

VNU Journal of Science: Earth and Environmental Sciences



Journal homepage: https://js.vnu.edu.vn/EES

Original Article

Facile and Effective Synthesis of Non-nobel Metal Oxide Composite Heterojunction Catalyst for CO₂ Reduction Reaction

Jenaidullah Batur¹, Le Duc Anh^{1,2,*}, Sebghatullah Mudaber¹

¹Department Beijing Key Laboratory for Green Catalysis and Separation, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, P. R. China ²Vietnam National Institute of Occupational Safety and Health, Vietnam

> Received 27th August 2024 Revised 14th November 2024; Accepted 7th May 2025

Abstract: Increasing CO_2 emmission leads to global warming. Effective and impotent strategies such as photocatalytic CO_2 reduction and utilization was proposed to solve this issue by using sustainable solar energy. We provided a novel, facile, and eco-friendly synthesis strategy to effectively synthesize TiO₂-organic composite materials to selectively reduce CO_2 to CO. This strategy not only improves TiO₂ photocatalytic activity but also shows potential to apply with alternate metal oxide composite catalyst.

Keywords: Photocatalyst, Heterogeneous Catalyst, Metal Oxide, TiO₂, Composite Materials.

1. Introduction

Green chemistry and green environment importance are widely increasing in our century. CO_2 emission, water purification, and heavy metal adsorption (1) are also important for industrial and environmental purification. As industrial growth rapidly increased fossil fuel use, parallelly CO_2 emissions increased in the atmosphere. Recent research indicates that over 60% of global warming can be attributed to both natural processes and industrial CO_2 production. The atmospheric concentration of CO_2 was already 48% above pre-industrial levels by 1850. Before the industrial age, the average atmospheric CO_2 concentration ranged from 172 ppm to 300 ppm. However, according to the latest Earth CO_2 report, the concentration has now reached 416.87 ppm as of May 20, 2020 (2; 3). The alarming rise in CO_2 emissions poses a

^{*} Corresponding author.

E-mail address: ducanh.nilp@gmail.com

https://doi.org/10.25073/2588-1094/vnuees.5236

significant threat to the delicate balance of our natural ecosystems (4; 5). Urgent action is needed to reduce atmospheric CO_2 levels and mitigate global warming and environmental damage (4) one of effective approaches is CO_2 utilization techniques, with carbon dioxide photoreduction being particularly attractive due to its sustainability, non-toxicity, and abundant availability. Implementing CO_2 photo reduction is straightforward and beneficial.

Currently, there is a list of catalysts that can reduce CO₂ to valuable chemicals and fuels, among them metal oxides such as TiO₂ known as promising photocatalysts to produce hydrogen and CO, unless they are at an earlier age and still need to promote activity to able for produce fabricated values. Titanium (IV) oxide (TiO₂), has been used as catalysts for environmental applications due it its low cost, photocatalytic efficiency, and nontoxicity properties (6). TiO_2 is used for several environmental experiments, insisted of Nobel metals catalysis with improving charge separation of photogenerated electrons and holes (7) such as environmental cleanup, water splitting, oxidization, reduced water molecules, organic synthesis, west water treatment (8) and, CO₂ photoreduction reaction. The TiO₂ bandgap is larger than 3.0 EV also can able to use for device applications (9), wettability control for self-cleaning(10), and electrochromic windows(11). Due to its limited photocatalytic activity research, adding impurities can improve the photocatalytic production of TiO₂. His group declared that the Schottky barrier formed at the metal-TiO₂ interface of Ag, Pt, and Au-doped TiO₂, and charge carrier recombination decreased (12; 13). Cheng et all 2007 reported non-metal-doped TiO₂ (C, N, S, B, P, F, and I) to compare with metal-doped TiO_2 (14), they may improve the extension of photocatalytic activity of TiO₂ under visible light due to their impurity state is near the valance bandgap, but they did not act as charge carriers or their role as recombination centre minimized. To improve the nunneries nonmetals-TiO₂ photo catalyst light absorption into visible light has been reported. Among them, N-TiO₂ and C-TiO₂ nanomaterials have improved photocatalysis activity (15; 16).

Ansari et all reported that the ball milling method can shift the light absorption ability from UV to visible light and red phosphorus can effectively improve the photocatalysis of TiO₂ (17-19). TiO₂ nano-wires (Ti-NWs) and nanflaks (Ti-NFs) Hydrothermal heat treatment increases the optical response and separation of photogenerated charge carriers (20). We have reported the first, fast, cheap, and effective synthesis method in our previous work (21) and we applied that method to our current work TiO₂/SAC nanocomposite material without using any harmful organic solvent with a low temperature of 8°C. We directly used titanium (IV) dioxide nanocrystals and Saccharin with LiBr salt without any further chemical process and purification. The CO₂ reduction process at the gas-solid interface on TiO₂-Sac-Li composite semiconductors is investigated by functional calculations and several characterization methods. Compared with nanosized TiO₂, the new TiO₂- Sac-Li indeed displays a high CO generation rate of 70.83 μ mol/g/h, which is 7 times higher than TiO₂ which shows enhancement in CO₂ reduction and an apparent improvement in charge carrier dynamic. The results indicate that CO₂ can be easily activated by the TiO₂-Sac-Li atoms on the surface. This work innovatively investigates CO₂ reduction in novel composite materials and helps to broaden the applications of composite materials semiconductors. Characterization. photoreduction activity, and mechanism of action of the new TiO₂/SAC/LiBr composite catalyst particles are discussed.

2. Material

Titanium dioxide (TiO₂, 99%) was purchased from Beijing Shiji as nanocrystal powders. Saccharine (SAC) from Energy chemical, Triethylamine (TEA 500 ml, 99%) from Sinopharm Chemical Reagent Co., Ltd, Water (18.2 $\mu\Omega$ /cm), lithium chloride (LiCl 96%), lithium bromide (LiBr) from Chemical Reagent, all chemical reagents above purchased commercially and used without further purification.

2.1. Synthesis of Metal Oxide/SAC Composite Catalysts

The composite materials were synthesized with a similar method to our previous report. TiO_2 was manually ground with commercial saccharin (300 mg each, mass ratio of 1:1) in mortar and pestle for 10 minutes under air and ambient conditions. The powder named sample N1. The acquired powder is then mixed with deionized water and LiBr salt (e.g., 0.3 mg sample powder in 10 mL water). The mixture was heated in a Teflon-lined stainless steel acid digestion bomb (ZhongKaiYa Instrument) at 80 °C.

2.2. Characterisation

The prepared sample phase pattern was collected by powder X-ray diffraction XRD-(Rigaku Co) Smart Lab 6000 x-rav diffractometer using Cu Ka ($\lambda = 1.5418$ Å) irradiation (40 kV, 30 mA) in the 2θ range from 20° to 80° with 0.02° scan step. To analyse the morphology and structure of the samples, scanning electron microscopes (SEM; Hitachi SU3500) operated at the accelerating voltage of PerkinElmer Fourier-transform 20.0 kV, infrared spectroscopy (FTIR) was measured Shimadzu using **IRAffinity-1S** а spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi XPS spectrometer (Thermo Fisher Scientific) using Al Ka radiation. The obtained spectra were calibrated based on the C 1s peak at 284.8 eV.

2.3. Catalytic Reaction

The catalytic reaction of the CO_2 reduction test was performed in a closed stainless reactor 120 mL in capacity with a connected top quartz glass for light irradiation. 1.4 mg of composite was weighed in a 60 mL quartz container, added 100 µL of deionized water and sacrificial agent (TEA) 1:1, the mixture was sonicated in a water bath for 5 minutes to attach water with the catalysis. Then, the reactor was filled with air, and the mixture container was evacuated by a pump before executing a carbon dioxide reduction reaction. The system washed with refilling into the reactor (0.1 MPa of pure CO₂, Beijing Beiwen Gas Comp. 99.999%) repeated 10 times. The performance of the provided catalyst was tested under full spectrum irradiation (300 W xenon with photocatalytic wav-length $\lambda > 320$ nm and optical density of 2550.4 mW cm⁻²). To keep the reaction at room temperature and control the temperature inside the reactor, connect cooling water to the reactor and set it at 24 °C. After the reaction, the formed products were collected every 2 hours. Produced CO was analysed by GC (Shimadzu GC2014C) with a TCD detector using argon gas as carrier gas.

3. Results and Discussion

Synthesis and characterisation of TiO₂/SacLi composite materials. The primary contact between materials obtains with grinding in mortal and pestle in 10 minutes. During the grinding of composite materials may instruct with the component. Saccharine is an organic sugar and it seems pesty during the grinding with TiO₂ nanoparticle powder, after 5 minutes of grinding did not observe a pesty feeling, which is probably because TiO₂ nanoparticles covered saccharine molecules and separated on the saccharin chunks.

The morphology of the TiO₂-Sac-LiBr materials provided with SEM, and Fig.1(A) denoted the ground TiO₂-SAC-LiBr materials. Fig.1A shows that after the hand grinded of the materials the saccharin looks like a large chalk that almost has a clean surface and TiO₂ separated on the saccharin molecules have low interaction with TiO₂ nanocrystals.

The schematic look of the saccharin is shown in Figure 1. The saccharin molecules have 3 oxygen functional groups after the hydrothermal treatment probably Lithium coordinated with the oxygen of the saccharin molecule similarly to Na-SAC. After milling these composite semiconductors, TiO_2 nanocrystals covered the saccharin molecules and changed the molecule's environment of the TiO_2 nanocrystals. The morphology studies of the materials have been studied in the SEM section. After hydrothermal treatment, TiO_2 nanocrystals interact deeply with saccharine molecules and are covered with the TiO_2 nanocrystals. Moreover, the saccharine molecules have reduced their size after hydrothermal treatment therefore the smaller size of the molecules made stronger instruction between each other. Instruction of smaller molecules also simplifies the electron transfer between molecules and this operation will provide better reduction ability for the semiconductors.



Figure 1. SEM images of (A) TiO₂-Sac-LiBr hand milled, (B) Hydrothermal synthesized TiO₂- Sac-LiBr.

3.1. XPS and FT-IR spectra

X-ray photoelectron spectroscopy (XPS) was utilized to measure compositions and surface functional groups of the composite materials to ensure the surface analysis. The xps peaks has been listed in below.

The measured xps data is as follows: TiO_2 (N0): (C-C and O-C=C Peaks at 284.80, 286.52eV. Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks at 459.40, and 465.10 eV. Ti-O and V_o peaks at 530.64 and 532.06 eV). N1: (C-C, C-N, and O-C=C Peaks at 284.80, 285.49, and 288.81 eV. Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks at 458.73, and 464.46 eV. Ti-O, Ti-OH, and Vo peak at 529.87, 530.32, and 531.97 eV. Nxps: 398.65, 400.09, 401.58, and S peaks are 168.57 and 169.67 respectively).

N3: (C-C, C-N, and O-C=C Peaks at 284.80, 285.28, and 288.79 eV. Ti 2p_{3/2} and Ti 2p_{1/2} peaks at 458.69, and 464.42 eV. Ti-O, Ti-OH, and Vo peak at 529.85, 530.46, and 531.91 eV. Nxps: 398.74, 399.97, 401.37, and S peaks are 168.39 and 169.65 respectively). N2: (C-C, C-N, and O-C=C Peaks at 284.80, 285.28, and 288.79 eV. Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks at 458.86, and 464.61 eV. Ti-O, Ti-OH, and Vo peak at 531.12, 530.46, and 532.79 eV. Nxps: 398.67, 399.95, 402.31, and S peaks are 168.17 and 169.14 respectively). As shown in Figure 3A, the full XPS shows four peaks of C 1s calibrated according to the reference 284.80 eV. The high-resolution XPS C1s spectra reveal that C exists mostly in the form of C-C and O-C=C in TiO₂ and C-N start to form after the addition of saccharine on TiO₂.

The XPS N 1s spectra could be decomposed into the 3 peaks. As shown in Figure 2d, the deconvolution of the S 2p spectra indicates the presence of the -C-SOx- group, which was located at 168.4 eV and 169.6 eV.



Figure. 2. XPS spectrum of the Carbon (A), Ti (B), and Oxygen (b).



Figure 3. XPS spectrum of Nitrogen (A), and Sulfur (B).

As shown in Figure 4 (4A and 4B), In the FT-IR spectrum of N1 and N2, the peaks at 1269-1126 cm-1 are attributed to the stretching of SO₂ bonds of the saccharin. The peaks at 1684 cm-1 are corresponding to the vibration of carboxylate groups of saccharin molecules. The

strong absorption at 1000 cm⁻¹ results from the amide bonds of saccharin molecules. the corresponding vibration of these bonds denoted the presence of the saccharin molecules in the composite materials with TiO_2 .



Figure 4. In powder XRD after adding TiO₂ and grinding it some of the XRD peak intensity has decreased showing that saccharine molecules covered TiO2 nanocrystals. (A) FT-IR spectrum of N1, (4B) N2, (4C) P-XRD pattern of the samples, and (4D) FT-RP spectrum of the N1 after calcination at 500 C.

After heating at 80 C in an autoclave it still shows the characteristic bands of the saccharin in the FT-IR spectrum, some changes have been observed after applying hydrothermal treatment, which may be because of the strong instruction with metal oxide during the heating period. Moreover, after the hydrothermal, the crystal form of the saccharin is impaired and milted and dissolved in the presence of water due to attaching the Li⁺¹ it becomes an ionic compound that may dissolve in water and heat. After calcination as shown in Figure 4.D the saccharin molecules were removed from the composite material at 500 C in the presence of oxygen. We did not observe any corresponding vibration band in the FT-IR after the calcination of the catalyst the reason is the oxidation of the saccharin during the calcination with air (O₂) figure. 4D which declared that saccharin molecules are no longer present in the system. due to the saccharin is an organic compound after calcination at 500 C, may decompose at high temperatures. The results after CO_2 reduction reaction experiments have dropped with less production of CO. This result also shows that after removing the saccharin

6

7

molecules the P-XRD pattern also conforms to the decomposition of the saccharin after calcination.

This reduction in impedance implies diminished electron-hole recombination, a crucial factor for efficient photoelectron transfer. Our observations collectively confirm the facilitated interphase photoelectron transfer in the semiconductor system. Furthermore, the efficiency of electron conduction followed the order of samples N2>N1. This trend was consistent with their CO₂ reduction reaction (CO₂RR) performance, where the photocatalytic activities of TiO₂-SAC-LiBr significantly outperformed the sample lacking Sac and Li metal (Figure 4B). Importantly, this correlation between catalytic activity and photoelectron transfer efficiency underscores the critical role of the latter as an indicator of interphase contact. Additionally, scanning electron microscopy (SEM) analysis of sample N2 revealed interdigitated TiO₂ on SAC surfaces, signifying decreased interfacial interaction compared to sample N1. These findings provide valuable insights for designing efficient semiconductor systems for energy-related applications.

Our newly synthesized TiO_2 -SAC-LiBr heterojunction photocatalyst demonstrates a significant enhancement in CO_2 reduction activity compared to previously reported Tibased composites, non- metal doped materials, and metal-organic frameworks (MOFs) as evidenced by data in Table 1.

This superior performance is attributed to the presence of the heterojunction, which facilitates efficient charge separation and transfer, extending the lifetime of photogenerated charges that drive the reaction. Additionally, LiBr is postulated to promote CO₂ adsorption and activation on the catalyst surface, further enhancing the overall CO₂RR process. To ensure the catalytic activity of the catalyst applied cycling process. The shows that the catalyst performance after 3th cycle still unchanged. Notably, the catalyst weight has been reduced after every cycle due the washing the samples that probably effect the activity of CO₂ reduction to CO. Moreover, the application confirmed the catalytic activity of the synthesized composite material. After photocatalyst performance we noticed the high selectivity of the composite catalyst after observing just CO without any other production. The N2 shows higher activity than the Ti and different catalysts reported as shown in the table 1. The successful application of the metal oxide organic sugar with a green synthesis method verifies a greet step to further usage of the saccharin in term of the industrial application.

Composition	Reaction system	Light source	CO (umol/g/h)	Ref
TiO ₂ -RP	Water/TEA	300 W Xe Lamp	54.60	(21)
TiO ₂ /C@ZnCo-Zif-L	Water	300 W Xe Lamp	28.60	(22)
Porous 2D ZnO@g-CN	Water vapor	300 W Xe Lamp $\lambda > 420 \text{ nm}$	30.50	(23)
P-doped g-C ₃ N ₄	Water	$300 \text{ W} \text{ Xe Lamp } \lambda \ge 420 \text{ nm}$	31.22	(24)
TiO ₂ -SAC-LiBr	Water/TEA	300 W Xe Lamp	70.83	This
				work

Table 1. Photocatalytic CO₂RR Performance of Selected Composite Catalysts Reported in 2020–2022

The promotion of the photocatalytic activity of N_2 over similar composite catalyst indicate the high efficiency of the novel synthesized Ti-SAC composite. The remarkable CO production activity positions the TiO₂-SAC-LiBr composite as a promising candidate for CO_2 reduction applications. Future research can focus on elucidating the underlying mechanisms and optimizing the material's properties to achieve even greater CO production and selectivity, paving the way for scalable and sustainable CO_2RR technologies for a carbon-neutral future.

4. Conclusion

The study aimed to evaluate different methods for preparing composite materials based on TiO_2 and to determine their toxicity profiles and complex methods. Our findings indicate that the presence of organic saccharin and Li metal is a crucial factor in determining the final composite materials. In particular, we found that the inclusion of organic saccharin played a critical role in enhancing the CO_2 reduction rate (CO₂RR) of the composite materials. This observation can be attributed to the fact that organic saccharin contains nitrogen and sulfur, which act as catalytic centres and help facilitate the reduction of CO₂ to CO. Likewise, the incorporation of Li metal also played a crucial role in enhancing the CO2RR of the composite materials. This can be attributed to the fact that Li metal can act as an electron donor and facilitate the reduction of CO_2 to CO. Moreover, Li metal has a high surface area and can provide a large number of active sites for CO₂ reduction.

Furthermore, we demonstrated that the most effective method to increase the CO₂RR and convert it to CO involves using a grinding and hydrothermal method with water solvent. This method is important to consider as it does not require the use of any organic solvents, which are often toxic and harmful to the environment. Instead, water is used as a solvent, making the method more sustainable and environmentally These friendly. findings highlight the significance of this novel method for preparing TiO₂-based composite materials and its potential benefits for the field of CO₂RR. The method has the potential to be applied in various industrial applications, including the production of fuels and chemicals from CO₂, which can contribute to mitigating climate change and reducing our dependence on fossil fuels. Overall, the study's findings demonstrate the importance of considering the toxicity profiles and complex

methods in the preparation of composite materials and the potential benefits of using sustainable and environmentally friendly methods in CO_2 reduction reactions.

References

- Batur J, Mudaber S. 2023. Differences in Heavy Metals Adsorption on Natural, Modified, and Synthetic Zeolites-A Review. Journal of the Turkish Chemical Society Section A: Chemistry 10:847-60
- [2] Gao W, Liang S, Wang R, Jiang Q, Zhang Y, et al. 2020. Industrial carbon dioxide capture and utilization: state of the art and future challenges. Chemical Society Reviews 49:8584-686
- [3] Yu D-G, He L-N. 2021. Introduction to CO2 utilisation. Green Chemistry 23:3499-501
- [4] Sun H, Wang A, Zhai J, Huang J, Wang Y, et al. 2018. Impacts of global warming of 1.5°C and 2.0°C on precipitation patterns in China by regional climate model (COSMO-CLM). Atmospheric Research 203:83-94
- [5] Li Y, Tao H, Su B, Kundzewicz ZW, Jiang T. 2019. Impacts of 1.5 °C and 2 °C global warming on winter snow depth in Central Asia. Science of The Total Environment 651:2866-73
- [6] Iwase M, Yamada K, Kurisaki T, Prieto-Mahaney OO, Ohtani B, Wakita H. 2013. Visible-light photocatalysis with phosphorus-doped titanium (IV) oxide particles prepared using a phosphide compound. Applied Catalysis B: Environmental 132-133:39-44
- [7] Doustkhah E, Assadi MHN, Komaguchi K, Tsunoji N, Esmat M, et al. 2021. In situ Blue titania via band shape engineering for exceptional solar H2 production in rutile TiO₂. Applied Catalysis B: Environmental 297:120380
- [8] Wang Z, Song J, Xu Y, Chen W, Zhang M, et al. 2024. Treatment of MB wastewater with a Fe– RGO/TiO2/PTFE photocatalytic composite membrane. New Journal of Chemistry
- [9] Guidetti G, Pogna EAA, Lombardi L, Tomarchio F, Polishchuk I, et al. 2019. Photocatalytic activity of exfoliated graphite–TiO₂ nanoparticle composites. Nanoscale 11:19301-14
- [10] Wang R, Hashimoto K, Fujishima A, Chikuni M, Kojima E, et al. 1997. Light-induced amphiphilic surfaces. Nature 388:431-2
- [11] Takagi S, Makuta S, Veamatahau A, Otsuka Y, Tachibana Y. 2012. Organic/inorganic hybrid

electrochromic devices based on photoelectrochemically formed polypyrrole/ TiO_2 nanohybrid films. Journal of Materials Chemistry 22:22181-9

- [12] Tang J, Durrant JR, Klug DR. 2008. Mechanism of Photocatalytic Water Splitting in TiO₂. Reaction of Water with Photoholes, Importance of Charge Carrier Dynamics, and Evidence for Four-Hole Chemistry. Journal of the American Chemical Society 130:13885-91
- [13] Mekasuwandumrong O, Jantarasorn N, Panpranot J, Ratova M, Kelly P, Praserthdam P. 2019. Synthesis of Cu/TiO₂ catalysts by reactive magnetron sputtering deposition and its application for photocatalytic reduction of CO₂ and H₂O to CH₄. Ceramics International 45:22961-71
- [14] Guo Z, Zhang L, Jiu H, Liang D, Wang C, et al. 2024. TiO₂-modified two-dimensional composite of nitrogen-doped molybdenum trioxide nanosheets as a high-performance anode for lithium-ion batteries. Dalton Transactions
- [15] Dong F, Guo S, Wang H, Li X, Wu Z. 2011. Enhancement of the Visible Light Photocatalytic Activity of C-Doped TiO₂ Nanomaterials Prepared by a Green Synthetic Approach. The Journal of Physical Chemistry C 115:13285-92
- [16] Arifin K, Yunus RM, Minggu LJ, Kassim MB. 2021. Improvement of TiO₂ anotubes for photoelectrochemical water splitting: Review. International Journal of Hydrogen Energy 46:4998-5024
- [17] Liu G, Niu P, Yin L, Cheng H-M. 2012. α-Sulfur Crystals as a Visible-Light-Active Photocatalyst.

Journal of the American Chemical Society 134:9070-3

- [18] Liu G, Niu P, Cheng H-M. 2013. Visible-Light-Active Elemental Photocatalysts. ChemPhysChem 14:885-92
- [19] Ansari SA, Cho MH. 2016. Highly Visible Light Responsive, Narrow Band gap TiO₂ Nanoparticles Modified by Elemental Red Phosphorus for Photocatalysis and Photoelectrochemical Applications. Scientific Reports 6:25405
- [20] Gopal NO, Basha MH. 2018. TiO₂ nano-flakes with high activity obtained from phosphorus doped TiO₂ nanoparticles by hydrothermal method. Ceramics International 44:22129-34
- [21] Li R, Batur J, Bian H, Wang Y-J, Duan Z, et al. 2022. Green and Facile Fabrication of Metal Oxide/Red Phosphorus Composite Catalysts for CO₂ Photoreduction. ACS Sustainable Chemistry & Engineering 10:8658-68
- [22] Zhou A, Dou Y, Zhao C, Zhou J, Wu X-Q, Li J-R. 2020. A leaf-branch TiO₂/carbon@MOF composite for selective CO₂ photoreduction. Applied Catalysis B: Environmental 264:118519
- [23] Guo Q, Fu L, Yan T, Tian W, Ma D, et al. 2020. Improved photocatalytic activity of porous ZnO nanosheets by thermal deposition graphene-like g-C3N4 for CO₂ reduction with H₂O vapor. Applied Surface Science 509:144773
- [24] Huang X, Gu W, Hu S, Hu Y, Zhou L, et al. 2020. Phosphorus-doped inverse opal $g-C_3N_4$ for efficient and selective CO generation from photocatalytic reduction of CO₂. Catalysis Science & Technology 10:3694-70