CHEMICAL ENGINEERING TRANSACTIONS
VOL. 106, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Peck Loo Kiew, Hon Huin Chin

ISBN 979-12-81206-05-2; **ISSN** 2283-9216
DOI: 10.3303/CET23106119

Photocatalytic CO_2 Reduction to Produce Cleaner Fuels Over Vanadium Aluminium Carbide (V_2AlC) Supported TiO_2 Composite

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Photocatalytic reduction of CO_2 to produce cleaner fuels is a promising approach for climate action to achieve sustainable development goals. Herein, noble metal-free vanadium aluminium carbide (V_2AlC) MAX as cocatalysts with TiO_2 to construct 2D/0D V_2AlC/TiO_2 heterojunction for photocatalytic CO_2 reduction with water to produce CO and CH_4 has been investigated. Coupling V_2AlC with TiO_2 was beneficial in increasing visible light absorbance capacity and charge separation efficiency. Using 10 % V_2AlC/TiO_2 composite, the highest CO and CH_4 production of 522 and 78.3 μmol g^{-1} h^{-1} were achieved, which were much higher than using pristine TiO_2 samples. This significant enhancement in photocatalytic efficiency was due to good interface interaction with proficient charge carrier separation. The findings of this work would be beneficial for further investigation in the design and fabrication of noble metal-free composite materials for energy and environmental applications.

1. Introduction

Photocatalytic CO_2 reduction using a semiconductor and energy source (light) produces various chemicals and fuels such as methane, methanol, carbon monoxide, acetic acid, and formic acid. For these processes, various photocatalysts including TiO_2, CdS, ZnO, and WO_3 were explored. Due to its low-cost, strong photostability, and suitable redox potential, TiO_2 is one of the most extensively researched semiconductors (Wang et al., 2023). TiO_2 has a number of advantages, however, its photoactivity and selectivity are reduced because of charge carrier recombination (Ren et al., 2023). As a result, TiO_2 photoactivity can be enhanced by loading with metals and using low-cost materials to develop TiO_2-based composites (Beenish et al., 2018).
MAX materials with the general formula $M_{n+1}AX_n$, are made of three elements, transition metals (M element), elements of group III or IV (A element) and either C or N elements (X element), which have layered structures and compact sheets. Multiple researchers have become interested in them due to their numerous distinctive qualities, including strong conductivity, charge carrier transfer ability, inexpensive cost, and improved stability (Bai et al., 2022). In the past, titanium aluminium carbide (Ti_3AlC_2) MAX was put to the test in photocatalytic applications and found to be effective in reducing CO_2 levels. Another significant MAX that is based on multiple oxidation states is V_2AlC because vanadium possesses several oxidation states. This MAX has various distinguishing qualities, including a greater capacity to absorb visible light, superior electrical conductivity, and chemical and thermal stability (Presser et al., 2012). Previous $V_2AlC/g\text{-}C_3N_4$ was invested for photocatalytic water splitting, and higher hydrogen production was achieved (Tahir et al., 2021). As a result, V_2AlC can be further investigated for use as a photocatalyst and producing a V_2AlC/TiO_2 heterojunction would improve the effectiveness of CO_2 reduction to yield useful chemicals and fuels.
In this work, V_2AlC supported TiO_2 composite for photocatalytic CO_2 reduction in a fixed bed photoreactor has been investigated. The composites were synthesized using a facile sol-gel single step method to get good interface interaction between both the materials. The composites were analyzed using XRD, UV, visible, SEM, and PL characterization techniques. The composite found promising for selective CO_2 reduction to cleaner fuels with higher efficiency. The reaction mechanism was proposed based on findings of characterization and experimental results.

Paper Received: 4 August 2023; Revised: 06 September 2023; Accepted: 25 September 2023
Please cite this article as: Tahir M., 2023, Photocatalytic CO2 Reduction to Produce Cleaner Fuels Over Vanadium Aluminium Carbide (V2AlC) Supported TiO2 Composite, Chemical Engineering Transactions, 106, 709-714 DOI:10.3303/CET23106119

2. Experimental

2.1 Catalyst Synthesis

V_2AlC/TiO_2 composite was synthesized using the sol-gel method. Titanium sol was obtained by hydrolyzing TTIP (Titanium (IV) isopropoxide (Sigma Aldrich)) in acetic acid (1 M) using 10 mL of TTIP that was dissolved in 2-propanol, in accordance with a procedure reported previously (Tahir 2020). Typically, specific amount of V_2AlC MAX (10 weight %) dispersed in 2-propanol was added to the titanium solution after stirring for 4 h. The suspension was then stirred for 24 h before being overnight oven dried at 100 °C. The final product was ground before being calcined at 500 °C for two hours and was given name V_2AlC/TiO_2 composite.

2.2 Catalyst Characterization

The purity and crystal phase structures were studied using X-ray powder diffraction (XRD) on a Bruker Advance D8 diffractometer (Rigaku Smart Lab-Cu-K, =0.154178 nm). The morphology was obtained using scanning electron microscopy (SEM, JEOL 6010 PLUS/LA). Using a 325 nm laser, photoluminescence (PI) spectroscopy was carried out (HORIBA Scientific) to measure the charges separation efficiency in the composite material. The UV-visible diffuse reflectance absorbance spectra were obtained using Carry 100 Agilent UV-vis spectrophotometer (model # G9821A).

2.3 Photoactivity test

The photocatalytic CO_2 reduction experiments were conducted using fixed bed photoreactor system. The primary reactor chamber, cooling fans integrated with lamps, mass flow controllers (MFC), and an online system for product analysis are all parts of the photocatalytic system. A water saturator was combined with the reactor system, in which CO_2 was passed to carry water vapours. A 150 mg photocatalysts was dispersed in the reactor bottom surface. The feed mixture entered the reactor from the top, passed over the catalyst surface, and then exited the reactor from the bottom surface. A feed combination (CO_2 and H_2O) was constantly fed into the reactor at 20 mL/min for 30 min prior to the experimentation to saturate the catalyst surface. The gas products were analyzed using GC which was integrated with TCD and FID detectors. After regular intervals of 30 min, samples were injected into GC using a gas-tight syringe and production of CO and CH_4 was calculated using GC results. All the experiments were conducted at normal temperature and atmospheric pressure.

3. Results and discussion

3.1 Materials analysis

Figure 1 (a) shows XRD patterns of TiO_2, V_2AlC and V_2AlC/TiO_2 composite samples. The XRD spectra of V_2AlC MAX shows two main peaks with 2-theta of 13.46° and 41.16° associated to (0 0 2) and (1 0 3) facets of V_2AlC MAX, and similarly reported previously in the literature (Madi et al., 2022). The XRD of TiO_2 confirms successful synthesis of anatase phase and was in accordance with JCPDS Card No. 01-084-1285. In V_2AlC/TiO_2 composite, all the original peaks were appeared, which confirm successful synthesis.

The UV-visible analysis of TiO_2 and V_2AlC/TiO_2 composite has been demonstrated in Figure 1 (b). TiO_2 was used to measure light absorption in the UV-visible range with a band edge just below 400 nm. The band edge was shifted to the visible light region, above 400 nm, when V_2AlC was coupled with TiO_2 to produce V_2AlC/TiO_2 composite with greater visible light absorbance. This is because pure V_2AlC MAX demonstrates higher visible spectrum light absorption because of its dark hue and conductive properties (Zhao et al., 2022). The band gap energies were estimated for pure TiO_2 and V_2AlC/TiO_2 composites were 3.40 and 2.96 eV. Previously, the energy of the band gap increased from 3.14 to 3.22 eV when Ti_3AlC_2 was added to TiO_2 (Tahir et al., 2022). All of these findings show that V_2AlC has features of visible light absorption and significantly lowers the band gap energy of TiO_2.

Figure 1 (c) discusses the findings of charges separation of TiO_2 and V_2Al/TiO_2 through photoluminescence (PI) analysis. Because charge recombination occurs at a faster rate in pure TiO_2, it is evident that it has the highest PL intensity. Loading V_2AlC into TiO_2, PI intensity was significantly decreased. This is because, MAX has greater ability to conduct electrons what keeps charges from recombining in the V_2AlC/TiO_2 composite, lowering the PL intensity noticeably. In a recent study, V_2C MXene and g-C_3N_4 were coupled and the PL intensity was significantly reduced as a result of effective charge carrier separation (Tahir, 2023).

Figure 2 shows the morphology of TiO_2, V_2AlC and V_2AlC/TiO_2 composites. The morphology of TiO_2 is depicted in Figure 2(a), where spherical-shaped particles of uniform size can be seen. The morphology of V_2AlC/TiO_2 composite is depicted in Figure 2(b-c). To give their strong interface interaction, TiO_2 particles are evenly dispersed throughout the V_2AlC structure. Further research revealed that the constant stirring during the sol-gel process in the presence of alcohols caused the bulk structure of V_2AlC to exfoliate. V_2AlC sheets were

completely covered with TiO_2 particles, providing good interaction that would be useful to transport charges. Figure 2 (d) shows EDX spectra of V_2AlC/TiO_2 composite, in which all the elements are present.

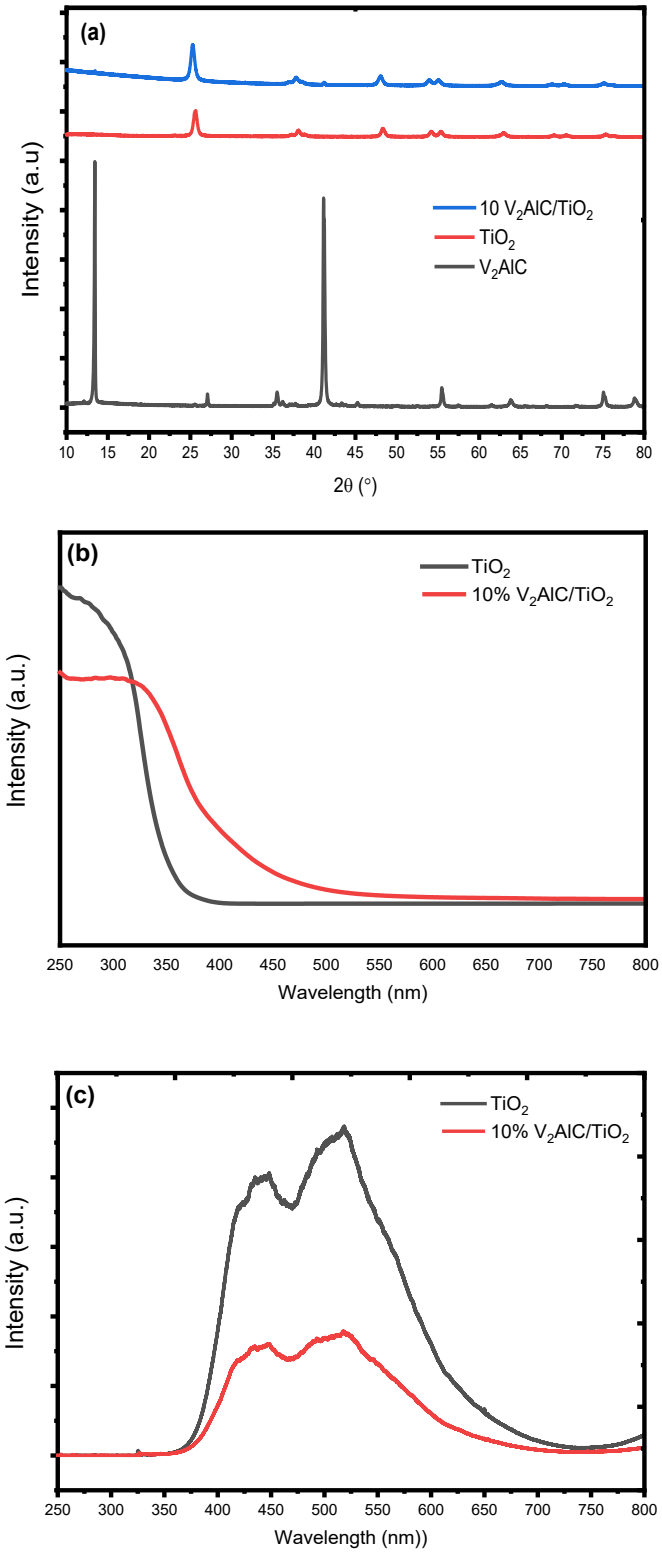

Figure 1: (a) XRD patterns of TiO_2 and V_2AlC/TiO_2, (b) UV-visible diffuse reflectance spectra of TiO_2 and V_2AlC/TiO_2 and (c) PL analysis of TiO_2 and V_2AlC/TiO_2 samples.

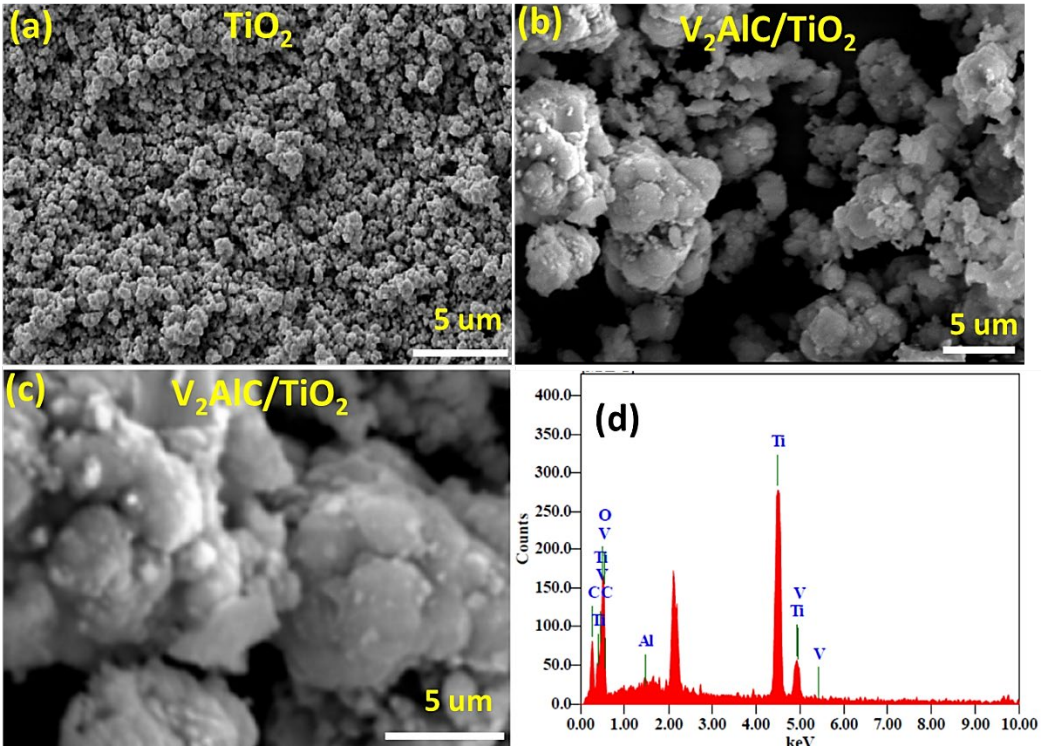

Figure 2: SEM analysis of (a) TiO_2, (b-c) V_2AlC/TiO_2, (d) EDX plot of V_2AlC/TiO_2 composite.

3.2 Photocatalytic hydrogen production

Blank experiments were first carried out to make sure that all of the products were produced only from the CO_2 and not from organic residues in the composite photocatalyst. These quality control tests show that the photocatalyst or feed mixture, both of which are necessary for any photocatalysis process, were not used to produce the products. The performance of TiO_2 and V_2AlC/TiO_2 composite for photocatalytic CO_2 reduction to CO and CH_4 is shown in Figure 3.

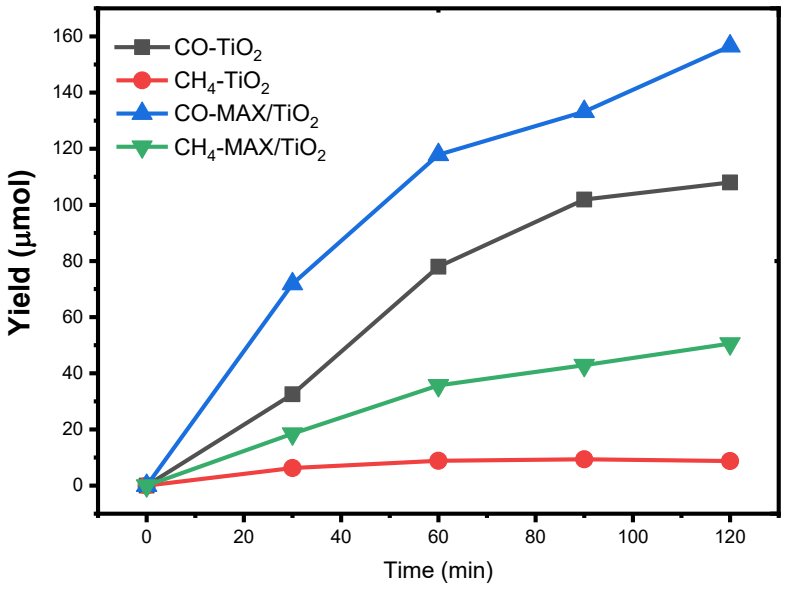

Figure 3: Performance comparison of TiO_2 and V_2AlC-loaded TiO_2 for photocatalytic CO_2 reduction to CO and CH_4 in a fixed bed reactor.

Using both the materials, CO was identified as the main product with lower amount of CH_4 formation. Obviously, production of CO and CH_4 was continuous over the entire irradiation time. Using pure TiO_2, lower amount of CO (108 µmol) and CH_4 (8.76 µmol) were produced, which were due to charge carrier recombination. When 10 % V_2AlC was loaded with TiO_2, CO and CH_4 production was increased to 156.53 and 50.6 µmol, respectively was achieved. Typically, production of CH_4 increment was much higher compared to CO, which was evidently due to more production and separation of photoinduced charge carrier. V_2AlC has potential to increase light absorbance and preventing the recombination of charges, which was beneficial to promote photocatalytic efficiency.

Numerous studies that are currently available discuss the use of TiO_2 based photocatalyst for photocatalytic CO_2 reduction to CO and CH_4 under UV and visible light irradiations. The photocatalytic activity for the selective reduction of CO_2 was shown to be improved in prior studies using 2D Ti_3AlC_2 MAX supported TiO_2 (Tahir 2020). Similar to this, when the photocatalytic CO_2 reduction were investigated using V_2AlC loaded g-C_3N_4 composite, the production of CO was greatly increased due to effective charge carrier separation (Tahir et al., 2022). In a different experiment, g-C_3N_4-loaded Ti_3C_2 was more effectively able to reduce CO_2 to CH_4 with high selectivity. In addition to improved light-harvesting ability, the greatly increased photoactivity was caused by improved CO_2 adsorption/activation (Hu et al., 2021). The performance of V_2AlC/TiO_2 for photocatalytic CO_2 reduction in view of production rate and selectivity are summarized in Table 1. Using TiO_2 and V_2AlC/TiO_2, CO was obtained as the main product during photocatalytic CO_2 reduction with H_2O. The highest CO and CH_4 production rates of 522 and 78.3 µmol g^{-1} h^{-1}, which was 1.45 and 2.68 folds higher for CO and CH_4 production than using pure TiO_2 samples. Similar to this, CO and CH_4 selectivity of 92.5 and 7.5 % over TiO_2, which was changes to 86.96 and 13.04 % when V_2AlC was coupled with TiO_2. This increase in CH_4 selectivity was due to more production and separation over V_2AlC/TiO_2 composite. Figure 4 shows photocatalytic CO_2 reduction over a V_2AlC/TiO_2 composite for the production of CO, and CH_4. The photogenerated charges on the TiO_2 under light irradiation can combine again because of their short life time. However, effective photoinduced charge separation was achieved by creating a heterojunction between V_2AlC and TiO_2 (Majhi et al., 2023). The holes were used for water oxidation, whereas, electrons were used for CO_2 reduction to CO and CH_4. Due to the increased electrical conductivity of MAX-based materials, higher separation of charges with their lowest recombination over TiO_2 can be achieved. The generation of CO was significantly higher than that of CH_4 because of the favourable reaction due to involving only two electrons, compared to eight electrons for CH_4 formation. Using V_2AlC/TiO_2 composite, production was CH_4 was higher due to more production and separation of charge carriers.

Table 1: Summary of yield rate and selectivity for CO and CH_4 production over TiO_2 and 10 % V_2AlC/TiO_2 composite in a fixed bed photoreactor

Catalyst	Production rate (µmol g^{-1} h^{-1})		Selectivity (%)	
	CO	CH_4	CO	CH_4
TiO_2	360	29.2	92.50	7.50
10 % V_2AlC/TiO_2	522	78.3	86.96	13.04

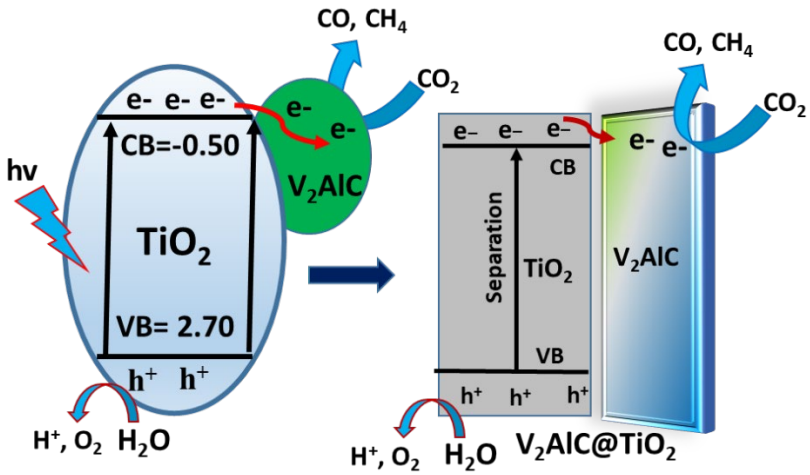

Figure 4: Schematic presentation of the proposed mechanism of V_2AlC/TiO_2 composite for photocatalytic CO_2 reduction to CO and CH_4 under UV-light irradiation.

4. Conclusions

The V_2AlC loaded TiO_2 composite was successfully synthesized suing sol-gel single step method. Higher light absorption and effective charge carrier separation during the photocatalytic process were responsible for increasing photocatalytic CO_2 reduction efficiency over V_2AlC/TiO_2 composite. CO and CH_4 were produced as the main products during CO2 reduction with water in a fixed bed photoreactor. The CO was produced at a significantly higher rate compared to methane due to using TiO_2 as a catalyst, which is supportive to produce more CO. When V_2AlC was coupled with TiO_2, production of CH_4 was increased. It can be concluded that to increase photocatalytic efficiency, V_2AlC MAX can be utilized directly as a cocatalyst with semiconductor materials rather than being converted into MXene using hazardous acids. The results of this research offer hope for developing more effective, structured photocatalytic systems that can be applied to both energy and environmental applications.

Acknowledgments

United Arab Emirates University (UAEU) provided funding for this work through a SURE PLUS grant (Grant # G00004006).

References

Bai J., Chen W., Shen R., Jiang Z., Zhang P., Liu W., Li X., 2022, Regulating interfacial morphology and charge-carrier utilization of Ti_3C_2 modified all-sulfide $CdS/ZnIn_2S_4$ S-scheme heterojunctions for effective photocatalytic H_2 evolution, Journal of Materials Science & Technology 112, 85-95.

Beenish T., Tahir M., and Amin N.A.S., 2018, Photocatalytic CO_2-Hydrogen Conversion via RWGSR over Ni/TiO_2 Nanocatalyst Dispersed in Layered MMT Nanoclay, Chemial Engineering Transactions 63, 115-120.

Hu J., Ding J., Zhong Q., 2021, Ultrathin 2D Ti_3C_2 MXene Co-catalyst anchored on porous $g\text{-}C_3N_4$ for enhanced photocatalytic CO_2 reduction under visible-light irradiation, Journal of Colloid and Interface Science 582(Pt B), 647-657.

Madi M., Tahir M., 2022, Fabricating $V_2AlC/g\text{-}C_3N_4$ nanocomposite with MAX as electron moderator for promoting photocatalytic CO_2-CH_4 reforming to CO/H_2, International Journal of Energy Research, 7666-7685.

Majhi S.M., Ali A., Greish Y.E., El-Maghraby H.F., Mahmoud S.T., 2023, V_2CT_x MXene-based hybrid sensor with high selectivity and ppb-level detection for acetone at room temperature, Scientific Reports 13(1), 3114.

Presser V., Naguib M., Chaput L., Togo A., Hug G., Barsoum M.W., 2012, First-order Raman scattering of the MAX phases: Ti_2AlN, $Ti_2AlC_{0.5}N_{0.5}$, Ti_2AlC, $(Ti_{0.5}V_{0.5})_2AlC$, V_2AlC, Ti_3AlC_2, and Ti_3GeC_2, Journal of Raman Spectroscopy, 43 (1), 168-172.

Ren G., Wei Z., Li Z., Zhang X., Meng X., 2023, Fabrication of S-scheme hollow $TiO_2@Bi_2MoO_6$ composite for efficiently photocatalytic CO_2 reduction, Materials Today Chemistry, 27, 101260.

Tahir B., Tahir M., Nawawi M.G.M., 2022, Highly stable honeycomb structured 2D/2D vanadium aluminum carbide MAX coupled $g\text{-}C_3N_4$ composite for stimulating photocatalytic CO_2 reduction to CO and CH_4 in a monolith photoreactor, Journal of Alloys and Compounds 927, 166908.

Tahir M., 2020, Enhanced photocatalytic CO_2 reduction to fuels through bireforming of methane over structured 3D MAX Ti_3AlC_2/TiO_2 heterojunction in a monolith photoreactor, Journal of CO_2 Utilization 38, 99-112.

Tahir M., 2023, Vanadium Carbide (V_2CT_x) MXene-Supported Exfoliated $g\text{-}C_3N_4$ with the Role of Hole Scavenger as a Rapid Electron Transfer Channel for Enhancing Photocatalytic CO_2 Reduction to CO and CH_4, Energy & Fuels 37(14), 10615-10630.

Wang Y., He W., Xiong J., Tang Z., Wei Y., Wang X., Xu H., Zhang X., Zhao Z., Liu J., 2023, MIL-68 (In)-derived $In_2O_3@TiO_2$ S-scheme heterojunction with hierarchical hollow structure for selective photoconversion of CO_2 to hydrocarbon fuels, Fuel 331.

Zhao R., Liu J., Nie Y., Wang H., 2022, Bismuth oxide modified V_2C MXene as a Schottky catalyst with enhanced photocatalytic oxidation for photo-denitration activities, Environmental Technologies, 1-12.