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In the past years, Ni(OH)₂ has been found an effective cocatalyst for photocatalytic hydrogen evolution. Herein, we report that it can also be used to enhance CO₂ photoreduction into chemical fuels. Vertically aligned Ni(OH)₂ nanosheets are deposited onto electrospinning TiO₂ nanofibers via simple wet-chemical precipitation to manufacture TiO₂/Ni(OH)₂ hybrid photocatalysts. The TiO2 nanofibers can direct the ordered growth of Ni(OH)2 nanosheets, which have thickness of 20 nm and uniformly cover the surface of TiO2 substrate. The TiO2/Ni(OH)2 hierarchical composite displays remarkably improved photocatalytic CO₂ reduction activity compared to pristine TiO₂ fibers. The bare TiO₂ can only produce methane and carbon monoxide (1.13 and 0.76 µmol h⁻¹ g⁻¹, respectively) upon CO₂ photoreduction. After loading 0.5 wt% Ni(OH)₂, the methane yield increases to 2.20 µmol h⁻¹·g⁻¹, meanwhile with the CO yield unchanged. Interestingly, alcohols (methanol and ethanol) also appear as products in addition to CH4 and CO over the TiO2/Ni(OH)2 hybrid, and the maximum yield is reached with 15 wt% Ni(OH)₂ loaded (0.58 and 0.37 μ mol·h⁻¹·g⁻¹ for methanol and ethanol, respectively). This can be ascribed to the enhanced charge separation efficiency and higher CO2 capture capacity owing to the presence of Ni(OH)2. These results demonstrate that Ni(OH)2 can not only improve the total CO2 conversion efficiency, but also can alter the product selectivity upon photocatalysis. This work opens a new pathway for achieving high-efficiency photocatalytic CO2 reduction with Ni(OH)2 as a cocatalyst.

Introduction

The harvest of solar energy and its subsequent conversion to hydrocarbon fuels is a promising strategy to remedy the energy shortage. Considering worsening greenhouse effect caused by the increasing CO₂ emission, photocatalytic CO₂ reduction using solar light is under extensive investigation to achieve renewable energy generation as well as to reduce environment pollution.¹⁻¹² For one thing, it is highly desirable to develop new photocatalyts for improving the CO₂ conversion efficiency. For another, due to the generation of many possible hydrocarbon compounds (methane, methanol, etc.), it is vital to control the photoreduction process so that products can be selectively obtained from CO₂ reduction.¹³⁻¹⁶ In particular, the photoconversion of CO₂ to methanol is quite preferable due to an increasing industrial demand for methanol such as the large utilization of MTO (methanol to olefin) process.^{17,18} Therefore, developing a high-efficiency photocatalyst for CO₂ reduction and ideally with high selectivity towards methanol is an

attractive issue.

In heterogeneous photocatalytic CO2 reduction, a hybrid material is often used as the photocatalyst to collect light, separate the photoinduced charge carriers and provide active sites.¹⁹ Usually, a semiconductor material is responsible for the first two functions while a cocatalyst serves as the active sites.^{13,20-22} Therefore, the rational assembling of a semiconductor and a corresponding cocatalyst is a potential way to reach high photocatalytic CO₂ reduction activity. The properly designed hybrid structures can harvest more solar light, accelerate molecules diffusion and increase the active sites.²³ As one type of efficient semiconductor photocatalyst, 1D TiO₂ nanofibers have been widely used as a substrate to construct heterostructured photocatalysts due to their extraordinary physiochemical properties.²⁴⁻³³ For instance, the electrospun TiO₂ nanofibers are composed of closely stacked nanoparticles with high porosity which is able to provide more active sites.³⁴ Further, the intimate alignment of TiO₂ nanocrystals in the nanofibers is favorable to the electron transport.³⁵

Recently, Ni(OH)₂ has been frequently used as an effective cocatalyst for enhancing photocatalytic H₂ evolution via water splitting due to more favorable electron transfer.³⁶⁻³⁹ However, to the best of our knowledge, it has not been utilized in photocatalytic CO2 reduction reaction. For CO2 reduction, effective adsorption and activation of CO2 is a key step for enhancing the efficiency.⁴⁰⁻⁴³ Since CO₂ is an acidic molecule, Ni(OH)₂ can be a promising adsorber for CO₂ molecules.

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Fig. 1 Schematic diagram for preparing hierarchical $TiO_2/Ni(OH)_2$ composite nanofibers.

Moreover, it was reported that transition metals can be efficient cocatalysts in enhancing the activity and product selectivity for CO_2 photoreduction, which also makes Ni(OH)₂ an alternative due to its easy transformation from Ni(OH)₂ to Ni cluster under illumination.^{39,44,45} Thus, constructing bicomponent hierarchical nanostructures that consists of TiO₂ and Ni(OH)₂ could be a promising method to improve the conversion efficiency and product selectivity for CO_2 photoreduction.

In this context, 1D $\text{TiO}_2/\text{Ni}(\text{OH})_2$ hybrid photocatalyst was prepared via a simple electrospinning and solution-precipitation method (Fig. 1). The Ni(OH)₂ nanosheets were vertically aligned and uniformly deposited onto the TiO₂ fibers. The TiO₂/Ni(OH)₂ heterostructure exhibited enhanced CO₂ photoreduction activity and noteworthy selectivity over alcohol production owing to the improved charge extraction and directed charge transfer in the presence of Ni(OH)₂ nanosheets. The photocatalytic mechanism and the significant role of Ni(OH)₂ in the CO₂ reduction were investigated and discussed.

Experimental

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TiO₂ nanofibers were prepared by an electrospinning method. Typically, a homogeneous precursor consisting of polyvinyl pyrrolidone (PVP), ethanol, glacial acetic acid and tetrabutyl titanate was prepared. Electrospinning was then conducted using the precursor solution, followed by calcination to remove the organic compositions, and the as-obtained TiO₂ nanofibers were denoted as T. TiO₂/Ni(OH)₂ composite samples with different weight ratios of Ni(OH)2 were synthesized by oil bath at 90 °C for 6 h with TiO2 nanofiber as the substrate and Ni(NO₃)₂·6H₂O as Ni source, the obtained samples were denoted as TN_x (x = 0.5, 1, 1.5, 2, 15 wt%), where x means the weight ratio of Ni(OH)₂ with respect to TiO₂. The Ni(OH)₂ nanosheets were also prepared via a similar oil bath process but without adding TiO₂ nanofibers and were denoted as N. The detailed fabrication procedure was given in Supporting Information. To facilitate investigation, TN15 was chosen as the typical sample due to its large weight ratio of Ni(OH)₂ and remarkable selective alcohol production.

Results and Discussion

Fig. 2a displays the X-ray diffraction (XRD) patterns of N, T and TN15. For sample N, three weak diffraction peaks located



Fig. 2 XRD patterns of samples T, N and TN15 (a). FESEM pictures (b, c), EDX mapping (d), TEM (e) and HRTEM (f) images of sample TN15.

at 24.6°, 34.9° and 59.7° can be ascribed to α-Ni(OH)₂ (JCPDS No. 38-0715). As for sample T and TN15, the diffraction patterns can be assigned to anatase TiO₂ (JCPDS, No. 21-1272) and rutile TiO₂ (JCPDS, No. 21-1276), exhibiting the coexistence of the two phases,^{35,46} with the rutile percentage of ca. 7%. The diffraction peaks of α -Ni(OH)₂ was unobservable in sample TN15 due to its weak crystallization. Besides, the peak positions of TiO₂ remained unchanged for sample TN15, suggesting the deposition of Ni(OH)₂ had no effect on the structure of the TiO₂ substrate. The morphology and microstructure of the hybrids were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM pictures (Fig. 2b, c) show the hierarchical nanostructure of TN15 that is composed of 1D TiO₂ nanofibers and 2D Ni(OH)₂ nanosheets with an overall diameter of 530 nm. The Ni(OH)₂ nanosheets had thicknesses around 20 nm and were vertically aligned onto the surface of the TiO₂ fibers. The specific orientation can promote the light-absorption due to multiple reflections and scattering of the incident light⁴⁷ and meanwhile maximize the exposed active sites of both TiO₂ and Ni(OH)₂, which is highly beneficial to reactants adsorption (CO₂ and H₂O) and the following photocatalysis reaction. 29,48,49 This architecture may also promote the possible charge transfer from TiO₂ to Ni(OH)₂ as well as from Ni(OH)₂ to CO₂.

The energy dispersive X-ray (EDX) elemental mapping (Fig. 2d) identified the spatial distributions of Ti, O and Ni,

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Fig. 3 (a) UV-vis spectra, (b) nitrogen adsorption-desorption isotherms of T, TN15 and N.



Fig. 4 XPS survey spectra (a) and high-resolution XPS spectra of Ti 2p (b), O 1s (c) and Ni 2p (d) of T and TN15 samples.

suggesting the homogeneous distributions of Ni(OH)₂ along with the TiO₂ fiber. The TEM images (Fig. 2e) further confirm the hierarchical morphology of the *in-situ* grown TiO₂/Ni(OH)₂ hybrid. High resolution TEM (HRTEM, Fig. 2f) image clearly demonstrates that the Ni(OH)₂ nanosheets were well attached to the TiO₂ substrate, which remained stable after 30 min bath sonication treatment. The low crystallinity of Ni(OH)₂ can also be observed, in accordance with the XRD results.

As a comparison, the morphology of individually prepared Ni(OH)₂ were also studied. The Ni(OH)₂ sample synthesized in the absence of the TiO₂ support was in the form of aggregated, nanosheets-assembled spheres with *ca*. 1 μ m in diameter (Fig. S1), completely distinct from the above observations. The vertical growth of Ni(OH)₂ can be explained by heterogeneous nucleation and subsequent oriented crystal growth. The TiO₂ fibers acted as backbones and provide sites for the preferential growth of Ni(OH)₂. At the beginning of the growth process, NH₃ and HCHO were generated from the decomposition of hexamethylenetetramine and then Ni²⁺ ions reacted with the OH⁻ that were released from NH₃ hydrolysis, forming amorphous Ni(OH)₂ nanocrystal nucleus, which anchored to the external surface of the TiO₂ fibers. Then the NH₃ molecules adsorbed on the surface of Ni(OH)₂ seeds by hydrogen bonds,

suppressing the outward growth of $Ni(OH)_2$ and facilitating inplane sheets growth⁵⁰. Thus, 2D $Ni(OH)_2$ nanosheets grown in a vertical mode, rather than covering on the surface of TiO_2 fibers.

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Further, light absorption of samples was measured by UV-vis absorption (Fig. 3a). The absorption edge of sample TN15 remains almost unchanged compared with pure TiO₂. Besides, a weak absorption shoulder at ~450 nm and an absorption band in the range of 600–800 nm were observed for sample TN15 and N, resulting from the d-d transition of Ni.³⁹

Fig. 3b presents the N₂ adsorption-desorption isotherms and corresponding pore-size distribution curves (inset). All samples exhibit isotherms of type IV, reflecting the existence of mesopores (2–50 nm). The hysteresis loops of T at relative pressures of 0.5~1 are of type H2, indicative of ink-bottle-like mesopores formed by TiO₂ nanocrystals. The hysteresis loops of TN15 and N samples vary from T: at relative pressures of 0.4~0.9, the shapes of hysteresis loops are of type H2, indicating that ink-bottle-like mesopores are formed by primary Ni(OH)₂ nanoparticles; at relative pressures of 0.9~1.0, The hysteresis loops are of type H3, implying that slit-like mesopores are formed by the stacking of Ni(OH)₂ nanosheets. The derived data including specific surface area, pore volume and pore size are summarized in Table S1.

XPS measurements were performed to identify the surface chemical status of elements of the photocatalysts. The survey spectrum (Fig. 4a) of sample T shows the presence of Ti 2p (459 eV) and O 1s (531 eV). For TN15, peaks attributed to Ni 2p (855 eV), O 1s (531 eV) and C 1s (285 eV) are found, while Ti peaks became much less noticeable, due to the shielding effect of the Ni(OH)2 nanosheets chemically grown on TiO2 surface. In fact, Ti element still exists with a lower intensity in TN15 according to the Ti 2p high-resolution spectrum of TN15 (Fig. 4b). Fig. 4c depicts the high resolution O 1s spectra of T and TN15. For pure TiO2, oxygen exists as lattice oxygen (Ti-O-Ti, 529.6 eV) and surface hydroxyl oxygen (Ti-OH, 531.5 eV).⁵¹ As Ni(OH)₂ nanosheets were deposited on TiO₂ surface, oxygen exists as lattice oxygen (M-O-M, M = Ti or Ni, 529.6 eV) and hydroxyl oxygen (Ni-OH, 531.6 eV). The intensity of the hydroxyl oxygen significantly increased.⁵² In the Ni 2p region of TN15 (Fig. 4d, top), the binding energies at 856.0 eV and 873.6 eV correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, indicating the generation of Ni(OH)₂ phase.⁵³ Moreover, the two shoulder peaks at about 861.8 eV and 880.2



Fig. 5 (a) FTIR spectra and (b) CO_2 adsorption isotherms of T, TN15 and N samples.

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Fig. 6 Yields of CH₄, CH₃OH, C₂H₅OH and CO for photocatalytic CO₂ reduction over sample T, N and TNx (x=0.5, 1, 1.5, 2 and 15) samples after 1 h irradiation (a). Time course of the products in the photocatalytic conversion of CO₂ over TN15 (b), T (c) and N (d).

eV can be ascribed to the satellite peaks of Ni $2p_{3/2}$ and Ni $2p_{1/2}$

Adsorption is the key step for the following photocatalytic CO₂ reduction processes. Fourier transform infrared spectroscopy (FTIR) spectra were measured to quickly assess the CO₂ uptake capabilities. As shown in Fig. 5a, for all the three samples, the broad peak at 3440 cm⁻¹ and the peak at 1623 cm⁻¹ are assigned to the O-H stretching vibration and H-O-H bending vibration of water, respectively. For sample T, the broad bands from 400 to 1000 cm⁻¹ correspond to the special vibration of TiO₂.⁵¹ Moreover, the peak of sample N centered at 647 cm⁻¹ is indicative of Ni-O-H bending vibration,⁵⁴ and the sharp peak at 1382 cm⁻¹ is attributed to the CO₂ stretching vibration owing to the strong CO2 adsorption.52 As a result, the TN15 shows an enhanced CO₂ capture capacity compared to pure TiO₂ indicated by the appearance of the CO₂ vibration peak. This is highly desirable for improving CO₂ photoreduction efficiency.

Quantitative CO₂ uptakes of the samples were evaluated by CO₂ adsorption isotherms. As shown in Fig. 5b, all samples exhibit an increase along with elevated CO₂ pressure. Notably, Ni(OH)₂ nanosheets demonstrate a much higher CO₂ adsorption capacity due to its alkalinity and consequently TN15 has a capacity almost twofold higher than that of TiO₂ nanofibers, agreeing well with the FTIR measurements. These results demonstrate that Ni(OH)₂ nanosheets can act as an effective CO₂ adsorbent and compensate the limited adsorption of TiO₂ nanofibers.

Finally, the photocatalytic CO_2 reduction activities of the asprepared hybrids (50 mg) were evaluated using self-designed setups with a 350 W Xenon lamp as simulated sunlight (Fig. S2 and S3). As displayed in Fig. 6a, CH₄ and CO were detected as products with a rate of 1.13 and 0.76 µmol h⁻¹ g⁻¹ when T was used as the photocatalyst. With 0.5 wt% Ni(OH)₂ deposited onto TiO₂ nanofibers (TN_{0.5}), the CH₄ yield increased to 2.20 μ mol·h⁻¹·g⁻¹, which nearly doubled the reduction rate of T. Besides, the CO yield almost remained unchanged (0.71 μ mol·h⁻¹·g⁻¹). Meanwhile, it is very interesting to note that CH₃OH and C₂H₅OH started to appear as coproducts with the deposition of Ni(OH)₂, with a generation rate of 0.11 and 0.15 μ mol·h⁻¹·g⁻¹, respectively. Further increase of the Ni(OH)₂ amount (up to 15 wt%) resulted in the slow decrease of CH₄ vield, but remained higher than bare TiO₂. On the other hand, it is noteworthy that the yield of CH₃OH and C₂H₅OH tended to improve with the increasing amount of Ni(OH)2 and the maximum yield was reached when 15 wt% Ni(OH)2 was loaded $(0.58 \ \mu mol \cdot h^{-1} \cdot g^{-1}$ and $0.37 \ \mu mol \cdot h^{-1} \cdot g^{-1}$ for CH₃OH and C_2H_5OH , respectively). As a control, the photocatalytic activity of pure Ni(OH)₂ was also evaluated. CH₃OH and C₂H₅OH were detected as major products (0.15 and 0.44 μ mol·h⁻¹·g⁻¹, respectively), while the total CO₂ conversion efficiency was much lower than that of the TiO₂/Ni(OH)₂ hybrids (Fig. 6a). Table 1 shows the photocatalytic CO₂ reduction performance of various TiO₂-based photocatalysts. It can be found that the $TiO_2/Ni(OH)_2$ hybrid exhibits higher or comparable photocatalytic CO2 conversion activities compared with most of the recently reported TiO₂-based photocatalyst. There are few showing higher CO₂ reduction efficiency, materials nevertheless, these photocatalysts were modified with noble metals such as Pt and Pd, which increased the cost and limited the large-scale usage. Therefore, the easily-prepared, non-noble metal cocatalyst of Ni(OH)2 can still be of great interest for achieving high-efficiency CO₂ reduction.

Moreover, the time courses of the photocatalytic chemical fuel generation over sample T, N and TN15 were investigated (Fig. 6b-d). The amounts of the evolved photocatalytic products increased with the illumination time, indicating the continuous photo-reduction of CO₂. These results clearly demonstrate that the overall photocatalytic CO₂ conversion efficiency (to CH₄, CH₃OH, C₂H₅OH and CO) can be greatly enhanced by hybridizing TiO₂ with Ni(OH)₂. Moreover, the selectivity over the products can be facilely tuned by adjusting the Ni(OH)₂ amount. The related mechanism involving the vital role of the vertically aligned Ni(OH)2 arrays is investigated and illustrated below. Further, the wavelength dependent CO₂ reduction efficiency over sample TN15 was measured by using a wavelength filter of 400 and 450 nm (Fig. S4), respectively. We can see that reasonable amount of photo-reduction products were still obtained, although the light with wavelength below 400 nm (the light that TiO_2 is able to absorb) was filtered. These result suggest that TiO2 played a major role for photocatalytic CO2 reduction under full-spectrum illumination with Ni(OH)₂ as a cocatalyst, whereas under long-wavelength illumination Ni(OH)2 alone can also be a photocatalyst for CO2 reduction.

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Photocatalyst ^a	Photocatalyst ^a Reductant ^b Light ^c		Light intensity (mW cm ⁻²)	Product	Yield (µmol h ⁻¹ g ⁻¹)	Year	Ref.
0.5% Ni(OH) ₂ -TiO ₂	6 Ni(OH) ₂ -TiO ₂ H ₂ O vapor 350 W Xe lamp		40	CH_4	2.20	2018	This report
				CO	0.71		
				CH ₃ OH	0.11		
				C_2H_5OH	0.15		
TiO ₂ nanosheet	H ₂ O vapor	350 W Xe lamp	/ (not given)	CH_4	1.35	2014	55
hydrogenated TiO ₂	H ₂ O vapor	550 W Xe lamp	100	CH_4	0.156	2014	56
				CO	0.241		
mesoporous Co/TiO ₂	H ₂ O vapor	300 W Xe lamp	/	CH_4	0.090	2015	57
				CO	1.94		
Pt/TiO ₂	H ₂ O vapor	300 W Xe lamp	100	CH_4	4.8	2015	58
				СО	0.1		
Carbon/TiO ₂	H ₂ O vapor	350 W Xe lamp	/	CH_4	4.22	2017	59
hollow spheres				CH ₃ OH	9.11		
Pd-TiO ₂	H ₂ O vapor	300 W Xe lamp	2.7	CH_4	4.10	2017	60
				СО	15.50		
1.5% Ag-TiO ₂	H ₂ O vapor	300 W Xe Lamp	/	CH_4	1.4	2016	61
1.2 nm CuPt-TiO ₂	H ₂ O vapor	150 W Xe lamp	/	CH_4	11.35	2016	62
Cu ₂ O/TiO ₂	H ₂ O vapor	1 kW Hg (Xe) lamp	/	СО	2.11	2017	63
Pt-Cu ₂ O/TiO ₂	H ₂ O vapor	300 W Xe lamp	20.5	CH_4	1.42	2017	64
				СО	0.05		
$TiO_2/g-C_3N_4$	H ₂ O vapor	300 W Xe lamp	/	CH_4	2.50	2017	65
				СО	9.30		

Table 1. Co	mparisons of	photocatalytic	O_2 reduction	performance of	of various	TiO ₂ -based	photocatalyst	s reported in	2014~2018.
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Notes: (a) TiO_2 based photocatalysts; (b) solid-gas reaction systems, with H_2O vapor as the reductant; (c) Xe lamps were used as the light source.

Oxidation reactions by holes were also investigated. Fig. S5 shows the gas chromatogram results after 4 h of irradiation for photocatalytic CO₂ reduction over sample T and TN15. It can be observed that O₂ was detected in the photocatalytic process for sample T (Fig. S5a), which was generated by water oxidation (2 H₂O \rightarrow O₂ + 4H⁺ + 4e⁻). However, no O₂ was observed for sample TN15 (Fig. S5b), and we consider that this is because the holes were captured and quenched by the hydroxyl groups from TiO₂.^{66,67}

To determine the actual carbon source of the photocatalytic products, isotope tracer experiment involving photocatalytic reduction of ${}^{13}CO_2$ (${}^{12}CO_2$ was also tested as a reference) was performed and examined by GC-MS. As shown in Fig. S6, peaks assigned to ${}^{13}CH_4$ (m/z = 17), ${}^{13}CH_3OH$ (m/z = 33) and ${}^{13}C_2H_5OH$ (m/z = 47) were clearly observed when using ${}^{13}CO_2$ as the carbon source. These results verified that the detected photo-reduction products over the as-prepared materials originated from the CO₂ source gas rather than any residual/contaminant carbon species. Moreover, it is worth mentioning that the TiO₂/Ni(OH)₂ hybrid remained stable

against the photocatalytic CO_2 reduction, indicated by no changing of the crystal structure and morphology before and after the photoreaction (Fig. S7).

In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out to monitor the CO₂ adsorption and conversion over the photocatalysts. As shown in Fig. 7a, without illumination (red line), only adsorbed H₂O, CO₂ and carbonate species were detected on the TN15 surface. The peaks at 1173 and 1272 cm^{-1} are ascribed to adsorbed H₂O and CO₂, respectively.⁶⁸ The peaks at 1394 and 1715 cm⁻¹ are assigned to symmetric stretching vibration of monodentate carbonate and bicarbonate species.^{69,70} Upon illumination for 60 min (blue line), additional peaks associated to the reaction intermediates were observed. The peak at 1053 cm⁻¹ is attributed to stretching vibration of methoxy.⁷¹ The peaks at 1107, 1509, 1745 cm⁻¹ belong to the vibration of formaldehyde.^{71,72} The peak at around 1458 cm⁻¹ was assigned to bending vibration of dioxymethylene.⁷¹ These results suggest that photocatalytic CO₂ conversion on the surface of TN15 undergoes a multi-electron reduction process (probably

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 CO_2 →HCOOH→HCHO→CH₃OH)^{8,59,73-76} involving reaction intermediates such as methoxy and formaldehyde. On the contrary, no vibrations bands at 1458 cm⁻¹ and below 1100 cm⁻¹ were observed for TiO₂ under illumination (Fig. 7b, blue line), suggesting the absence of the dioxymethylene and methoxy intermediate, corresponding to the generation of CH₃OH and C₂H₅OH over the TN15. Although several peaks associated with formaldehyde were also seen on the TiO₂ surface (1506 and 1745 cm⁻¹), the final product contained only CH₄ and CO. These results demonstrate the conversion paths of CO₂ and the intermediates (e.g. formaldehyde) upon the photocatalyst surfaces can be changed by the addition of Ni(OH)₂, agreeing with the aforementioned photocatalytic activity measurements.

The transient photocurrent response (I-t) of the electrodes deposited with sample T and TN15 was measured and recorded (Fig. S8) under the irradiation of 365 nm LED light to evaluate the separation and transfer efficiency of photogenerated charge carriers. The on-off cycles of photocurrent response were reproducible over the chopped light illumination. The photocurrent density of TN15 was over 7 times higher than that of pure TiO₂, suggesting the promoted charge migration



Fig. 7 In-situ DRIFTS of sample (a) TN15 and (b) T. Black lines: light off, without introducing CO_2 gas. Red lines: light off, flowing CO_2 gas for 60 min. Blue lines: light on, flowing CO_2 gas for 60 min.



Fig. 8 Schematic illustration for the separation and transfer of photoinduced charge carriers over the $TiO_2/Ni(OH)_2$ nanofiber system.

efficiency after loading of Ni(OH)2 nanosheets.

Based on the above results, we propose a mechanism to better understand the CO₂ photocatalytic process. On one hand, TiO₂ nanofibers alone (without Ni(OH)₂) can harvest light and reduce CO₂ into CH₄ and CO with a rather low efficiency. On the other, after the deposition of the Ni(OH)2 nanosheets, the photogenerated electrons in TiO₂ tend to migrate to Ni(OH)₂, resulting in partial reduction of Ni2+ ions into Ni0 atoms, forming Ni(OH)₂/Ni clusters (step 1), Fig. 8).³⁹ The Ni(OH)₂/Ni clusters can be a cocatalyst and serve as electron sinks and accelerate the separation of photogenerated electrons from TiO₂ to the Ni(OH)₂/Ni cluster and to the CO₂ molecules. The modified electron transfer is highly beneficial to the photocatalytic CO₂ conversion, leading to much improved generation rate of the reduction products. Further increase of the Ni(OH)₂ loading amount suppressed the formation of CH₄ while CH_3OH and C_2H_5OH was preferably generated (step (2)). Herein, the formation of Ni⁰ clusters can be confirmed by XPS measurement of the TN15 sample before and after photocatalysis reaction. As shown in Fig. 4d (bottom), after photocatalytic reaction, the Ni 2p_{3/2} binding energy of TN15 shifted to a lower binding energy of 855.3 eV, which can be attributed to NiO. This can be explained by the fact that the Ni clusters are unstable in air and they can be easily oxidized. Therefore, it is reasonable that NiO (instead of Ni) was detected after photocatalytic reaction.

Conclusions

In summary, a hierarchical TiO₂/Ni(OH)₂ hybrid photocatalyst is prepared by depositing vertically aligned Ni(OH)2 nanosheets onto the electrospun TiO₂ fibers with a simple solution precipitation method. We show that Ni(OH)₂ can not only enhance photocatalytic H₂ evolution as previously reported, but also can remarkably improve the photocatalytic CO₂ reduction as a cocatalyst on TiO₂ nanofibers. It is found that the hybrids possess stronger CO₂ capture capacity compared with pure TiO₂ nanofibers. Further, a part of Ni(OH)₂ can be reduced by the photo-induced electrons from TiO₂ and then Ni(OH)₂/Ni clusters are formed, which can act as vital active sites and decrease the recombination rate of photogenerated charge carriers during photocatalytic process. Hence, the functions of $Ni(OH)_2$ are proposed to be increasing the density of CO_2 on the photocatalyst surface and favoring the charge transfer from TiO₂ nanofibers to Ni(OH)₂ nanosheets and finally to CO₂ molecules. Moreover, an enhanced alcohols generation (CH₃OH and C₂H₅OH) upon the hybrid photocatalyst can be achieved, resulting from the Ni(OH)2 induced changing of the CO2 conversion paths, which can be detected using the in-situ DRFITS. We believe this work provides a potential approach to enhance both the efficiency and selectivity of photocatalytic CO₂ reduction by developing more transition metal based compounds as cocatalysts.

Acknowledgements

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Graphical abstract



Hierarchical porous $TiO_2/Ni(OH)_2$ composite fiber photocatalyst with dramatically improved photocatalytic CO_2 reduction activity and prominent alcohol production selectivity.