

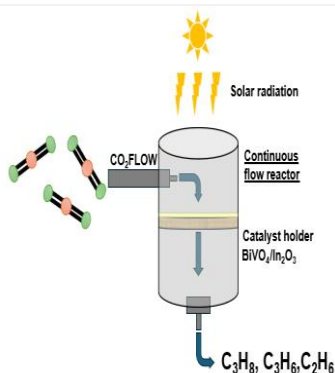
Synthesis and characterization of the BiVO₄/In₂O₃ heterojunction for photocatalytic CO₂ conversion in a continuous flow reactor.

POSTER

Ph.D. Student: Y

Journal: NONE

Perez-Magdalenó, M.¹, Hernández-Ramírez, A.,^{*1} Guzmán-Mar, J.,¹ Murillo-Sierra, J.C.² (1) Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Lab. de Fotocatálisis y Electroquímica Ambiental, Av. Universidad S/N, Ciudad Universitaria, San Nicolás de los Garza, N. L., México. Aracely.hernandezrm@uanl.edu.mx (2) Universidad Tecnológica Metropolitana, Facultad de Ciencias Naturales, Matemáticas y Medio Ambiente, Las Palmeras 3360, Ñuñoa, Santiago, Chile.



In this study, the BiVO₄/In₂O₃ heterojunction was synthesized by the solvothermal method for photocatalytic CO₂ reduction. For comparative purposes, the semiconductors In₂O₃ and BiVO₄ were also synthesized. The prepared materials were characterized by XRD, UV-Vis-DRS, SEM, and N₂ physisorption. Electrochemical studies were conducted to evaluate the conduction band potentials of the materials. The highest conversion of CO₂ was achieved using the heterojunction compared with individual In₂O₃ and BiVO₄ catalysts. The main product generated from the CO₂ conversion was carbon monoxide using the individual and coupled semiconductors. However, in addition to CO, the BiVO₄/In₂O₃ photocatalyst was able to produce light hydrocarbons such as propane (C₃H₈), propylene (C₃H₆), and ethane (C₂H₆).

Introduction

Over the last few years, many strategies have been studied to decrease the CO₂ emissions into the atmosphere. Among them, photocatalytic CO₂ reduction for obtaining valuable hydrocarbons represents one of the most promising strategies to reduce CO₂ emissions using solar radiation as an energy source [1]. Recently, monoclinic BiVO₄ (E_g = 2.4 eV) and hexagonal In₂O₃ (E_g = 2.85 eV) have been considered viable candidates for photocatalytic processes due to its advantageous characteristic such as good stability and excellent electrical properties. Also, these materials exhibit activity under visible light irradiation [2,3]. Due to the aforementioned reasons, the purpose of this study was to synthesize BiVO₄/In₂O₃ heterojunction via the solvothermal method to evaluate its photocatalytic performance in the CO₂ conversion to value-added products.

Material and Methods

All the chemicals including bismuth nitrate (Bi(NO₃)₃·5H₂O), ammonium metavanadate (NH₄VO₃), In(NO₃)₃·XH₂O and urea (CO(NH₂)₂) were purchased from Sigma Aldrich. All materials were of analytical grade and used without further purification.

Preparation by BiVO₄

The BiVO₄ (BVO) was synthesized by the hydrothermal method according to Obregon *et al.* [4]. 1.5 g of Bi(NO₃)₃·5H₂O were dissolved in 30 mL of HNO₃ 0.02 M (solution A). At the same time, 0.6 g of NH₄VO₃ was dissolved in 30 mL of water (solution B). Solution B was added dropwise to solution A to form a yellowish suspension. The pH was adjusted

to 9 using NH₄OH 7.5 M. The resultant suspension was transferred into a Teflon recipient inside of stainless-steel autoclave at 100 °C for 2 hours. The product was washed and dried. The obtained sample was calcinated at 400 °C for 2 hours.

Preparation of BiVO₄/In₂O₃

The 10 % BiVO₄/In₂O₃ (BVO/InO) was synthesized by a simple hydrothermal method. The previously synthesized BiVO₄ was dispersed in a mixture of 25 mL of diethylene glycol and 10 mL of H₂O under magnetic stirring for 1 h. Lately, 2.16 g of In(NO₃)₃·XH₂O was added and stirred for an additional hour. Subsequently, 2.0 g of urea was added to the mixture and stirred for one hour. The precipitate was transferred into a Teflon recipient inside of stainless-steel autoclave at 200 °C for 18 h. The final product was washed, dried, and calcinated at 500°C for 3 hours.

Photocatalytic CO₂ reduction

The experiments were performed in a photocatalytic CEL-GPRT100 reactor. Diluted CO₂ was fed to the reactor (He 10% v/v balance) with a flow rate of 2 mL min⁻¹ and passed through a bubbler to obtain the water vapor. The catalyst (250 mg) was evenly supported over the catalyst holder. A 300 W Xe lamp was used as radiation source (300-1100 nm). The generated products were analyzed using a gas chromatography system (GC-FID/TCD Agilent Technologies 8890).

Results and Discussion

Fig. 1a) shows the diffraction patterns of the synthesized photocatalysts. The main reflections of

single BVO are observed at $2\theta = 28.80^\circ$ (013), 30.39° (004), 34.38° (200) and 35.10° (020) corresponding to monoclinic phase of BiVO_4 (marked with a circle, PDF 01-074-4894). The pure In_2O_3 was indexed to the cubic phase (marked with a cross, PDF 01-071-2194) with the main peaks at 21.14° (211), 30.74° (222), 35.54° (400) and 50.98° (440). However, the BVO/In heterojunction presents the reflections corresponding to monoclinic BVO (circle marks) and those at 30.84° (104), 32.49° (110), 45.62° (024) and 50.16° (116) correspond to InO hexagonal phase (marked with an asterisk, PDF-00-022-0336). In the heterojunction, incorporating BiVO_4 causes a re-arrangement of the In_2O_3 crystalline phase from cubic to hexagonal phase. The hexagonal phase is more beneficial than the cubic phase due to its six square faces generating different surface absorption sites, improving its absorption and conversion of solar energy [3].

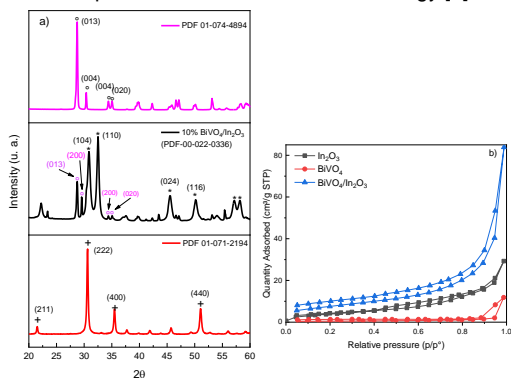


Fig. 1 a) XRD patterns and b) N_2 adsorption-desorption isotherms of the prepared photocatalyst.

Fig. 1b) shows the N_2 adsorption-desorption isotherms of synthesized materials. According to IUPAC classification, the BVO/InO and BVO photocatalysts exhibit a type III isotherm, characteristic of non-porous or macroporous solids. Otherwise, InO presents an isotherm type IV that is characteristic of mesoporous materials. When the oxides were coupled an increase in the specific surface area was observed compared with the individual semiconductors (Table 1). This is a critical parameter because specific surface area could increase the number of adsorption sites, beneficial to CO_2 conversion [4].

Fig. 2a shows the results from the CO_2 photocatalytic reduction, where CO was detected as the main product generated by all photocatalysts. However, additional to CO, the heterojunction BVO/InO (Fig.2b) produced secondary products as C_3H_8 ($336 \mu\text{mol m}^{-2} \text{h}^{-1}$), followed by C_3H_6 ($64.60 \mu\text{mol m}^{-2} \text{h}^{-1}$) and C_2H_6 ($3.39 \mu\text{mol m}^{-2} \text{h}^{-1}$). This behavior was attributed to an improvement in the charge separation of electron-hole pairs, suppressing the recombination phenomenon.

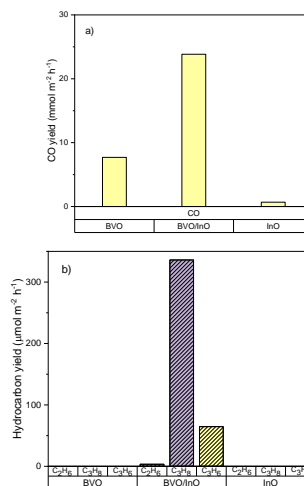


Fig. 2 Yield production of continuous photocatalytic reaction for 3 h at 80°C and 2 mL/min flow rate. a) CO, b) C_2H_6 , C_3H_6 and C_3H_8 .

Table 1. Textural and electronic properties of the synthesized catalyst

Photo-catalyst	E_g (eV)	Specific surface area (m^2/g)	Average pore size (nm)	E_{CB} (V)
BVO	2.20	1.73	24.84	-0.55
InO	2.86	15.84	9.21	-0.10
BVO/InO	2.89	27.62	17.17	-0.30

Conclusions

$\text{BVO}_{10\%}/\text{InO}$ heterojunction was prepared by the solvothermal method. The CO_2 conversion experiments using individual and coupled oxides indicated that BVO and InO only produce CO under UV-Vis light. The coupling of BVO and InO promoted the generation of light hydrocarbons due to the improvement of the charge carrier transfer being more selective to propane production.

References

- [1] Lingampalli S & Ayyub M. ASC Omega. 7 (2017). 2740.
- [2] Trinh D & Channei D. Res. Chem. Intermed. 45 (2019). 1.
- [3] Chang P, Wang Y. Chem. Eng. J. 450 (2022).
- [4] Obregón S., Caballero A. Appl Catal B-environ. (2012)
- [5] Chico-Vecino M *et al.* J. Environ Chem Eng. 11 (2023).

Acknowledgements

Authors acknowledge CONAHCYT Project No. A1-S-4026.