Photocatalytic CO$_2$ Reduction to Produce Cleaner Fuels Over Vanadium Aluminium Carbide (V$_2$AlC) 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$_2$AlC) MAX as cocatalysts with TiO$_2$ to construct 2D/0D V$_2$AlC/TiO$_2$ heterojunction for photocatalytic CO$_2$ reduction with water to produce CO and CH$_4$ has been investigated. Coupling V$_2$AlC with TiO$_2$ was beneficial in increasing visible light absorbance capacity and charge separation efficiency. Using 10 % V$_2$AlC/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). TiO$_2$ can be improved 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 Mn$+1$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$_3$AlC$_2$) 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$_2$AlC 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$_2$AlC/g-C$_3$N$_4$ was invested for photocatalytic water splitting, and higher hydrogen production was achieved (Tahir et al., 2021). As a result, V$_2$AlC can be further investigated for use as a photocatalyst and producing a V$_2$AlC/TiO$_2$ heterojunction would improve the effectiveness of CO$_2$ reduction to yield useful chemicals and fuels.

In this work, V$_2$AlC 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.
2. Experimental

2.1 Catalyst Synthesis

V2AlC/TiO2 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 V2AlC 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 V2AlC/TiO2 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-Kα =0.154178 nm). The morphology was obtained using scanning electron microscopy (SEM, JEOL 6010 PLUS/LA). Using a 325 nm laser, photoluminescence (PL) 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 CO2 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 CO2 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 (CO2 and H2O) 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 CH4 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 TiO2, V2AlC and V2AlC/TiO2 composite samples. The XRD spectra of V2AlC 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 V2AlC MAX, and similarly reported previously in the literature (Madi et al., 2022). The XRD of TiO2 confirms successful synthesis of anatase phase and was in accordance with JCPDS Card No. 01-084-1285. In V2AlC/TiO2 composite, all the original peaks were appeared, which confirm successful synthesis. The UV-visible analysis of TiO2 and V2AlC/TiO2 composite has been demonstrated in Figure 1 (b). TiO2 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 V2AlC was coupled with TiO2 to produce V2AlC/TiO2 composite with greater visible light absorbance. This is because pure V2AlC 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 TiO2 and V2AlC/TiO2 composites were 3.40 and 2.96 eV. Previously, the energy of the band gap increased from 3.14 to 3.22 eV when Ti3AlC2 was added to TiO2 (Tahir et al., 2022). All of these findings show that V2AlC has features of visible light absorption and significantly lowers the band gap energy of TiO2.

Figure 1 (c) discusses the findings of charges separation of TiO2 and V2AlC/TiO2 through photoluminescence (PL) analysis. Because charge recombination occurs at a faster rate in pure TiO2, it is evident that it has the highest PL intensity. Loading V2AlC into TiO2, PL intensity was significantly decreased. This is because, MAX has greater ability to conduct electrons what keeps charges from recombining in the V2AlC/TiO2 composite, lowering the PL intensity noticeably. In a recent study, V2C MXene and g-C3N4 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 TiO2, V2AlC and V2AlC/TiO2 composites. The morphology of TiO2 is depicted in Figure 2(a), where spherical-shaped particles of uniform size can be seen. The morphology of V2AlC/TiO2 composite is depicted in Figure 2(b-c). To give their strong interface interaction, TiO2 particles are evenly dispersed throughout the V2AlC structure. Further research revealed that the constant stirring during the sol-gel process in the presence of alcohols caused the bulk structure of V2AlC to exfoliate. V2AlC 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$_2$AlC/TiO$_2$ composite, in which all the elements are present.

Figure 1: (a) XRD patterns of TiO$_2$ and V$_2$AlC/TiO$_2$, (b) UV-visible diffuse reflectance spectra of TiO$_2$ and V$_2$AlC/TiO$_2$ and (c) PL analysis of TiO$_2$ and V$_2$AlC/TiO$_2$ samples.
Figure 2: SEM analysis of (a) TiO₂, (b-c) V₂AlC/TiO₂, (d) EDX plot of V₂AlC/TiO₂ 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 CO₂ 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 TiO₂ and V₂AlC/TiO₂ composite for photocatalytic CO₂ reduction to CO and CH₄ is shown in Figure 3.

Figure 3: Performance comparison of TiO₂ and V₂AlC-loaded TiO₂ for photocatalytic CO₂ reduction to CO and CH₄ in a fixed bed reactor.
Using both the materials, CO was identified as the main product with lower amount of CH₄ formation. Obviously, production of CO and CH₄ was continuous over the entire irradiation time. Using pure TiO₂, lower amount of CO (108 µmol) and CH₄ (8.76 µmol) were produced, which were due to charge carrier recombination. When 10 % V₂AlC was loaded with TiO₂, CO and CH₄ production was increased to 156.53 and 50.6 µmol, respectively was achieved. Typically, production of CH₄ increment was much higher compared to CO, which was evidently due to more production and separation of photoinduced charge carrier. V₂AlC 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 TiO₂ based photocatalyst for photocatalytic CO₂ reduction to CO and CH₄ under UV and visible light irradiations. The photocatalytic activity for the selective reduction of CO₂ was shown to be improved in prior studies using 2D Ti₃AlC₂ MAX supported TiO₂ (Tahir 2020). Similar to this, when the photocatalytic CO₂ reduction were investigated using V₂AlC loaded g-C₃N₄ composite, the production of CO was greatly increased due to effective charge carrier separation (Tahir et al., 2022). In a different experiment, g-C₃N₄-loaded Ti₃C₂ was more effectively able to reduce CO₂ to CH₄ with high selectivity. In addition to improved light-harvesting ability, the greatly increased photoactivity was caused by improved CO₂ adsorption/activation (Hu et al., 2021). The performance of V₂AlC/TiO₂ for photocatalytic CO₂ reduction in view of production rate and selectivity are summarized in Table 1. Using TiO₂ and V₂AlC/TiO₂, CO was obtained as the main product during photocatalytic CO₂ reduction with H₂O. The highest CO and CH₄ production rates of 522 and 78.3 µmol g⁻¹ h⁻¹, which was 1.45 and 2.68 folds higher for CO and CH₄ production than using pure TiO₂ samples. Similar to this, CO and CH₄ selectivity of 92.5 and 7.5 % over TiO₂, which was changes to 86.96 and 13.04 % when V₂AlC was coupled with TiO₂. This increase in CH₄ selectivity was due to more production and separation over V₂AlC/TiO₂ composite. Figure 4 shows photocatalytic CO₂ reduction over a V₂AlC/TiO₂ composite for the production of CO and CH₄. The photogenerated charges on the TiO₂ under light irradiation can combine again because of their short life time. However, effective photoinduced charge separation was achieved by creating a heterojunction between V₂AlC and TiO₂ (Majhi et al., 2023). The holes were used for water oxidation, whereas, electrons were used for CO₂ reduction to CO and CH₄. Due to the increased electrical conductivity of MAX-based materials, higher separation of charges with their lowest recombination over TiO₂ can be achieved. The generation of CO was significantly higher than that of CH₄ because of the favourable reaction due to involving only two electrons, compared to eight electrons for CH₄ formation. Using V₂AlC/TiO₂ composite, production was CH₄ was higher due to more production and separation of charge carriers.

Table 1: Summary of yield rate and selectivity for CO and CH₄ production over TiO₂ and 10 % V₂AlC/TiO₂ composite in a fixed bed photoreactor

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Production rate (µmol g⁻¹ h⁻¹)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>CH₄</td>
</tr>
<tr>
<td>TiO₂</td>
<td>360</td>
<td>29.2</td>
</tr>
<tr>
<td>10 % V₂AlC/TiO₂</td>
<td>522</td>
<td>78.3</td>
</tr>
</tbody>
</table>

Figure 4: Schematic presentation of the proposed mechanism of V₂AlC/TiO₂ composite for photocatalytic CO₂ reduction to CO and CH₄ under UV-light irradiation.
4. Conclusions

The V2AlC loaded TiO2 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 CO2 reduction efficiency over V2AlC/TiO2 composite. CO and CH4 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 TiO2 as a catalyst, which is supportive to produce more CO. When V2AlC was coupled with TiO2, production of CH4 was increased. It can be concluded that to increase photocatalytic efficiency, V2AlC 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.

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References


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