

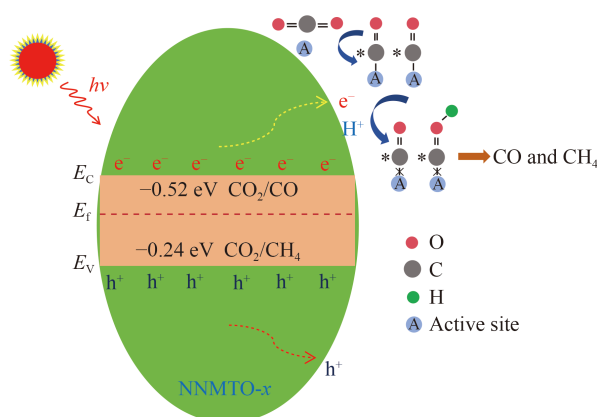
Facile synthesis of $\text{Na}_{0.9}\text{Mg}_{0.45}\text{Ti}_{3.55}\text{O}_8\text{-Na}_2\text{Ni}_2\text{Ti}_6\text{O}_{16}$ solid solutions for improving photocatalytic CO_2 reduction

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Abstract: In this study, a straightforward one-step hydrothermal method was successfully utilized to synthesize the solid solution $\text{Na}_{0.9}\text{Mg}_{0.45}\text{Ti}_{3.55}\text{O}_8\text{-Na}_2\text{Ni}_2\text{Ti}_6\text{O}_{16}$ (NNMTO- x), where x denotes the molar percentage of $\text{Na}_2\text{Ni}_2\text{Ti}_6\text{O}_{16}$ (NNTO) within $\text{Na}_{0.9}\text{Mg}_{0.45}\text{Ti}_{3.55}\text{O}_8$ (NMTO), with x values of 10, 20, 30, 40, and 50. Both XPS (X-ray Photoelectron Spectroscopy) and EDX (Energy Dispersive X-ray Spectroscopy) analyses unequivocally validated the formation of the NNMTO- x solid solutions. It was observed that when x is below 40, the NNMTO- x solid solution retains the structural characteristics of the original NMTO. However, beyond this threshold, significant alterations in crystal morphology were noted, accompanied by a noticeable decline in photocatalytic activity. Notably, the absorption edge of NNMTO- x ($x < 40$) exhibited a shift towards the visible-light spectrum, thereby substantially broadening the absorption range. The findings highlight that NNMTO-30 possesses the most pronounced photocatalytic activity for the reduction of CO_2 . Specifically, after a 6 h irradiation period, the production rates of CO and CH_4 were recorded at 42.38 and 1.47 $\mu\text{mol/g}$, respectively. This investigation provides pivotal insights that are instrumental in the advancement of highly efficient and stable photocatalysts tailored for CO_2 reduction processes.

Key words: photocatalytic conversion; hydrothermal method; optical response range; solid solution; charge separation



The widespread utilization of fossil fuels has significantly transformed human lifestyle. Regrettably, it releases a substantial quantity of the greenhouse gas CO_2 into the atmosphere. The climate issues resulting from the massive emission of CO_2 have drawn global attention. Addressing the environmental crisis and advancing the development of renewable green energy have emerged as critical challenges that demand immediate attention and resolution^[1]. The important way of closing carbon cycle and achieve carbon neutrality is to carbon capture, utilization and storage technology (CCUS)^[2-3]. Converting CO_2 into carbonaceous fuel is a win-win solution for addressing environmental pollution and energy crisis^[4-5]. CO_2 has emerged as a valuable feedstock for synthesizing hydrocarbon fuels and

high-value chemical products. Notably, the catalytic conversion of CO_2 into value-added chemicals, including methanol^[3], ethylene carbonate^[6] and propylene carbonate^[7], represents a promising strategy for CO_2 resource utilization. Compared to conventional hydrocarbon feedstocks, CO_2 offers distinct advantages as a raw material, including its abundant availability, low cost, and environmentally benign nature^[8]. The catalytic hydrogenation of CO_2 using renewable hydrogen has attracted substantial interest from both academic and industrial sectors. Photocatalytic CO_2 reduction to renewable fuels is particularly promising, offering a dual solution to energy sustainability and climate change mitigation^[9]. Among various reduction products, C_1 compounds such as CO and formic acid (HCOOH) exhibit

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remarkable selectivity at elevated current densities, presenting promising commercialization potential for CO_2 utilization^[10–11]. However, the direct synthesis of C_{2+} products from CO_2 remains a significant scientific and technological challenge, requiring further breakthroughs in catalyst design and process optimization^[12–13]. The intrinsic stability of CO_2 , competition from side reactions pose challenges in photocatalytic reduction of CO_2 . Although CO_2 contains two polar $\text{C}=\text{O}$ double bonds, it is an overall centrosymmetric and nonpolar linear molecule. The thermodynamic stability and chemical inertness make the cleavage of the $\text{C}=\text{O}$ double bond in CO_2 highly challenging.

Photocatalytic CO_2 reduction is a solar-driven process that converts CO_2 into valuable carbon-based fuels using water as the reducing agent under ambient conditions, offering a sustainable alternative to conventional methods that depend on fossil fuels or hazardous chemicals. The transport and separation of photogenerated carriers and the redox potential of semiconductors play a crucial role in the process of photocatalytic reduction of CO_2 . The surface of catalyst involves the interaction between catalyst and CO_2 or intermediate, which is the main core region of photocatalytic reduction of CO_2 . Therefore, the surface properties of the catalyst will significantly affect the reaction pathway^[14]. In recent years, various photocatalysts, including $\text{Bi}_2\text{Sn}_2\text{O}_7/\text{NiAl-LDH}$ heterojunction^[15], $\text{CN}^{[16]}$, $\text{g-C}_3\text{N}_4$ ^[17], metal based catalysts (MOF-derived defective Ni/TiO_2 ^[18]), pyridine-nitrogen^[19] and bismuth-based^[20] etc. have demonstrated remarkable efficacy in CO_2 reduction. However, on account of their low charge separation efficiency, the poor light absorption or high cost substantially largely constrain its photocatalytic efficiency. Then, some optimization of catalyst structure approaches, such as, metal or non-metallic modification^[21], surface engineering^[22] and heterojunction construction^[23], defective structures etc., were employed to improve the photocatalytic activity.

NMTO, a wide-bandgap semiconductor nanocomposite based on $\text{TiO}_2(\text{B})$ ^[24], has demonstrated exceptional photocatalytic properties. In this study, we developed a novel solid solution system, NNMTO- x , through a hydrothermal synthesis approach to enhance catalytic performance. The formation of solid solutions represents a promising strategy for optimizing the photocatalytic efficiency of CO_2 reduction, offering enhanced charge carrier separation and tailored band structure engineering.

1 Experimental methods

1.1 Chemicals

Titanium dioxide (TiO_2 , 98.50%), sodium hydroxide (NaOH , 96.00%), light magnesium oxide (MgO , 98.50%), nickel nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.70%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultra-high purity CO_2

(>99.99%) was supplied by Xuzhou Hongfeng Gas Co., Ltd. The distilled water employed in our experiments exhibits a conductivity of $0.82 \mu\text{S/cm}$ ($\pm 0.1 \mu\text{S/cm}$ measurement uncertainty) at 25°C , meeting the requirements for analytical grade purity.

1.2 Characterization methods

X-ray Diffraction (XRD) analysis was performed on a D/Max-2550 diffractometer ($\text{Cu K}\alpha$, $\lambda=0.15 \text{ nm}$) from 10° – 80° 2θ at 40 kV and 100 mA. The sample morphology was examined using an FEI Nova Nano SEM 450 field emission scanning electron microscope (SEM) at 10.00 kV accelerating voltage. The morphology and crystal structure of samples were investigated using field emission high-resolution transmission electron microscopy (FE-HRTEM) with SAED attachment (G2F20). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MKII (VG Scienta USA) system ($\text{Mg K}\alpha$ source), with energy calibration referenced to C 1s at 284.60 eV. Data analysis was performed with DigitalMicrograph software and optical properties were characterized by UV-vis spectroscopy (Lambda 950) across the 200–800 nm spectral range. The specific surface area (S_{BET}) was determined by N_2 adsorption-desorption isotherms measured at -196°C (77 K) using a Micromeritics ASAP 2010 analyzer (USA). The photoluminescence (PL) spectra were acquired on a Cary-Eclipse 500 system (325 nm excitation) to characterize the separation efficiency of photoinduced electron-hole pairs. The CHI 660E electrochemical workstation was employed to record both transient photocurrent and Nyquist plots under simulated solar irradiation. The elemental composition of the samples was determined by inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) analysis.

1.3 Synthesize NNMTO- x solid solutions

A series of nano-catalysts comprising NNMTO- x solid solutions with varying molar ratios of NNTO and NMTO were synthesized via a one-step hydrothermal method. Typically, MgO and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in a 1.20 mol/L NaOH aqueous solution, while maintaining a constant mass of TiO_2 . The mixture was subjected to ultrasonication for 10 min followed by magnetic stirring for 30 min, transferred into a 130 mL stainless steel autoclave and hermetically sealed. The autoclave was gradually heated to 300°C at a controlled heating rate of 3°C/min and maintained isothermally for 80 min to ensure complete reaction. After natural cooling to room temperature, the samples were collected. The NNMTO- x solid solution nanocrystals were isolated through sequential washing with distilled water and ethanol (three times), then dried at 60°C for 8 h in oven.

1.4 Evaluation of photodegradation activity

The photocatalytic activity for CO_2 reduction was evaluated under xenon lamp irradiation (300 W) without the addition of sacrificial reagents. In a typical procedure, 15 mg of catalyst was uniformly dispersed on a quartz sand plate and subsequently transferred to a 100 mL static reactor equipped with a quartz window. Prior to irradiation, 2 mL of deionized water was injected into the reactor, followed by purging with high-purity CO_2 (99.99%) at a constant flow rate (20 mL/min) for 30 min to ensure complete removal of atmospheric gases. The photocatalytic reaction was conducted under full-spectrum xenon lamp irradiation (350–780 nm) for 6 h, with the light intensity being enhanced by an internal reflector system. The gaseous products were quantitatively analyzed at 1 h intervals using gas chromatography. The quantification of CO and CH_4 products was performed by gas chromatography (GC-7920, AuLight, China) equipped with a flame ionization detector.

2 Results and discussion

2.1 Phase and morphology

Due to the absence of a reference XRD pattern for NNTO in the standard powder diffraction database, its theoretical diffraction pattern was computationally simulated employing the Vienna Ab-initio Simulation Package

(VASP) based on density functional theory (DFT) calculations. The atomic structure of NNTO, as shown in Figure 1(a), was constructed based on the isostructural analog of NMTO^[25]. The simulated XRD pattern of NNTO, presented in Figure 1(b), demonstrates excellent agreement with the diffraction pattern of NMTO (PDF No. 44-0007), confirming their structural similarity.

Figure 2(a) presents the XRD patterns of NNMTO-*x* samples with varying mass concentrations. The diffraction peaks of NNMTO-*x* show excellent agreement with the standard pattern of NMTO^[24], indicating consistent crystal structures across the different compositions. The structures of NMTO and NNTO are similar and their XRD diffraction patterns almost coincide, the XRD diffraction patterns remain nearly unchanged with increasing Ni content. The characteristic diffraction peak of NNMTO-*x*, as indicated within the circled region, exhibits modification, presumably attributed to the interstitial incorporation of Ni atoms into the NMTO crystal lattice. The magnified view of the strongest peak at approximately 24.5° provides conclusive evidence for the successful synthesis of NNMTO-*x* continuous solid solutions. As illustrated in Figure 2(b), the diffraction peaks of NNMTO-*x* solid solutions exhibit a slight angular shift compared to pure NMTO, which attributable to the interstitial incorporation of Ni ions within the crystal lattice.

Figure 3(a) presents the scanning electron microscopy (SEM) image of NMTO, revealing well-defined hexagonal plate-like morphology with smooth surfaces.

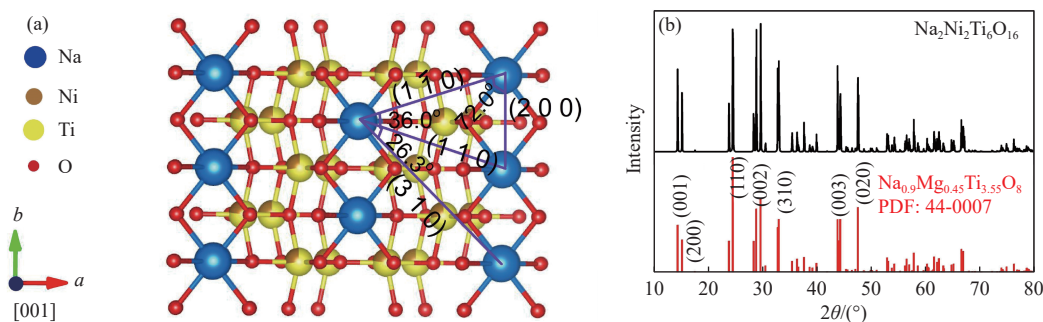


Fig. 1 (a) Crystal structure model of NNTO, (b) simulated XRD diffraction pattern of NNTO and standard diffraction pattern of NMTO

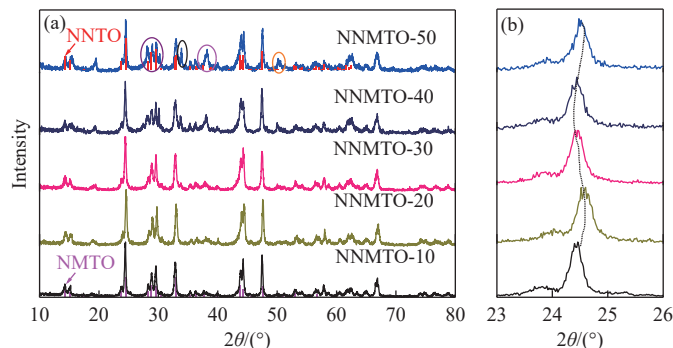


Fig. 2 (a) XRD patterns of NNMTO-*x*, (b) magnified NNMTO-*x* peak near 24.5°

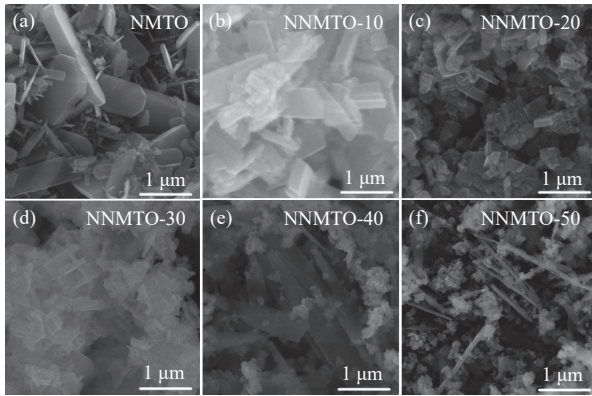


Fig. 3 SEM images of (a) NMTO, (b)–(f) NNMT0- x

The observed morphological characteristics are in excellent agreement with those of pure NMTO^[24], demonstrating the preservation of the distinctive hexagonal structure. The morphological characteristics of NNMT0- x solid solutions remain virtually identical to those of pure NMTO when the NNTO molar ratio is maintained below 40% (Figure 3(b)–(d)). However, a significant morphological transformation is observed when the Ni molar ratio exceeds 40% (Figure 3(e)–(f)). This structural evolution can be

attributed to the interstitial incorporation of Ni atoms into the NMTO crystal lattice, which presumably alters the surface energy and growth kinetics of the crystals.

Figure 4(a) shows the TEM image of NNMT0-30 at 200 kV, with Figure 4(b) presenting the HRTEM image from the red rectangular area. The measured lattice spacings of 1.73, 2.39 and 1.99 Å correspond to the (113), (401) and (403) planes of NMTO, respectively. As evidenced by Figure 4(c), (d), the interplanar spacing remains virtually unchanged, demonstrating that NNMT0- x ($x < 40$) retains the structural characteristics of pure NMTO. Figure 4(f) presents the corresponding HRTEM image obtained from the region delineated by the yellow rectangle in Figure 4(e). The crystal fringes of $d = 3.63$, 3.63 and 5.87 Å are determined as (110), ($1\bar{1}0$) and (200) crystal planes of NNMT0-40. Measurable variations in interplanar spacing were observed among the samples, resulting from localized strain induced by the incorporation of Ni^{2+} ions into the NMTO lattice through ionic radius mismatch with host cations. The chemical composition analysis, as determined by the EDX spectrum in Figure 4(i), (j), confirms the presence of Na, Mg, Ti, Ni and O elements in the NNMT0- x samples.

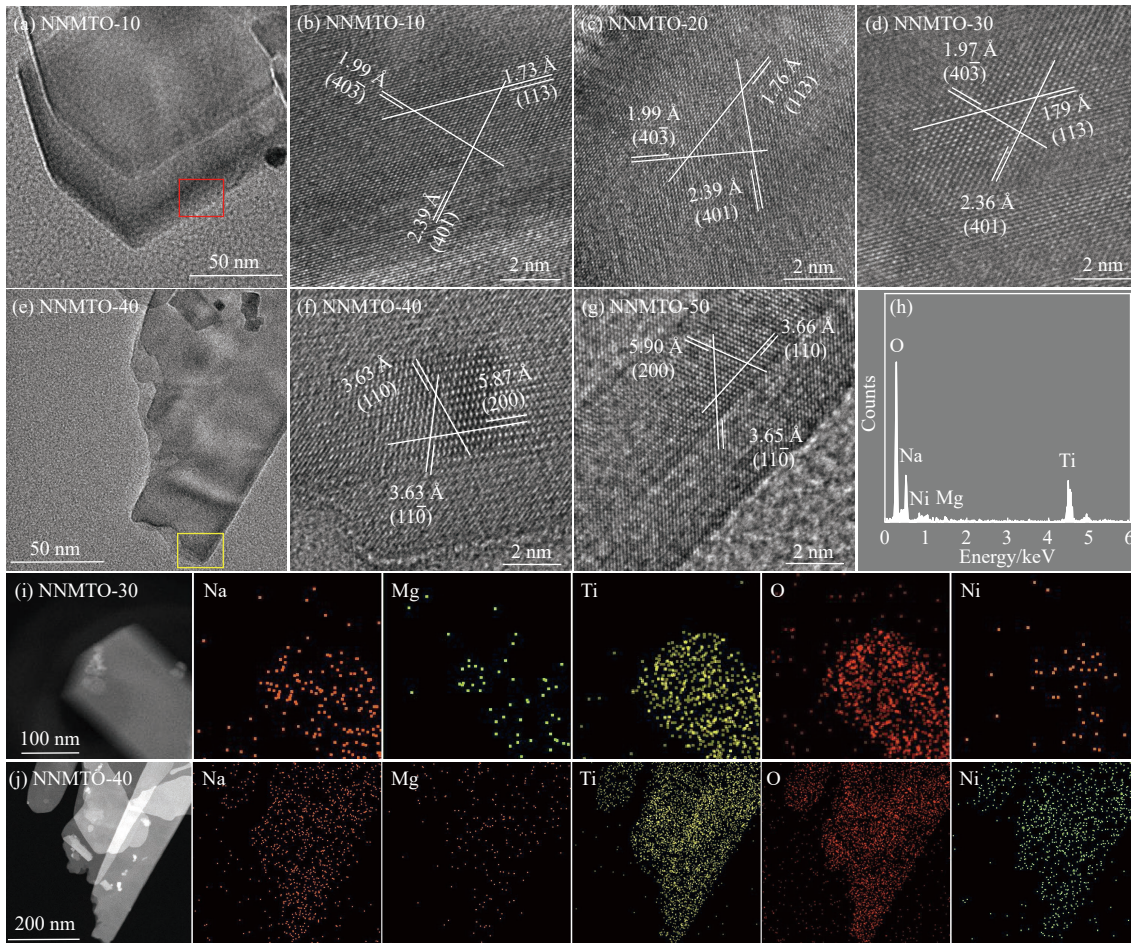


Fig. 4 (a) TEM image of NNMT0-10, (b) HRTEM images from the red rectangular area in (a), (c), (d) HRTEM images of NNMT0-20 and NNMT0-30, (e) TEM image of NNMT0-40, (f) HRTEM images from the yellow rectangular area in (e), (g) HRTEM images of NNMT0-50, (h) EDX near the red rectangular area in (a), (i)–(j) element mappings of NNMT0-30 and NNMT0-40

Moreover, the intensity of the Ni characteristic signal exhibits a proportional increase with the rising molar concentration of Ni, demonstrating the successful incorporation of nickel into the crystal structure. The ICP-OES/MS analysis results are summarized in Table 1, the measured mass fractions of all constituent elements (Na, Ni, Mg, Ti, O) show relatively agreement with the theoretical stoichiometric ratios, confirming the successful formation of the target solid solution phase.

XPS measurements were conducted for both NMTO and NNMTO- x samples.

Table 1 ICP-OES/MS analysis of NNMTO-30 and NNMTO-40

Photocatalyst	Element	Theo. content w/%	Exp. content w/%
NNMTO-30	Na	6.35	8.35
	Ni	2.29	3.72
	Mg	5.00	3.50
	Ti	48.36	56.18
NNMTO-40	Na	6.36	9.16
	Ni	6.68	9.61
	Mg	1.97	1.07
	Ti	47.26	59.62

The XPS spectra in Figure 5(a)–(c) reveal characteristic binding energies corresponding to the primary oxidation states of constituent elements in NMTO: Na $1s$ at 1071.20 eV (Na^+), Mg $2p$ at 49.20 eV (Mg^{2+}) and Ti $2p$ doublet at 458.20 and 464.00 eV (Ti^{4+}). The O $1s$ spectrum presented in Figure 5(d) can be fitted to three distinct components with binding energies at 529.20, 531.30 and 533.10 eV, corresponding to lattice oxygen (O^{2-}) in the crystal structure, surface-adsorbed water molecules (H_2O), and surface hydroxyl groups ($-\text{OH}$) of NMTO, respectively. The Ni $2p$ XPS spectrum in Figure 5(e) was deconvoluted into four characteristic peaks at binding energies of 855.20 eV (Ni $2p_{3/2}$), 86.80 eV (satellite), 873.40 eV (Ni $2p_{1/2}$) and 879.50 eV (satellite), confirming the presence of Ni^{2+} species within the solid solution.

2.2 UV-vis diffuse reflectance spectra

Figure 6 presents the UV-visible absorption spectra of NMTO and NNMTO- x samples, recorded using a UV-visible spectrophotometer in the wavelength range of 200–800 nm. The pristine NMTO exhibits the highest absorption intensity, which can be attributed to its characteristic gray coloration.

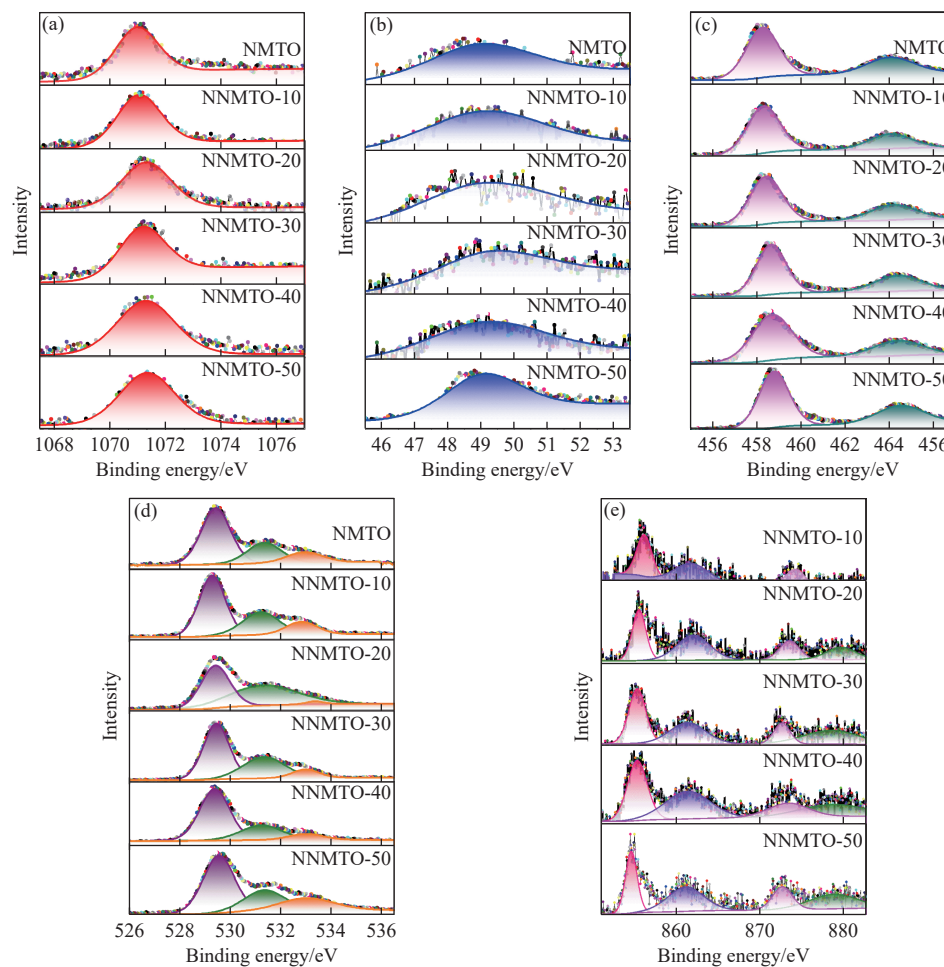


Fig. 5 XPS spectra of (a) Na $1s$, (b) Mg $2p$, (c) Ti $2p$, (d) O $1s$ for NMTO and NNMTO- x , (e) Ni $2p$ for NMTO- x

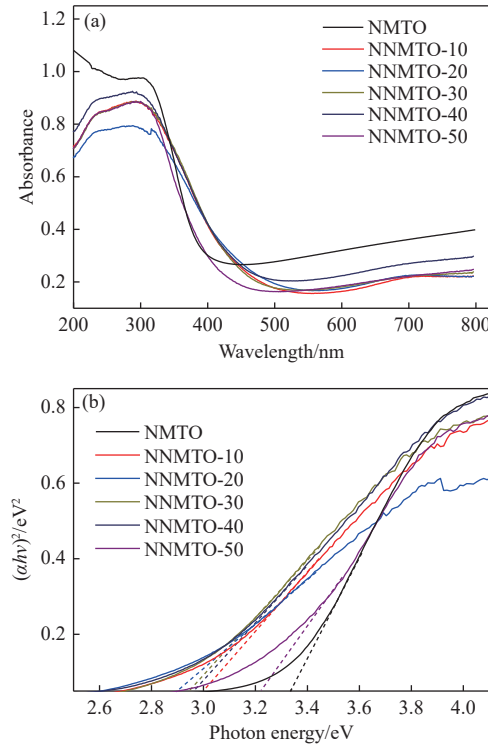


Fig. 6 (a) UV-vis diffuse reflectance spectra of NMTO and NNMTO- x , (b) Kubelka-Munk function versus energy $h\nu$ to determine the NNMTO- x bandgap

Notably, the absorption edge demonstrates a progressive red shift with increasing NNTO content, indicating enhanced visible light absorption capability in the NNMTO- x solid solutions. The optical band gap energies were determined using the Tauc plot method based on the following equation^[26]:

$$\alpha h\nu = B(h\nu - E_g)^{n/2} \quad (1)$$

The physical significance of the parameters α , ν , B and E_g in the Tauc equation is summarized in Table 2. The parameter n , which determines the transition type, is fundamentally related to the electronic band structure of the semiconductor. Specifically, a value of $n=1$ corresponds to a direct bandgap transition, where the minimum conduction band energy aligns with the maximum valence band energy in momentum space. Conversely, a value of $n=4$ indicates an indirect bandgap transition, requiring phonon assistance due to the misalignment of the conduction band minimum and valence band maximum in the Brillouin zone. Figure 6(a) demonstrates that NNTO exhibits significantly higher optical absorbance compared to the NNMTO- x samples, primarily attributed to its intrinsic gray coloration resulting from enhanced light absorption characteristics.

Table 2 The parameters in equation (1)

Parameter	Physical meaning	Unit
α	absorption coefficient	$\text{L} \cdot \text{g}^{-1} \cdot \text{cm}^{-1}$
ν	absorption frequency	Hz
B	proportional constant	—
E_g	band gap energy	eV

Figure 6(b) illustrates the Tauc plot representation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), where the optical band gap is determined by extrapolating the linear region of the curve to intersect with the $h\nu$ axis. Also, this indicates the prepared NNMTO- x is a direct bandgap transition semiconductor. Notably, the absorption edges of NNMTO- x samples exhibit a significant red shift compared to pristine NMTO, indicating an extended visible light absorption range. This enhanced optical property is particularly advantageous for photocatalytic applications, as it facilitates more efficient utilization of solar energy.

2.3 N_2 adsorption-desorption measurement

Figure 7 presents the nitrogen adsorption-desorption isotherms of NMTO and NNMTO- x , measured using the Brunauer-Emmett-Teller (BET) method for specific surface area determination. As summarized in Table 3, the formation of solid solutions leads to a noticeable enhancement in specific surface area. Among the synthesized samples, NNMTO-30 demonstrates optimal textural properties, exhibiting the maximum specific surface area ($31.77 \text{ m}^2/\text{g}$), the highest total pore volume ($0.12 \text{ cm}^3/\text{g}$), and the smallest average pore diameter (3.86 nm). However, a gradual decrease in specific surface area is observed with increasing NNTO molar ratio. It is mainly due to the proper ratio of NNTO to NMTO ensures the dispersion of Ni species on the surface of NMTO, forming a stable NNTO-NMTO interface.

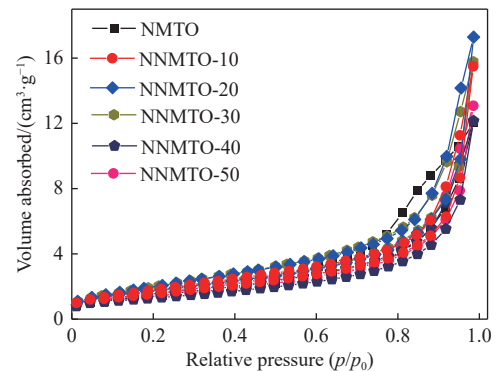


Fig. 7 Nitrogen adsorption-desorption isotherms of NMTO and NNMTO- x

Table 3 Pore characteristics of solid products varying with heating temperature

Sample	$S_{\text{BET}} / (\text{m}^2 \cdot \text{g}^{-1})$	Total pore volume $v / (\text{cm}^3 \cdot \text{g}^{-1})$	Average pore size d / nm
NMTO	25.71	0.09	10.30
NNMTO-10	29.27	0.12	3.06
NNMTO-20	30.31	0.12	3.08
NNMTO-30	31.77	0.12	3.86
NNMTO-40	25.06	0.10	3.58
NNMTO-50	26.99	0.10	3.86

However, excessive NNTO, due to agglomeration or coverage of the surface sites and mesopores of NMTO, reduces both the specific surface area and the number of effective NNTO-NMTO interfaces. Nevertheless, the overall variation in specific surface area across the NNMTO- x series remains relatively modest compared to pristine NMTO.

2.4 Transient photocurrent and electrochemical impedance

The photoelectrochemical performance of the samples was evaluated through chronoamperometric measurements under ultraviolet-visible light irradiation ($\lambda=365\text{ nm}$) using a $0.5\text{ mol/L Na}_2\text{SO}_4$ aqueous solution as the electrolyte. Figure 8(a) demonstrates a rapid photocurrent response upon illumination, characterized by an immediate increase when the light source is activated and a sharp decrease upon light termination. This reproducible on-off photocurrent behavior clearly indicates the efficient generation and separation of charge carriers under light irradiation, followed by their rapid recombination when the illumination ceases. A photocurrent spike was found in NMTO and NNMTO- x photocatalyst when the light was on, which is due to the recombination of holes and electrons. The NNMTO-30 sample exhibits significantly enhanced photocurrent density compared to pristine NMTO, demonstrating superior charge separation efficiency and reduced electron-hole recombination rates, which can be attributed to its optimized electronic structure and improved light absorption characteristics^[27].

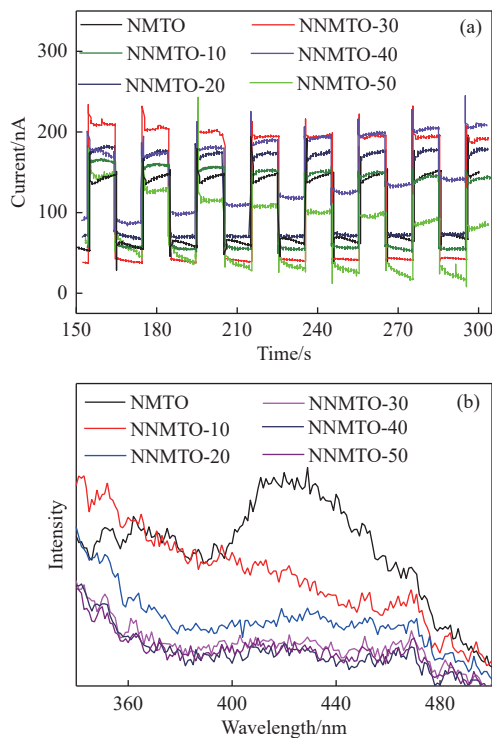


Fig. 8 (a) Transient photocurrent of NMTO and NNMTO- x , (b) Photoluminescence spectra of NMTO and NNMTO- x

The formation of solid solutions significantly suppresses the recombination kinetics of photogenerated electron-hole pairs, thereby enhancing charge carrier utilization efficiency and consequently improving the overall photocatalytic performance. Figure 8(b) reveals that NNMTO-30 exhibits the smallest semicircle diameter in the Nyquist plot, indicating the lowest charge transfer resistance among the samples. This reduced impedance can be attributed to the effective suppression of electron-hole recombination, which is in excellent agreement with the enhanced photocurrent response observed in the transient photocurrent measurements.

2.5 Electrochemical characteristics

Figure 9(a) demonstrates that NNMTO-30 exhibits the smallest arc radius in the electrochemical impedance spectroscopy (EIS) Nyquist plot, indicating superior charge transfer characteristics resulting from effective suppression of electron-hole recombination. The interfacial charge transfer properties can be further analyzed through Mott-Schottky measurements, where the relationship between the space charge layer capacitance (C) and the applied potential (V) is described by the following equation:

$$\frac{1}{C_{sc}} = \frac{2}{\epsilon\epsilon_0 N_D} \left(E - E_{FB} - \frac{Tk_B}{q} \right) \quad (2)$$

The physical significance and corresponding units of the parameters in the Mott-Schottky equation are summarized in Table 4.

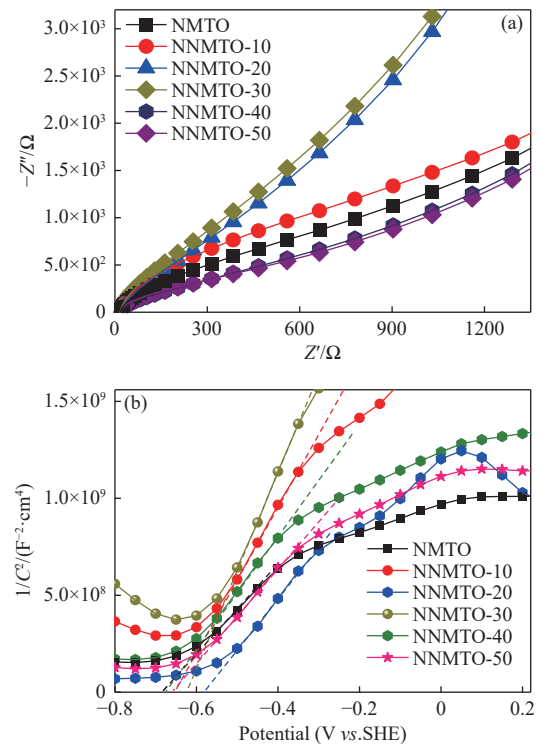


Fig. 9 (a) Electrochemical impedance of NMTO and NNMTO- x , (b) Mott-Schottky curves of NMTO and NNMTO- x

Table 4 The parameters in equation (2) and (3)

Parameter	Physical meaning
C_{SC}	capacitance of space charge region
ε	dielectric constant
ε_0	vacuum dielectric constant
q	elementary charge quantity
N_{D}	electron concentration
E	bias voltage applied
k_{B}	Boltzmann constant
T	absolute temperature
N_{C}	effective state density
m_{n}^*	effective mass of electrons
$\hbar$	reduced Planck constant

The thermal voltage term ($\frac{Tk_{\text{B}}}{q}$), which has a nominal value of approximately 25 mV at room temperature (298 K), can be neglected in the calculation. The correlation between the donor density (ND), conduction band edge potential (ECB), and Fermi level (EF) can be expressed by the following relationship:

$$E_{\text{CB}} = E_{\text{F}} + k_{\text{B}} \ln \frac{N_{\text{C}}}{N_{\text{D}}}, \quad N_{\text{C}} = 2 \left(\frac{m_{\text{n}}^* k_{\text{B}} T}{2\pi \hbar^2} \right)^{3/2} \quad (3)$$

As shown in Figure 9(b), the positive slope of the Mott-Schottky plot confirms the *n*-type semiconductor characteristics of NNMTO-*x*. Furthermore, a distinct positive shift in the flat band potential is observed for the NNTTO-*x* solid solutions compared to pristine NMTO, suggesting an upward movement of the Fermi level towards the conduction band, which corresponds to an increase in electron energy within the material system.

2.6 Photothermal catalytic performance for CO₂ reduction

The photocatalytic performance for CO₂ conversion was evaluated under UV-visible light irradiation without the addition of any sacrificial reagents. As demonstrated in Figure 10, the NNMTO-*x* series exhibits remarkable CO₂ photoreduction activity, suggesting efficient utilization of photogenerated charge carriers for the photocatalytic conversion process. As presented in Figure 10(a), (b), the photocatalytic CO₂ reduction process demonstrates significantly higher CO production compared to CH₄ generation during the initial hour of illumination across all catalyst samples.

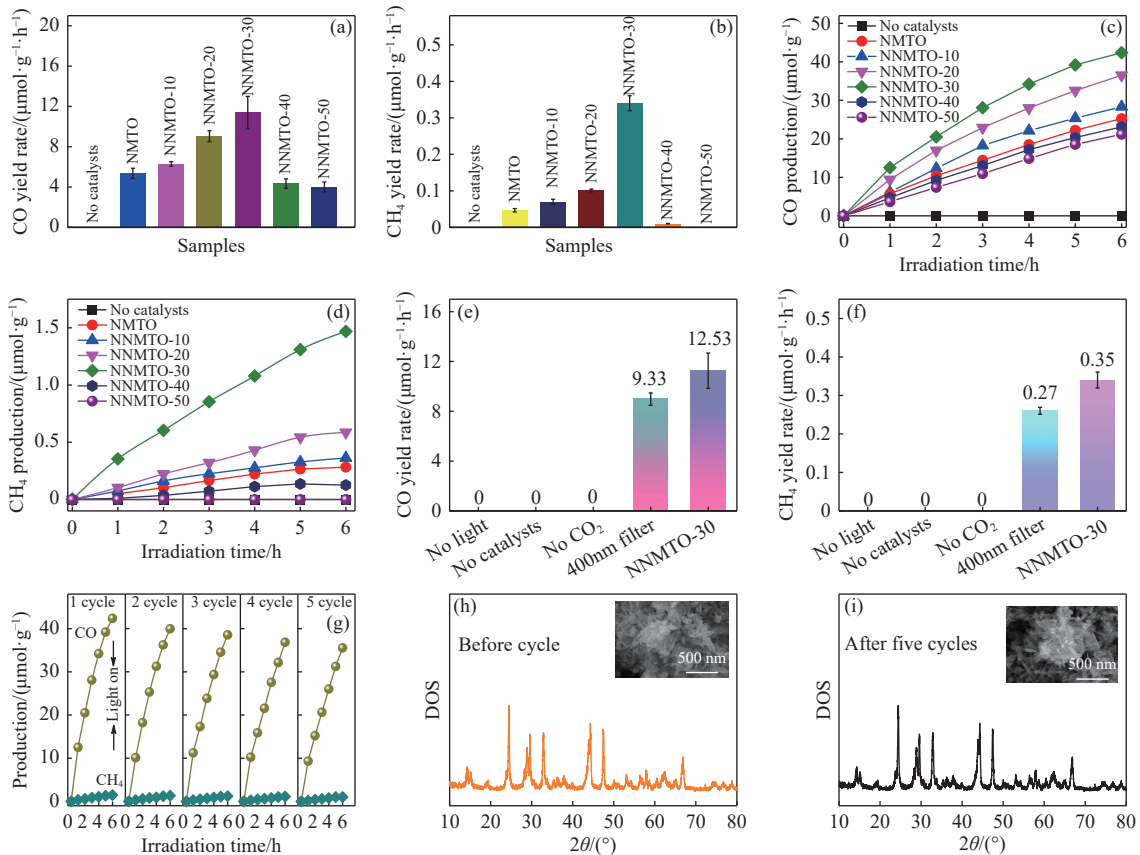


Fig. 10 Gas yield per unit time of (a) CO and (b) CH₄ over samples NMTO and NNMTO-*x*, Gas production at different times with (c) CO and (d) CH₄, Gas yield per unit time of (e) CO and (f) CH₄ under different experimental conditions, (g) Photocatalytic CO₂ reduction over NNMTO-30 for 5 times, XRD patterns of NNMTO-30 (h) before and (i) after 5 cycles. The insets show the corresponding SEM images

Notably, the formation of solid solutions substantially enhances the CO_2 reduction performance, which can be primarily attributed to the effective suppression of electron-hole recombination and the consequent improvement in charge carrier utilization efficiency. Among the synthesized catalysts, NNMT0-30 exhibits optimal photocatalytic performance, achieving remarkable CO_2 reduction rates of $10.26 \mu\text{mol}/(\text{g}\cdot\text{h})$ for CO and $0.33 \mu\text{mol}/(\text{g}\cdot\text{h})$ for CH_4 during the initial hour of illumination. As illustrated in Figure 10(c), (d), the extended photocatalytic evaluation over 6 h of continuous irradiation reveals that the NNMT0-*x* series maintains superior CO_2 conversion efficiency compared to both pristine NMTO and other reference catalysts, demonstrating its exceptional photocatalytic stability and performance. The photocatalytic performance exhibits a gradual degradation when the Ni molar ratio surpasses 40%, primarily due to the excessive coverage of active surface sites on NNMT0-*x*. This surface modification leads to diminished light absorption capacity and consequently reduces the generation of photogenerated charge carriers, ultimately impairing the overall photocatalytic efficiency. As evidenced by the control experiments presented in Figure 10(e), (f), no detectable CO or CH_4 production was observed in the absence of any essential photocatalytic components (light irradiation, catalyst, or CO_2), confirming that the reduction products are exclusively generated through photocatalytic processes. Furthermore, the significant decrease in CO and CH_4 yields when employing a 400 nm cutoff filter demonstrates the crucial role of ultraviolet light in driving the photocatalytic reactions, as the energy of visible light photons is insufficient to excite the catalyst effectively. Figure 10(g) presents the cyclic stability evaluation of NNMT0-30 through five consecutive CO_2 photocatalytic reduction tests, maintaining consistent production rates of $42.38 \mu\text{mol}/\text{g}$ for CO and $1.47 \mu\text{mol}/\text{g}$ during the 6 h irradiation period in the final cycle. As demonstrated in Figure 10(h)–(i), both the XRD patterns and morphological characteristics remain virtually unchanged after five reaction cycles, confirming the exceptional photostability and structural integrity of NNMT0-30 in photocatalytic CO_2 reduction applications. Comparative analysis with literature-reported catalysts revealed a modest performance gap in our system (Table 5),

primarily attributable to the differences in experimental conditions (e.g., the quality of the photocatalyst, sacrificial agent, et al.) and variations in co-catalyst loading, et al. In subsequent studies, we propose to construct a g- C_3N_4 or pyridine-nitrogen modified NMTO heterojunction system, where g- C_3N_4 or pyridine-nitrogen will serve as cocatalyst to enhance CO_2 reduction performance through improved charge separation and visible-light absorption.

2.7 Fundamentals and reaction mechanisms

Figure 11 illustrates the proposed mechanism for photocatalytic CO_2 reduction over NNTO-*x*. The fundamental principle governing photocatalytic reactions requires that: the semiconductor's conduction band minimum should exceed the reaction's reduction potential, while its valence band maximum must surpass the oxidation potential. These energetic alignments facilitate the efficient transfer of photogenerated electrons from the conduction band to CO_2 molecules while enabling hole migration from the valence band to electron donors. Consequently, the appropriate alignment between the semiconductor's band edge positions and the redox potentials of reactants represents a crucial prerequisite for effective photocatalytic reactions.

The oxygen atom of CO_2 supply electrons to the Lewis acid center, while the carbon atom receives electrons from the Lewis base center^[28]. The adsorption of CO_2 molecules on the catalyst surface initiates the formation of $\ast\text{CO}$ radical anions, which subsequently undergo a series of proton-coupled electron transfer processes to generate key reaction intermediates^[29]. The surface-bound intermediates may undergo two distinct pathways: (1) desorption from the catalyst surface to form CO as the final product, or (2) further reduction through sequential proton-electron transfer processes to generate C–H bond-containing intermediates, which ultimately lead to hydrocarbon formation^[30]. The CO_2 reduction mechanism proceeds through a series of well-defined steps: Initially, CO_2 undergoes single-electron reduction to form an activated $\text{CO}_2^{\cdot-}$ radical anion^[31]. This reactive intermediate is subsequently protonated to generate the carboxyl radical ($\text{COOH}^{\cdot}$).

Table 5 Comparative analysis of photocatalytic CO_2 conversion performance

Photocatalyst	Sacrificial agent	Light source	CO yield $/(\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1})$	CH_4 yield $/(\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1})$	Ref.
NNMT0-30 (15 mg)	no	300 W xenon lamp	10.26	0.33	this paper
$\text{Bi}_2\text{Sn}_2\text{O}_7/\text{NiAl-LDH}$	triethanolamine	300 W xenon lamp	37.91	1.18	[15]
heterojunction (50 mg)	no	300 W xenon lamp	0	0	
g- $\text{C}_3\text{N}_4@/\text{NaNbO}_3$ (20 mg)	no	300 W xenon lamp	<1.00	<1.00	[17]
8Ni/ TiO_2 (40 mg)	no (H_2/He)	300 W xenon lamp	1.40	279.10	[18]
Pyridine-nitrogen (20 mg)	no	300 W xenon lamp	261.00	0	[19]
BNB/BWO (30 mg)	no	300 W xenon lamp	34.38	—	[20]

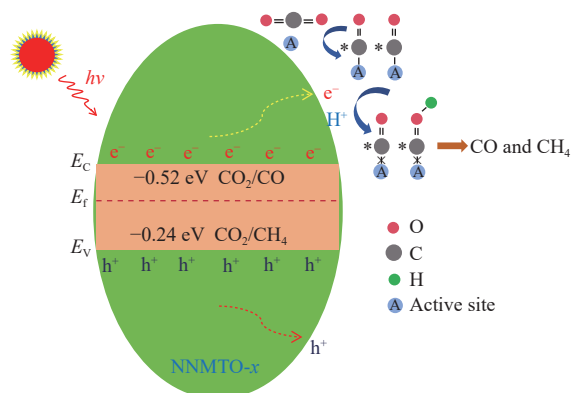


Fig. 11 Schematic diagram NNMT0-x photocatalytic reduction of CO_2 to prepare CO and CH_4

The carboxyl radical then undergoes further protonation to form formic acid (HCOOH), which dehydrates to produce the formyl radical ($\text{HCO}\cdot$). Through sequential two-electron reduction and protonation, $\text{HCO}\cdot$ is converted to formaldehyde (HCHO). Subsequent hydrogenation reactions transform formaldehyde into methanol (CH_3OH)^[32]. The final step involves methanol reduction followed by dehydration, yielding methane (CH_4) as the end product.

3 Conclusions

The solid solution of NNMT0-x were successfully synthesized by hydrothermal method. NNMT0-x maintain NMTO-like morphology at $\leq 40\%$ Ni, but undergoes significant transformation beyond this threshold, which attributable to the interstitial incorporation of Ni ions within the crystal lattice. NNMT0-x shows a red-shifted absorption edge compared with NMTO, enhancing visible-light response. The photocatalytic reduction activity of CO_2 is greatly improved after the formation of solid solution NNMT0-x ($x < 40$) due to the recombination of electron hole pairs were effectively suppressed. The optimum molar ratio of Ni is 30, which shows the best ability of CO_2 reduction and the yields of CO and CH_4 are 42.38 and 1.47 $\mu\text{mol/g}$ after 6 h irradiation, respectively. This study demonstrates the successful multifunctional application of the developed material, exhibiting simultaneous enhancements in photocatalytic activity. The next work will focus on developing g- C_3N_4 or pyridine-N modified NMTO heterostructures to enhance interfacial charge transfer.

Declaration of Competing Interest

The authors declare no conflict of interest.

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$\text{Na}_{0.9}\text{Mg}_{0.45}\text{Ti}_{3.55}\text{O}_8\text{-Na}_2\text{Ni}_2\text{Ti}_6\text{O}_{16}$ 固溶体的制备及光催化 CO_2 还原性能研究

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摘要: 本研究通过一步水热法制备了 $\text{Na}_{0.9}\text{Mg}_{0.45}\text{Ti}_{3.55}\text{O}_8\text{-Na}_2\text{Ni}_2\text{Ti}_6\text{O}_{16}$ (NNMTO) 固溶体, 其中, x 表示 $\text{Na}_2\text{Ni}_2\text{Ti}_6\text{O}_{16}$ (NNTO) 在固溶体 NNMTO- x 中的物质的量比, x 值分别为 10、20、30、40 和 50。通过综合运用 X 射线光电子能谱 (XPS) 和能量色散 X 射线光谱 (EDX) 技术进行表征分析, 证实了 NNMTO- x 系列固溶体的有效形成。实验结果表明, 当 x 值低于 40 时, NNMTO- x 固溶体能够保持原始 $\text{Na}_{0.9}\text{Mg}_{0.45}\text{Ti}_{3.55}\text{O}_8$ (NMTO) 的结构特征; 当 x 值超过 40 时, 晶体形态发生显著变化, 并伴随光催化性能的明显下降。当 x 值低于 40 时, NNMTO- x 固溶体的吸收边带向可见光区域显著偏移, 从而明显拓宽了其光吸收范围。NNMTO-30 表现出最优异的光催化还原活性, 在 6 h 光照条件下, 其 CO 和 CH_4 的生成速率分别达到 42.38 和 1.47 $\mu\text{mol/g}$ 。本研究为开发高效、稳定的二氧化碳还原光催化剂提供了重要的理论依据和实践指导, 对推动光催化 CO_2 还原技术的发展具有重要的科学意义和应用价值。

关键词: 光催化转化; 水热法; 光相应范围; 固溶体; 电荷分离

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