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https://doi.org/10.1016/j.apcatb.2018.02.042
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PII: S0926-3373(18)30163-2
DOI: https://doi.org/10.1016/j.apcatb.2018.02.042
Reference: APCATB 16437

To appear in: Applied Catalysis B: Environmental

Received date: 12-12-2017
Revised date: 2-2-2018
Accepted date: 19-2-2018

Please cite this article as: Xu F, Zhang J, Zhu B, Yu J, Xu J, CuInS$_2$ sensitized TiO$_2$ hybrid nanofibers for improved photocatalytic CO$_2$ reduction, Applied Catalysis B, Environmental (2010), https://doi.org/10.1016/j.apcatb.2018.02.042

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**CuInS$_2$ sensitized TiO$_2$ hybrid nanofibers for improved photocatalytic CO$_2$ reduction**

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A novel TiO\textsubscript{2}/CuInS\textsubscript{2} hybrid is synthesized by an in-situ hydrothermal approach, with the TiO\textsubscript{2} nanofibers coated by few-layer CuInS\textsubscript{2} nanoplates. A direct Z-scheme heterojunction is generated between TiO\textsubscript{2} and CuInS\textsubscript{2} which results in superior photocatalytic activity for CO\textsubscript{2} reduction under irradiation.

**Highlights**

1. In-situ deposition of CuInS\textsubscript{2} nanoplates onto TiO\textsubscript{2} nanofibers.
2. Direct Z-scheme TiO\textsubscript{2}/CuInS\textsubscript{2} heterostructure was generated.
3. The prepared photocatalyst with enhanced photocatalytic CO\textsubscript{2} reduction activity.
4. The photocatalytic mechanism investigated by XPS and DFT calculation.

**Abstract**

Photocatalytic CO\textsubscript{2} reduction into solar fuels over photocatalysts has theoretically and
practically become a hot research topic. Herein, we fabricated a novel hybrid TiO$_2$ nanofiber coated by CuInS$_2$ nanoplates through a hydrothermal method. The materials were characterized by X-ray diffraction, electron microscopes, UV-vis absorption spectra, nitrogen sorption, X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy. The resulting TiO$_2$/CuInS$_2$ hybrid nanofibers exhibit superior photocatalytic activity for CO$_2$ reduction under irradiation, due to the generation of direct Z-scheme heterojunction between TiO$_2$ and CuInS$_2$. This work may provide an alternate methodology to design and fabricate multicomponent TiO$_2$-based photocatalyst for high-efficiency CO$_2$ photoreduction.

**Keywords**: TiO$_2$ nanofiber, CuInS$_2$ nanoplates, direct Z-scheme heterojunction, photocatalytic CO$_2$ reduction

1. Introduction

Photocatalytic CO$_2$ reduction over well-designed catalysts has been considered an emerging way for recycling CO$_2$ back to renewable fuels, e.g., CH$_4$ and CH$_3$OH with the aid of solar energy, which is regarded as one of the most promising strategies to overcome the energy and environmental crises [1-7]. For example, metal-organic frameworks (MOF), a type of micro-mesoporous hybrid materials, are recently emerging as a new category of materials for CO$_2$ photo-reduction due to their special structural characteristics and remarkable adsorption capability for CO$_2$ [8-10]. Besides, TiO$_2$ as a typical semiconductor photocatalyst, has been frequently studied for CO$_2$ reduction due to its high stability, nontoxicity and abundant
availability [11-14]. However, TiO$_2$ can only absorb UV-light because of its large band gap [15, 16]. Moreover, it shows a fast recombination of the photogenerated electron-hole pairs, which leads to low photocatalytic performance [17-19]. Several approaches have been explored to improve the photocatalytic activities of TiO$_2$, including noble metal deposition (e.g. Pt, Au, Pd, Ag) [20-24], nonmetal doping (e.g. N, C) [25-28], surface sensitization [29, 30], coupling with narrow-bandgap semiconductors (e.g. CdS, g-C$_3$N$_4$, Cu$_2$O) [31-36] and so on. Among these, hybridizing TiO$_2$ with other semiconductors is believed to be an effective method to broaden the light absorption and meanwhile improve the separation and extraction of the photogenerated carriers.

Differing from TiO$_2$, CuInS$_2$ has a narrow direct band gap of 1.50 eV, close to the optimal band gap (1.45 eV) for solar light harvesting [37-39], and meanwhile shows an ultrahigh absorption coefficient ($1 \times 10^5$ cm$^{-1}$). Besides, CuInS$_2$ shows a pronounced defect tolerance and exceptional radiation hardness as compared to other semiconductors [40-42]. CuInS$_2$ does not contain any toxic heavy metals and has been investigated for photovoltaics [43], bioimaging [44], and photocatalytic water splitting [45]. For instance, Kudo and coworkers have prepared a ZnS-CuInS$_2$-AgInS$_2$ ternary solid solution which exhibited 7.4% quantum yield of hydrogen production under 520 nm irradiation [45]. In addition, CuInS$_2$ has been combined with other semiconductors to make composite photocatalysts, such as MoS$_2$/CuInS$_2$ [46], g-C$_3$N$_4$/CuInS$_2$ [47], Bi$_2$WO$_6$/CuInS$_2$ [48] and ZnO/CuInS$_2$ [49, 50], for enhanced H$_2$ generation from water splitting or organic pollutants degradation. In these cases, CuInS$_2$ was presented as nanosheets or quantum dots. It is also reported that CuInS$_2$ thin films can function as cathodes for photoelectrochemical reduction of CO$_2$ [51]. However,
CuInS$_2$ involved photocatalysts for direct CO$_2$ reduction have been rarely demonstrated and more efforts are required to improve the solar driven CO$_2$-to-fuel conversion efficiency.

Herein, we report the facile synthesis of TiO$_2$ nanofibers sensitized with CuInS$_2$ nanoplates through an *in-situ* hydrothermal process. The obtained TiO$_2$/CuInS$_2$ hybrid nanofibers show increased optical absorption and enhanced charge separation, and thus improved photocatalytic CO$_2$ reduction was achieved. Based on the experimental data and DFT calculation, we propose a direct Z-scheme heterojunction formed between the TiO$_2$ nanofiber and the CuInS$_2$ nanoplates.

2. Experimental details

2.1. Materials and synthesis of electrospun TiO$_2$ nanofibers

Poly(vinyl pyrrolidone) with an average molecular weight of 1300000 was purchased from Tianjin Bodi Chemical Co., Ltd. The other chemicals were of analytical grade and purchased from Shanghai Chemical Company. Electrospun TiO$_2$ nanofibers were prepared according to our previous work [11]. Typically, 2.0 g of Tetrabutyl titanate (TBT) and 0.75 g of PVP were dissolved in the solvent containing 10.0 g of ethanol and 2.0 g of acetic acid. The mixture became a transparent light yellow solution after magnetically stirring for 5 h at room temperature. The solution was then poured into a 10 mL syringe in the electrospinning setup. The steel needle had a distance of 10 cm and a voltage of 15 kV with respect to the static collector. And the solution feeding rate is maintained at 2.5 mL·h$^{-1}$. The collected electrospun samples (TiO$_2$ precursors) were calcinated at 550 °C in air for 2 h with a ramping rate of 2 °C·min$^{-1}$.

2.2. Preparation of TiO$_2$/CuInS$_2$ heterostructures
TiO$_2$ nanofibers were first chemically etched to increase surface roughness. Briefly, TiO$_2$ nanofiber was immersed in a concentrated NaOH solution (10 M) at 160 °C for 15 min, and washed with dilute HCl solution and water for several times. As-etched TiO$_2$ fibers were then annealed at 450 °C in air for 1 h with a ramping rate of 2 °C min$^{-1}$. The rough TiO$_2$ nanofibers are labeled as T.

TiO$_2$/CuInS$_2$ heterostructures were synthesized through a hydrothermal method. Typically, a transparent solution was formed by mixing 0.0125 mmol Cu(NO$_3$)$_2$ (the mass ratio of CuInS$_2$ was 1 wt. %), 0.0125 mmol In(NO$_3$)$_2$ and 0.025 mmol L-cysteine hydrochloride with 80 mL deionized water. Then 0.1 g TiO$_2$ nanofibers were added to the above solution under vigorous stirring. The obtained suspension was transferred to a Teflon cup of 100 mL inner volume in a stainless steel-lined autoclave. The autoclave was maintained at 160 °C for 12 h and then was allowed to cool to room temperature. The solid product was washed with deionized water and ethanol several times and dried at 80 °C for 4 h to obtain TiO$_2$/CuInS$_2$ heterostructures. For comparison, TiO$_2$/CuInS$_2$ samples with various mass ratios of CuInS$_2$ were synthesized by varying the amount of Cu(NO$_3$)$_2$ from 0.03, 0.06 to 0.12 mmol while fixing the molar ratio of Cu(NO$_3$)$_2$ : In(NO$_3$)$_2$ : L-cysteine hydrochloride at 1:1:2. The nominal mass ratios of CuInS$_2$ were 2.5 wt.%, 5 wt.% and 10 wt.%, respectively. These TiO$_2$/CuInS$_2$ samples were labeled as TC$_x$ ($x = 1, 2.5, 5, 10$). The actual compositions of the samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) by using a Prodigy 7 spectrometer (see Table 1).

2.3. Characterization

The X-ray diffraction (XRD) patterns were recorded on a D/Max-RB X-ray diffractometer
(Rigaku, Japan) with Cu Kα radiation (λ = 0.15418 nm) with a scan rate (2θ) of 0.05 °·s⁻¹. The morphology was observed on a JSM 7500F field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) images and energy dispersive X-ray (EDX) spectrometer were recorded on a Titan G2 60-300 electron microscope. Nitrogen adsorption-desorption data were recorded on a Micromeritics ASAP 3020 nitrogen adsorption apparatus (USA) at 77 K. Prior to measurements, the samples were degassed at 150 °C for 12 h. The specific surface areas (S_BET) calculated by the Brunauer-Emmett-Teller (BET) method using adsorption data in a relative pressure range from 0.05 to 0.3. The total pore volumes were estimated from nitrogen adsorption volume adsorbed at the relative pressure of 0.97. The pore size distributions were calculated from desorption data of isotherms using the Barret-Joyner-Halender (BJH) method. UV-visible diffuse reflectance spectra of samples were recorded on a Shimadzu UV-2600 UV-visible spectrophotometer (Japan) using BaSO₄ as a reference. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo ESCALAB 250Xi instrument with Al Kα X-ray radiation. The binding energy was calibrated with reference to C 1s signal (284.8 eV).

2.4. Photoelectrochemical measurements

The photoelectrochemical measurements were conducted in 0.5 M Na₂SO₄ aqueous solution on a CHI660C electrochemical workstation (Shanghai CH Instruments), with a 3W LED lamp (365 nm) as the light source. A Pt wire and saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. For preparing the working electrode, 80 mg of the photocatalysts (T, TC1, TC2.5, TC5 and TC10) were ground with 1.0 mL ethanol to form a slurry. The slurry was blade-coated onto a 2 cm × 1.5 cm F-doped SnO₂-coated (FTO) glass.
with an active area of 1 cm², followed by drying at 100 °C for 1 h. All the electrodes used had a similar thickness. The EIS measurements was carried out by applying the bias of the open circuit potential and recorded over a frequency range of 0.01-10⁵ Hz with an ac amplitude of 10 mV.

2.5. Analysis of hydroxyl radicals (·OH)

A terephthalic acid (TA) fluorescence probe method was used to quantitatively analyze the production of ·OH. Typically, 0.1 g of photocatalyst was dispersed in a 20 mL solution containing 0.5 mM TA and 5 mM NaOH. The suspension was placed in a dish with a diameter of 9 cm. A 350 W Xe arc lamp (Zhenjian Silver Jewelry Chemical, China) was positioned 25 cm above the dish. The light intensity on the solution was measured to be 2.0 mW cm⁻² with a UV radiometer with the peak intensity of 365 nm (model: UV-A, Photoelectric Instrument Factory of Beijing Normal University). TA easily reacts with ·OH and produces a highly fluorescent 2-hydroxyterephthalic acid (TAOH). The amount of ·OH was determined by measured the concentration of TAOH (fluorescence peak at 425 nm with an excitation wavelength of 315 nm) using a Hitachi F-7000 fluorescence spectrophotometer after centrifugation.

2.6. Photocatalytic reduction of CO₂

The photocatalytic reduction of CO₂ was carried out in a 200 mL home-made Pyrex reactor with two openings. A 350 W simulated solar Xe arc lamp was used as the light source and positioned 10 cm above the reactor. A suspension was firstly placed in the reactor by ultrasonically mixing 50 mg of the catalyst and 10 mL of deionized water. After drying at 80 °C for 2 h, the catalyst formed a uniform film coating on the bottom of the reactor. Prior to
irradiation, the reactor was purged with nitrogen for 30 min to ensure an anaerobic circumstance. CO₂ together with H₂O vapor was in-situ produced through the reaction of NaHCO₃ (0.12 g, introduced into the reactor before seal) and the injected H₂SO₄ solution (0.25 mL, 2 M). The product (1 mL) was automatically collected at given intervals (1 h) and analyzed using a Shimadzu GC-2014C gas chromatograph (Japan) equipped with an FID detector and a methanizer. Blank experiments in the absence of CO₂ or light irradiation confirmed the CO₂ and light were the key factors for the CO₂ reduction. Control experiment was also performed to determine whether the carbon resource came from CO₂.

¹³CO₂ isotope tracer experiment was conducted to verify the carbon source of the products by using ¹³C isotope-labelled sodium bicarbonate (NaH¹³CO₃, Cambridge Isotope Laboratories Inc., USA) and H₂SO₄ aqueous solution for the photocatalytic examinations. After 1 h of photocatalytic reaction, 500 μL of mixed gas was taken out from the reactor and examined by a gas chromatography-mass spectrometer (GC-MS) (6980N network GC system-5975 inert mass selective detector, Agilent technologies, USA) to analyze the products.

2.7. Computational details

The density functional theory (DFT) calculations were performed by using the Cambridge Serial Total Energy Package (CASTEP). Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was utilized to describe the exchange-correlation interaction. The energy cutoff and Monkhorst-Pack k-point mesh were set to as 440 eV and 7 × 7 × 1, respectively. During the geometry optimization, the convergence tolerance was set as 1.0 × 10⁻⁵ eV/atom for energy and 0.03 eV/Å for maximum force. For the construction of
surface models, a vacuum of 20 Å was used to eliminate interactions between periodic images. The geometric structures of TiO$_2$ (101) surface and CuInS$_2$ (004) surface are illustrated in Figure 1. The work function is defined as $\Phi = E_V - E_F$, where $E_V$ and $E_F$ are the electrostatic potentials of the vacuum and Fermi levels, respectively.

![Figure 1](image)

**Figure 1.** Geometric structure of (a) TiO$_2$ (101) surface and (b) CuInS$_2$ (004) surface. The grey, red, orange, brown and yellow spheres stand for Ti, O, Cu, In and S atoms, respectively.

3. Results and discussion

3.1 Crystalline phase and morphology of materials

Figure 2 shows the XRD patterns of the resultant samples with various loadings of CuInS$_2$. For the original TiO$_2$ nanofibers, the diffraction peaks can be assigned to anatase TiO$_2$ (JCPDS file No. 21-1272) or rutile TiO$_2$ (JCPDS file No. 21-1276). No other diffraction peaks were observed for TC1 and TC2.5 because of the quite low loading of CuInS$_2$. In contrast, TC5 and TC10 which had higher loadings of CuInS$_2$ show a new diffraction peak at around 32.1°, which correspond to the (004) plane of tetragonal CuInS$_2$ (JCPDS file No.85-1575). The results confirm the formation of CuInS$_2$ by hydrothermal deposition, which
can be further verified by TEM observation below.

![Figure 2. XRD patterns of the samples: (a) T, (b) TC1, (c) TC2.5, (d) TC5 and (e) TC10.](image)

The morphologies of the resultant samples were investigated by SEM and TEM. The SEM image of the pristine TiO$_2$ before and after NaOH etching was shown in Figure 3a and b, illustrating nanofibers with diameters around 150 nm and lengths of tens of micrometers. After the hydrothermal growth, CuInS$_2$ nanoplates were deposited onto the TiO$_2$ nanofibers, as shown in Figure 3c and d. The very thin CuInS$_2$ nanoplates had high surface area and more active sites can be exposed, which will be highly favourable for the photocatalytic reactions. The microstructure of the TiO$_2$/CuInS$_2$ hybrid can be further revealed by TEM image (Figure 3e), showing a TiO$_2$ nanofiber coated by CuInS$_2$ nanoplates with thickness of ca. 10 nm.
Figure 3. SEM images of (a-b) T and (c-d) TC2.5. TEM image (e) and HRTEM image (f) of TC2.5. EDX element mappings of (g) Ti, O, Cu, In and S elements for TC2.5.

The crystalline phase of the hybrid material was also examined by high-resolution TEM (HRTEM). As shown in Figure 3f, the lattice fringes with a spacing of 0.352 and 0.324 nm corresponded to the (101) plane of anatase TiO$_2$ and (110) plane of rutile TiO$_2$, respectively. In addition, lattice fringes with a spacing of 0.279 nm were also observed, which was attributed to the (004) plane of CuInS$_2$. The HRTEM analysis further confirmed the
generation of CuInS$_2$ over the TiO$_2$ nanofibers, agreeing with the XRD results as above. The EDX mapping (Figure 3g) of the nanofiber indicates the co-existence of Ti, O, Cu, In and S elements, resulting from the heterostructured TiO$_2$/CuInS$_2$ composite.

3.2 UV-vis absorption and nitrogen sorption

UV-vis diffuse reflectance spectra were measured to study the optical absorption properties of the samples, as shown in Figure 4. As expected, the pristine TiO$_2$ sample can only absorb UV light (wavelength below 400 nm). After deposition of CuInS$_2$, the hybrid nanofibers show enhanced visible-light absorption with the increased loading of CuInS$_2$, resulting from the low bandgap and strong absorption capability of the CuInS$_2$ nanoplates. The significantly improved optical absorption of the hybrid can potentially result in higher photocatalytic activity for CO$_2$ reduction, as described below.

![Diffuse reflectance spectra of the samples.](image)

Figure 4. Diffuse reflectance spectra of the samples.

Figure 5 shows the nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) for T, TC1, TC2.5, TC5 and TC10. All the isotherms can be identified as type IV according to the BDDT (Brunauer, Deming, Deming and Teller) classification and having H3-type hysteresis loops at $P/P_0$ between 0.45 and 0.9, indicating
the presence of narrow slit-shaped mesopores that may originate from the random distribution of CuInS$_2$ nanoplates on the TiO$_2$ nanofibers [52]. The inset of Figure 5 shows the corresponding pore size distributions of the samples calculated according to the desorption isotherms. All the samples show mesoporous structures with the pore size increasing from ~10 nm to ~20 nm after the coating of CuInS$_2$ nanoplates. Table 1 summarizes the specific surface areas ($S_{\text{BET}}$), pore volumes and pore sizes of the samples. The $S_{\text{BET}}$ of the samples shows a volcano shape and reaches the maximum value of 102 m$^2$·g$^{-1}$ for TC2.5, as the loading of CuInS$_2$ was increased.

**Figure 5.** Left: nitrogen adsorption-desorption isotherms (inset: pore size distributions) of the samples. Right (Table 1): specific surface area ($S_{\text{BET}}$), pore volume (PV) and average pore size (APS) derived from the isotherms.

### 3.3 XPS analysis
Figure 6. (a) XPS survey spectra of T and TC2.5. XPS spectra of (b) Ti 2p and (c) O 1s of T and TC2.5. XPS spectra of (d) Cu 2p, (e) In 3d and (f) S 2p of CuInS$_2$ and TC2.5.

The surface composition and chemical states of the resultant samples were investigated by XPS. The survey XPS spectrum (Figure 6a) shows the presence of Cu and In elements for TC2.5, in addition to Ti and O, confirming the generation of CuInS$_2$. Figure 6b shows the high-resolution Ti 2p spectrum with two symmetrical peaks corresponding to Ti 2p$_{3/2}$ at 458.8 eV and Ti 2p$_{1/2}$ at 464.5 eV, respectively. The O 1s XPS spectra of both samples (Figure 6c) can be deconvoluted to lattice oxygen (529.8 eV) in TiO$_2$ and –OH species (531.6 eV). Note that the binding energies of both Ti 2p and O 1s for TC2.5 shifted by 0.5 eV to lower values as compared to T, suggesting the presence of electron transfer from CuInS$_2$ to TiO$_2$ after hybridization, which will build an internal electric field at the interface of the hybrid. The directed electron transfer between the two components of the hybrid can be further verified
by the DFT calculation shown below. The electron transfer and the associated electric field would play a role in the heterojunction formation and hence affect the photocatalytic activities for CO$_2$ reduction.

The Cu 2p XPS spectrum of TC2.5 shown in Figure 6d contained two signals at 932.0 and 951.5 eV, corresponding to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$, respectively. The two strong photoelectron signals at 444.8 and 452.3 eV in the In 3d XPS spectrum (Figure 6e) of TC2.5 were assigned to In 3d$_{5/2}$ and In 3d$_{3/2}$, respectively. For comparison, the XPS of pure CuInS$_2$ were also measured and shown in Figure 6d-f. The binding energies of Cu and In for TC2.5 showed clear shift to higher values compared to those of CuInS$_2$, implying the electron transfer from CuInS$_2$ to TiO$_2$, which agree with the above analysis and suggest the formation of build-in electric field and direct Z-scheme heterojunction between them, as detailed below. Figure 6f shows the XPS signal of sulfur, which can be assigned to the presence of S$^{2-}$ and SO$_3^{2-}$ species. Apparently, S$^{2-}$ derived from the formation of CuInS$_2$, and SO$_3^{2-}$ may be generated during the disproportionation of L-cysteine hydrochloride. The results further prove the existence of CuInS$_2$ in TC2.5, which are in good agreement with the XRD and HRTEM analyses.

3.4 Photocatalytic CO$_2$ reduction and in-situ DRIFTS measurement

For the photocatalytic CO$_2$ reduction tests, control experiments were first conducted in the absence of photocatalysts, carbon source, irradiation or H$_2$O (N$_2$ was used as the reference gas). We found that hydrocarbons were produced only in the presence of the photocatalysts, irradiation, H$_2$O and CO$_2$, which verified that the hydrocarbons resulted exclusively from the photoreduction of CO$_2$. Here, CO$_2$ can be reduced to CH$_4$ and CH$_3$OH upon the as-prepared
materials under Xe lamp irradiation. Figure 7a shows the yields of CH$_4$ and CH$_3$OH after 1 h of irradiation over the samples. It can be seen that the hydrocarbon yield increased with the loading of CuInS$_2$ and reached a maximum value over TC2.5, with the production rate of 2.5 $\mu$mol h$^{-1}$ g$^{-1}$ for CH$_4$ and 0.86 $\mu$mol h$^{-1}$ g$^{-1}$ for CH$_3$OH. We consider the improvements resulted from the enhanced light absorption, increased surface area and possible improved charge separation and extraction after the growth of CuInS$_2$. We note that the generation rate of CH$_4$ by TC2.5 almost doubled the generation rate by T, while the yield of CH$_3$OH only showed a minor increase. Further rising of the CuInS$_2$ amount would result in a decrease of photocatalytic efficiency (sample TC5 and TC10).

We note that the product (CH$_4$ and CH$_3$OH) distribution of CO$_2$ reduction over TiO$_2$/CuInS$_2$ varied with the loading amount of CuInS$_2$. From the thermodynamic point of view, the reduction potential of CO$_2$ $\rightarrow$ CH$_4$ (-0.24 V vs. NHE, pH7) is more positive than that of CO$_2$ $\rightarrow$ CH$_3$OH$_4$ (-0.38 V vs. NHE, pH7). We speculate that with increasing amount of CuInS$_2$, more electrons can be generated and/or transferred to react with CO$_2$ molecules. Meanwhile, since the CO$_2$ $\rightarrow$ CH$_4$ is energetically more favourable than CO$_2$ $\rightarrow$ CH$_3$OH$_4$ as mentioned above, the CH$_4$ generation rate was improved with the loading of CuInS$_2$, and meanwhile the generation rate of CH$_3$OH remained unchanged.
Figure 7. (a) Photocatalytic activities of the CO\(_2\) reduction over different photocatalysts. (b) The GC-MS patterns of the produced CH\(_4\) over TC2.5 using \(^{12}\)CO\(_2\) and \(^{13}\)CO\(_2\) as the carbon source, respectively. (c) The long-term photocatalytic activities of TC2.5 for CO\(_2\) reduction.

Further, to verify the real carbon source of the photocatalytic products, isotope tracer experiment involving photo-reduction of \(^{13}\)CO\(_2\) (\(^{12}\)CO\(_2\) was also tested as a reference) was conducted and examined by GC-MS. As shown in Figure 7b, a strong peak assigned to \(^{13}\)CH\(_4\) (m/z = 17) was clearly observed when using \(^{13}\)CO\(_2\) as the carbon source, while the corresponding peak using \(^{12}\)CO as the carbon source was much weaker. These results confirmed that the detected products over the as-prepared photocatalyst originated from the CO\(_2\) source gas rather than any residual/contaminant carbon species.

Table 2. Photocatalytic CO\(_2\) reduction performances of various TiO\(_2\)-based photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
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<th>Light</th>
<th>Product</th>
<th>Yield ((\mu)mol g(^{-1}) h(^{-1}))</th>
<th>Ref.</th>
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<td>350 W Xe lamp</td>
<td>CH(_4)</td>
<td>2.5</td>
<td>This work</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>H(_2)O vapor</td>
<td>300 W Xe lamp</td>
<td>CH(_4)</td>
<td>1.135</td>
<td>[53]</td>
</tr>
<tr>
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<td>H(_2)O vapor</td>
<td>300 W Xe lamp</td>
<td>CH(_4)</td>
<td>4.8</td>
<td>[54]</td>
</tr>
<tr>
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<td></td>
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<td>CO</td>
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</tr>
<tr>
<td>1.5 % Ag/TiO(_2)</td>
<td>H(_2)O vapor</td>
<td>300 W Xe lamp</td>
<td>CH(_4)</td>
<td>1.4</td>
<td>[55]</td>
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<tr>
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</tbody>
</table>
Table 2 shows the photocatalytic CO\textsubscript{2} reduction performance of various TiO\textsubscript{2}-based photocatalysts. It can be found that the TiO\textsubscript{2}/CuInS\textsubscript{2} hybrid exhibits higher or comparable photocatalytic CO\textsubscript{2} conversion activities compared with most of the recently reported TiO\textsubscript{2}-based photocatalysts. There are few materials showing higher CO\textsubscript{2} reduction efficiency, nevertheless, these photocatalysts were modified with noble metals such as Pt and Ag, which increased the cost and limited the large-scale usage. Further, the long-term stability of the TiO\textsubscript{2}/CuInS\textsubscript{2} hybrid was checked and we found that the photocatalytic CO\textsubscript{2} reduction rate was largely remained after 12 hours illumination (Figure 7c). Therefore, the easily-prepared, noble-metal-free cocatalyst of CuInS\textsubscript{2} can still be of great interest for achieving high-efficiency CO\textsubscript{2} reduction.

Further, we conducted in-situ DRIFTS measurement to explore the CO\textsubscript{2} photoreduction mechanism over TC2.5. As shown in Figure 8, no absorption bands can be found in the absence of CO\textsubscript{2} and H\textsubscript{2}O (Figure 8a) in the dark. When CO\textsubscript{2} and water vapor were introduced into the reactor for 20 minutes in the dark, the molecules can be adsorbed onto TC2.5, evidenced by the presence of the monodentate bicarbonate species at 1650 cm\textsuperscript{-1} ($\nu_{\text{as}}$(CO\textsubscript{3})) and 1420 cm\textsuperscript{-1} ($\nu_{\text{s}}$(CO\textsubscript{3})) as well as bidentate bicarbonate species at 1515 cm\textsuperscript{-1} ($\nu_{\text{as}}$(CO\textsubscript{3})) and 1395 cm\textsuperscript{-1} ($\nu_{\text{s}}$(CO\textsubscript{3})) [59-61] (Figure 8b). The absorption spectra showed no changes when the exposure time was further increased to 40 and 60 minutes (Figure 8c-d).
without illumination. Under the photoirradiation, the intensities of monodentate and bidentate bicarbonate species increase with irradiation time (Figure 8e-g) due to the large thermodynamic tendency for the conversion of CO$_2$ to CO$_3^{2-}$. Meanwhile, some new absorption bands appear at 1540 and 1340 cm$^{-1}$, which are attributed to $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ of bidentate formic acid species [59]. The absorption bands located at 1456 and 1365 cm$^{-1}$ are assigned to $\nu_{as}(COO)$ and $\nu_s(COO)$ of absorbed formic acid species [60]. The bands at 1699 and 1740 cm$^{-1}$ can be ascribed to $\nu_{as}(CO)$ of absorbed formate and formic acid species, respectively [61]. It can be concluded that formate and formic acid were generated as the intermediates on the surface of TiO$_2$/CuInS$_2$ nanohybrids during the CO$_2$ reduction.

![Figure 8](image-url)  
**Figure 8.** In-situ DRIFTS spectra of TC2.5 under the flow CO$_2$/H$_2$O: (a) in the absence of CO$_2$/H$_2$O in the dark, (b-d) after the introduction of CO$_2$/H$_2$O for 20, 40 and 60 minutes in the dark, and (e-g) after the photo-irradiation for 20, 40 and 60 minutes.

3.5 EIS measurement, EPR analysis and DFT calculation
Electrochemical impedance spectra (EIS) were measured to investigate the photogenerated charge transfer dynamics. Figure 9 shows the EIS spectra of the samples and the semicircles observed in the Nyquist plots correspond to the charge transfer resistance in the sample/electrode interface. In general, a smaller semicircle implies a better charge transfer across this interface. As can be seen, the semicircle became smaller as the content of CuInS$_2$ was increased, indicating that the hybridization with CuInS$_2$ was able to improve the electron transfer which thus led to a significant photocatalytic enhancement for the CO$_2$ reduction.

Figure 9. Nyquist plots of the samples measured in 0.5 M Na$_2$SO$_4$ aqueous solution under Xe lamp irradiation.

Moreover, terephthalic acid (TA) was used as a probe molecule to examine the ·OH free radicals produced over the samples under illumination. The ·OH radicals can easily react with TA to produce a luminescent TAOH adduct, with fluorescence emission centered at 425 nm. Hence, the corresponding photoluminescence (PL) spectra recorded after UV illumination for different time (0~60 min) over TC2.5 were recorded and shown in Figure 10a. The PL
intensity boosted with increasing irradiation time, implying the continuous generation of hydroxyl radicals upon TC2.5 under illumination. Figure 10b shows the time courses of the PL intensity from TAOH for different samples. Clearly, TC2.5 generated the highest amount of ·OH as compared to other samples and in contrast, while T showed minor PL increase even after 60 min illumination. Based on these results, we proposed a direct Z-scheme heterojunction formed between TiO_2 and CuInS_2, i.e. the photo-generated electrons in the conduction band of TiO_2 can transfer to the valence band of CuInS_2, reducing the recombination rate of electron/hole pairs and facilitating the production of ·OH in aqueous solution. In the process of CO_2 reduction, we suppose that the ·OH radicals were captured and quenched by the hydroxyl groups from TiO_2 [62, 63].

Figure 10. (a) PL spectra of TA aqueous solution (5×10^{-4} M) in the presence of TC2.5 upon illumination for 0, 15, 30, 45 and 60 min. (b) PL intensity variation (425 nm) of the TA aqueous solution against time in the presence of different samples.

The Z-scheme charge transfer pathway can be more directly evidenced by in-situ XPS measurement under light irradiation. As shown in Figure 6b and c, the binding energies of Ti 2p and O 1s for TC2.5 under irradiation shifted positively by 0.2 eV as compared to the
values in dark. Accordingly, the binding energies of Cu 2p and In 3d (Figure 6d, e) for TC2.5 showed a negative shift of ca. 0.1 eV under irradiation. Such shifts clearly confirm the presence of electron transfer from TiO$_2$ to CuInS$_2$ under light irradiation driven by the direct Z-scheme heterojunction, agreeing well with the above analyses.

DFT calculations further confirm the generation of the Z-scheme heterostructure between TiO$_2$ and CuInS$_2$. Generally, electrons will transfer from the semiconductor with higher Fermi energy ($E_F$) level to the other semiconductor with lower $E_F$ level at the interface of two semiconductors. In our case, the $E_F$ level of CuInS$_2$ is higher than that of TiO$_2$ (Figure 11). This means the electrons can transfer from CuInS$_2$ to TiO$_2$ upon contact, creating a built-in electric field in the TiO$_2$/CuInS$_2$ interface with the orientation from CuInS$_2$ to TiO$_2$ upon contact. These analyses agree well with the XPS results as discussed above, that the electrons transfer from CuInS$_2$ to TiO$_2$ after hybridization to form a built-in electric field resulting from the shift of binding energies of Ti 2p, O 1s, Cu 2p and In 3d.

![Figure 11](image-url). Calculated electrostatic potentials for (a) TiO$_2$ (101) face and (b) CuInS$_2$ (004) face. The red and blue dashed lines denote Fermi level and the vacuum energy level, respectively.
According to the above results and discussion, we propose a mechanism of the photocatalytic CO$_2$ reduction upon the hybrid materials. Under light irradiation, the electrons in the valence band (VB) of TiO$_2$ and CuInS$_2$ were excited to the conduction band (CB). Owing to the presence of the internal electric field pointing from CuInS$_2$ to TiO$_2$, the electrons in TiO$_2$ CB would transfer and recombine with the holes in CuInS$_2$ VB, instead of the electrons in CuInS$_2$ CB transfer to TiO$_2$ CB. This Z-scheme configuration can improve the separation and extraction of the charge carriers (electrons from CuInS$_2$ and holes from TiO$_2$) [64-66]. Therefore, the photo-induced electrons from CuInS$_2$ CB would react with the adsorbed CO$_2$ molecules, with the CO$_2$ reduced to CH$_4$ and CH$_3$OH with water as the proton source [67-69]. The photocatalytic mechanism and the charge transfer for the TiO$_2$/CuInS$_2$ Z-scheme heterostructures are schematically illustrated in Figure 1.

**Figure 12.** Schematic illustration of the charge transfer and separation in TC2.5 under simulated sunlight light irradiation.
4. Conclusions

In summary, novel TiO$_2$/CuInS$_2$ core-shell nanofibers were fabricated through an electrospinning and subsequent hydrothermal methods. The resulting TiO$_2$/CuInS$_2$ hybrid nanofibers exhibit superior photocatalytic activity for CO$_2$ reduction under irradiation, due to the enhanced light absorption, increased surface area and most importantly, the generation of Z-scheme heterojunction between TiO$_2$ and CuInS$_2$. The formation of the Z-scheme heterojunction was verified by XPS measurement, DFT calculation and free radical analysis. The direct Z-scheme heterojunction could significantly promote the charge separation and extraction upon photo-excitation, resulting in improved hydrocarbon production from CO$_2$ reduction. Our work provides a new insight into the design and synthesis of TiO$_2$-based photocatalysts with Z-scheme pathways for high-efficiency solar-fuel conversion.

Acknowledgements

This work was supported by NSFC (51320105001, 21573170, U1705251 and 21433007), NSFHP (2015CFA001) and Innovative Research Funds of SKLWUT (2017-ZD-4). J.X. is grateful to Discovery Early Career Researcher Award (DECRA) by Australian Research Council (DE160101488). The project is also supported by the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing (Wuhan University of Technology) (2018-KF-17).

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Table 1. Physical properties of the samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>CuInS$_2$ (mol%)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>PV (m$^3$/g)</th>
<th>APS (nm)</th>
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<tbody>
<tr>
<td>T</td>
<td>-</td>
<td>43</td>
<td>0.14</td>
<td>10</td>
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<tr>
<td>TC1</td>
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<tr>
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<td>TC10</td>
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<td>51</td>
<td>0.25</td>
<td>20.1</td>
</tr>
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</table>

PV: pore volume, APS: average pore size