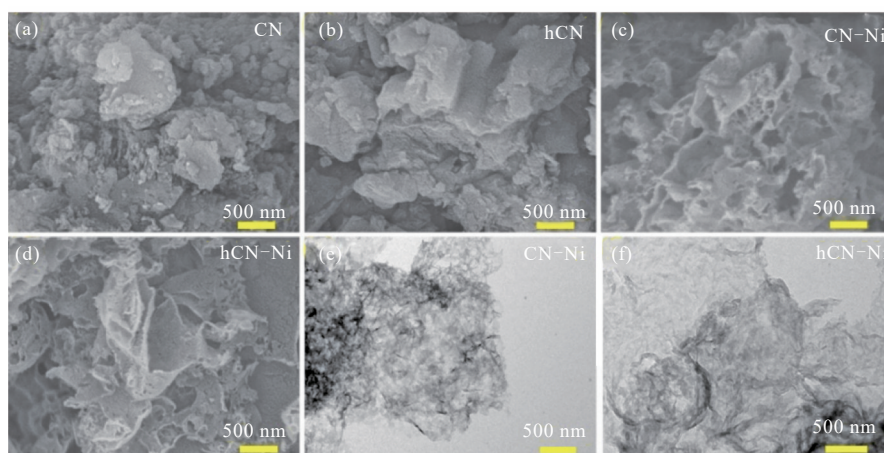


Fig.2 SEM images of (a) CN, (b) hCN, (c) CN-Ni, and (d) hCN-Ni; TEM images of (e) CN-Ni and (f) hCN-Ni

To verify whether hydroxylation of CN-Ni disrupts the single-atom Ni species in the nanosheets, the hCN-Ni sample was further characterized by AC-STEM. As shown in Fig. 3a, highly dispersed bright dots (circled in red) are clearly observed, with an approximate size of 0.2 nm, consistent with the atomic radius of Ni ($R_{\text{Ni}} = 1.62 \text{ \AA}$). Elemental mapping further confirms that the catalyst surface is composed of C, N, O, and Ni elements (Fig. 3b), where red, blue, green, and purple correspond to C, N, O, and Ni, respectively. These results indicate that hydrothermal treatment does not alter the existing state of the metallic species.

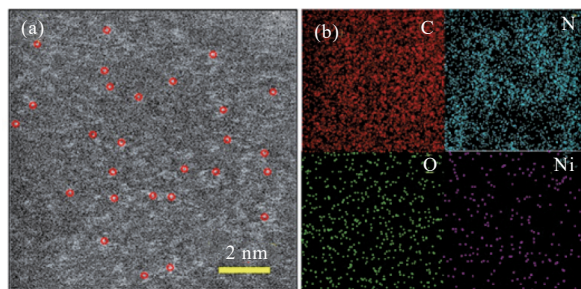


Fig.3 (a) AC-STEM image and (b) element mapping of hCN-Ni catalyst

XPS was used to investigate the abundant surface hydroxyl groups and their locations in the hCN-Ni sample. As shown in Fig. 4a, the high-resolution C 1s spectrum of hCN-Ni can be deconvoluted into three peaks (N=C—N, C—NH_x, and C—C), and the peak at 284.8 eV corresponds to the C—C bond from adventitious carbon. The N=C—N bond (287.9 eV) and C—NH_x bond (286.2 eV) are two different spatial positions of carbon in polymeric carbon nitride^[19]. It is clearly observed from the figure that compared with CN-Ni, the binding energy of C in N=C—N of hCN-Ni shifts to a lower value, indicating that after grafting —OH onto CN-Ni, the electron density around the C element in N=C—N increases, which may be due to the grafting of hydroxyl groups onto C atoms^[20]. Fig. 4b shows the high-resolution N 1s spectra, which can be divided into four types of N with centers at 398.2, 399.7, 400.9, and 403.7 eV, corresponding to the energy of C=N—C, N—(C)₃, C—NH_x, and π -excited N 1s energy bands, respectively^[21]. Compared with Ni-CN, the N 1s peak of the C=N—C bond in hCN-

Ni also shifts to a lower binding energy after the introduction of $-OH$, which is also attributed to the increase in electron density and consistent with the negative shift of the C 1s peak at the $N=C-N$ site. At the same time, it is observed that the peak of edge-defect amino groups connected to C atoms ($C-NH_x$) does not change significantly, thus inferring that hydroxyl groups do not replace the edge-defect amino groups of the sample. Fig. 4c shows the XPS spectra of O 1s, in which the peak at 530.5 eV is attributed to the C—O bond. In addition, there is another peak at 532.4 eV in the catalyst, which corresponds to the O—H bond^[22]. For the C—O peak, it is caused not only by the unavoidable O doping during thermal polymerization in air but also by the surface $-OH$ bonded to C atoms ($C-O-H$), and at the same time, it is clearly observed that the intensity of the O—H bond increases. Although the C—O component in the C 1s spectrum (Figure 4a) was not

clearly resolved, likely owing to the relatively low abundance of surface C—O bonds, whose signal (~ 284.6 eV) may be masked by the strong C—C main peak (284.8 eV)—the O 1s analysis provided conclusive evidence confirming the successful grafting of hydroxyl species onto the carbon framework. In the Ni 2p spectra (Fig. 4d), the peaks at binding energies of 855.0 and 872.6 eV correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively. The binding energy of Ni 2p_{3/2} lies between that of metallic Ni (853.1 eV) and Ni²⁺ (856.0 eV)^[23], indicating that Ni exists in the sample in the form of cations and its valence state is lower than +2. The hydrothermal treatment does not change the valence state of Ni atoms. Synthesizing the above XPS analysis results, it can be concluded that hydroxyl groups are successfully modified in the CN-Ni material and mainly bind selectively to the non-amino-coordinated carbon sites ($N=C-N$) in the framework.

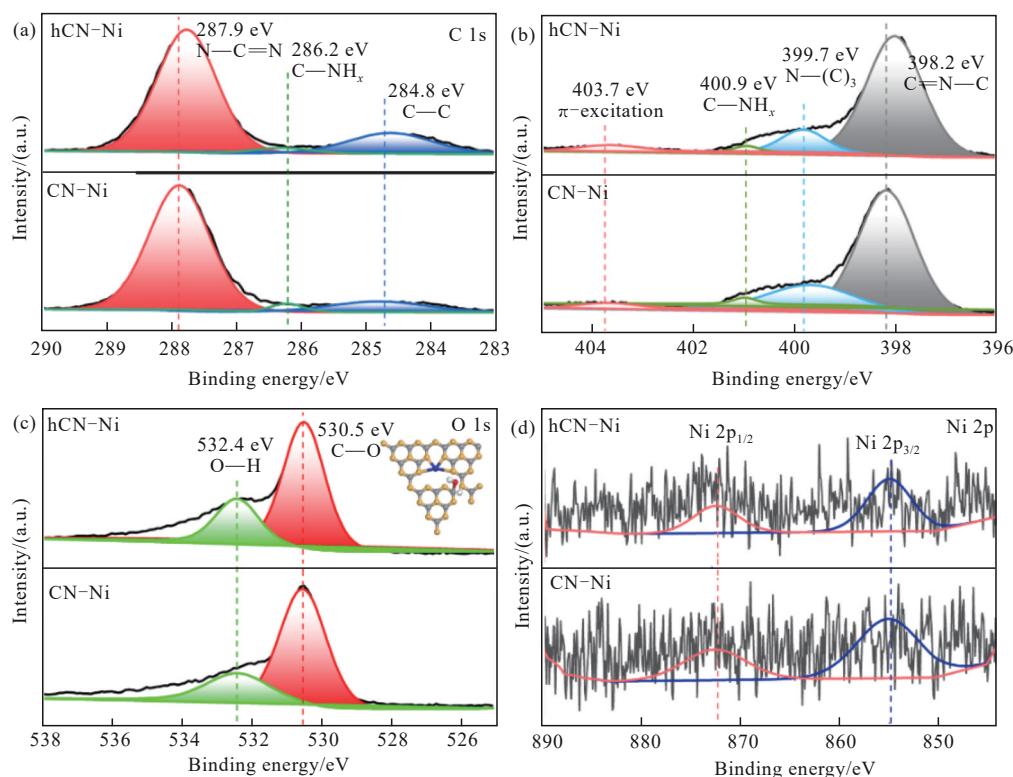


Fig. 4 (a) C 1s, (b) N 1s, (c) O 1s, and (d) Ni 2p spectra of hCN-Ni and CN-Ni catalysts

In addition, it can be seen from the XPS relative elemental contents in Table 1 that the relative content of O element in hydroxylated hCN-Ni increases from 3.8% (in CN-Ni) to 4.2%, confirming the successful introduction of oxygen-containing groups via

hydroxylation; the contents of C and N decrease slightly since the increased proportion of O, and the overall impact on the proportions of C and N in the C_3N_4 framework was minor; while the relative content of Ni element was 0.2% in both materials, indi-

cating that hydroxylation did not significantly change the relative content of Ni on the material surface.

Table 1 XPS element relative content of CN-Ni and hCN-Ni(%)

Material	C	N	O	Ni
CN-Ni	55.6	40.4	3.8	0.2
hCN-Ni	55.5	40.1	4.2	0.2

2.2 Photocatalytic CO₂ reduction performance of hCN-Ni

To evaluate the photocatalytic CO₂ reduction performance of CN, hCN, CN-Ni, and hCN-Ni, the samples were tested under irradiation with a 300 W Xe lamp, using H₂O and CO₂ as reactants without any sacrificial agents. In addition, the electron selectivity of the reduction products was calculated to further analyze the effect of hydroxyl groups on the cata-

lytic performance of CN. As shown in Fig.5a, all catalysts can convert CO₂ into CO and CH₄ under simulated sunlight irradiation. The rates of CO production via photocatalytic CO₂ reduction over CN, hCN, CN-Ni, and hCN-Ni are 1.56, 1.36, 19.8, and 22 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively, while the rates of CH₄ production are 0.1, 0.15, 1.73, and 3.3 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively. It can be observed that with the introduction of hydroxyl groups into CN-Ni, the rates of photocatalytic CO₂ reduction to CO and CH₄ are both significantly increased: the CO production rate of hCN-Ni is 14, 16, and 1.1 times that of CN, hCN, and CN-Ni, respectively, while its CH₄ production rate is 33, 22, and 1.9 times that of CN, hCN, and CN-Ni, respectively.

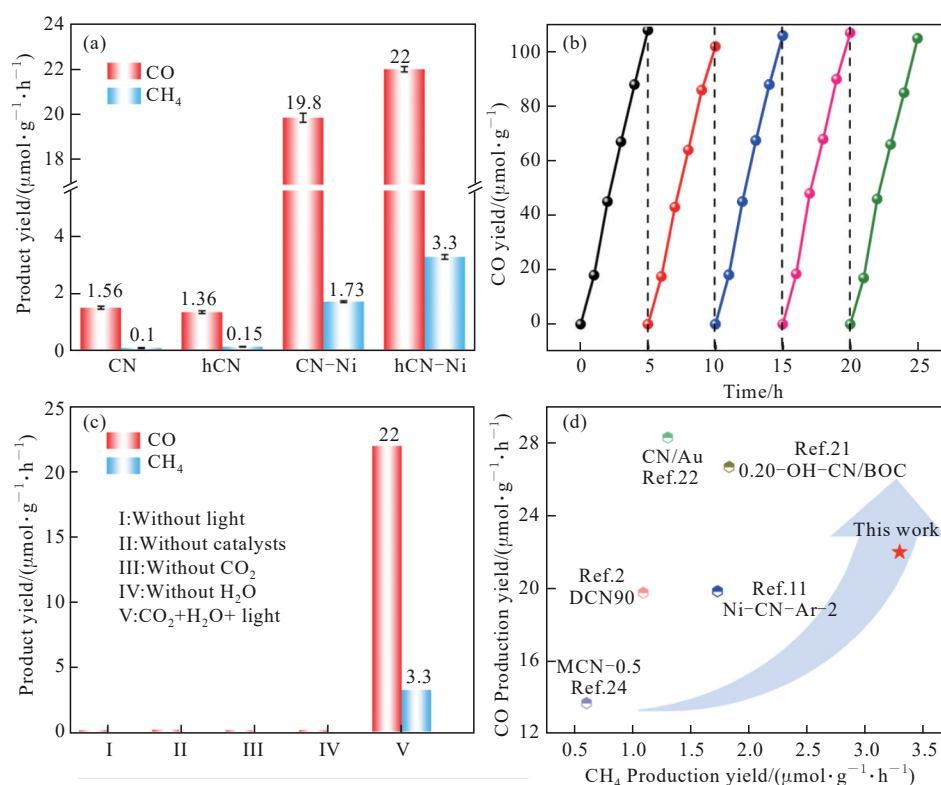


Fig.5 (a) Generation rate of photocatalytic reduction of CO₂ gas products of samples; (b) Photocatalytic cycle stability plot of hCN-Ni; (c) Blank control test for hCN-Ni sample; (d) Comparison of photocatalytic performance with modified g-C₃N₄ samples reported in literature

After the reaction, the photocatalyst samples were collected, centrifuged, and dried to test their stability in CO₂ reduction. As shown in Fig.5b, it is found that after 5 cycles of experiments, the CO production rate remains almost unchanged, indicating that the introduction of hydroxyl groups does not affect the stability of the catalyst. In addition, to verify

the effect of photocatalytic conditions on performance, the photocatalytic performance of hCN-Ni was tested with the following conditions: (I) without light, but with photocatalyst, CO₂, and H₂O; (II) without catalyst, but with light, CO₂, and H₂O; (III) without CO₂, but with light, catalyst, and water; (IV) without H₂O, but with light, catalyst, and

CO₂; (V) with light, catalyst, CO₂, and H₂O. As shown in Fig. 5c, no obvious reduction products are generated under the first three conditions, which indicates that light, catalyst, CO₂, and H₂O are all key factors for effective photocatalytic CO₂ reduction in this experiment. In addition, the performance of this sample was compared with that of the reported functional group-modified g-C₃N₄, and its performance outperforms most of the similar photocatalysts^[2,11,21,22,24] (Fig. 5d).

In this experiment, the electron selectivity of the CH₄ product was evaluated using the following formula^[25]:

$$\text{Selectivity} = \frac{8V(\text{CH}_4)}{8V(\text{CH}_4) + 2V(\text{CO})} \times 100\% \quad (1)$$

where $V(\text{CO})$ and $V(\text{CH}_4)$ represent the reaction rates of CO and CH₄, respectively. Table 2 presents the selectivities of CN, hCN, CN-Ni, and hCN-Ni for photocatalytic CO₂ reduction to CO and CH₄. It can be observed that with the introduction of hydroxyl groups into CN-Ni, the production rates of CO and CH₄ are improved to a certain extent, and the CH₄ electron selectivity increases from 20.4% (of the pristine CN sample) to 37.5%.

Table 2 Activity and electron selectivity for photocatalytic reduction of CO₂ over samples

Photocatalyst	Average production rate/ ($\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$)		Electron selectivity of CH ₄ products/%
	CO	CH ₄	
CN	1.52	0.1	20.4
hCNCN-Ni	1.36	0.15	30.6
CN-Ni	19.8	1.73	25.9
hCN-Ni	22	3.3	37.5

2.3 Light absorption capacity of hCN-Ni

UV-vis DRS was used to investigate the light absorption capacity of the catalyst samples. As shown in Fig. 6a, all samples exhibit strong absorption peaks in the ultraviolet region, with the absorption edges of CN, hCN, CN-Ni, and hCN-Ni being 464.3, 457.9, 556.8, and 524.2 nm, respectively. Owing to the significant expansion of the material's light response range induced by the introduction of single-atom Ni, both CN-Ni and hCN-Ni exhibit superior light absorption capacity compared to CN. The light absorption capacity of hCN-Ni decreases slight-

ly compared to CN-Ni, which may be due to the reduced defect state density in the material caused by the introduction of hydroxyl groups. The band gap of the catalyst can be determined using the Kubelka-Munk equation and Tauc plot, with the formula given below^[26]:

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (2)$$

where α , h , ν , E_g , and A represent the absorption coefficient, Planck constant, light frequency, band gap, and constant, respectively. Fig. 6(b) shows the band gap values of CN, hCN, CN-Ni, and hCN-Ni. The band gaps of CN, hCN, CN-Ni, and hCN-Ni are 2.78, 2.80, 2.60, and 2.67 eV, respectively. The flat-band potential (E_b) of the catalyst can be determined by extrapolating the linear region of the M-S curve, and for n-type semiconductors, E_b is generally considered to be approximately equal to its conduction band position^[27]. As shown in Fig. 6c, the conduction band positions of CN, hCN, CN-Ni, and hCN-Ni relative to the normal hydrogen electrode (NHE) are -1.1, -0.87, -0.87, and -0.80 eV, respectively, thus all of them meet the potential requirements for CO₂ reduction to CO and CH₄. In addition, the valence band (VB) positions of the samples can be calculated using the following formula^[28]:

$$E_{\text{VB}} = E_{\text{CB}} + E_g \quad (3)$$

By combining the band gap and conduction band position of the samples, the valence band positions of the catalysts can be obtained. The valence band positions of CN and hCN-Ni relative to the normal hydrogen electrode (NHE) are 1.68 and 1.87 eV, respectively. By integrating the valence band and conduction band positions, the band structure diagram of the catalysts, as shown in Fig. 6d, is finally obtained.

2.4 Efficient photogenerated charge carrier separation capabilities of samples

For the photocatalytic CO₂ reduction reaction, the transport behavior of photogenerated charges directly affects the kinetics of photocatalytic CO₂ reduction. The photoelectric conversion capability and charge carrier separation capability of semiconductor photocatalysts can usually be evaluated by photoelectrochemical tests. As shown in Fig. 7a, the transient photocurrent curves of the photocatalysts reveal that

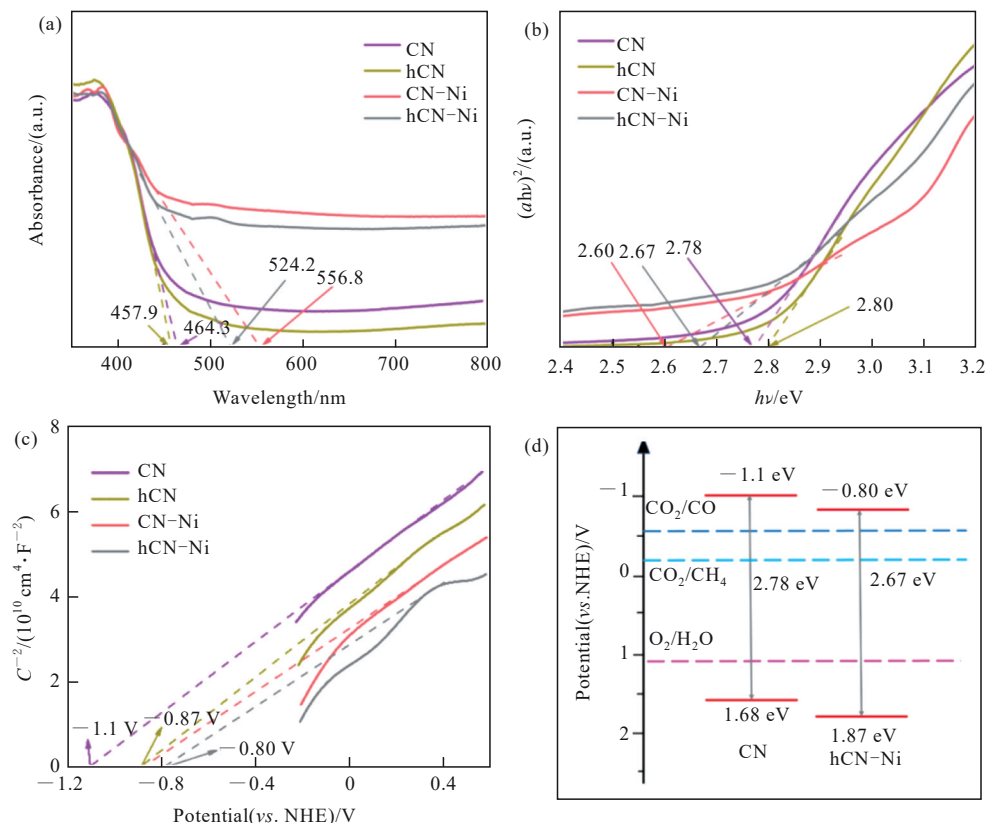


Fig.6 (a) UV-vis absorption spectra of CN, hCN, CN-Ni, and hCN-Ni; (b) Bandgaps of samples; (c) Mott - Schottky analysis curves of samples; (d) Energy band structure diagram of CN and hCN-Ni

the photocurrent intensities follow the order: hCN-Ni > CN-Ni > hCN > CN. This indicates that the introduction of hydroxyl groups into CN and CN-Ni can significantly increase their photocurrent intensities, remarkably improve the separation efficiency of photogenerated charge carriers^[29], and accelerate the migration of electron-hole pairs, thereby providing more photogenerated charges for the photocatalytic CO_2 reduction reaction.

EIS is an effective method to study the charge carrier separation kinetics in photocatalysts. As shown in Fig. 7b, the EIS curves of the samples exhibit a typical semicircular feature. The diameter of the semicircle directly reflects the charge transfer resistance (R_{ct}) at the catalyst/electrolyte interface; a smaller diameter corresponds to a lower R_{ct} , which is more favorable for the catalytic reaction^[30]. The test results show that the semicircle diameters of the four samples (CN, hCN, CN-Ni, and hCN-Ni) decrease in sequence, among which hCN-Ni exhibits the smallest R_{ct} value, indicating its optimal charge separation efficiency. This result is highly consistent

with the conclusion from the transient photocurrent test. Analysis shows that hydroxyl modification can significantly enhance the charge carrier separation and migration capabilities of the material, thereby effectively promoting the improvement of CO_2 reduction performance.

PL spectroscopy is an effective technique to characterize the recombination behavior of photogenerated charge carriers. When electron-hole pairs generated by light excitation undergo radiative recombination, characteristic fluorescence is emitted, and its intensity directly reflects the carrier recombination rate. The higher the PL peak intensity, the more severe the recombination and the lower the carrier separation efficiency. Fig. 7c shows the PL spectra of the prepared samples, and it can be observed that their peak intensities follow the order from highest to lowest: CN > hCN > CN-Ni > hCN-Ni. hCN-Ni exhibits the lowest peak intensity, which means it has the smallest photogenerated carrier recombination rate and also indicates the best migration rate of photogenerated electrons and holes. With the introduc-

tion of hydroxyl groups, the recombination rate of photogenerated electrons and holes in CN-Ni is significantly suppressed, which is attributed to the accelerated charge transfer rate from the interior of the ultrathin nanosheets to the surface and the trapping of photogenerated charges by surface states, thereby significantly improving their migration rate. Meanwhile, TRPL spectroscopy analyses were performed on CN-Ni and hCN-Ni, and the variation trend of decay time is shown in Fig. 7d. The fluorescence lifetime of CN-Ni is 3.89 ns, while that of hCN-Ni is 2.05 ns, which is 1.84 ns shorter than that of CN-Ni.

The shortened lifetime of hCN-Ni indicates more efficient separation of electrons and holes, meaning that photogenerated carriers are trapped by the hydroxylated substrate and thus can drive redox reactions. The fluorescence decay of the prepared samples is completely consistent with the decrease in their photoluminescence intensity. These results confirm that the charge separation of CN-Ni is significantly improved via surface hydroxyl modification, which contributes to the enhancement of its photocatalytic activity.

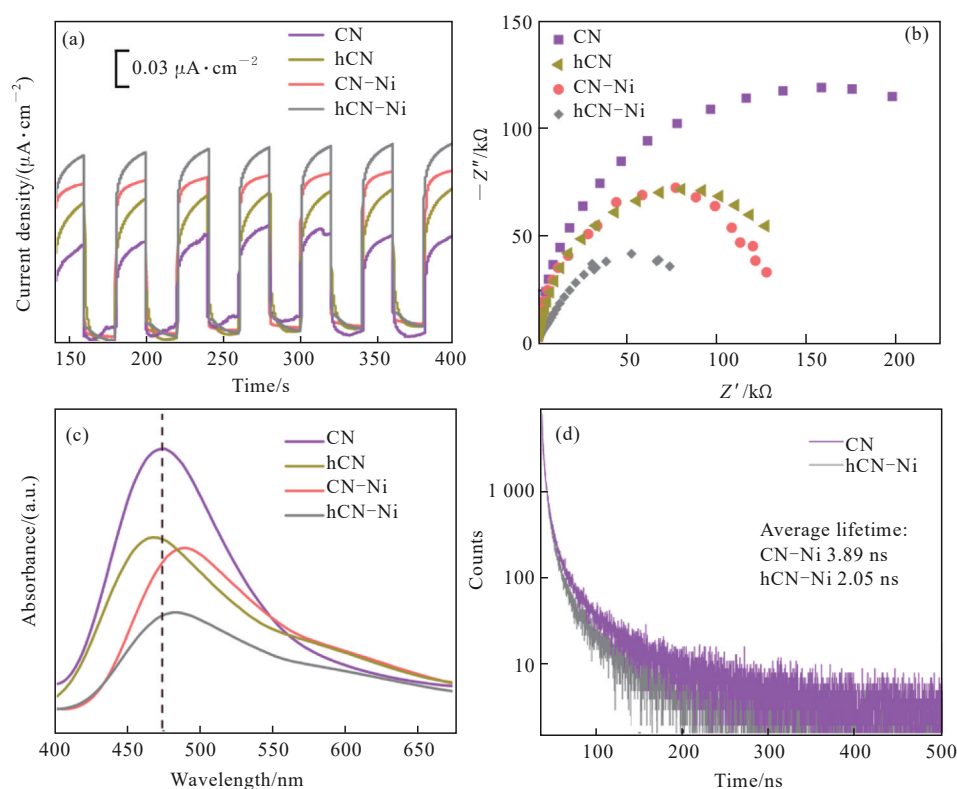


Fig. 7 (a) Transient photocurrent curves; (b) EIS curves; (c) PL spectra of CN, hCN, CN-Ni, and hCN-Ni; (d) TRPL spectra of CN and hCN-Ni catalysts

2.5 Water adsorption capacities of samples

The adsorption capacity of catalyst surfaces for reactant molecules (H_2O and CO_2) significantly influences the reaction rate and product distribution in catalytic processes. The water contact angles of CN, hCN, CN-Ni, and hCN-Ni samples are shown in Fig. 8. Hydrophilicity is inversely proportional to the contact angle, meaning smaller angles indicate stronger water adsorption capacity. The contact angles of CN and CN-Ni are 58.14° and 58.73° , respectively,

while those of hCN and hCN-Ni decrease to 53.46° and 52.96° , respectively. This reduction in contact angle after hydrothermal treatment confirms enhanced hydrophilicity and improved water adsorption ability.

Previous studies have demonstrated that hydroxyl group introduction can enhance both hydrophilicity and photogenerated charge carrier separation efficiency. The increased hydrophilicity of hCN-Ni promotes water adsorption, providing a richer hydrogen source for CO_2 photoreduction to CH_4 . Additionally,

hydroxyl groups accelerate the combination of photo-generated electrons with hydrogen protons and reaction intermediates, facilitating the conversion of intermediates into hydrocarbons. These synergistic effects

explain why hCN-Ni exhibits higher CH_4 electron selectivity, which is attributed to its improved charge separation efficiency and water adsorption capacity.

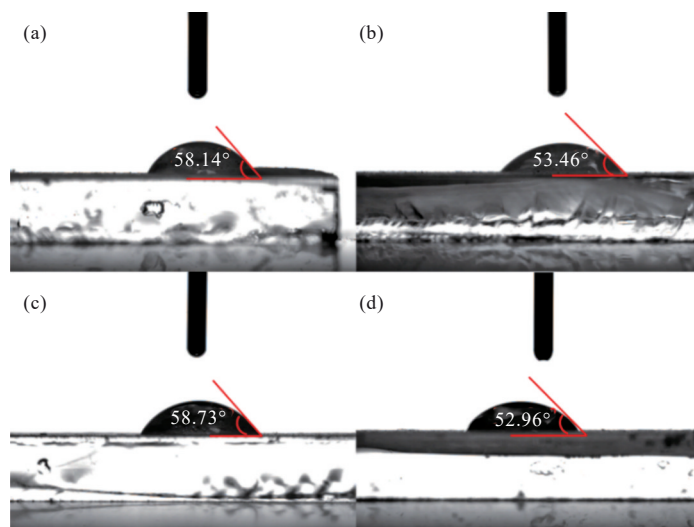


Fig.8 H_2O contact angles of (a) CN, (b) hCN, (c) CN-Ni, and (d) hCN-Ni

2.6 CO_2 reduction mechanism of hCN-Ni

According to the analysis of hCN-Ni's morphological structure, light absorption properties, photoelectric properties, and catalytic performance, it is found that the introduction of hydroxyl groups plays a crucial role in the photocatalytic conversion of CO_2 to CH_4 . As shown in Fig. 9, under light irradiation, with the small band gap of the hCN-Ni semiconductor photocatalyst (note: corrected “hNi-CN” to “hCN-Ni” for consistency with previous sections), more electrons absorb photons with energy greater than the band gap, then jump from the valence band to the conduction band to form electron-hole pairs, and quickly migrate to the catalyst surface. Meanwhile, single-atom Ni acts as charge accumulation sites, which promote the separation of photogenerated carriers and reduce their recombination rate, thereby allowing more photogenerated carriers to participate in the CO_2 reduction reaction. In addition, the introduction of hydroxyl groups exerts two key effects: On one hand, it enhances the hydrophilicity of the catalyst surface, promotes the adsorption of water molecules, and forms a local water-rich environment; at the same time, its asymmetric steric hindrance effectively inhibits the recombination of photo-generated carriers. On the other hand, the well-dis-

persed single-atom Ni on the hCN-Ni surface serves as active sites for CO_2 adsorption and activation. Protons enriched by hydroxyl groups can be rapidly transferred to the Ni active sites, significantly promoting the conversion process of CO_2 hydrogenation to CH_4 , thus enhancing the catalyst's electron selectivity for CH_4 .

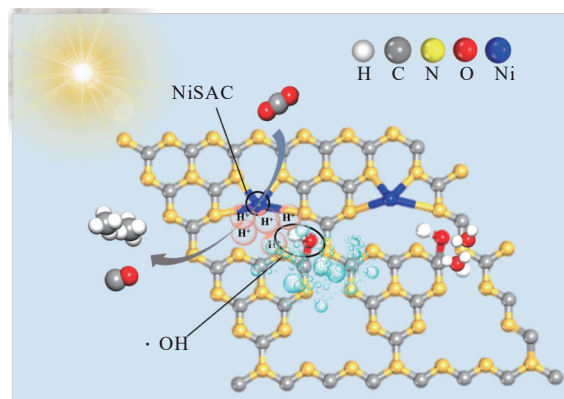


Fig.9 Schematic illustration of photocatalytic conversion processes of CO_2 and H_2O on hCN-Ni for CO and CH_4 productions

3 Conclusions

In conclusion, in this work, hydroxyl functional groups were introduced onto single-atom Ni-modified g-C₃N₄ nanosheets by using hydrothermal method to obtain the catalyst hCN-Ni. hCN-Ni exhibits excellent CO_2 reduction performance, with CO and

CH₄ production rates of 22 and 3.3 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively, and the electron selectivity for CH₄ reaches 37.5%. The introduction of hydroxyl groups not only promotes the separation of photogenerated charge carriers and provides an electron-rich environment for CO₂ conversion but also enhances the hydro-

philicity of single-atom Ni-modified g-C₃N₄ nanosheets. Water molecules accumulated on the hydroxyl-modified surface can serve as a hydrogen proton source for the reduction of CO₂ to CH₄, facilitating the formation of CH₄.

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