Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Photocatalytic reduction of CO_2 over facet engineered TiO_2 nanocrystals supported by carbon nanofibers under simulated sunlight irradiation

Ze Lei, Zhuo Xiong, Yicheng Wang, Yuxiao Chen, Dingshan Cao, Yongchun Zhao*, Junying Zhang, Chuguang Zheng

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science & Technology, 1037 Luoyu Road, Wuhan 430074, China

ARTICLE INFO

Keywords: Photocatalysis CO₂ reduction CNFs TiO₂ Facet engineering

ABSTRACT

Carbon nanofibers (CNFs) supported facet engineered TiO₂ nanocrystals (NCs) were one-step synthesized by a solvothermal method and their photocatalytic CO_2 reduction performance were investigated under simulated sunlight irradiation. The results show that anatase TiO₂ NCs with {001} and {101} facets coexposure were homogeneously dispersed on CNFs and combined firmly with CNFs. The enhanced photocatalytic CO_2 reduction activity of the composites can be attributed to the formation of TiO₂-carbon heterojunction and the surface heterojunction between the {001}/{101} facets of TiO₂ crystals, which accelerate the separation of photogenerated electron-hole pairs and extend the light response of TiO₂ to the visible light region simultaneously.

1. Introduction

Photocatalytic reduction of CO_2 with water into renewable fuels is a promising technology to reduce CO_2 emission and produce organic fuels. Among a variety of photocatalysts, TiO₂ is most frequently evaluated for the CO_2 photocatalytic reduction process because it is inexpensive, photo-stable and low toxic [1,2]. However, TiO₂ still has limitations that include low light absorption in the visible range due to its large band gap (3.2 eV for anatase) and low photocatalytic conversion efficiency by reason of the rapid recombination rate of photoexcited electrons and holes.

Recently, it has been reported that photocatalytic activity of TiO_2 crystals could be enhanced by engineering coexposed multiple facets [3]. Yu et al. [4] reported enhanced CO_2 photocatalytic reduction over anatase TiO_2 crystals with coexposed {001} and {101} facets and found that it could be attributed to the effect of surface heterojunction in a single TiO_2 particle with {001} and {101} facets coexposure, which is conducive to the photogenerated electrons and holes separation.

Another effective approach to enhance photocatalytic activity of TiO_2 is to combine it with other materials to form composite materials, for instance noble metals [5], oxide semiconductor [6], and carbon materials [7]. Among them, carbon material is more abundant and cheaper, meanwhile, some of them have several extraordinary properties, such as large specific area, rapid mobility of charge carriers, and tunable surface properties [8,9]. Therefore, combining TiO₂ with carbon materials has been widely used to enhance the photocatalytic

activity of TiO₂ [10,11]. For example, Zhang et al. [12] reported the enhanced photocatalytic activity on degradation and H₂ evolution over mesoporous TiO₂ layer coated on multiwall carbon nanotubes. Our group previously reported the synthesis and characterization of graphene supported TiO₂ with coexposed {101} and {001} facets and their enhancement of photocatalytic CO₂ reduction performance [13]. Among a variety of carbon materials, carbon nanofiber has been reported in several researches for photocatalysis degradation and H₂ evolution because it has strong visible light absorption and can effectively capture and transport photogenerated electrons [14,15]. Pant et al. [16] reported the fabrication of CNFs decorated with CdS/TiO2 heteroarchitecture by electrosping process and found that the nanocomposites exhibited high photocatalytic hydrolysis of ammonia borane due to their favorable electrons-transfer properties, good dispersion, and strong adsorption property. Kim et al. [17] synthesized trilayer CdS/CNF/Pt-TiO₂ heterostructures for photocatalytic H₂ production from water splitting and demonstrated that the CNF acted as an efficient electron-transfer mediator which promotes the separation of excited electron-hole pairs. Moreover, comparing to other carbon materials such as graphene reported in many researches for CO2 photocatalytic reduction, CNF is cheaper and easier to prepare [13]. Therefore, it is possible to load facet engineered TiO₂ NCs onto CNFs to achieve enhanced CO2 photocatalytic reduction. However, as far as we know, very few papers have reported the synthesis and application of this kind of catalyst for CO₂ photocatalytic reduction.

In this paper, a one-step solvothermal method was employed to

https://doi.org/10.1016/j.catcom.2018.01.025





^{*} Corresponding author. *E-mail address:* yczhao@hust.edu.cn (Y. Zhao).

Received 31 August 2017; Received in revised form 28 December 2017; Accepted 21 January 2018 1566-7367/ © 2018 Elsevier B.V. All rights reserved.

Fig. 1. TEM and HR-TEM images of 001/101TiO₂ (A), 5CNF-001/101TiO₂ (B) catalysts.



synthesize CNFs supported TiO₂ NCs with {001} and {101} facets coexposure (CNF-001/101TiO₂). The photocatalytic CO₂ reduction activity of as-prepared CNF-TiO₂ composites was evaluated under simulated sunlight. The effect of CNFs introduction on CO₂ reduction photocatalytic performance of CNF-001/101TiO₂ was investigated. A possible photocatalytic CO₂ reduction mechanism of CNF-001/101TiO₂ was analyzed.

2. Experimental

2.1. Catalyst preparation

CNFs supported TiO_2 NCs with {001} and {101} facets coexposure were prepared by a one-step solvothermal method. Firstly, different amounts of CNFs were dispersed into 90 mL ethanol by ultrasonic treatment for 30 min, and then 1.2 mL hydrofluoric acid solution and 3 mL titanium butoxide dropped into the homogeneous suspension. After sonication for other 1 h, the mixed suspension was then transferred to a 200 mL Teflon-lined autoclave and heated at 180 °C for 24 h. After the autoclave was cooled down, the obtained precipitates were collected by centrifugation, washed with ethanol and deionized water for several times, respectively, and then dried at 60 °C for overnight. Finally the fluoride ions on the surface of the as-prepared sample were removed by calcination at 500 °C for 2 h in the nitrogen atmosphere. The mass ratio of CNF to $\rm TiO_2$ is 1%, 5%, and 10% in the mixed suspension, the samples prepared by solvothermal from these suspensions were labeled as 1CNF-001/101TiO₂, 5CNF-001/101TiO₂, and 10CNF-001/101TiO₂, respectively. The preparation of CNFs supported TiO₂ NCs with {101} facet exposure (CNF-101TiO₂) was carried out in a similar manner without the addition of HF solution. Pure TiO₂ NCs with {101} and {001} facets coexposure (denoted as $001/101TiO_2$) was prepared using the same procedure without CNF. Pure TiO₂ NCs with {101} facets exposure (denoted as 101TiO₂) was prepared using the same procedure without CNF and HF.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on an Empyrean diffractometer. Specific surface area (BET) measurement was performed on a Micromeritics ASAP2010 analyzer. An FEI Tecnai G^2 F30 instrument was used to obtain transmission electron microscopy (TEM) images. UV–Vis absorbance spectra were measured by a Hitachi U3900 spectrophotometer. Photoluminescence (PL) spectra were collected using a confocal laser Raman microscope (Horiba Jobin Yvon, LabRAM HR800). Electrochemical impedance spectra (EIS) were obtained by an electrochemical system (CHI-660D). Fourier transform infrared (FTIR) spectra were recorded by a Bruker VERTEX 70 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Shimadzu/KRATOS AXIS-ULTRA DLS-600W instrument.

2.3. Photocatalytic reduction of CO_2

 CO_2 photocatalytic reduction was performed under simulated sunlight irradiation (18.7 mW cm⁻², 300 nm < λ < 400 nm; 45.0 mW cm⁻², 400 nm < λ < 800 nm) in an internal circulated reaction system reported in our previous work [18]. First, 10 mL of deionized water was added to the reactor, and then 20 mg of catalyst dispersed uniformly on a Petri plate was placed on above the water. Prior to illumination, the reactor was first vacuumed through a vacuum pump and then was performed a purification process with ultra-pure CO_2 (99.999%). The amounts of H₂, CO, and CH₄ in the reactor were analyzed every 30 min by the GC during 6 h of light irradiation.

First, background tests were conducted using CO_2 and water as reactants for the cases of (1) empty reactor and (2) blank Petri plate in the reactor. No hydrocarbons were detected under simulated sunlight irradiation in these two cases. This indicated that the CO_2 reduction reaction could not occur in the absence of catalyst. Second, test was performed using carbon nanofibers under simulated sunlight irradiation, no hydrocarbons were detected with or without CO_2 and water, This demonstrated that the carbon nanofibers did not produce hydrocarbons under simulated sunlight irradiation, Third, instead of CO_2 , N_2 was used to be purged gas, no hydrocarbons were detected under simulated irradiation in the presence of water and catalyst. This confirms that any produced hydrocarbons must be derived from the purged CO_2 .

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns are presented in Fig. S1, only diffraction peaks indexed to anatase appeared and all samples exhibited similar diffraction peaks, indicating that the obtained samples were anatase TiO_2 and CNFs would not affect the crystal structure of the TiO_2 nanocrystals. The BET surface of composites decreased with the increase of content of CNF because the BET surface of CNF is smaller than that of TiO_2 (Table S1).

The TEM images in Fig. 1A clearly shows the facet engineered TiO_2 NC is a truncated tetragonal bipyramidal with coexposed {001} and {101} facets. The HR-TEM images exhibited that the fringe spacing of 0.23 nm parallel to the top and bottom facets corresponds to the {001} plane of anatase TiO_2 [19]. Fig. 1A also showed another set of the lattice fringes with spacing of 0.35 nm corresponding to the {101} plane of anatase TiO_2 [20]. For 5CNF-001/101TiO_2 samples (Fig. 1B), the TiO_2 NCs with {001} and {101} facets coexposure were homogenously dispersed on CNFs. And the formation of TiO_2 -carbon heterojunction can be clearly observed in the HR-TEM images of 5CNF-001/101TiO_2 composites.

The UV–Vis absorbance spectra are shown in Fig. 2A. The absorption intensities of the composites were higher than of pure TiO_2 at visible wavelengths. This can be attributed the presence of CNFs in the composites, reducing reflection of light due to the black color of CNFs



Fig. 2. UV-Vis absorbance spectra of the as-prepared catalysts.

[21]. The absorption edges of pure TiO_2 is higher than the CNF-TiO₂ composites (Fig. S2), and the band gaps for the composites are further narrowed by the increase of CNF content (Table S1), which is attributed to the formation of Ti–C bonds, as indicated by XPS analysis (Fig. S4C). The formation of Ti–C bonds results in the upward shift of the valence band top, which is beneficial for band-gap narrowing [22].

The PL spectra of the samples are presented in Fig. 3. The CNF-TiO₂ composites show the diminished PL intensities compared with that of pure TiO₂. This can be explained by the carbonaceous species bound to TiO₂ in the TiO₂-carbon heterojunction that can receive the photogenerated electrons easily to efficiently suppress the recombination of the photogenerated electron-hole pairs [12,23], which is beneficial to the separation of photogenerated charges on TiO₂.

The EIS spectra are presented in Fig. 4, it is observed that the arc radius of the EIS Nyquist plot of the CNF-TiO₂ composites are smaller than that of pure TiO₂, indicating that the interface layer resistance and the charge transfer resistance on the surface are diminished [24], which reveals that charge migration is facilitated due to the interfacial interaction between the TiO₂ and CNF caused by the TiO₂-carbon heterojunction. The FTIR spectra are presented in Fig. S3. The broad peaks located at 3422 and 1625 cm⁻¹ are assigned to the physically adsorbed H₂O and the stretching mode of hydroxyl groups [25]. The weak peak



Fig. 3. PL spectra of the as-prepared catalysts.



Fig. 4. Electrochemical impedance spectroscopy Nyquist plots of the as-prepared catalysts.

at 1056 cm⁻¹ of all samples corresponds to the vibration of C–O stretching [26]. The peak at 1383 cm⁻¹ of the spent 5CNF-001/101TiO₂ composite is attributed to the C=O stretching mode of COOH groups [27]. The presence of wide transmittance band at 500–700 cm⁻¹ in the composites is ascribed to Ti–O bonding [28].

The XPS spectra of Ti 2p in Fig. S4A exhibit that the binding energy (BE) are located around 458.6 eV (Ti 2p_{3/2}) and 464.3 eV (Ti 2p_{1/2}), indicating a chemical state of Ti^{4+} in the TiO_2 [29]. The spectra of O 1 s shown in Fig. S4B reveal that the peak at around 529.7 and 531.0 eV are assigned to lattice oxygen in TiO2 and the surface hydroxyl of CNF and TiO₂, respectively [30]. There are four peaks in the spectra (Fig. S4C) of CNF-001/101TiO₂ composites with the binding energies centered around 290.0 eV, 287.8 eV, 286.4 eV, and 285.0 eV, respectively. The peaks at 285.0 eV and 286.4 eV is ascribed to the delocalized alternant hydrocarbon (C-C) and C-O bond, while the other two peaks at 287.8 and 290.0 eV are attributed to the C=O bond and carboxyl or ester carbon (O=C-O), respectively [8,25]. The peak at 283.4 eV in 1CNF-001/101TiO₂ can be attributed to the Ti-C bond [31]. It is notable that the chemical states of C on the surface of pristine CNF do not change obviously after the solvothermal process (Fig. S4C), demonstrating that CNF were stable during the solvothermal process. However, in comparison with the XPS spectra of CNF, a positive shift of the C-O and C=O bond peaks of CNF-001/101TiO₂ catalysts can be observed, demonstrating the oxidation of the CNFs in CNF-001/101TiO₂ catalysts during the solvothermal process, which could be caused by introduction of TiO2. A similar phenomenon in the hydrothermal synthesis of carbon nanotubes-TiO2 nanocomposites was also found by Jitianu et al. [32]. This also indicated that the good combination of TiO₂ and CNF, which might be beneficial for the formation of TiO₂-carbon heterojunction.

3.2. CO_2 photocatalytic reduction

Fig. 5 shows the photocatalytic CO yield of as-prepared catalysts after 6 h. CO was found to be the main product and the generation of CH₄ and H₂ was not detected. It can be seen that CNF-TiO₂ composites exhibit higher photocatalytic activity than pure $001/101TiO_2$ and 101TiO₂, suggesting that the support of CNF promotes the migration of electron from TiO₂ to CNF leading to the restrained recombination of electrons and holes, as evident in PL spectra and EIS analysis. However, the photocatalytic activity of $10CNF-001/101TiO_2$ is lower than that of $5CNF-001/101TiO_2$ even though the PL intensity of $10CNF-001/101TiO_2$ is lower than that of $5CNF-001/101TiO_2$. The reason for this phenomenon may be due to the decreased active component TiO2



Fig. 5. Photocatalytic CO yield of as-prepared catalysts after 6 h irradiation.

content in the composites. In addition, the $101TiO_2$ and $CNF-101TiO_2$ has lower photocatalytic than $001/101TiO_2$ and $CNF-001/101TiO_2$ respectively, which is attributed to the "surface heterojunction" within the facet engineered TiO_2 NCs that can facilitate the spatial migration of photogenerated electrons and holes [13]. The CO yield of $CNF-001/101TiO_2$ is much higher than that of RGO-TiO_2 composite reported by Tomoaki Takayama [33]. Moreover, the quantum yield of $CNF-001/101TiO_2$ is higher than that of graphene oxide-supported TiO_2 catalysts reported by Lling-Lling Tan [34]. Quantum yield of the CO₂ photocatalytic reduction over the composites were calculated by the following Eqs. [35].

$\Phi CO(\%) = 100\% \times 2 \times CO$ yield/moles of photon reached the catalyst

As shown in Table S1, For 001/101TiO₂, the quantum efficiency is calculated to be 0.09%, which is much higher than that of the rutile TiO₂ nanocrystals with exposed high-index facets reported by Quang Duc Truong [36]. Fig. S5 shows the cycle performance of 5CNF-001/101TiO₂ catalyst. After the first cycle, the reactor was vacuumed and the same experimental process was repeated. The CO yield in the second and the third cycle only slightly decreased, indicating good stability of 5CNF-001/101TiO₂ catalyst. As shown in Fig. S6 and Table S2, the chemical states of Ti, O and C on the surface of 5CNF-001/101TiO₂ catalyst do not show clearly change after photocatalytic reaction, which can well explain the stability of the catalyst.

On the basis of the above experimental results, a simple mechanism to explain the observed enhancement in the photocatalytic activity of CNF-001/101TiO₂ catalysts was proposed and shown in Fig. 6. Firstly, the introduction of CNF into composites can extend the spectral response of TiO₂ to visible light region and enhance the visible absorption capability. Secondly, the photogenerated electron and hole pairs can efficiently migrate to {101} and {001} facets, respectively, due to the formation of surface heterojunction [4]. Then the electrons continued to accumulate on {101} facets and transfer to CNFs owing to its high exhibit electron storage capacity, electron conductivity, and the formation of TiO₂-carbon heterojunction [37]. Thus, the combination of photogenerated electron-hole pairs is more effectively suppressed. Finally, the hydrocarbons are produced by the reaction of CO₂ with the electrons on CNFs and the generation of O₂ is due to the oxidation of H₂O by the hole on the TiO₂ NCs.

4. Conclusions

In this paper, CNFs supported TiO_2 NCs with {001} and {101} facets coexposure were synthesized by one-step solvothermal method. The



TiO₂ NCs with {001} and {101} facets coexposure were uniformly loaded on the CNFs after the solvothermal reaction. The photocatalytic activity of facet engineered TiO₂ catalyst was effectively improved after the supporting of CNF. The CO yield can effectively enhanced by adding an appropriate amount of CNFs in the catalyst. The optimization CO yield of 2.4 μ mol g⁻¹ was obtained by 5CNF-001/101TiO₂ after simulated sunlight irradiation for 6 h. The enhanced photocatalytic activity of CNF-001/101TiO₂ catalysts can be attributed to the formation of {001}/{101} surface heterojunction within TiO₂ crystals and TiO₂-carbon heterojunction between TiO₂ and CNF, which effectively promote the separation of photogenerated charges and extend the light response of TiO₂ from UV to visible light region.

Acknowledgments

This project was supported by the National Natural Science Foundation of China (U1610110, 51706082), the Foreign Science and Technology Cooperation of Hubei Province (2016AHB021), and China Postdoctoral Science Foundation (2017M620319). The Analytical and Testing Center of Huazhong University of Science & Technology were acknowledged by the authors.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2018.01.025.

References

- M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1993) 341–357.
- [2] I.H. Tseng, J.C.S. Wu, H.Y. Chou, Effects of sol-gel procedures on the photocatalysis of Cu/TiO₂ in CO₂ photoreduction, J. Catal. 221 (2004) 432–440.
- [3] L. Liu, Y. Jiang, H. Zhao, J. Chen, J. Cheng, K. Yang, Y. Li, Engineering coexposed {001} and {101} facets in oxygen-deficient TiO₂ nanocrystals for enhanced CO₂ photoreduction under visible light, ACS Catal. 6 (2016) 1097–1108.

- [4] J. Yu, J. Low, W. Xiao, P. Zhou, M. Jaroniec, Enhanced photocatalytic CO₂-reduction activity of anatase TiO₂ by coexposed {001} and {101} facets, J. Am. Chem. Soc. 136 (2014) 8839–8842.
- [5] Z. Xiong, Z. Lei, S. Ma, X. Chen, B. Gong, Y. Zhao, J. Zhang, C. Zheng, J.C.S. Wu, Photocatalytic CO₂ reduction over V and W codoped TiO₂ catalyst in an internalilluminated honeycomb photoreactor under simulated sunlight irradiation, Appl. Catal. B Environ. 219 (2017) 412–424.
- [6] S.Y. Chai, Y.S. Kim, W.I. Lee, Photocatalytic property of TiO₂ loaded with SnO₂ nanoparticles, J. Electroceram. 17 (2006) 323–326.
- [7] Y. Xu, Y. Zhuang, X. Fu, New insight for enhanced photocatalytic activity of TiO₂ by doping carbon nanotubes: a case study on degradation of benzene and methyl orange, J. Phys. Chem. C 114 (2010) 2669–2676.
- [8] C.H. Kim, B.H. Kim, K.S. Yang, TiO₂ nanoparticles loaded on graphene/carbon composite nanofibers by electrospinning for increased photocatalysis, Carbon 50 (2012) 2472–2481.
- [9] R. Leary, A. Westwood, Carbonaceous nanomaterials for the enhancement of TiO₂ photocatalysis, Carbon 49 (2011) 741–772.
- [10] Y. Wang, J. Yu, W. Xiao, Q. Li, Microwave-assisted hydrothermal synthesis of graphene based Au–TiO₂ photocatalysts for efficient visible-light hydrogen production, J. Mater. Chem. A 2 (2014) 3847–3855.
- [11] W.J. Ong, L.L. Tan, S.P. Chai, S.T. Yong, A.R. Mohamed, Self-assembly of nitrogendoped TiO₂ with exposed {001} facets on a graphene scaffold as photo-active hybrid nanostructures for reduction of carbon dioxide to methane, Nano Res. 7 (2014) 1528–1547.
- [12] X. Zhang, S. Cao, Z. Wu, S. Zhao, L. Piao, Enhanced photocatalytic activity towards degradation and H₂ evolution over one dimensional TiO₂@MWCNTs heterojunction, Appl. Surf. Sci. 402 (2017) 360–368.
- [13] Z. Xiong, Y. Luo, Y. Zhao, J. Zhang, C. Zheng, J.C. Wu, Synthesis, characterization and enhanced photocatalytic CO₂ reduction activity of graphene supported TiO₂ nanocrystals with coexposed {001} and {101} facets, Phys. Chem. Chem. Phys. 18 (2016) 13186–13195.
- [14] A.A. Taha, A.A. Hriez, Y.N. Wu, H. Wang, F. Li, Direct synthesis of novel vanadium oxide embedded porous carbon nanofiber decorated with iron nanoparticles as a low-cost and highly efficient visible-light-driven photocatalyst, J. Colloid Interface Sci. 417 (2014) 199–205.
- [15] B. Pant, N.A. Barakat, H.R. Pant, M. Park, P.S. Saud, J.W. Kim, H.Y. Kim, Synthesis and photocatalytic activities of CdS/TiO₂ nanoparticles supported on carbon nanofibers for high efficient adsorption and simultaneous decomposition of organic dyes, J. Colloid Interface Sci. 434 (2014) 159–166.
- [16] B. Pant, H.R. Pant, M. Park, Y. Liu, J.W. Choi, N.A.M. Barakat, H.Y. Kim, Electrospun CdS–TiO₂ doped carbon nanofibers for visible-light-induced photocatalytic hydrolysis of ammonia borane, Catal. Commun. 50 (2014) 63–68.
- [17] Y.K. Kim, S.K. Lim, H. Park, M.R. Hoffmann, S. Kim, Trilayer CdS/carbon nanofiber (CNF) mat/Pt-TiO₂ composite structures for solar hydrogen production: effects of CNF mat thickness, Appl. Catal. B Environ. 196 (2016) 216–222.

- [18] Z. Xiong, Z. Lei, C.C. Kuang, X. Chen, B. Gong, Y. Zhao, J. Zhang, C. Zheng, J.C.S. Wu, Selective photocatalytic reduction of CO₂ into CH₄ over Pt-Cu₂O TiO₂ nanocrystals: the interaction between Pt and Cu₂O cocatalysts, Appl. Catal. B Environ. 202 (2017) 695–703.
- [19] M. Chen, J. Ma, B. Zhang, G. He, Y. Li, C. Zhang, H. He, Remarkable synergistic effect between {001} facets and surface F ions promoting hole migration on anatase TiO₂, Appl. Catal. B Environ. 207 (2017) 397–403.
- [20] J. Pan, G. Liu, G.Q. Lu, H.M. Cheng, On the true photoreactivity order of {001}, {010}, and {101} facets of anatase TiO₂ crystals, Angew. Chem. 50 (2011) 2133–2137.
- [21] J.W. Shi, H.J. Cui, J.W. Chen, M.L. Fu, B. Xu, H.Y. Luo, Z.L. Ye, TiO₂/activated carbon fibers photocatalyst: effects of coating procedures on the microstructure, adhesion property, and photocatalytic ability, J. Colloid Interface Sci. 388 (2012) 201–208.
- [22] F. Dong, H. Wang, Z. Wu, One-step "Green" synthetic approach for mesoporous Cdoped titanium dioxide with efficient visible light photocatalytic activity, J. Phys. Chem. C 113 (2009) 16717–16723.
- [23] J. Shi, J. Chen, G. Li, T. An, H. Yamashita, Fabrication of Au/TiO₂ nanowires@ carbon fiber paper ternary composite for visible-light photocatalytic degradation of gaseous styrene, Catal. Today 281 (2017) 621–629.
- [24] Z. Xiong, Z. Lei, Z. Xu, X. Chen, B. Gong, Y. Zhao, H. Zhao, J. Zhang, C. Zheng, Flame spray pyrolysis synthesized ZnO/CeO₂ nanocomposites for enhanced CO₂ photocatalytic reduction under UV–Vis light irradiation, J. CO₂ Utilization 18 (2017) 53–61.
- [25] J. Cheng, Y. Wang, Y. Xing, M. Shahid, W. Pan, A stable and highly efficient visiblelight photocatalyst of TiO₂ and heterogeneous carbon core–shell nanofibers, RSC Adv. 7 (2017) 15330–15336.
- [26] P.K. Dubey, P. Tripathi, R.S. Tiwari, A.S.K. Sinha, O.N. Srivastava, Synthesis of reduced graphene oxide–TiO₂ nanoparticle composite systems and its application in hydrogen production, Int. J. Hydrog, Energy 39 (2014) 16282–16292.
- [27] J. Fu, S. Cao, J. Yu, J. Low, Y. Lei, Enhanced photocatalytic CO₂-reduction activity of electrospun mesoporous TiO₂ nanofibers by solvothermal treatment, Dalton Trans. 43 (2014) 9158–9165.
- [28] H. Meng, W. Hou, X. Xu, J. Xu, X. Zhang, TiO₂-loaded activated carbon fiber:

hydrothermal synthesis, adsorption properties and photo catalytic activity under visible light irradiation, Particuology 14 (2014) 38-43.

- [29] L. Zuniga, V. Agubra, D. Flores, H. Campos, J. Villareal, M. Alcoutlabi, Multichannel hollow structure for improved electrochemical performance of TiO₂/Carbon composite nanofibers as anodes for lithium ion batteries, J. Alloys Compd. 686 (2016) 733–743.
- [30] X. Liu, X. Ma, L. Zhu, D. Li, Photocatalysis, microstructure, and surface characterization of TiO₂-loaded wooden-activated carbon fibers, Polym. Compos. 36 (2015) 62–68.
- [31] E.M. Rockafellow, X. Fang, B.G. Trewyn, K. Schmidt-Rohr, W.S. Jenks, Solid-state ¹³C NMR characterization of carbon-modified TiO₂, Chem. Mater. 21 (2009) 1187–1197.
- [32] A. Jitianu, T. Cacciaguerra, R. Benoit, S. Delpeux, F. Béguin, S. Bonnamy, Synthesis and characterization of carbon nanotubes–TiO₂ nanocomposites, Carbon 42 (2004) 1147–1151.
- [33] T. Takayama, K. Sato, T. Fujimura, Y. Kojima, A. Iwase, A. Kudo, Photocatalytic CO₂ reduction using water as an electron donor by a powdered Z-scheme system consisting of metal sulfide and an RGO-TiO₂ composite, Faraday Discuss. 198 (2017) 397–407.
- [34] L.-L. Tan, W.-J. Ong, S.-P. Chai, A.R. Mohamed, Photocatalytic reduction of CO₂ with H₂O over graphene oxide-supported oxygen-rich TiO₂ hybrid photocatalyst under visible light irradiation: process and kinetic studies, Chem. Eng. J. 308 (2017) 248–255.
- [35] Z. Xiong, H. Wang, N. Xu, H. Li, B. Fang, Y. Zhao, J. Zhang, C. Zheng, Photocatalytic reduction of CO₂ on Pt²⁺ -Pt⁰/TiO₂ nanoparticles under UV/Vis light irradiation: a combination of Pt²⁺ doping and Pt nanoparticles deposition, Int. J. Hydrog. Energy 40 (2015) 10049–10062.
- [36] Q.D. Truong, H.T. Hoa, T.S. Le, Rutile TiO₂ nanocrystals with exposed {331} facets for enhanced photocatalytic CO₂ reduction activity, J. Colloid Interface Sci. 504 (2017) 223–229.
- [37] J. Liu, J. Li, A. Sedhain, J. Lin, H. Jiang, Structure and photoluminescence study of TiO₂ nanoneedle texture along vertically aligned carbon nanofiber arrays, J. Phys. Chem. C 112 (2008) 17127–17132.