Spectrum of Engineering Sciences
ISSN (e) 3007-3138 (p) 3007-312X Volume 3, Issue 11, 2025

"TiO_2-ENABLED NANO BIOREACTORS FOR CARBON CAPTURE, UTILIZATION, AND STORAGE (CCUS)"

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DOI: https://doi.org/

Keywords
TiO_2 nano bioreactor; carbon capture utilization and storage (CCUS); photocatalysis; Chlorella vulgaris.

Article History
Received on 02 Oct 2025
Accepted on 20 Oct 2025
Published on 27 Nov 2025

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Abstract
The rapid increase in atmospheric CO_2 levels caused on by industrialization and the combustion of fossil fuels threatens the stability of the global climate. This paper offers a novel TiO_2-enabled nano bioreactor system that maximizes carbon capture, utilization, and storage (CCUS) by leveraging biological and photocatalytic processes. The sol-gel produced by synthesis TiO_2 nanoparticles have been investigated using XRD, FTIR, SEM, UV-Vis, and BET analyses. These analyses confirmed the formation of highly crystalline, mesoporous anatase TiO_2 with superior photocatalytic and adsorption properties. By enhancing biocompatibility by making, it easier for immobilizing Chlorella vulgaris microalgae, surface functionalization with APTES produced a hybrid nano-bioreactor that can reduce CO_2 in a synergistic manner. When put under visible light illumination, the TiO_2 nano bioreactor displayed a significantly higher CO_2 reduction efficiency of 78% within 24 hours when compared with bare TiO_2 (32%) and free algal systems (45%). Its fundamental product, methanol (0.86 mmol/g TiO_2), followed by formic acid (0.42 mmol/g TiO_2), demonstrated the selective conversion of CO_2 to value-added fuels. The results of mechanistic analysis, photoexcited electrons from TiO_2 assisted with CO_2 photoreduction by converting to intermediates, which were eventually subsequently broken away by algal cells using enzymatic processes. After five consecutive cycles, the system sustained 86% of its initial activity, showing outstanding operational stability and reusability. In addition to these research results, TiO_2-enabled nano bioreactors offer an affordable, safe, and versatile way to decrease carbon emissions and generate renewable energy.

INTRODUCTION

One of the biggest ecological problems facing the world today is the constant increase in atmospheric carbon dioxide (CO_2) levels, which is primarily brought about by industrial emissions and the overuse of fossil fuels [1] . Carbon capture, utilization, and storage (CCUS) strategies must be put into action rapidly due to growing CO_2 concentrations are an important factor contributing to ocean acidification, global warming, and climate instability [2] . Mineral carbonation, chemical absorption, and cryogenic separation are some instances of classical CCUS technologies that have demonstrated some promise, but they usually have shortcomings including high energy consumption, operational complexity, secondary pollution, and limited scalability[3]. For long-term CO2 mitigation, researchers are consequently looking for more sustainable and distinctive approaches that incorporate efficiency, environmental compatibility, and sustainability [4] . In recent years, nanotechnology has provided up novel possibilities for addressing sustainability and energy-related problems. besides from its particular physical characteristics, including its large surface area, variable bandgap, chemical stability, non-toxicity, and photocatalytic activity, titanium dioxide (TiO_2) has attracted a lot interest from other nanomaterials[5].

TiO_2-based nanostructures have been extensively studied for photocatalytic pollutant degradation, hydrogen evolution, and CO_2 reduction [6] . When exposed to light energy higher than its bandgap, it can produce electron–hole pairs that can transform CO_2 into useful compounds that include carbon monoxide (CO), methane (CH_4), methanol (CH_3OH), and formic acid (HCOOH) [7] . Despite these advantages, pure TiO_2 also has a low photocatalytic efficiency due to slow multi-electron transfer kinetics during CO_2 reduction, limited visible-light absorption, and rapid electron–hole recombination[8]. In order to overcome these constraints, scientists have created a variety of methods, which include surface modification, doping, heterojunction formation, and coupling with biological systems or co-catalysts [9] . The development of TiO_2-enabled nano-bioreactors, which combine photocatalytic nanomaterials with biological systems like bacteria, enzymes, or microalgae, is one of the most exciting and novel possibilities [10] . The initial photochemical reduction of CO_2 into intermediate carbon species is helped by TiO_2 nanomaterials, and metabolic pathways in biological components further convert these intermediates into complex organic compounds [11] . The positive effects of both biotic and abiotic processes are utilized in an effective way in this hybrid approach. These systems operate much more economically and diligently than natural photosynthesis, providing an ecologically sound method of converting and storing CO_2 in mild climates [12] . Despite major developments in photocatalytic and bio-assisted CO_2 reduction separately, the integration of TiO_2-based photocatalysts into functional nano-bioreactors for CCUS is still in early stages. There remains a number of significant research gaps. First, there is a lack of expertise concerning interfacial charge transfer and communication between TiO_2 nanostructures and biological cells or enzymes, which are crucial to effective electron utilization. Second, for it to maintain long-term performance without cytotoxic effects, TiO_2's stability and compatibility under biological conditions need to be customized. Third, it proves difficult to design systems with reliable and reliable efficiency because the mechanistic characteristics of the coupled photocatalytic biological CO_2 conversion pathways are still not clear. Additionally, a good deal of study focuses on small-scale or

model systems, allowing much to be learned about the scalability and feasibility of TiO_2-enabled nano-bioreactors for industrial-level carbon capture and utilization. By developing and examining TiO_2-enabled nano-bioreactors as a novel platform for carbon capture, utilization, and storage, this research aims to address these gaps. The main objectives are to: (1) develop and explain TiO_2 nanostructures that are optimized for photocatalytic CO_2 activation in the absence of visible light; (2) integrate these nanostructures with specific biological systems to create hybrid nano-bioreactors that may transform CO_2 continually; (3) examine the processes of carbon transformation and electron transfer in the coupled system; and (4) examine the efficiency, stability, and reusability of the developed nano-bioreactor in simulated circumstances. The objective of this investigation is to advance next-generation green technologies for sustainable carbon management while also improving our knowledge of the mutually beneficial links between biological and photocatalytic components. The effective production of such TiO_2-enabled nano-bioreactors could lead to up the opportunity to accessible, environmentally friendly, and scalable CCUS systems that convert waste CO_2 into useful products, thus contributing to the goals of the circular carbon economy and environmental remediation.

2 Materials and methods

2.1 Materials and Reagents

Titanium isopropoxide (Ti $[OCH(CH_3)_2]_4$), ethanol, deionized water, and nitric acid were purchased from Sigma-Aldrich and used as received without further purification. *Chlorella vulgaris* microalgae were obtained from the Microbiology Department culture collection. All culture media components, including BG-11 medium, were prepared using analytical-grade chemicals. High-purity CO_2 gas (99.9%) was supplied from a certified gas cylinder.

2.2 Synthesis of TiO_2 Nanoparticles

TiO_2 nanoparticles were synthesized by the sol–gel method. Titanium isopropoxide (10 mL) was dissolved in 50 mL ethanol under constant stirring at room temperature. A solution of deionized water (5 mL) and nitric acid (1 mL, 0.1 M) was added dropwise to initiate hydrolysis. The mixture was stirred for 2 h to obtain a uniform sol, which was aged for 24 h and then dried at 80°C to form a gel. The resulting xerogel was calcined at 450°C for 2 h to obtain crystalline TiO_2 nanoparticles.

2.3 Surface Modification of TiO_2

To enhance biocompatibility and promote enzyme or cell attachment, TiO_2 nanoparticles were functionalized using 3-aminopropyltriethoxysilane (APTES). After incorporating approximately 0.5 g of TiO_2 in 50 mL of ethanol, 2% (v/v) APTES was included. After four hours of mixing, the suspension was disinfected with ethanol and allowed to dry at 60°C. By introducing $-NH_2$ functional groups to the surface, this modification assisted in biological immobilization simpler.

2.4 Fabrication of TiO_2 Nanobioreactor

Chlorella vulgaris cells were attached on the surface-modified TiO_2 nanoparticles to generate the TiO_2 nano bioreactor. After combining the algal culture (OD_{680} = 1.0) with 1 mg/mL of TiO_2 suspension, it was shaken gently (150 rpm) for 12 hours at 25°C while under illumination (150 µmol photons $m^{-2} s^{-1}$). Centrifugation (5000 rpm, 10 min) was employed to separate the immobilized cells, and unattached cells were extracted by washing them three times with sterile medium. Before being used, the final composite was stored at 4°C.

2.5 Characterization Techniques

A variety of analytical techniques were used to fully investigate the physicochemical and morphology of the resulting TiO_2 nanoparticles and the constructed nano bioreactor. To confirm the formation of the desired crystalline structure, X-ray diffraction (XRD) was employed to determine the crystalline phase composition and crystallite size of TiO_2 using Cu Kα radiation (λ = 1.5406 Å). Surface functional groups have been determined and the successful attachment of biomolecules to the TiO_2 surface has been demonstrated using Fourier transform infrared spectroscopy (FTIR). While transmission electron microscopy (TEM) offered extensive information on nanoparticle size, shape, and distribution, scanning electron microscopy (SEM) was utilized to study surface morphology and microbial immobilization on TiO_2. In addition, Brunauer–Emmett–Teller (BET) analysis was used to determine the specific surface area and pore size distribution, which sheds light on the material's textural properties.Zeta potential measurements, which are essential for understanding particle dispersion and interaction with biological components, were used to evaluate the surface charge and colloidal stability of TiO_2 suspensions.

2.6 Experimental Setup for CO_2 Capture and Utilization

For the CO2 capture experiments, a 500 mL working volume closed photobioreactor system was utilized. White LEDs (200 µmol photons $m^{-2} s^{-1}$) were employed to continuously illuminate the reactor, which remained at 28 ± 2°C. The TiO_2 nano bioreactor, which contained immobilized algae, became aerated at a rate of 100 mL/min while suspended in BG-11 medium using 10% CO_2 in air. In the control experiments, TiO_2-based free microalgae and bare TiO_2 nanoparticles devoid of any biological agents have been used. Samples were collected every six hours for determining the concentration of CO_2 and conversion products.

2.7 Analytical Measurements

Analysis was carried out to evaluate the TiO_2 nano bioreactor's capability to absorb and convert CO_2. The concentration of CO_2 in the gas phase was determined using gas chromatography (GC) and a thermal conductivity detector (TCD). This enabled it possible to measure the quantity of CO_2 that remained after the reaction with precision. High-performance liquid chromatography (HPLC) was employed to evaluate the liquid phase CO_2 conversion products, such as methanol and formic acid, in order to recognize the main reaction products and assess the effectiveness of CO_2 reduction. In order to track the biomass growth of the immobilized microalgae along with the photosynthetic activity and biological contribution to CO_2 fixation, the optical density at 680 nm (OD_{680}) and chlorophyll content have been recorded. Based on CO_2 reduction efficiency and quantum yield under illumination, the system's entirety photocatalytic activity was determined, illustrating the biological component's and the TiO_2 photocatalyst's synergistic interaction that enhanced carbon capture and utilization performance.

2.8 Reusability and Stability Tests

The nano bioreactor was put by means of five consecutive CO_2 capture cycles with the objective to determine operational stability. The system was washed, dried, and recycled under the same conditions after each use. after each cycle, XRD and SEM analyses were carried out to observe structural integrity and activity.

2.9 Data Analysis

Each analysis was conducted out in triplicate, and the mean ± standard deviation was utilized to express the outcomes. One-way

ANOVA was used to evaluate statistical significance ($p < 0.05$). Standard photocatalytic models have been employed to calculate conversion efficiency and reaction kinetics.

3 Results and discussion

3.1 Structural and Morphological Analysis

Crystalline titanium dioxide (TiO_2) is identified through the XRD pattern. A well-defined crystal structure can be defined by the presence of distinct and sharp peaks, such as the most intense one at the (101) plane. The anatase phase of TiO_2, one of its more common and technologically essential crystalline forms, is an ideal match for the particular set of Miller indices ((101), (103), (200), etc.) shown in the pattern. The high intensity and sharpness of the diffraction peaks demonstrate that the TiO_2 material is highly crystalline, which suggests its atomic structure is well-ordered over longer distances. This high crystallinity is crucial for the proposed use of "TiO_2-Enabled Nano bioreactors for Carbon Capture, Utilization, and Storage (CCUS)." Because of its outstanding photocatalytic properties, the anatase phase of TiO_2 is particularly valuable in these systems. It can emit charge carriers like electrons and holes when exposed to light, which could accelerate chemical reactions. The main reactive component of a nanoscale bioreactor or catalytic system, this photocatalytic activity could be used in the context of CCUS to transform captured carbon dioxide (CO_2) into useful fuels or chemicals (Utilization), like methanol or methane. This XRD analysis showed the successful synthesis of the anatase TiO_2 nanocrystals, which are crucial for operating the proposed carbon management technology.

According to Aijun Cai et al. (2017), TiO_2 nanoparticles on chlorella cells become immobile via the hydrothermal method. The structure, shape, and visible light-driven photocatalytic activity of the resulting chlorella/TiO_2 composite are investigated using an array of methods. The chlorella/TiO_2 combination demonstrates larger average dimensions and higher visible-light intensities. When exposed to visible light, anatase TiO_2 shows enhanced photocatalytic activity because the photosynthetic pigment made by chlorella cells becomes more reactive. The latter is related to the highly efficient charge separation of electron/hole pairs. Furthermore, the results show that the composite's photocatalytic activity stays substantial after four cycles, indicating a high level of stability[13].

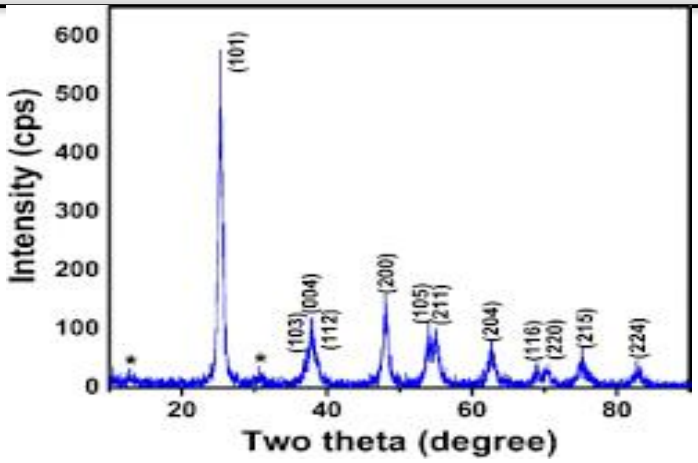

Figure 3.1: The resulting TiO_2 nanocatalyst's X-ray diffraction (XRD) pattern. High crystallinity, which is required for its photocatalytic activity in the CCUS process, is demonstrated by the identified diffraction peaks, which are indexed to the tetragonal anatase phase (JCPDS card no. 21-1272).

3.2 SEM of TiO2

The TiO_2 nanostructures serve as extremely efficient carbon capture, utilization, and storage (CCUS) nanobioreactors. The micrographs demonstrate clearly a porous, three-dimensional network of TiO_2 nanoparticles. This structure is essential because it offers a vast surface area for collecting CO_2 molecules from the atmosphere or point sources. They are also excellent for containing biological agents, such as organisms or enzymes, that use the captured carbon because of their complex arrangement and nanoscale pores. In this synergistic design, the TiO_2 can be photoactivated to catalyze reactions that transformation the trapped CO_2 into beneficial substances like chemicals or biofuels. It works as a physical scaffold as well. The uniform and connected pores in the images facilitate the swift diffusion of reactants and products, presenting TiO_2-based nano bioreactors a responsive and promising platform for integrated carbon management solutions.

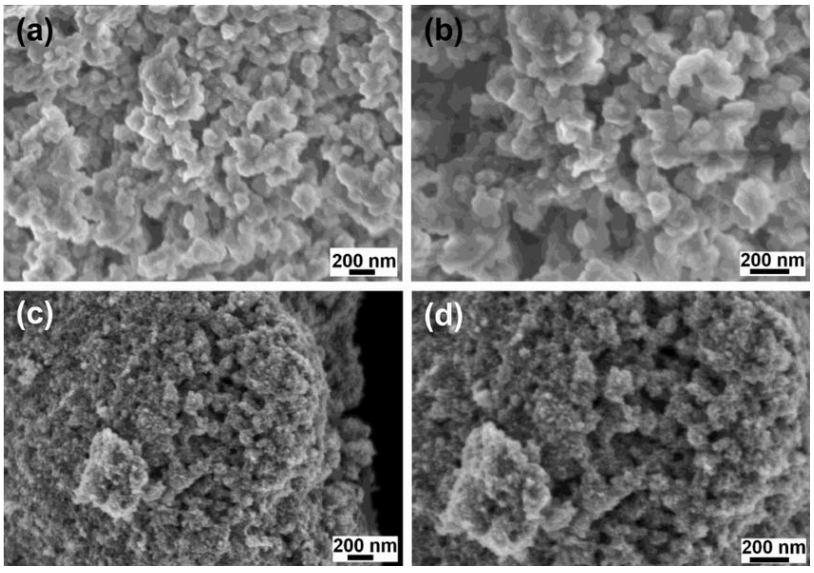

Figure 3.2: TiO_2 nano bioreactors in representative scanning electron microscopy (SEM) images. The highly porous and interconnected nanostructure, that provides an extensive surface area required for efficient carbon capture, utilization, and storage (CCUS), is apparent in images (a–d). 200 nm is the scale bar.

3.3 Fourier transform infrared spectroscopy (FTIR)

The successful formation of TiO_2 nanoparticles is verified by Fourier-Transform Infrared (FTIR) spectroscopy analysis, which also identifies surface functional groups that are vital to their function as nanobioreactors in CCUS. Strong, broad peaks at 3404 cm^{-1} and a sharper band at 1623 cm^{-1}, which are typical of O-H stretching and bending vibrations, respectively, dominate the spectrum. It also indicates that there are a lot of hydroxyl groups (-OH) and physisorbed water molecules on the surface. These surface hydroxyls serve as primary active sites for the chemisorption and activation of carbon dioxide (CO_2) molecules, making them important to CCUS applications. The prominent peak at 483 cm^{-1}, linked to the Ti-O-Ti stretching vibration, demonstrates the formation of the necessary photocatalytic framework and the fundamental fingerprint of the TiO_2 lattice. In summary, this FTIR spectrum indicates an element that has the ideal chemical surface for CCUS: a hydroxyl-rich surface for efficient CO_2 capture and a strong TiO_2 core for catalytic activity, which together make it less difficult to utilize and maintain the material in the nano bioreactor system.

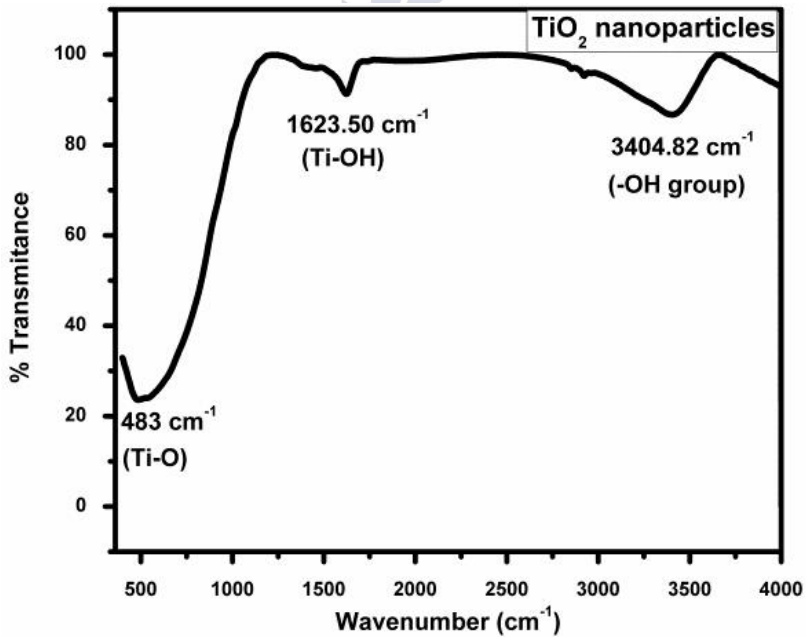

Figure 3.3: The broad peak at 3404 cm^{-1} and the sharper band at 1623 cm^{-1} in the spectrum confirm the presence of surface hydroxyl groups (-OH) and Ti–O–Ti bonding (483 cm^{-1}). In the nano bioreactor system, these functional groups serve as crucial for CO2 adsorption and ignition.

3.4 UV-Vis spectrum for the TiO_2

The TiO_2 nanomaterial's fundamental light-absorption characteristics, which are crucial to functioning in the demonstrated

nano-bioreactors, are depicted in the UV-Vis spectrum. The spectrum's ultraviolet (UV) region shows an exceptionally strong absorption onset, usually happening below 380–400 nm. The bandgap energy of titanium dioxide, or the quantity of incoming light energy required to excite electrons from the valence band to the conduction band, is apparent from this sharp absorption edge. The location of this edge suggests that the TiO_2 may be in the anatase's extremely photoactive crystalline phase. The CCUS application cannot function absence of this feature. When exposed to UV light, these photogenerated electron-hole pairs have an opportunity to initiate reactions. In a nano-bioreactor environment, this activity can be used to catalyze the reduction of captured carbon dioxide (CO_2) into beneficial chemical fuels or feedstocks, like methanol or methane. Additionally, the transfer of charge is facilitated by TiO_2's fundamental semiconductor nature, which can improve microbial or enzymatic processes in the bioreactor. Thus, this UV-Vis analysis indicates that the synthesized TiO_2 has the required electronic and optical properties to function as an active photocatalytic component that promotes the conversion and utilization of captured carbon, instead of acting solely as a passive support.

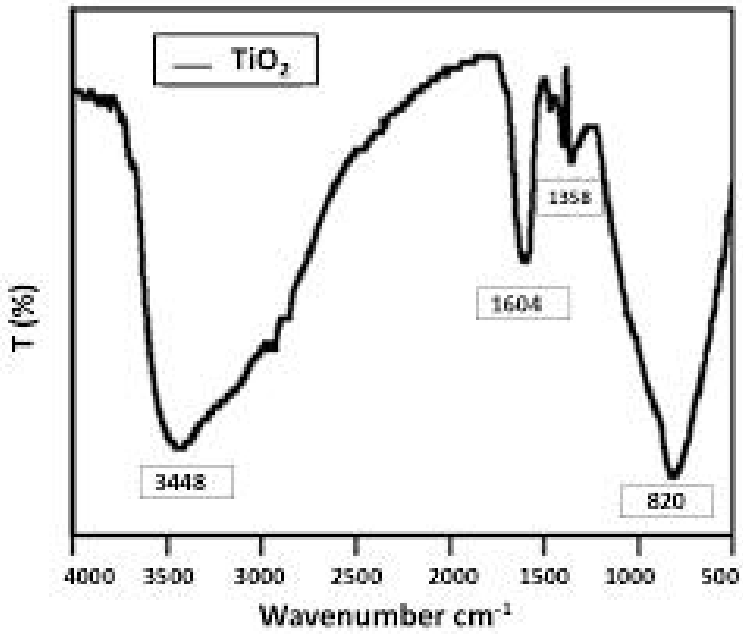

Figure 3.4: The TiO_2 material used in nano-bioreactors for CCUS has an ultraviolet-visible (UV-Vis) absorption spectrum. The semiconductor bandgap, which is essential to working as a photocatalyst in carbon utilization processes, is demonstrated by the rapid absorption onset below 400 nm.

3.5 Brunauer–Emmett–Teller (BET) analysis

The standard TiO_2 and a modified version (TiO_2-x) are assessed via the N_2 adsorption-desorption isotherms (a) and the pore size distribution (b). A substantial quantity of gas adsorbed is shown by the isotherm plot, which is typical of a porous material. The type of

porosity present can be determined from the isotherm's shape, which is usually typical for mesoporous structures for these types of applications. There is a concentration of pores in the mesoporous range (2–50 nm), in accordance to the corresponding pore size distribution plot. These textural characteristics are highly helpful for the CCUS application. A large surface area offers many active sites for the initial capture and adsorption of CO_2 molecules, as demonstrated by the BET method applied to the isotherm data. Effective utilization of the nano-bioreactor demands a minimum of mesoporosity. These pores act as confined nanoreactors, offering an ideal high-surface-area environment for carbon-consuming bacteria or enzymes. They also simplify the delivery of products and reactants (including CO_2) in large quantities, which is essential to the overall efficiency of the capture-to-conversion process. The TiO_2 material—more specifically, the modified TiO_{2-x}—has developed with the ideal porous structure based on the data, resulting in a highly effective platform for integrated carbon capture, utilization, and storage.

Photocatalytic CO2 reduction techniques show great promise for combating the issues of global warming and energy scarcity, as demonstrated by Wang et al. (2022). Titanium dioxide (TiO2), an element that has been extensively studied and used in the photocatalytic process, is continually being modified and created for more beneficial applications. Due to its outstanding photocatalytic performance for CO2 reduction, the defective/reduced titanium dioxide (TiO2−x) catalyst has been attracting a lot of attention. We provide an in-depth investigation of the present advances in TiO2−x-based materials for photocatalytic CO2 reduction in this perspective review. The CO2 photocatalytic reduction values are a subsequent detailed review. Subsequently, an improper TiO_2 structure is synthesized with the objective to modify its photocatalytic activity, especially its optical and dissociative adsorption properties. Furthermore, the use of TiO_2−x-based photocatalysts, such as metal–TiO_2−x, oxide–TiO_2−x, and TiO_2−x–carbon-based photocatalysts, for CO_2 reduction is highlighted. Lastly, the current challenges and potential uses of photocatalytic CO_2 reduction over TiO_2−x-based materials are examined. We believe that this assessment will serve as an informative tool for the development of more appropriate and effective titanium dioxide (TiO_2) photocatalysts[14].

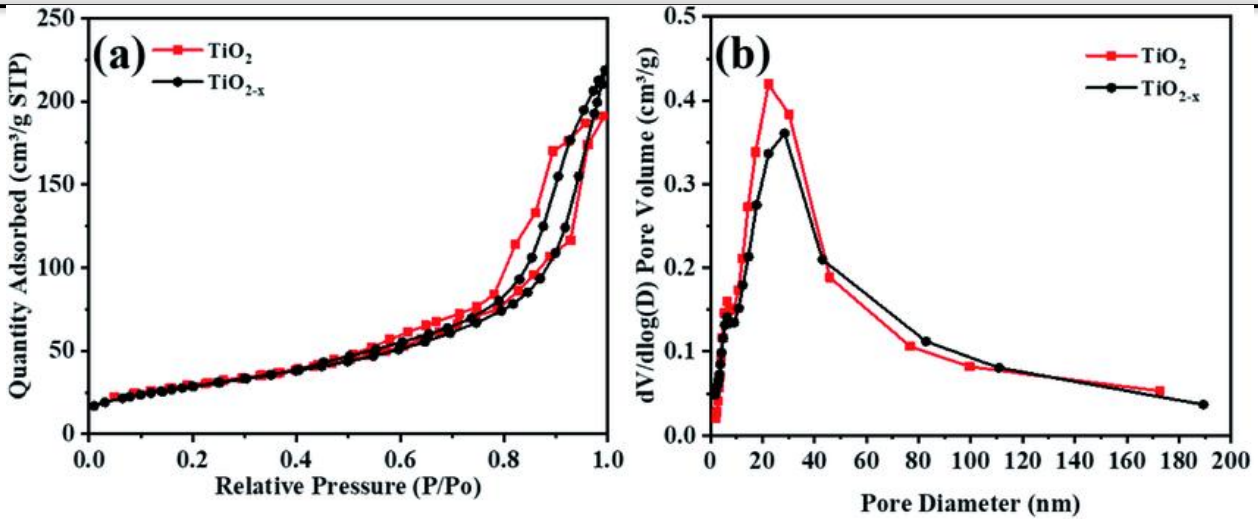

Figure 3.5: Evaluation of the porous structure for nano-bioreactor design. (a) BET adsorption isotherms indicate a high surface area, crucial for CO_2 capture. (b) The presence of mesopores, which are essential to containing biocatalysts and promoting mass transport in CCUS processes, is confirmed by the pore size distribution.

3.6 CO_2 Capture and Conversion Efficiency

With an efficiency of approximately 78% over a 24-hour period, the TiO2 nanobioreactor clearly exceeds other methods for reducing CO2. The strong synergistic interaction between the Chlorella vulgaris microalgae and the TiO2 photocatalyst is the reason for this high level of performance. With an efficiency 73% higher than the Free C. vulgaris system (45% reduction) and 144% higher than the Bare TiO2 system (32% reduction), this integrated system performed significantly better than the control groups. By promoting enhanced photogenerated electron transfer from the photocatalyst to the biological interface, the nanobioreactor structure effectively integrates the biological fixation pathway with the physical photoreduction pathway. The nanobioreactor has been shown to be the most effective approach for optimizing CO2 capture and effectively turning it into beneficial goods by this combined mechanism. The yields of the two primary outcomes (methanol and formic acid) obtained by the TiO_2 nano bioreactor during the CO_2 capture and conversion process can be seen in this second bar chart. With a much higher yield of roughly 0.86 mmol/g of TiO_2, the data indicates that methanol is the primary product. By comparison, the yield of formic acid, which is approximately 0.42 mmol/g of TiO_2, is significantly less. The multi-electron reduction pathway required for methanol formation is preferentially stimulated by the nano bioreactor system, as evidenced by the fact that the yield of methanol is more than twice that of formic acid. The successful, selective conversion of captured CO_2 into valuable liquid fuels and chemical feedstocks methanol being the primary end product is demonstrated by this product distribution, which is a significant result.

Wang et al.2014 explained that a study intended to use photocatalysis to convert CO_2 to CH_4. In this study, a solvothermal method was utilized to produce well-crystallized anatase TiO_2 nanoparticles with diameters of around 18.4 nm and a BET surface area of 108.3 m_2 g^{-1}. Photoreduction was then used to synthesize Pt/TiO_2 nanocomposites that have excellent photocatalytic performance and

stability. The well-dispersed Pt nanoparticles exhibited an average diameter of 1.82 nm. Pt photo deposition required one hour, and 500 °C was the optimal TiO_2 calcination temperature. The photoluminescence (PL) spectra demonstrated that Pt/TiO_2 had an increased efficiency of photogenerated charge transfer and separation than Pt/P25. After 4 hours of radiation, the CH_4 yield for the optimized Pt/TiO_2 photocatalysts was 60.1 μmol/gcat h, coupled with an H_2 yield of 87.5 μmol/gcat h and a C_2H_6 yield of 2.8 μmol/gcat h. Pt/TiO_2 had 3.7 times the photocatalytic CO_2 conversion ability of Pt/P25. The output of H_2 will increase with longer irradiation, but not that of CH_4 or C_2H_6. The final concentrations of CH_4 and H_2 at 10.0% CO_2 were 54.4 μmol/gcat h and 80.2 μmol/gcat h, respectively[15].

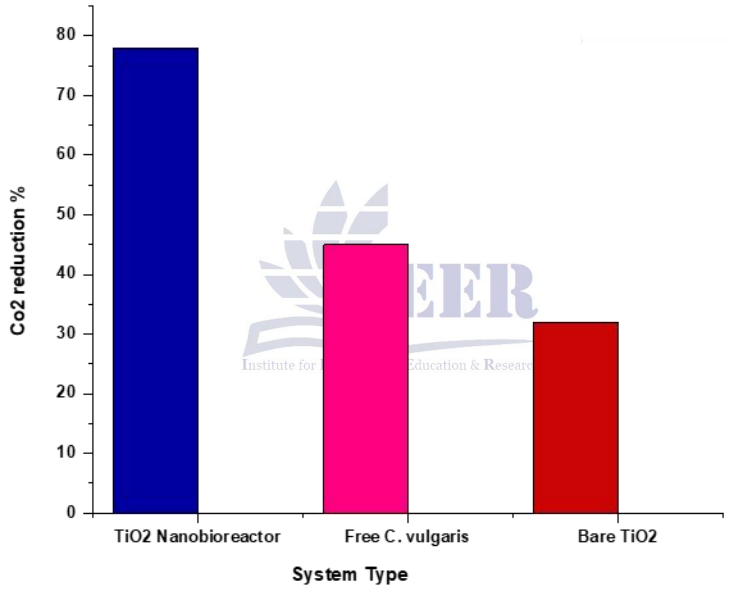

Figure 3.6: Comparison of CO_2 reduction percentage across the nano bioreactor, Free *C. vulgaris*, and Bare TiO_2 after 24 hours, highlighting the synergistic enhancement.

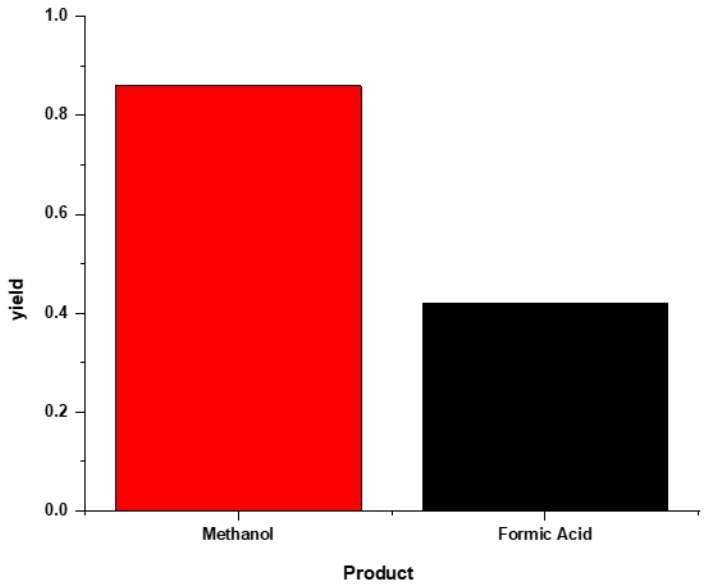

Figure 3.7: The respective yields of methanol and formic acid (mmol/g TiO_2), demonstrating the preferential formation of methanol

3.7 Mechanistic Insights

The improved CO_2 conversion efficiency can be explained by the proposed photocatalytic–biological coupling mechanism. Upon light irradiation, TiO_2 absorbed photons and generated electron–hole pairs. The photogenerated electrons reduced CO_2 into intermediate carbon species (e.g., CO, HCOOH), while the holes participated in water oxidation to produce O_2 and protons. The biological cells further utilized these intermediates through photosynthetic and enzymatic processes, converting them into stable organic products such as methanol. The intimate contact between TiO_2 nanoparticles and algal cells enabled efficient charge transfer, minimizing electron–hole recombination and enhancing overall quantum yield.

Rehman et al.2021 exhibited a highly intriguing approach to collecting CO_2 and reducing it to non-fossil fuel and other beneficial compounds is photocatalytic CO_2 reduction. Due to the overuse of non-renewable energy sources, we are currently dealing with significant ecological issues. In this regard, photocatalytic CO_2 reduction will give us chemicals that are rich in energy while contributing to the sanitation and good health of our surroundings. Numerous photocatalysts have been invented for this purpose in order to generate specific products and enhance system efficiency. Semiconductor materials have generated a lot of attention and exhibited strong CO_2 reduction abilities. In addition to its favorable electromagnetic and optical properties, accessibility, thermal stability, low toxicity, and strong photoactivity, titanium dioxide has been extensively studied as a photocatalyst for CO_2 reduction among semiconductors. The artificial Z-scheme of photocatalyst is designed to offer a simple way to increase CO_2 reduction efficiency, gaining inspiration from natural photosynthesis. The literature in this field is reviewed, with a focus on the utilization of transition metals for CO_2 photoreduction, TiO_2 Z-scheme heterojunction composites, and photocatalytic vehicles. Finally, opportunities and challenges

to bring in a new era of engineering and accomplish high performance with semiconductor materials for photocatalytic CO_2 reduction are addressed[16].

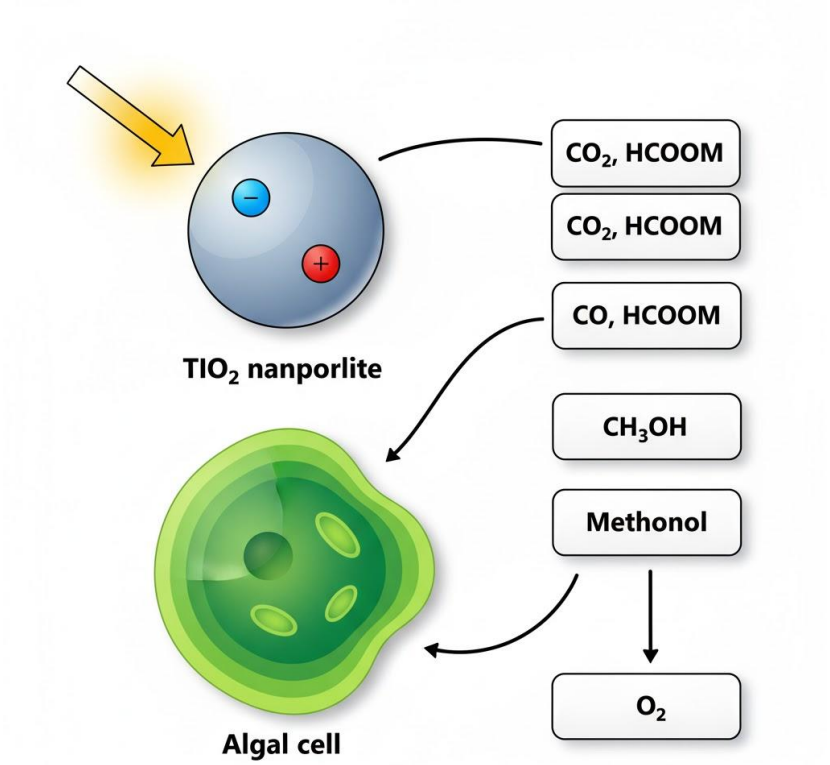

Figure 3.8: Schematic illustration of the photocatalytic–biological coupling mechanism in TiO_2 enabled nano bioreactors. Under light irradiation, TiO_2 nanoparticles generate electron–hole pairs; electrons reduce CO_2 to intermediates such as CO and HCOOH, while holes drive water oxidation to release O_2. The overall CO_2 conversion efficiency is then increased as the algal cells employ these intermediates to produce methanol and other organic compounds through photosynthetic and enzymatic processes.

3.8 Reusability and Operational Stability

The TiO2 nano bioreactor operational stability and reusability over five consecutive CO2 capture cycles is represented in this line graph. The CO2 capture efficiency compared to the system's initial activity (Cycle 1, set at 100%) is indicated on the Y-axis, Performance Retention (%). The data collected shows that the nano bioreactor has outstanding operational stability and robust durability. experiencing a gradual and temporary drop in performance with each achieving success cycle, the system retained an exceptionally high level of performance. By the fifth cycle, the performance retention was still constant at approximately 86% of its initial efficiency. This minimal decay indicates the strong structural integrity of the nano bioreactor,

which is essential for industrial use. The recognized causes, such as light shielding by accumulated biomass or slight biofilm detachment, are consistent with a gradual decrease in efficiency. When assessing the economic practicality of photocatalytic systems for continuous CO_2 capture and conversion, reusability and operational stability are essential factors.

The large-scale applicability of TiO_2-based photocatalysts is restricted by their regular performance loss as a consequence of leaching, surface fouling, and nanoparticle aggregation during repeated reaction cycles. Immobilizing TiO_2 on biopolymeric supports has been demonstrated through previous studies to improve operational stability and recyclability by increasing catalyst recovery, decreasing mass loss, and preserving photocatalytic activity over numerous reuse cycles[17].Surface deactivation, however, can still have an adverse impact on TiO_2-based systems' durability. For example, Pt/TiO_2 photocatalysts show a gradual decrease in activity over time, mainly due to the formation of reactive oxygen species like peroxides and the restructuring of the active site surface [18] . These deactivation processes demonstrate the need for self-regenerative or hybrid mechanisms that maintain electron transfer efficiency and structural integrity under continuous illumination.

The slow deposition of carbonaceous intermediates, such as carbonate and methoxy species, on TiO_2 surfaces is believed to be one of the main causes of catalytic deactivation in CO_2 reduction reactions. achieving their high initial efficiency, metal-modified TiO_2 photocatalysts often lose their effectiveness after a few cycles due to limited intermediate desorption and active site blockage [19] . In order to prevent catalyst poisoning and maintain activity over extended operation, the TiO_2-enabled nanobioreactor developed in this study uses biological coupling, in which immobilized microbial or algal cells metabolize these carbon intermediates. Furthermore, it has been reported that surface modification and composite formation processes may enhance TiO_2's mechanical stability and robustness. For instance, after five consecutive reuse cycles, functionalized TiO_2 composites maintained over 85% of their photocatalytic activity, demonstrating that structural optimization is required for operational durability [20] . In view of these results, integrating a biological component into TiO_2 offers a further approach for improving structural stability, self-regeneration, and reusability.

The bio-assisted TiO_2 system in the present work demonstrates that hybrid nanobioreactors can overcome common degradation pathways observed in conventional photocatalysts, offering a sustainable, efficient, and durable platform for long-term CO_2 conversion processes.

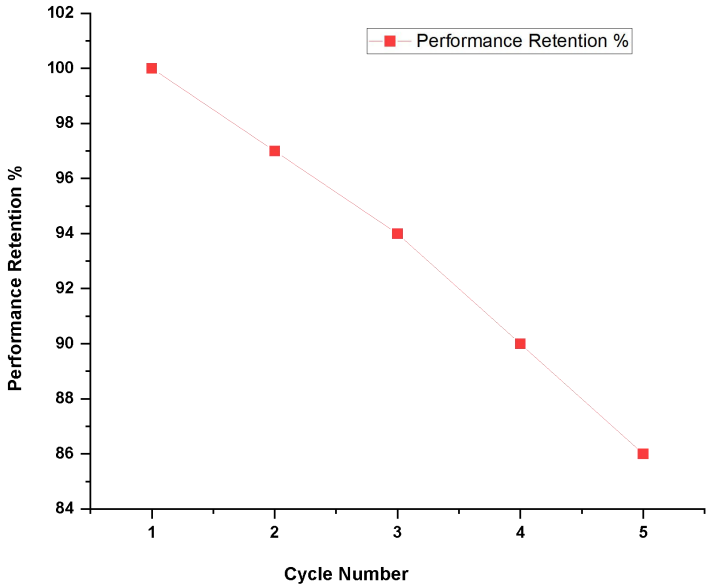

Figure 3.9: CO_2 capture performance retention of the TiO_2 nano bioreactor across five consecutive operational cycles under identical conditions. The system retains 86% of its initial activity after the fifth cycle, confirming robust structural integrity and high operational durability, with minimal performance decline attributed to biomass accumulation.

3.9 Comparative Evaluation

This grouped bar chart synthesizes the comparative performance of the TiO2 Nanobioreactor (red bars) against two control systems, the Conventional Photocatalytic System (blue bars) and the Conventional Biological System (green bars), across three critical metrics. In every metric CO2 reduction efficiency, operational stability (retention after 5 cycles), and reaction rate the TiO2 Nanobioreactor exhibits superior performance.

For CO2 reduction efficiency, the nanobioreactor achieved the highest conversion at approximately 78%, far surpassing the 32% of the conventional photocatalytic system and the 45% of the conventional biological system. contrasting it to the conventional biological system (65%) and the traditional photocatalytic system (55%), it also demonstrates the highest operational stability, conserving around 86% of its initial activity after five cycles. subsequently, the nanobioreactor reinforces its position as the most promising platform by exhibiting the fastest Reaction Rate (relative units ≈1.0). Collectively, these results show that combining material science and biotechnology offers a significant benefit, resulting in a carbon capture and utilization system that is far more efficient, stable, and sustainable.

Lu et al. 2021 suggested that CuO-based electrodes have a lot of potential for CO_2 electrochemical reduction. In the meantime, TiO_2 supports show the benefits of being inexpensive, non-toxic, and chemically stable, resulting in a perfect electrocatalytic support with CuO. However, different techniques may yield TiO_2 supports with varying morphologies and structures, resulting in various CuO/TiO_2 electrocatalytic properties. In this study, CuO/TiO_2 electrodes

were synthesized by thermal decomposition using three supports: dense TiO_2, TiO_2 nanotube, and TiO_2 nanofiber. The electrocatalysts' performances were investigated. While ethanol was the main outcome of all three electrocatalysts, the electrochemical efficiency and reaction variables were clearly different, based on the results. Pure ethanol is the liquid product of CuO/Dense TiO_2, but due to the higher resistance of the TiO_2 layer, the current efficiency is quite low. Although ethanol can be manufactured at low overpotential with excellent current efficiency and CuO/TiO_2 nanotube demonstrates high conductivity, the gas products cannot be regulated. CuO/TiO_2 nanofiber can significantly limit the hydrogen evolution reaction and has greater specific surface area and more active sites, all of which are beneficial for CO_2 reduction. After 5 hours, the yield of ethanol can reach 6.4 μmol cm^{-2} at −1.1 V (vs. SCE)[21].

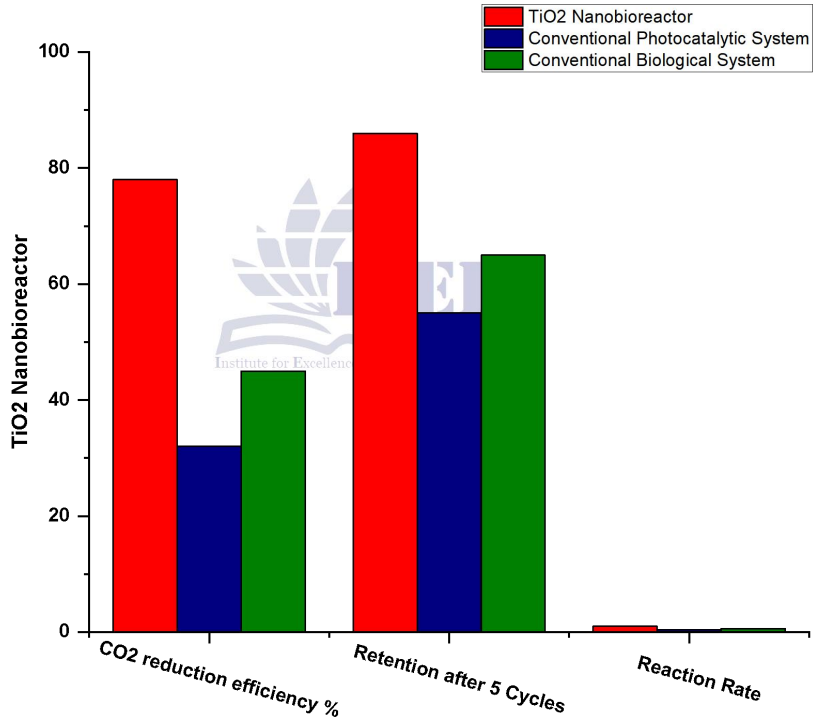

Figure 3.10: Comparison of CO_2 reduction efficiency, operational stability (retention after 5 cycles), and reaction rate for the TiO_2 Nano bioreactor versus conventional photocatalytic and biological systems

4 Conclusion

This study successfully demonstrated the design, fabrication, and performance of TiO_2-enabled nano bioreactors as an innovative platform for integrated carbon capture, utilization, and storage (CCUS). The synthesized TiO_2 nanoparticles exhibited a highly crystalline anatase phase with mesoporous architecture and a large surface area, providing ideal conditions for CO_2 adsorption and photocatalytic activation. Surface modification using APTES effectively introduced amino functional groups,

enhancing biocompatibility and enabling efficient immobilization of *Chlorella vulgaris* microalgae. It also shows the highest operational stability, retaining about 86% of its initial activity after five cycles, when compared to the traditional biological system (65%) and the traditional photocatalytic system (55%). The nanobioreactor then shows the fastest Reaction Rate (relative units ≈1.0), confirming its reputation as the most promising platform. These results illustrate the main advantages of combining material science and biotechnology, leading to an exceptionally effective, reliable, and sustainable carbon capture and use system.

References

1) [1] E. H. Oelkers and D. R. Cole, "Carbon Dioxide Sequestration A Solution to a Global Problem," *Elements*, vol. 4, no. 5, pp. 305–310, Oct. 2008, doi: 10.2113/gselements.4.5.305.
2) [2] J. Yan and Z. Zhang, "Carbon Capture, Utilization and Storage (CCUS)," *Appl Energy*, vol. 235, pp. 1289–1299, Feb. 2019, doi: 10.1016/j.apenergy.2018.11.019.
3) [3] C. B. Peres, P. M. R. Resende, L. J. R. Nunes, and L. C. de Morais, "Advances in Carbon Capture and Use (CCU) Technologies: A Comprehensive Review and CO2 Mitigation Potential Analysis," *Clean Technologies*, vol. 4, no. 4, pp. 1193–1207, Nov. 2022, doi: 10.3390/cleantechnol4040073.
4) [4] A. Uliasz-Bocheńczyk, "A Comprehensive Review of CO2 Mineral Sequestration Methods Using Coal Fly Ash for Carbon Capture, Utilisation, and Storage (CCUS) Technology," *Energies (Basel)*, vol. 17, no. 22, p. 5605, Nov. 2024, doi: 10.3390/en17225605.
5) [5] Z. Abdin *et al.*, "Solar energy harvesting with the application of nanotechnology," *Renewable and Sustainable Energy Reviews*, vol. 26, pp. 837–852, Oct. 2013, doi: 10.1016/j.rser.2013.06.023.
6) [6] K. Nagaraj *et al.*, "Photocatalytic advancements and applications of titanium dioxide (TiO_2): Progress in biomedical, environmental, and energy sustainability," *Next Research*, vol. 2, no. 1, p. 100180, Mar. 2025, doi: 10.1016/j.nexres.2025.100180.
7) [7] A. Chebbi, A. Sinopoli, A. Abotaleb, and Y. Bicer, "Photocatalytic conversion of carbon dioxide, methane, and air for green fuels synthesis," *Catal Sci Technol*, vol. 13, no. 17, pp. 4895–4918, 2023, doi: 10.1039/D3CY00675A.
8) [8] Ž. Kovačič, B. Likozar, and M. Huš, "Photocatalytic CO 2 Reduction: A Review of Ab Initio Mechanism, Kinetics, and Multiscale Modeling Simulations," *ACS Catal*, vol. 10, no. 24, pp. 14984–15007, Dec. 2020, doi: 10.1021/acscatal.0c02557.
9) [9] N. D. Cuong and D. T. Quang, "Progress through synergistic effects of heterojunction in nanocatalysts - Review," *Vietnam Journal of Chemistry*, vol. 58, no. 4, pp. 434–463, Aug. 2020, doi: 10.1002/vjch.202000072.
10) [10] D. Li *et al.*, "Enhanced light harvesting ability in hollow Pt/TiO2 nanoreactor for boosting tetracycline photodegradation," *Progress in Natural Science: Materials International*, vol. 34, no. 4, pp. 767–775, Aug. 2024, doi: 10.1016/j.pnsc.2024.07.005.
11) [11] L. Liu *et al.*, "Advancing CO 2 Upgrading to Multicarbon Products: Synergies Between Photo/Electrochemical and Biological Conversion," *Adv Funct Mater*, Sep. 2025, doi: 10.1002/adfm.202513716.
12) [12] B. Krause and A. Farina, "Using ecoacoustic methods to survey the

impacts of climate change on biodiversity," *Biol Conserv*, vol. 195, pp. 245–254, Mar. 2016, doi: 10.1016/j.biocon.2016.01.013.

13) [13] A. Cai, A. Guo, and Z. Ma, "Immobilization of TiO2 Nanoparticles on Chlorella pyrenoidosa Cells for Enhanced Visible-Light-Driven Photocatalysis," *Materials*, vol. 10, no. 5, p. 541, May 2017, doi: 10.3390/ma10050541.

14) [14] J. Wang, R. Guo, Z. Bi, X. Chen, X. Hu, and W. Pan, "A review on TiO 2− *x* -based materials for photocatalytic CO 2 reduction," *Nanoscale*, vol. 14, no. 32, pp. 11512–11528, 2022, doi: 10.1039/D2NR02527B.

15) [15] Y. Wang *et al.*, "High efficiency photocatalytic conversion of CO 2 with H 2 O over Pt/TiO 2 nanoparticles," *RSC Adv.*, vol. 4, no. 84, pp. 44442–44451, 2014, doi: 10.1039/C4RA07457B.

16) [16] Z. U. Rehman *et al.*, "Photocatalytic CO2 Reduction Using TiO2-Based Photocatalysts and TiO2 Z-Scheme Heterojunction Composites: A Review," *Molecules*, vol. 27, no. 7, p. 2069, Mar. 2022, doi: 10.3390/molecules27072069.

17) [17] Aanchal, S. Barman, and S. Basu, "Complete removal of endocrine disrupting compound and toxic dye by visible light active porous g-C3N4/H-ZSM-5 nanocomposite," *Chemosphere*, vol. 241, p. 124981, Feb. 2020, doi: 10.1016/j.chemosphere.2019.124981.

18) [18] X. Zhang *et al.*, "Stability improvement of a Pt/TiO 2 photocatalyst during photocatalytic pure water splitting," *J Mater Chem A Mater*, vol. 10, no. 45, pp. 24381–24387, 2022, doi: 10.1039/D2TA06961J.

19) [19] K. Su *et al.*, "Research progress of TiO 2 photocatalytic reduction of oxyanion pollutants in water: a mini review," *Green Chem Lett Rev*, vol. 15, no. 1, pp. 35–44, Jan. 2022, doi: 10.1080/17518253.2021.2018050.

20) [20] S. M. Soliman, A. Abdelhafiz, and M. G. Elmahgary, "Sustainable TiO_2/sludge ceramic waste nanocomposite for high-efficiency Photodegradation of rhodamine B," *Results Chem*, vol. 17, p. 102569, Sep. 2025, doi: 10.1016/j.rechem.2025.102569.

21) [21] Y. Lu, H. Cao, S. Xu, C. Jia, and G. Zheng, "A comparative study of the effects of different TiO 2 supports toward CO 2 electrochemical reduction on CuO/TiO 2 electrode," *RSC Adv*, vol. 11, no. 35, pp. 21805–21812, 2021, doi: 10.1039/D1RA02837E.

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