CHEMICAL ENGINEERING TRANSACTIONS
VOL. 113, 2024
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Bohong Wang, Guo Ren Mong, Petar S. Varbanov
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**ISBN** 979-12-81206-14-4; **ISSN** 2283-9216
DOI: 10.3303/CET24113033

# Photocatalytic Carbon Dioxide Reduction with Water to CO and CH4 over Bio-sludge Modified TiO2 Composite

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Photocatalytic reduction of carbon dioxide ($CO_2$) is a promising strategy for converting greenhouse gases into valuable fuels and chemicals, contributing to sustainable energy solutions and climate change mitigation. In a continuous flow photoreactor system, this work investigates the use of waste-bio-sludge (BS) supported $TiO_2$ (BS/$TiO_2$) composite for photocatalytic reduction of $CO_2$ using water as the reducing agent. The bio-sludge acted as a cocatalyst, promoting efficient charge separation and transfer in addition to higher visible light absorbance. Using optimized BS/$TiO_2$ composite, the highest CO and $CH_4$ yield rates of 3.82 and 4.39 μmol $g^{-1}$ $h^{-1}$ at selectivity 46.50 and 53.50 % were achieved. When compared to pure $TiO_2$, the composite BS/$TiO_2$ was able to produce $CH_4$ at a higher yield rate. This was caused by the effective separation of charge carriers. This work contributes to the growing body of research on sustainable photocatalytic technologies, emphasizing the importance of designing efficient and robust photocatalysts for practical applications in $CO_2$ utilization and renewable energy production.

## 1. Introduction

Greenhouse gas carbon dioxide (CO2) is a major driver of climate change and photocatalytic CO2 reduction using solar energy offers an innovative solution to combat climate change by converting CO2 into useful fuels and chemicals (Zhou et al., 2024). Current photocatalytic systems using semiconductor materials often suffer from low efficiency in converting solar energy into chemical energy, resulting in low yields of desired products. Among the semiconductors, titanium dioxide (TiO2) is most promising due to its several benefits such as low cost, high stability under extreme environments and higher oxidation potential. In addition to TiO2 several benefits, it generally exhibits low efficiency and is unable to effectively harvest solar energy (Wang et al., 2023). There are several methods available to enhance TiO2 photocatalytic efficiency such as loading with metals and coupling with other semiconductors to construct heterojunction. For example, photocatalytic CO2 reduction over the TiO2/CsPbBr3 heterojunction, because of effective charge separation, enables higher CO production (Wang et al., 2023). In another work, V2AlC MAX was used as a cocatalyst with TiO2 and enhanced photocatalytic CO2 to CO was obtained (Tahir 2023). A composite of C/Ag@ urchin-like TiO2 was promising for photocatalytic CO2 reduction to CO (Yuan et al., 2023). In another work, reduced TiO2 coupled with 1T/2H-MoS2 enables efficient CO2 reduction to CO during the photocatalysis process (Park et al., 2023). Instead of using expensive metals, it would be promising to use low-cost and waste materials as a cocatalyst with TiO2 to maximize photocatalytic efficiency.

As a low-cost substrate for various applications, waste sewage sludge (WSS), a by-product of wastewater purification, has garnered significant attention among organic wastes. (Mahanna et al., 2024). Sludge management in wastewater processing systems is a significant difficulty due to the enormous volume of output, accounting for approximately 50–60 % of total operating expenses for wastewater treatment (Teoh et al., 2020). In addition, the majority of the sewage sludge from municipal waste is made up of heavy metals like zinc, copper, nickel, lead, and chromium along with organic matter, nitrogen, phosphorus, and other nutrients. To ensure long-term treatment, it is crucial to use special waste sewage sludge (WSS) techniques. Remarkably, solid waste sewage sludge can be employed with other semiconductors as a cocatalyst to promote photocatalytic hydrogen generation under solar energy (Zerga et al., 2023). Similarly, solid waste-derived carbon fibers were

Paper Received: 15 May 2024; Revised: 16 July 2024; Accepted: 29 October 2024
Please cite this article as: Tahir B., Tahir M., Alraeesi A., Kumar N., 2024, Photocatalytic Carbon Dioxide Reduction with Water to CO and CH4 over Bio-sludge Modified TiO2 Composite, Chemical Engineering Transactions, 113, 193-198 DOI:10.3303/CET24113033

coupled with $TiO_2$ and a significantly higher $H_2$ yield was reported in another work (Tahir et al., 2023). The biomass sludge recycled from paper mills was used to produce carbonaceous support, which was promising for $CO_2$ conversion (Ribeiro et al., 2024). In recent work, sludge-derived biochar was coupled with $TiO_2$ which resulted in a significantly higher photocatalytic hydrogen evolution rate under visible light irradiation (Zerga et al., 2023). Investigating the utilization of bio-sludge as a cocatalyst with $TiO_2$ for photocatalytic $CO_2$ reduction would be a fruitful approach.

This study looks into the use of bio-sludge-supported TiO2 composite for photocatalytic CO2 reduction in a continuous flow photoreactor with visible light. To create the BS/$TiO_2$ composite, which was synthesized utilizing a self-assembly technique, the biowaste sewage sludge was first dried in an oven. Under visible light irradiation, the photocatalysts' efficacy for $CO_2$ reduction with water was evaluated in a fixed bed photoreactor. Due to increased visible light absorbance and effective separation of photoinduced charge carriers, better photocatalytic $CO_2$ reduction efficiency was achieved using BS with $TiO_2$.

## 2. Experimental

### 2.1 Preparation of Bio-sludge (BS)and BS/$TiO_2$ composite

The industrial waste bio-sludge (BS), collected from the local wastewater treatment plant contains 75-85 % moisture. The BS was dried for 24 h at 100 °C in an oven to remove moisture (until a moisture content of 2 to 5 %) (Zerga et al., 2023). The product obtained was ground into fine powder and given the name bio-sludge (BS). The BS/$TiO_2$ composite was synthesized using a self-assembly approach. In a typical procedure, 20 mL of methanol was used to disperse 50–100 mg of $TiO_2$, which was then vigorously stirred for one hour. Concurrently, a certain quantity of BS dispersed in methanol was added to the $TiO_2$ dispersion and stirred for an extra three hours to achieve good interface interaction. The suspension was then dried at 100 °C overnight and was named BS/$TiO_2$ composite. The schematic illustration for the preparation of BS/$TiO_2$ composite is shown in Figure 1. The synthesized materials were characterized using scanning electron microscopy (SEM, SEM, JEOL), X-ray diffraction (XRD, Bruker Advance D8 diffractometer), UV-visible diffuse reflectance absorbance (V-750 UV−Visible Spectrophotometer) and Photoluminescence (PL, laser wavelength 532 nm) for the sludge, $TiO_2$ and BS/$TiO_2$ samples.

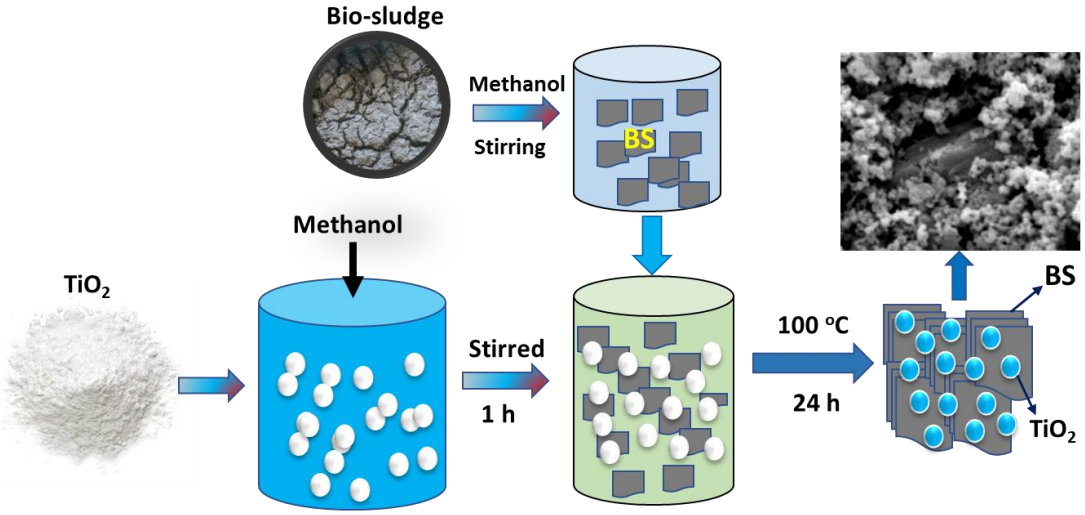


*Figure 1: Schematic of BS/$TiO_2$ composite synthesis*

### 2.2 Photoactivity test

Experiments on photocatalytic $CO_2$ reduction were carried out in a continuous-flow photoreactor setup. The reactor is made up of a stainless-steel chamber that is coupled to a 35-watt Xenon bulb it was used without UV-cut filters and it consists of UV and visible light irradiation. The reactor bottom, saturated with a steady supply of $CO_2$, was loaded specific amount of catalyst (100 mg). To transfer moisture, the $CO_2$ was first run via a water saturator. The feed mixture crossed the catalyst surface as it went from the top of the reactor intake to the bottom of the reactor outflow. The primary exposed area for the catalytic reaction was the bottom surface of the reactor chamber, which is where the catalyst, reactants, and light source interact. A consistent flow of $CO_2$ of 15 mL $min^{-1}$ was used for each experiment, and it was passed via a water saturator to carry moisture before entering the reactor. The atmospheric pressure was used for all of the experiments. The reactor outlet was

connected with the online GC (INFICON µGC) for continuous product analysis. The products were analyzed after a regular interval of 30 min for all the photocatalysts.

## 3. Results and discussion

### 3.1 Materials Characterization

XRD patterns of BS, $TiO_2$, and BS/$TiO_2$ samples are displayed in Figure 2a. For the BS, the main peaks appeared at 2θ of 12.44°, 20.85°, 24.97°, 26.69°, 25.08°, 45.82° and 50.24°, which can be associated with sludge elements such as $SiO_2$, $Al_2O_3$, and others as discussed previously (Zerga et al., 2023). For the XRD of $TiO_2$, the diffraction peaks that correspond to the lattice plans of (101), (004), (200), (220), and (215) represent the anatase phase of $TiO_2$. In the case of BS/$TiO_2$ composite with 3 % BS loading, all the $TiO_2$ peaks appeared, and peaks related to BS were not identified. Due to their small loading, there were no extra peaks associated with BS and similar observations have been reported previously (Pan et al., 2024).
The UV-visible absorbance spectra of BS, TiO2, and BS/TiO2 composite are displayed in Figure 2b. The BS shows strong absorbance in the visible region due to the presence of organics in the bio sludge. The UV-visible results of $TiO_2$ indicate that the band edge was below 400 nm, while absorption was observed in the UV region (390 nm). When BS was added to $TiO_2$, the light absorbance in the visible region was increased. However, there was no effect on the absorbance band edge and it was slightly decreased towards the region (387 nm).

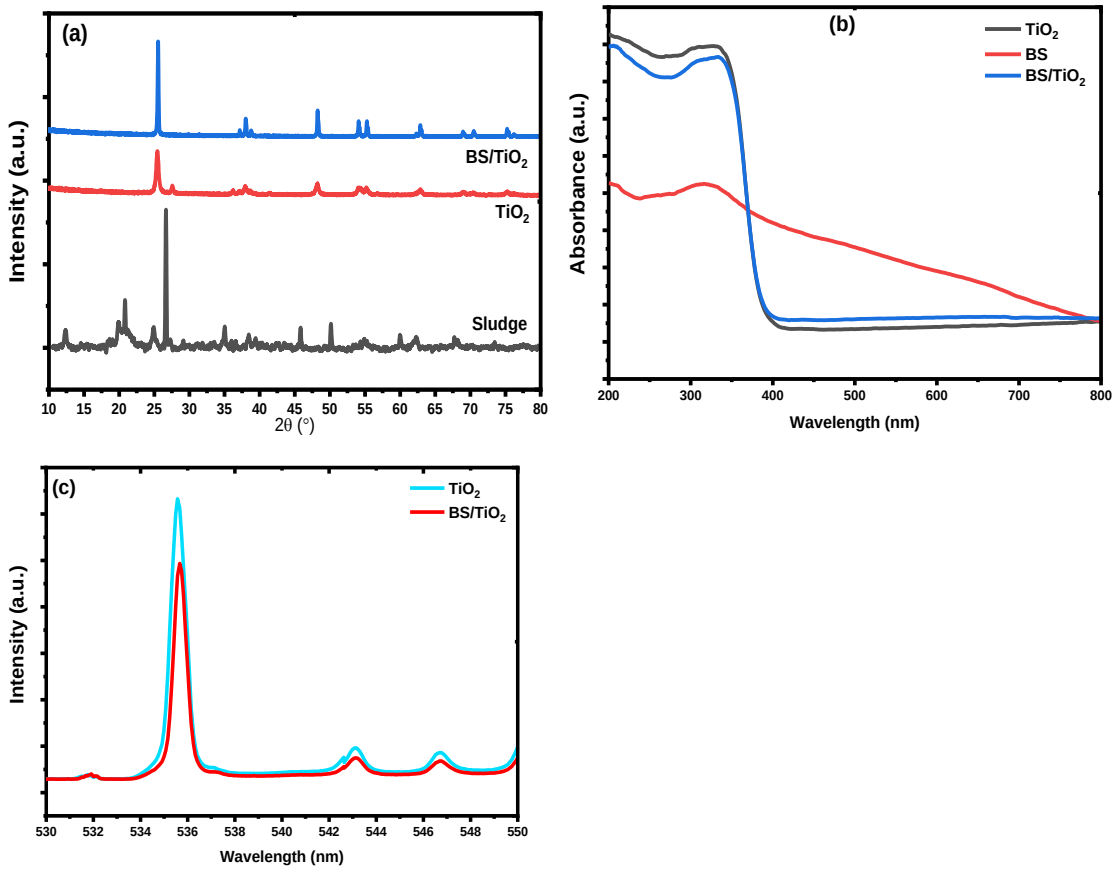


*Figure 2: (a) XRD patterns of $TiO_2$, Bio-sludge and BS/$TiO_2$ composite, (b) UV-visible analysis of $TiO_2$, $TiO_2$ and BS/$TiO_2$ composites, (c) PL analysis of $TiO_2$ and BS/$TiO_2$ composite.*

PL is often used to assess the segregation and transfer efficiency of photogenerated charge carriers. Lowering recombination rates is therefore not favoured by stronger peaks in PL analysis. Reduced peak intensity is thought to be a sign of increased charge separation efficiency, decreased recombination rates, and increased photocatalytic stimulation. Figure 2c shows photoluminescence (PL) analysis of $TiO_2$ and BS-loaded $TiO_2$ composite. Pure $TiO_2$ shows higher PL intensity, which was due to charge recombination within the $TiO_2$ structure. A reduced PL intensity was observed when BS was added to $TiO_2$, which was caused by effective

charge carrier separation. Sludge was added to g-$C_3N_4$ in a previous study, and this resulted in a reduced PL intensity. This was caused by effective charge carrier separation (Yuan et al., 2023).
Scanning electron microscopy of TiO2, BS, and BS/TiO2 composites is shown in Figure 3. The morphology of $TiO_2$ is exhibited in Figure 3a, where uniform-sized $TiO_2$ particles are visible. Figure 3b illustrates the 2D layered structure that BS displays. The morphology of the BS/$TiO_2$ composite is displayed in Figure 3c. The $TiO_2$ particles are entirely distributed with BS to provide good interface interaction. The EDS analysis of sludge is reported in our previous work, which confirms the presence of several metal elements inside the sludge (Zerga et al., 2023). This would be beneficial to maximize the light absorbance and charge separation efficiency of the composite during the $CO_2$ reduction process. Previously, sheets like the structure of bio-sludge were obtained from the paper mill biomass sludge (Ribeiro et al., 2024). In another work, the core-shell lightweight aggregate of bio-sludge has been reported with various structures and morphologies (Mahanna et al., 2024).

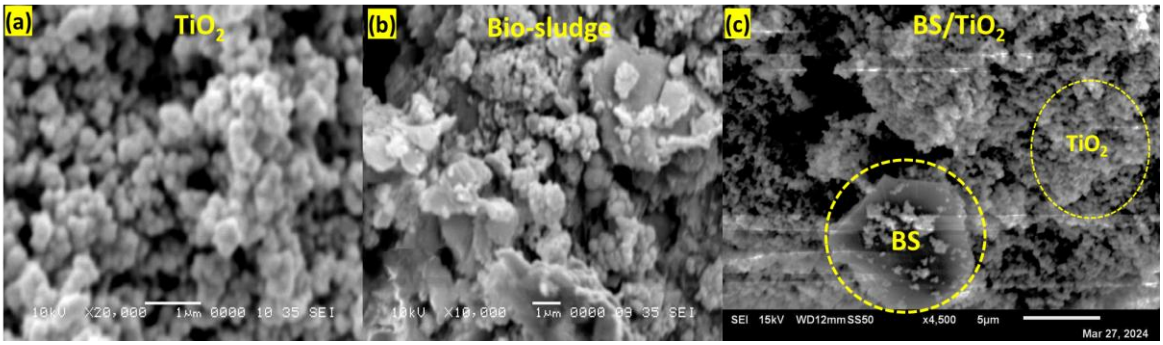


*Figure 3: SEM images of (a) $TiO_2$, (b) Bio-sludge, (c) BS/$TiO_2$ composite.*

### 3.2 Photocatalytic $CO_2$ reduction

With 100 mg of photocatalysts and $CO_2$/water as the feed combination, the photocatalytic $CO_2$ reduction studies were carried out in a continuous flow photoreactor system. After two hours of reaction time, Figure 4a illustrates photocatalytic $CO_2$ reduction with $H_2O$ to yield CO and $CH_4$. Using pure $TiO_2$, the CO and $CH_4$ yield of 2.18 and 2.12 µmole $g^{-1}$ were produced. When 1 % BS was added to $TiO_2$, the CO and $CH_4$ yield was increased to 4.09 and 3.14 µmole $g^{-1}$ using the $CO_2$-$H_2O$ feed mixture. The highest CO and $CH_4$ were produced with the optimized 3wt. % BS loading. Using an optimized 3 %BS/$TiO_2$ composite, the highest CO yield of 7.63 µmole $g^{-1}$ was produced, which is 1.87 and 3.5 folds more than using pure $TiO_2$. Similarly, the $CH_4$ yield of 8.78 µmole $g^{-1}$ was obtained over 3 % BS/$TiO_2$ composite, which is 2.8 and 4.14 folds more than using only $TiO_2$. Higher visible light absorbance and effective charge separation were the main causes of this noticeably increased photocatalytic $CO_2$ to CO and $CH_4$ over BS/$TiO_2$ composite. The yield of $CH_4$ and CO decreased when the BS loading was increased to 5 and 10 %. This was due to creating of charge recombination centers within the BS/$TiO_2$ composite, resulting in lower photocatalytic efficiency. In a recent study, we reported on the biochar (BC)/$TiO_2$ composite generated from bio-sludge and discovered that the inclusion of sludge materials led to much-increased hydrogen production (Zerga et al., 2024). In recent work, CO was identified as the main product during photocatalytic CO2 reduction over FePc/MXene in a flow cell-type reactor (Gao et al., 2024).
The yield rate and selectivity of CO and CH4 over a range of photocatalyst types are displayed in Table 1. It can be seen that TiO2 was favourable to producing more CO than CH4 at a selectivity of 50.70 %. The yield of CO rose further when 1 % BS was added to TiO2 because the charge carriers within the surface of TiO2 were effectively separated, resulting in 56.57 % selectivity for CO under the same operating conditions. However, when further BS loading was increased to 3wt. %, the CH4 yield rate was increased higher than CO, giving CH4 selectivity 53.50 %. This was possibly due to more production of electrons and their separation in the presence of sludge metal ions, which enables more production of CH4 (Yuan et al., 2023), for the production of CO and CH4, 2 and 8 electrons are conducted, which were obtained from the TiO2 during the photocatalysis process. Due to the presence of BS as a cocatalyst with metal elements, these electrons were effectively trapped and transported, which enables more production of CH4 (Zerga et al., 2024).
In previous work, TiO2 has been widely used in photocatalytic CO2 reduction applications most of the work used higher light power and a batch process and the exact comparative analysis of efficiency enhancement could not be possible. In several reports' sludge was used as a cocatalyst and support to promote catalytic efficiency. For example, dewatered sludge showed higher electrocatalytic degradation efficiency due to the presence of Fe and Mn metals (Guo et al., 2022). The Fe and Mn were beneficial to maximize the transfer of electrons. In another work, higher production of hydrogen was reported over the sludge-based composite due

to the synergistic effect of sludge metal ions, enabling efficient separation of charge carriers (Zerga et al., 2023). Using g-$C_3N_4$ with $Ti_3C_2$ MXene, higher photocatalytic $CO_2$ reduction was achieved in the presence of efficient production and separation of photoinduced charge carriers (Zhong et al., 2023).

*Table 1: $TiO_2$ and BS-loaded $TiO_2$ sample yield rate and selectivity*

| Photocatalyst | Yield rate (µmol $g^{-1}$ $h^{-1}$) | | Selectivity | |
|---|---|---|---|---|
| | CO | $CH_4$ | CO | $CH_4$ |
| $TiO_2$ | 1.09 | 1.06 | 50.70 | 49.30 |
| 1 % BS/$TiO_2$ | 2.05 | 1.57 | 56.63 | 43.37 |
| 3 % BS/$TiO_2$ | 3.82 | 4.39 | 46.53 | 53.47 |
| 10 % BS/$TiO_2$ | 2.03 | 2.95 | 40.76 | 59.24 |

The charge separation and utilization over the BS/$TiO_2$ composite for the generation of CO and $CH_4$ during the photocatalysis process is schematically illustrated in Figure 4b. Over the surface of $TiO_2$, light irradiation produces holes and electrons. The electrons are trapped because of the BS, which makes charge carrier separation effective. The BS has several metal elements, which enables efficient separation of charge carriers, resulting in higher $CO_2$ reduction efficiency. Using BS/$TiO_2$ composite, a higher yield of $CH_4$ was produced. Eight electrons are required for $CH_4$ formation, which was not provided by $TiO_2$, a lower yield rate was obtained. Due to the presence of BS with higher light absorbance and more charge separation, a significantly higher yield of $CH_4$ was obtained. All these findings confirm BS as a promising waste co-catalyst which can be combined with other semiconductors to enhance photocatalytic efficiency. When loaded with BS with $TiO_2$, BC plays an exceptional function in photocatalysts and photoactive heterojunctions, as per the previously described characteristics. In previous work, higher hydrogen production was reported over $TiO_2$ by loading MXenes, which was associated with the efficient separation of photoinduced charge carriers (Zaka et al., 2023). Because of these benefits, BS is a great co-catalyst material for the dispersion of nanoparticles. It also increases the exposed surface area, transports electrons, acts as an electron sink, and enhances charge separation.

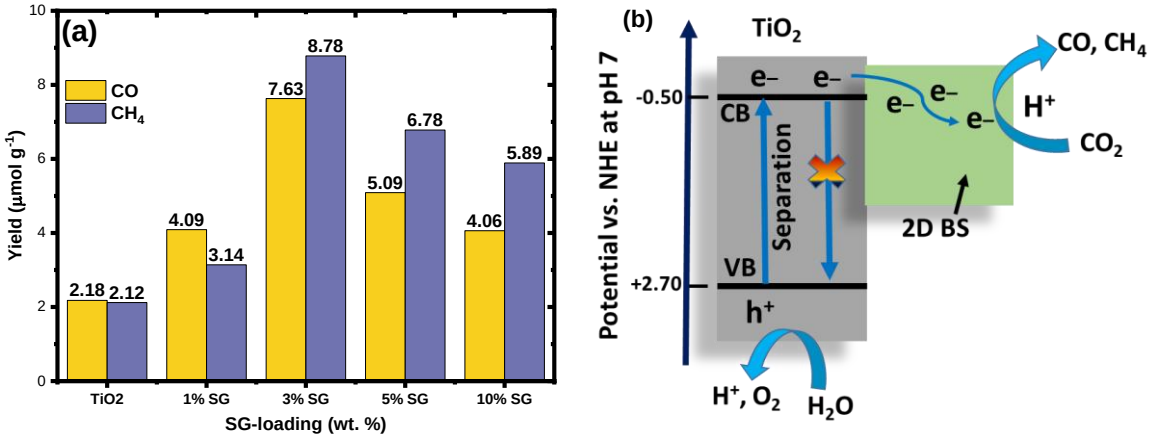


*Figure 4: (a) Photocatalytic $CO_2$ reduction with $H_2O$ to CO and $CH_4$ over sludge-loaded $TiO_2$ samples, (b) Schematic proposed mechanism for photocatalytic $CO_2$ reduction over BS/$TiO_2$ composite under visible light.*

## 4. Conclusion

The waste bio-sludge assisted $TiO_2$ composited was successfully synthesized using a self-assembly approach and found promising for photocatalytic $CO_2$ reduction. During the $CO_2$ reduction process, the main products identified were CO and $CH_4$, while using a continuous flow photoreactor system. Using $TiO_2$ and a lower amount of BS loading, CO was identified as the potential product. With the optimized 3 % BS/$TiO_2$ composite, a higher yield of $CH_4$ was produced compared to CO. After two hours of irradiation, the largest CO and $CH_4$ yields, 7.63 and 8.78 µmol $g^{-1}$, were generated. The enhanced BS/$TiO_2$ photocatalytic efficiency was caused by better visible light absorption and effective charge carrier separation. This study's main goal was to examine the huge potential of bio-sludge as a cocatalyst with a semiconductor material to be utilized for photocatalytic $CO_2$ reduction under visible light irradiation. The finding of this work would be promising to use bio-sludge as a cocatalyst in energy and environment-related applications.

**Acknowledgements**

United Arab Emirates University funded this investigation with a research grant under the Sure Plus program (vote # 12N229).

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