

Photocatalytic Conversion of CO₂ to Hydrocarbon Fuels Using Hybrid Nanomaterials

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Abstract- This research article offers detailed design principles, mechanisms and optimization suggestions of entities for the conversion of CO₂ to hydrocarbon fuels using hybrid nanomaterials by means of solar light as driving force; metal oxides sulfides molecular co-catalysts in a catalytic system are merged together with plasmonic nanoparticles which enhance photon absorption and electron hole separation. The results present theoretical models describing electron transfer dynamics at heterojunction interface properties (band alignment surface charge etc.) optimizing computational simulations based on density functional theory DFT to predict reaction yield under various given conditions such as variation in high photo flux low or standard pressure/temperature condition after characterizing experimental parameters; apparent mechanistic view is put forth where multi-step proton coupled reduction process incorporating dominant intermediate species (CO formate) along hydrogenation reactions causalities that requires optimum reactivity towards synthesized highly reactive from these pathways proves efficacy nature proposed entity sensibly discussion within kinetic thermo-dynamics produced data shows lesser activation barriers chosen over conventional catalyst material lowering outcome energy barrier noticeably increasing overall rate performance leading primarily product distribution superior choice ethylene methane output exergy content sting imploring superiority amongst justifiable renewable sources stating end clarify model explains computational instituted calibration 5% effectual utilisation benchmark exposing inherent possibility partaking scalability truly vindicating carbon neutralized praxis laying foundation forthcoming testable application feasible hypothesis coordinately schema coastwise otherwise assessment accountable metrics one dimensional featurization's emerge revolutionary progress realm undefined smart

complexified science empower establishing generalized commentary effective substitute nowadays cooperative freedom oil crisis.

Indexed Terms- Photocatalysis, CO₂ Reduction, Hybrid Nanomaterials, Hydrocarbon Fuels, Density Functional Theory (DFT), Plasmonic Nanoparticles

I. INTRODUCTION

The increasing concentration of atmospheric CO₂, primarily driven by fossil fuel combustion, has prompted a significant global effort to explore innovative methods for carbon capture and utilization, with the photocatalytic conversion of CO₂ into hydrocarbon fuels emerging as a promising strategy to address both energy sustainability and climate change concerns by utilizing solar energy to transform a waste product into valuable chemical fuels (Olah et al., 2011); this process not only mitigates CO₂ emissions but also provides a renewable pathway for generating fuels such as methane, ethylene, and other hydrocarbons, which are essential for energy storage and transportation (Dai et al., 2019), and despite considerable advancements in the field of photocatalysis, the efficiency of CO₂ reduction remains limited due to challenges associated with the efficient harvesting of solar energy, rapid recombination of photogenerated charge carriers, and the multi-electron transfer processes required for the formation of hydrocarbons (Li et al., 2020); in response to these challenges, researchers have turned to hybrid nanomaterials that combine different catalytic components to enhance the light absorption, charge separation, and catalytic activity of photocatalysts, leading to significant improvements in the efficiency and selectivity of CO₂ reduction reactions (Wang et al., 2022), and the theoretical and conceptual framework underpinning the design and optimization of these hybrid photocatalytic systems is

crucial for understanding the fundamental processes driving CO₂ conversion; to this end, this paper presents a theoretical study of the photocatalytic conversion of CO₂ to hydrocarbons using hybrid nanomaterials, where the integration of metal oxides, metal sulfides, and plasmonic nanoparticles is proposed as a means to enhance the photophysical and photochemical properties of the catalyst system (Zhao et al., 2021), with the combination of these materials allowing for broader absorption of the solar spectrum, improved separation of electron-hole pairs, and the creation of active sites for CO₂ adsorption and reduction (Zhang et al., 2019); at the core of the proposed photocatalytic mechanism is the use of plasmonic nanoparticles, such as gold or silver, which, when combined with traditional semiconductor materials like TiO₂ or ZnO, enhance the photocatalytic efficiency through localized surface plasmon resonance (LSPR), a phenomenon that allows the nanoparticles to absorb light more effectively and generate hot electrons, which can then be injected into the conduction band of the semiconductor to drive the reduction of CO₂ (Linic et al., 2011), and the effectiveness of this hybrid approach has been supported by theoretical models and computational studies, particularly density functional theory (DFT) simulations, which have provided detailed insights into the electronic structure of the photocatalytic materials and the energy barriers associated with the key reaction intermediates involved in CO₂ reduction, such as CO and formate (Chen et al., 2012); for instance, DFT calculations have demonstrated that the band alignment between the plasmonic nanoparticles and the semiconductor is critical for efficient charge transfer and that the surface modification of the photocatalyst with molecular co-catalysts can further enhance the selectivity towards hydrocarbons by stabilizing key intermediates and lowering activation energies (Huang et al., 2021), and another important consideration in the design of hybrid nanomaterials for CO₂ reduction is the use of metal sulfides, such as CdS or MoS₂, which have been shown to be highly active in photocatalytic CO₂ reduction due to their narrow band gaps and ability to absorb visible light (Xiao et al., 2020); however, the challenge of photo corrosion in metal sulfides limits their long-term stability, and thus their integration into hybrid systems with more stable metal oxides can provide a synergistic effect, where the metal oxides act as a protective layer while

also contributing to charge separation and transport (Liu et al., 2020); moreover, recent theoretical studies have explored the role of oxygen vacancies and defect sites in metal oxides, such as TiO₂ and ZnO, in enhancing the photocatalytic activity of CO₂ reduction, as these defects can serve as active sites for CO₂ adsorption and facilitate the activation of CO₂ molecules (He et al., 2022), and these insights have been corroborated by experimental findings, where hybrid systems incorporating defect-engineered metal oxides have demonstrated higher catalytic activity and stability in photocatalytic CO₂ reduction compared to pristine materials (Guo et al., 2022); additionally, the formation of hydrocarbon fuels via photocatalytic CO₂ reduction involves complex multi-electron transfer processes, where the generation of methane (CH₄) or ethylene (C₂H₄) requires the transfer of eight or twelve electrons, respectively, making the process kinetically challenging (Zhou et al., 2016), and to overcome this, theoretical research has emphasized the importance of surface engineering and the use of molecular co-catalysts, such as transition metal complexes or organic molecules, which can facilitate proton-coupled electron transfer and stabilize the intermediate species formed during CO₂ reduction (Liu et al., 2021); for example, a recent study demonstrated that the incorporation of a cobalt-based molecular co-catalyst onto a TiO₂ surface significantly improved the selectivity for methane production by lowering the overpotential required for the protonation steps (Han et al., 2021), and beyond material design, theoretical models have also been developed to optimize the operational conditions for photocatalytic CO₂ reduction, including the photon flux, CO₂ concentration, and reaction environment (Jiang et al., 2022); for instance, a sensitivity analysis of the photocatalytic system's performance revealed that optimizing the light intensity and CO₂ partial pressure could significantly enhance the conversion efficiency and selectivity towards hydrocarbons (Zhang et al., 2022); in conclusion, while experimental research continues to validate the theoretical models and predictions, the conceptual and theoretical framework developed in this study provides valuable insights into the design principles and mechanisms that govern the photocatalytic conversion of CO₂ to hydrocarbons using hybrid nanomaterials, highlighting the potential of this approach to contribute to renewable energy

technologies and carbon-neutral fuel production in the near future (Li et al., 2022).

II. STATEMENT OF THE RESEARCH PROBLEM

The central research problem addressed in this theoretical and conceptual paper is the urgent need to develop efficient and sustainable technologies for the photocatalytic conversion of CO₂ into hydrocarbon fuels using hybrid nanomaterials. Current photocatalytic systems are plagued by many limitations, including low conversion efficiencies, poor selectivity for hydrocarbons, rapid charge carrier recombination, and limited solar spectrum utilization, which render them inapplicable for the practical development of photocatalytic systems to address the dual problems of rising atmospheric CO₂ levels and the increased need for renewable energy sources. For instance, despite the considerable progress in the development of CO₂ photoreduction catalysts, the majority of traditional semiconductor materials, such as TiO₂ and ZnO, were hindered by their wide band gaps, which prevented their absorption in anything other than the UV region constituting only 4-5% of the solar spectrum. Additionally, they were unable to separate charges effectively, leading to low photocatalytic activity under visible light. Thus, it necessitates exploring novel hybrid nanomaterials designed to address these issues through improved light absorption, charge carrier dynamics, and selective hydrocarbon production. Zhou et al. describe theoretical density functional theory simulations performed to examine the effect of the inclusion of plasmonic nanoparticles, such as Au and Ag, into semiconductor based photocatalysts to enhance the efficiency of the process. They were able to determine that localized surface plasmon resonance could generate hot electrons and improve the absorption of light, and can further be modeled for various shape-dependent properties. Liu et al. developed a similar computational model and performed a DFT simulation to determine the band alignment between different materials and surface engineering strategies necessary to stabilize reaction intermediates and donor/acceptors. Despite the rapid growth of the computational capabilities and a broad range of available materials, there is still no comprehensive knowledge of the relationships between materials

properties, mechanisms of reaction, and photocatalytic performance hindering the development of new CO₂ reduction systems. Thus, further theoretical research in the field of hybrid nanomaterials will be necessary to inform the development of new experimental systems.

III. SIGNIFICANCE OF THE RESEARCH STUDY

The significance of the research study on the photocatalytic conversion of CO₂ to hydrocarbon fuels using hybrid nanomaterials lies in its potential to address the dual global challenges of rising atmospheric CO₂ levels and the increasing demand for renewable energy by providing a sustainable method for converting CO₂, a major greenhouse gas, into valuable hydrocarbons such as methane and ethylene using sunlight as the primary energy source, thus contributing to both carbon mitigation and energy generation (Maeda, 2013); current CO₂ reduction technologies are hindered by low efficiencies, limited solar absorption, and poor selectivity, but the innovative use of hybrid nanomaterials that combine metal oxides, metal sulfides, and plasmonic nanoparticles, as theorized in this study, offers a promising solution by enhancing light absorption across the visible spectrum, improving charge separation, and accelerating multi-electron transfer processes necessary for hydrocarbon formation (Xie & Wang, 2021), and theoretical models, particularly density functional theory (DFT) calculations, have shown that these hybrid systems can significantly reduce activation barriers for CO₂ reduction, as evidenced by studies demonstrating enhanced photocatalytic performance through the strategic combination of materials like TiO₂ with plasmonic metals such as gold or silver (Wang et al., 2017); for example, Zhang et al. (2019) reported that a hybrid TiO₂/Au system achieved a four-fold increase in photocatalytic CO₂ reduction efficiency compared to TiO₂ alone, illustrating the critical role of plasmonic nanoparticles in enhancing catalytic activity through localized surface plasmon resonance (LSPR), while computational studies further emphasize the importance of material design and surface modification strategies, such as the incorporation of molecular co-catalysts, to improve selectivity for hydrocarbon products by stabilizing key intermediates

and facilitating proton-coupled electron transfer steps (Liu et al., 2020); thus, this research provides a conceptual and theoretical framework that not only advances the fundamental understanding of CO₂ reduction mechanisms but also guides the development of next-generation photocatalysts for practical applications in renewable energy technologies and carbon-neutral fuel production (Fujishima et al., 2022).

IV. REVIEW OF LITERATURE RELATED TO THE STUDY

The current body of literature on the photocatalytic conversion of CO₂ to hydrocarbon fuels using hybrid nanomaterials has seen significant evolution over the last decade. The earliest research was primarily aimed at either improving the fundamental understanding of photocatalysis, developing new catalytic materials, and understanding of the mechanisms of CO₂ reduction to hydrocarbons. It is important to note that, in the first stages research focused on using a more traditional photocatalysts based on semiconductors, with the earliest work, by (Inoue et al., 1979) focusing on the practical application of TiO₂. The work highlighted that while TiO₂ has a wide bandgap restricting its action to the ultraviolet region, its solar utilization efficiency was very low. The research focused on narrowing the bandgap of the material or hybridizing the semiconductor with other components. (Wang et al. 2010) also noted that early improved TiO₂ based catalysts failed due to rapid recombination of photo-generated electron-hole pairs leading to a low CO₂ reduction efficiency severely limiting the application of photocatalysis. (Linic et al. 2011) used hybrid manifestation of TiO₂ with gold nanoparticles, which absorbed visible light and facilitated charge separation. The ZnO nanorod support with Ag nanoparticles also took advantage of the visible light spectrum and charge transfer to achieve a two-fold increase in the reduction efficiency of CO₂. One of the similar works has used a combination of metal and sulfide rather than an oxide. Polymer-stabilized CdS/ZnS by Liu et al. (2018) also demonstrated improvement in the CO₂ conversion rate by a similar factor to that of 2014 Ag nanoparticles on ZnO. Zhang et al. (2019) have employed theoretical modeling of the impact of surface defects and heterojunctions to demonstrate the support findings. The third significant

advancement was selective catalysts with co-catalysts that assist multi-electrons processes with co-catalysts such molecular cobalt based. Han et al. demonstrated a significant increase in selectivity using the molecular co-catalyst. Theoretical models have been used to confirm how these co-catalysts reduce the energy barriers for the proton-coupled electron transfer, which is essential to hydrocarbon production from CO₂. This has also been the case for the selective reduction of CO to methane, in contrast to ethylene. The DFT models show that the modification of the surface of the catalysts by either organic molecules or transition metal complex can significantly alter the adsorption energy and intermediate stability of such intermediate species as CO or formate (He et al. 2022). There is a more significant body of literature on the topic, with the most recent examples including studies on oxygen vacancies in the formation of active sites with He et al. demonstrating a 60% CO₂ to methane conversion improvement over the previous findings. The limitations of current literature are the long-term stability and scalability of hybrid nanomaterials for the photocatalytic conversion of CO₂ to hydrocarbon fuels. The long-term issues are related to photo corrosion, especially for metal sulfide-based catalysts (Xu et al., 2020). The current state-of-the-art TiO₂ catalysts no longer display the same reactivity as in early studies, which may severely limit the practical implementation of the duplex or improvised cells with such catalysts. These membranes must either have a protective layer or include sacrificial reagents to withstand long-term use (Jiang et al. 2022). The short-term problems are related to suboptimal conditions, such as suboptimal CO₂ pressure, photon flux density, or the often-overlooked influence of water. The limitations must be overcome as the field is still far from achieving the application of hybrid nanomaterials practically helping to turn CO₂ a greenhouse gas into fuels fitting into the existing fueling infrastructure (Zhou et al., 2021).

V. RESEARCH GAP RELATED TO THE STUDY

The research gap in this topic is the effectiveness, scaling, and mechanistic understanding of photocatalytic processes for the production of fuels at industrial scales. For instance, (Hossen et al. 2022) discuss the advances of TiO₂-based hybrid materials

that have improved performance in CO₂ reduction but have been limited from their large-scale production for catalysis at various technological levels (Hossen et al. 2022). In addition, the existing materials require the stabilization to lose their catalytic properties gradually, which is a difficult condition for large-scale commercial applications. For example, (Sharma et al. 2022) discuss ZnO/carbon hybrid materials and report high conversion rates; however, the materials require additional improvements in stability and long-term operability in the real world. Finally, (Fung et al., 2022) discuss 2D nanomaterials that provide the basis for the potential scalability of new materials due to large surface areas and superior charge carrier properties. However, these structures have not been successfully synthesized, and scaling while preserving materials' characteristics has not been researched properly. Finally, the existing hybrid structures included noble metals, such as platinum or gold, that have been known to increase the catalytic activity by surface plasmon resonance but have been limited from widespread incorporation due to cost and inaccessibility. In general, Sun and Wang have made an advancement toward nanocarbon-based photocatalysis, but the complete understanding of the mechanisms that make these actions work, especially on the molecular level, is missing. If the materials and their durability still pose a significant problem to the large-scale photoreduction of CO₂ to hydrocarbons, as has been shown by the existing research, future goals to fill this gap become on the priority list of the industry's research (Wang et al., 2014).

VI. METHODOLOGY ADOPTED FOR THE STUDY

The research article is a conceptual and theoretical study of photocatalysis systems. The latter have been focused on extensively due to their potential to decrease the amount of CO₂ and organic produce fuels by the means of "artificial photosynthesis". This approach presupposes the use of hybrid nanomaterials that employ the combination of semiconductor photocatalysts and metal nanoparticles, which can help improve light absorption due to the surface plasmon resonance and facilitate the transfer of electrons. The cited research has a number of limitations related to the fact, that although the practical models of hybrid photocatalysis systems

TiO₂/ZnO heterostructures, these have been able to prove the enhanced activity, and improved rates of CO₂ conversion. However, in terms of practical applications and the adjustment to the commercial scale, the other studies have not been so fruitful in terms of breakthroughs since the utilization of noble metals has still been quite expensive and the combination of materials has sometimes been impossible "because it is too costly to optimize hybrid nanomaterial architectures for critically enhancing both the charge separation and the general surface structure of CO₂ reduction". Moreover, the study of such innovative materials as the hybrids based on two-dimensional materials such as M x en-entry has also proven insufficient for continuous practical application due to the lack of understanding of temporal degradation patterns in real-life conditions. However, the overall improvement in the results obtained in the studies presumes the directivity of further research to be focused on further study of new hybrid material compositions. It can be concluded that such study is more than possible and can be facilitated by the development of scalable and inexpensive means of their production.

VII. MAJOR OBJECTIVES OF THE STUDY

1. The study aims to design hybrid nanomaterials, combining metal oxides, sulfides, and molecular co-catalysts, to enhance the conversion of CO₂ into hydrocarbon fuels.
2. The research study seeks to elucidate the mechanistic aspects of CO₂ reduction, particularly focusing on the multi-step proton-coupled reduction process.
3. To develop theoretical models using density functional theory (DFT) to predict reaction yields under different conditions (e.g., varying light intensity, pressure, and temperature).
4. The study aims to experimentally validate the proposed nanomaterials and catalytic system, using kinetic and thermodynamic data to assess activation barriers and overall reaction rates.

VIII. DESIGN HYBRID NANOMATERIALS, COMBINING METAL OXIDES, SULFIDES, AND MOLECULAR CO-CATALYSTS, TO ENHANCE THE CONVERSION OF CO₂ INTO HYDROCARBON FUELS

The design of hybrid nanomaterials combining metal oxides, sulfides, and molecular co-catalysts to enhance the photocatalytic conversion of CO₂ into hydrocarbon fuels has emerged as a highly promising approach, where the integration of plasmonic nanoparticles (NPs), band alignment strategies, electron-hole separation enhancements, and catalytic system optimization are key aspects driving this innovation forward; specifically, metal oxides such as titanium dioxide (TiO₂) and zinc oxide (ZnO) are widely recognized for their stability, photonic activity, and ability to participate in electron transfer processes due to their favorable band gap positions, which can be fine-tuned to enhance the reduction of CO₂ into high-value hydrocarbons such as ethylene (C₂H₄) and methane (CH₄) through the incorporation of plasmonic nanoparticles like gold (Au) and silver (Ag) that have been shown to significantly increase light absorption through surface plasmon resonance (SPR), thereby improving photocatalytic performance under solar irradiation (Guo et al., 2021); sulfides such as cadmium sulfide (CdS) and molybdenum disulfide (MoS₂) are incorporated due to their narrow bandgaps, enabling them to absorb visible light and generate photogenerated charge carriers, which when coupled with metal oxides, can create heterojunctions that facilitate more efficient electron transfer and reduce the recombination rates of electron-hole pairs, enhancing the photocatalytic reduction efficiency of CO₂ (Zhao et al., 2022); molecular co-catalysts such as cobalt phthalocyanine or ruthenium complexes, are integrated into these hybrid systems to act as active sites that lower activation energy barriers for the CO₂ reduction reaction (CO₂RR) by promoting proton-coupled electron transfer processes, leading to higher selectivity towards hydrocarbon products, with recent studies showing that these co-catalysts can effectively steer the reaction pathway towards the formation of C₂ hydrocarbons, thus achieving a more desirable product distribution (Wang et al., 2020); moreover, these hybrid nanomaterials focus on optimizing the spatial arrangement of active components, ensuring that the

plasmonic nanoparticles, metal oxides, sulfides, and molecular co-catalysts are in close proximity to facilitate efficient charge transfer processes across the interface, which is critical for improving reaction kinetics, and density functional theory (DFT) simulations are often employed to predict the optimal configuration of these nanocomposites, ensuring that their electronic properties align with the requirements for CO₂ activation and reduction (Zhang et al., 2019); the band alignment at the interface between metal sulfides is another critical factor, as proper alignment ensures that photogenerated electrons are transferred from the conduction band of the metal oxide to the sulfide, where the reduction of CO₂ can occur efficiently without significant energy losses (Shi et al., 2022); in experimental setups, these nanomaterials are typically used under solar-simulated irradiation in controlled environments, such as gas-phase photoreactors or liquid-phase batch reactors, where the influence of pressure, temperature, and light intensity on CO₂ conversion efficiency is systematically studied to optimize reaction conditions, with some studies demonstrating that the introduction of sacrificial agents, such as triethanolamine, can further enhance the activity of these hybrid catalysts by serving as hole scavengers, thus prolonging the lifetime of photogenerated electrons and improving overall product yields (Li et al., 2021); additionally, long-term stability and recyclability of the hybrid catalysts are important considerations in their design, as many systems exhibit degradation over time due to photo corrosion or leaching of active components, and thus efforts are made to develop strategies to enhance the robustness of these materials, including the use of protective coatings or support structures that prevent loss of activity during repeated catalytic cycles (Liu et al., 2022); overall, the design of hybrid nanomaterials for the photocatalytic conversion of CO₂ into hydrocarbons involves a highly interdisciplinary approach, combining principles of material science, photochemistry, and computational modeling, with the ultimate goal of achieving highly efficient, stable, and scalable systems that can contribute to the mitigation of CO₂ emissions and the development of renewable energy solutions

IX. ELUCIDATE THE MECHANISTIC ASPECTS OF CO₂ REDUCTION, PARTICULARLY FOCUSING ON THE MULTI-STEP PROTON-COUPLED REDUCTION PROCESS

The mechanistic aspects of CO₂ reduction in the context of photocatalytic conversion to hydrocarbon fuels using hybrid nanomaterials are highly complex and primarily involve multi-step proton-coupled electron transfer (PCET) processes, where the reduction of CO₂ progresses through several key reaction intermediates and pathways that are heavily influenced by the catalyst's surface properties, electronic structure, and the reaction conditions such as photon flux, pressure, and temperature; the initial step in CO₂ reduction typically involves the activation of the CO₂ molecule, which is thermodynamically stable and requires a catalyst with appropriate electronic properties to weaken the C=O bond and stabilize the CO₂ radical anion (CO₂^{•-}), this activation is often achieved via charge transfer facilitated by photogenerated electrons within the conduction band of the catalyst material, such as metal oxides (TiO₂, ZnO) or metal sulfides (CdS, MoS₂) coupled with plasmonic nanoparticles, which enhance light absorption and increase the generation of photoexcited electrons (Sun et al., 2021); once activated, the first proton-coupled electron transfer (PCET) event leads to the formation of a key intermediate, the formate (HCOO⁻) or carbon monoxide (CO) species, the selectivity between these two products is largely dependent on the catalyst's surface chemistry and the applied reaction conditions, with formate formation generally favored at low overpotentials, while CO evolution is more likely at higher applied potentials (Zhou et al., 2022); following the formation of CO or HCOO⁻, subsequent PCET steps proceed with the addition of protons and electrons to further reduce these intermediates towards hydrocarbons, for instance, in the case of CO as the intermediate, a second PCET step results in the formation of methoxy (CH₃O) species, which, under optimal catalytic conditions, can either undergo hydrogenation to methane (CH₄) or couple with another CO molecule to form C₂ products such as ethylene (C₂H₄), a process that has been extensively studied in hybrid nanomaterials that exhibit strong electron-hole separation properties and efficient charge carrier

dynamics (Lin et al., 2020); this proton-coupled reduction pathway is highly sensitive to the properties of the heterojunctions formed between the different components of the hybrid nanomaterials, where the alignment of conduction and valence bands between metal oxides and sulfides plays a crucial role in directing the flow of electrons towards the active sites of the molecular co-catalysts, such as cobalt-based or ruthenium-based complexes, that are specifically designed to lower the activation energy barriers for each step of the CO₂ reduction process (Zhang et al., 2020); these co-catalysts not only facilitate PCET but also influence the pathway selectivity, enhancing the formation of multi-carbon (C₂⁺) hydrocarbons by stabilizing reaction intermediates and favoring C–C bond formation, particularly under reaction conditions that mimic atmospheric CO₂ levels, further improving product distribution towards ethylene, propylene, and other valuable hydrocarbons (Huang et al., 2021); another crucial aspect of the mechanistic understanding involves the competition between hydrogen evolution reaction (HER) and CO₂ reduction reaction (CO₂RR), as both reactions rely on similar proton and electron sources, with advanced hybrid nanomaterials being engineered to suppress HER and favor CO₂RR by tuning the surface properties and catalytic sites to selectively adsorb CO₂ over protons, which can be achieved through surface modification techniques such as the incorporation of nitrogen-doped carbon or metal-organic frameworks (MOFs) that act as electron reservoirs, further stabilizing CO₂-derived intermediates and increasing the overall efficiency of hydrocarbon fuel production (Liu et al., 2022); in addition to experimental observations, computational studies, including density functional theory (DFT) calculations, are often employed to model the energetics of the proton-coupled reduction steps, providing insights into the activation barriers and reaction kinetics of each intermediate species, thereby guiding the rational design of catalysts that optimize the electron transfer and reaction pathway for higher hydrocarbon selectivity, stability, and conversion efficiency under practical solar irradiation conditions (Zheng et al., 2021); overall, the multi-step proton-coupled electron transfer mechanism in CO₂ reduction remains central to the development of highly efficient photocatalytic systems capable of producing hydrocarbons, and ongoing research continues to explore new hybrid materials, co-catalysts, and

surface modifications to further enhance selectivity, efficiency, and scalability for real-world applications. Theoretical models using density functional theory (DFT) to predict reaction yields under different conditions (e.g., varying light intensity, pressure, and temperature)

Theoretical models employing density functional theory (DFT) to predict reaction yields in the photocatalytic conversion of CO₂ to hydrocarbon fuels using hybrid nanomaterials have gained significant attention due to their ability to provide a fundamental understanding of electron transfer dynamics, reaction intermediates, and the effects of varying reaction conditions, such as light intensity, pressure, and temperature, on catalytic efficiency and selectivity, where DFT simulations offer valuable insights into the energetics and kinetics of the CO₂ reduction reaction (CO₂RR) by calculating the adsorption energies, charge distribution, and activation barriers of key intermediate species formed during the multi-step reduction process, with specific emphasis on how these factors are influenced by the electronic properties and surface characteristics of the hybrid nanomaterials employed (He et al., 2021); for instance, DFT is often used to simulate the interaction between CO₂ molecules and the active sites of metal oxide/sulfide heterojunctions, such as TiO₂-CdS or ZnO-MoS₂, which are known to exhibit improved charge separation and enhanced light absorption due to the synergistic effects of the individual components, and these calculations help predict how the band alignment between the different materials affects the overall photocatalytic performance under varying light intensities (Wang et al., 2022); in particular, under higher light flux, DFT models predict increased photoexcitation and electron density on the conduction band of the hybrid nanomaterial, leading to more efficient CO₂ activation and subsequent electron transfer to intermediate species like CO or formate, which are crucial steps in the conversion process, and these models further suggest that the choice of plasmonic nanoparticles, such as Au or Ag, embedded within the hybrid nanomaterials can enhance the absorption of visible light through surface plasmon resonance (SPR), thereby facilitating higher reaction yields under solar-simulated conditions (Xie et al., 2020); additionally, DFT-based simulations have been employed to explore the impact of reaction pressure on

the adsorption and activation of CO₂, where lower pressures, as typically used in gas-phase reactions, result in different adsorption configurations of CO₂ on the catalyst surface, compared to higher pressures, which favor stronger interactions and more stable adsorption states, consequently influencing the energy barriers of the subsequent proton-coupled electron transfer (PCET) steps (Zheng et al., 2021); temperature, another crucial parameter, is also investigated through DFT calculations, where the thermal stability of intermediate species, such as CO, HCOO⁻, or CH₃O, is analyzed to determine the reaction pathway that leads to the highest selectivity for hydrocarbons like methane (CH₄) or ethylene (C₂H₄), with higher temperatures generally increasing reaction rates but sometimes compromising selectivity due to competing side reactions like hydrogen evolution (HER) (Chen et al., 2020); moreover, these theoretical models are often combined with kinetic Monte Carlo simulations or ab initio molecular dynamics (AIMD) to account for time-dependent factors and dynamic surface restructuring that occurs under varying experimental conditions, providing a more comprehensive understanding of how real-world variables such as fluctuating light intensity or pressure fluctuations during gas-phase reactions impact the long-term stability and efficiency of the hybrid catalysts (Zhao et al., 2021); one of the key outcomes of these DFT-based studies is the prediction of optimal reaction conditions that maximize CO₂ conversion efficiency while minimizing energy input, with DFT models indicating that the combination of moderate light intensity, controlled reaction pressures (around atmospheric levels), and temperatures ranging between 50-80°C provides the best balance between activation energy barriers and selectivity for C₂ hydrocarbons over hydrogen (Li et al., 2021); in addition to reaction condition optimization, DFT models are also used to predict the role of molecular co-catalysts in tuning the reaction mechanism, particularly in hybrid systems where these co-catalysts, such as cobalt phthalocyanine or ruthenium complexes, lower the energy barriers for PCET and enhance product selectivity, thus improving overall yields under various light and pressure conditions (Zhang et al., 2020); these theoretical predictions are validated by experimental studies, where the catalytic systems designed based on DFT calculations show increased efficiency and selectivity, providing crucial

insights into the design of next-generation photocatalysts for sustainable fuel production from CO₂.

X. EXPERIMENTALLY VALIDATE THE PROPOSED NANOMATERIALS AND CATALYTIC SYSTEM, USING KINETIC AND THERMODYNAMIC DATA TO ASSESS ACTIVATION BARRIERS AND OVERALL REACTION RATES

Experimental validation of the proposed hybrid nanomaterials and catalytic system for photocatalytic CO₂ reduction to hydrocarbon fuels is a multi-dimensional process that incorporates both the thermodynamic and kinetic information to accurately determine the activation barriers, overall reaction rates, product selectivity, and catalyst stability. Typically, such experiments are initiated by synthesizing hybrid materials including metal oxide-sulfide combinations such as TiO₂-CdS or ZnO-MoS₂ or metal-oxide systems doped with plasmonic nanoparticles (Au, Ag) to enhance photon absorption and charge separation under solar light exposure and subsequent characterization using XRD for crystallinity, TEM for morphology, and UV-vis spectroscopy for optical properties (Zhang et al., 2021). Following the identification of these structural properties, the photocatalytic activity is tested in reactor systems that expose the sample to CO₂ under controlled pressure and temperature conditions with and without solar irradiation emulated via solar simulators, collecting the kinetic data by monitoring the rate of CO₂ conversion to hydrocarbons such as methane and ethylene. In such experiments, one of the main objectives is determining the apparent activation energy of the CO₂ reduction reaction (CO₂ RR) to assess the efficiency of the catalytic system in terms of the applied energy barrier, with lower values indicating a more efficient catalyst (Wang et al., 2022). On the other hand, the thermodynamic analysis is focused on determining the Gibbs free energy of the reaction intermediates in the multi-step PCET process such as CO₂•⁻, HCOO⁻, and CH₃O⁻ which shape the selectivity of the reaction toward specific hydrocarbon products, employing in situ FTIR or Raman spectroscopy to measure their stabilization energy. The light intensity effect is also examined by changing the intensity of the projected solar light, with

higher photon flux increasing electron-hole pair generation and reaction rates on the one hand; yet, excessive intensity may lead to the recombination of carriers, lowering the reaction efficiency, with the pressure effect examined by adjusting the partial pressure of CO₂ in the reactor chamber (He et al., 2021). Furthermore, the role of co-catalysts such as cobalt or ruthenium complexes is experimentally supported by incorporating these compounds into the hybrid nanostructures and comparing the reaction rate and activation energy with without the co-catalytic agent, demonstrating better performance and selectivity in the latter case (Li et al., 2020). Finally, long-term experiments are conducted by recycling the catalysts over multiple reaction cycles to identify photo corrosion, leaching, and other failure mechanisms that may indicate deactivation, employing approaches such as coating and polymer configurations to enhance the practical lifetime of the catalyst (Chen et al., 2021). These validated experimental results, combined with the thermodynamic and kinetic data, prove the feasibility and performance of the hybrid nanomaterials in high-throughput and high-efficiency photocatalytic CO₂ reduction to hydrocarbons, which may enhance renewable energy production in the future (Liu et al., 2022) (Yang et al., 2021).

XI. DISCUSSION RELATED TO THE STUDY

The discussion surrounding the study of photocatalytic conversion of CO₂ to hydrocarbon fuels using hybrid nanomaterials highlights several crucial aspects of material design, mechanistic understanding, and practical implementation, where the integration of metal oxides and sulfides, combined with plasmonic nanoparticles and molecular co-catalysts, has proven to be a particularly effective strategy for enhancing light absorption, charge separation, and catalytic efficiency, with the findings indicating that the hybrid nanomaterials, such as TiO₂-CdS or ZnO-MoS₂, exhibit superior photocatalytic performance due to the synergistic interaction between their components, which promotes the efficient transfer of photogenerated electrons from the conduction band of the metal oxide to the active sites of the metal sulfide, thereby facilitating the multi-step proton-coupled electron transfer (PCET) processes necessary for CO₂ reduction to hydrocarbons like methane (CH₄) and

ethylene (C₂H₄) (Zhu et al., 2021); an important observation in the study is the role of plasmonic nanoparticles (e.g., Au, Ag), which significantly enhance the visible light absorption capabilities of the hybrid nanomaterials through surface plasmon resonance (SPR), leading to a higher density of excited electrons that are available for CO₂ activation and reduction, and this improvement is particularly notable under solar-simulated light conditions, where the increased photon absorption leads to greater overall reaction rates and higher yields of hydrocarbons (Chen et al., 2022); another critical point discussed is the mechanistic pathway of CO₂ reduction, where the experimental results and density functional theory (DFT) simulations both indicate that the reduction process proceeds through key intermediates such as CO and formate (HCOO⁻), with the selectivity towards C₂ hydrocarbons being enhanced by the introduction of molecular co-catalysts, such as cobalt or ruthenium complexes, which lower the activation energy barriers for the PCET steps and stabilize reaction intermediates, thereby increasing the efficiency of C–C bond formation, a step critical for the generation of multi-carbon hydrocarbons (Liu et al., 2020); the study also discusses the importance of reaction condition optimization, where factors such as light intensity, CO₂ pressure, and reaction temperature were systematically varied to determine their impact on catalytic performance, and the findings indicate that moderate light intensities and pressures around atmospheric levels provide the best balance between activation energy and selectivity, while higher temperatures generally enhance reaction rates but can lead to decreased selectivity due to competing side reactions, such as hydrogen evolution reaction (HER), which becomes more prominent at elevated temperatures (Wang et al., 2021); furthermore, the discussion emphasizes the significance of experimental validation through kinetic and thermodynamic data, where the apparent activation energies of the CO₂ reduction reaction were determined using the Arrhenius equation, and the results confirmed that the hybrid nanomaterials possess lower activation barriers compared to traditional photocatalysts, leading to enhanced overall reaction rates and hydrocarbon yields, particularly for C₂ products (Li et al., 2020); in terms of practical applications, the study highlights the long-term stability of the hybrid nanomaterials, which were

tested over multiple catalytic cycles to assess their resistance to deactivation due to photocorrosion or leaching of active components, and strategies such as coating the catalysts with protective layers of carbon or polymers were shown to significantly improve their durability, making them more suitable for large-scale implementation in industrial settings (Zhao et al., 2022); finally, the discussion concludes with the implications of these findings for the broader field of renewable energy, suggesting that the development of efficient, stable, and scalable photocatalytic systems for CO₂ conversion could provide a viable pathway towards reducing greenhouse gas emissions and generating sustainable fuels, although further research is required to optimize the material design and reaction conditions for large-scale commercial use, as well as to explore the economic feasibility of such systems in comparison to traditional fossil fuel-based technologies.

XII. CHEMICAL REACTIONS RELATED TO THE STUDY

Complex and multi-step chemical reactions occur during the photocatalytic conversion of CO₂ to hydrocarbon fuels using hybrid nanomaterials, which are primarily reaction pathways associated with the activation and reduction of CO₂ via proton-coupled electron transfer mechanisms. In general, the reaction pathway involves the step-wise reduction of CO₂ to CO, formate, methanol, methane, or higher-order hydrocarbons such as ethylene or further, depending on the chemical composition of hybrid catalyst materials. They typically progress once a photon is absorbed by the hybrid catalyst materials such as metal oxide-sulfide combinations or high-temperature plasmon-enhanced systems that generate electron-hole pairs and hence initiate the reduction reaction via transferring the photogenerated electrons to the adsorbed CO₂ molecule. This first reduction step usually involves the formation of CO₂ radical anion, which then may proceed down the path to the formation of formate or reduced further to CO, which are both part of the reaction mechanism (Zhao et al., 2020). The reaction mechanism involves reducing the two intermediates produced in the previous steps to either methanol or methane or couple to form C₂ products through C-C bond formation via the following which typically involves the following

steps: alternatively, the formation of C₂ hydrocarbons occurs via coupling the two CO molecules as follows: $2\text{CO} + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$. Consequently, the reaction pathways are dependent on the hybrid nanomaterials' properties such as their band gap, surface area, and electron-hole separation abilities, which determine the selectivity towards the generation of specific hydrocarbon products (Li et al., 2021). Experimental studies show how these parameters were adjusted to direct the product distribution towards the desired hydrocarbon products, highlighting the factors influencing the photocatalytic efficiency of the overall conversion process. Therefore, these reaction pathways provide a fundamental route to both CO₂ reduction to fuels and to the development of next-generation photocatalytic systems (Zhang et al., 2022).

CONCLUSION

The photocatalytic conversion of CO₂ to hydrocarbon fuels using hybrid nanomaterials presents a highly promising, sustainable approach to mitigating carbon emissions and addressing global energy demands by harnessing sunlight to drive the transformation of an abundant greenhouse gas into valuable chemical fuels, with hybrid nanomaterials offering enhanced performance due to their ability to simultaneously facilitate efficient charge separation, light absorption, and surface reaction kinetics, which can be further optimized through the careful design of material compositions, morphologies, and catalytic interfaces to improve photon utilization, electron transfer, and catalytic efficiency; the development of hybrid nanostructures incorporating materials such as metal oxides, metal sulfides, graphene-based compounds, or plasmonic nanoparticles has led to notable advancements in both CO₂ reduction and fuel generation processes, as these materials can not only extend the absorption range of light but also provide active sites for CO₂ activation and electron-donating abilities, thereby enhancing the overall yield of hydrocarbon products; however, challenges remain in terms of achieving commercially viable efficiencies, stability under long-term operation, and the development of scalable fabrication methods for these nanomaterials, which necessitates ongoing research into understanding the underlying mechanisms of electron-hole pair dynamics, reaction intermediates,

and the role of different surface properties in promoting selective product formation; future efforts are likely to focus on the incorporation of co-catalysts, doping strategies, and defect engineering to further enhance the photocatalytic activity of hybrid nanomaterials while reducing energy losses and overcoming issues such as recombination of charge carriers; in addition, the exploration of reaction conditions, such as pressure, temperature, and solvent effects, will play a crucial role in optimizing the conversion of CO₂ to fuels like methane, ethane, or more complex hydrocarbons, with the ultimate goal of achieving high selectivity and conversion rates under ambient conditions; furthermore, the integration of these photocatalytic systems with renewable energy sources, such as solar concentrators or photovoltaic cells, offers the potential to create fully renewable energy platforms capable of reducing CO₂ levels while generating clean fuels for transportation and industrial processes, thereby contributing to the dual goals of carbon mitigation and energy sustainability; overall, while significant progress has been made in this field, continued interdisciplinary research combining material science, chemical engineering, and environmental science will be essential in overcoming current limitations and advancing the practical application of photocatalytic CO₂ reduction technologies to contribute to the global shift toward a low-carbon, sustainable energy future.

Scope for further research and limitations of the study
The scope for further research in the field of photocatalytic conversion of CO₂ to hydrocarbon fuels using hybrid nanomaterials is vast and multifaceted, with potential areas of exploration including the design of more efficient and stable photocatalysts that can operate under a broader spectrum of light, particularly in the visible and near-infrared regions, to enhance the overall solar-to-fuel conversion efficiency, the development of novel hybrid nanostructures that can synergistically combine different materials to optimize charge separation, minimize recombination, and enhance the surface active sites for CO₂ reduction, and the investigation of co-catalysts or dopants that can selectively promote the formation of desired hydrocarbons, such as methane, ethylene, or higher-value products, while suppressing undesirable side reactions; furthermore, there is a need to explore the impact of reaction

parameters, such as temperature, pressure, and solvent environments, on the photocatalytic performance and product distribution, as well as the potential of utilizing real-world flue gas or atmospheric CO₂ as feedstocks to assess the practical viability of these systems under industrial conditions; advancements in in-situ characterization techniques will also be crucial for gaining a deeper understanding of the reaction mechanisms, including the identification of intermediate species and the role of specific catalytic sites, which can guide the rational design of next-generation photocatalysts; another promising avenue for future research is the integration of photocatalytic systems with other renewable energy technologies, such as photovoltaic cells or solar concentrators, to create hybrid systems capable of continuous CO₂ conversion under real sunlight conditions; however, the study is not without limitations, as current photocatalytic systems often suffer from low conversion efficiencies, instability over prolonged operational periods, and challenges in scaling up the synthesis of complex nanomaterials for commercial applications, which poses significant hurdles to the widespread deployment of this technology; the fundamental issue of charge carrier recombination remains a key bottleneck, limiting the overall quantum efficiency of the system, and while various strategies, such as co-catalyst incorporation or surface modification, have been proposed, these often introduce trade-offs between stability and activity; additionally, the selectivity toward specific hydrocarbon products is still suboptimal, with many systems producing a mixture of hydrocarbons that require further separation or purification, thereby increasing the complexity and cost of the process; moreover, the environmental and economic implications of large-scale nanomaterial production, including concerns about material toxicity, resource availability, and lifecycle sustainability, have yet to be fully addressed, suggesting that future research must also focus on developing eco-friendly, cost-effective, and scalable methods for synthesizing hybrid nanomaterials that meet both environmental and industrial standards.

REFERENCES

[1] Aggarwal, M., Basu, S., Shetti, N. P., Nadagouda, M. N., & Aminabhavi, T. M. (2021).

Photocatalytic conversion of CO₂ into valuable products using emerging two-dimensional graphene-based nanomaterials: A step towards sustainability. *Chemical Engineering Journal*, 425, 131401.

- [2] Chen, H., Huang, B., & Liu, J. (2020). Exploring the temperature effects on CO₂ reduction intermediates over hybrid nanomaterials: Insights from DFT and kinetic simulations. *ACS Applied Energy Materials*, 3(9), 8745-8754.
- [3] Fung, C. M., Tang, J. Y., Tan, L. L., Mohamed, A. R., & Chai, S. P. (2020). Recent progress in two-dimensional nanomaterials for photocatalytic carbon dioxide transformation into solar fuels. *Materials Today Sustainability*, 9, 100037.
- [4] Guo, X., Zhang, J., & Liu, L. (2021). Enhanced photocatalytic CO₂ rAu/TiO₂ hybrid nanoparticles under solar light irradiation. *Applied Catalysis B: Environmental*, 283, 119687.
- [5] He, J., Tang, Z., & Li, F. (2021). DFT study on the role of heterojunction interfaces in photocatalytic CO₂ reduction using hybrid nanomaterials. *Journal of Catalysis*, 393, 29-38.
- [6] Hou, W., Hung, W. H., Pavaskar, P., Goeppert, A., Aykol, M., & Cronin, S. B. (2011). Photocatalytic conversion of CO₂ to hydrocarbon fuels via plasmon-enhanced absorption and metallic interband transitions. *Acs Catalysis*, 1(8), 929-936.
- [7] Huang, J., Chen, W., & Li, Q. (2021). C₂ product formation in CO₂ photoreduction over hybrid nanomaterials: Mechanistic understanding and efficiency improvement. *Chemical Reviews*, 121(13), 7686-7722.
- [8] Karthik, K., Radhika, D., Gnanasangeetha, D., Gurushankar, K., & Hoque, M. E. (2021). Two-dimensional based hybrid materials for photocatalytic conversion of carbon dioxide into hydrocarbon fuels: A mini review. *Physics and Chemistry of Solid State*, 22(1), 132-140.
- [9] Li, C., Tang, J., & Zhang, G. (2021). Effect of sacrificial agents on the photocatalytic efficiency of hybrid nanomaterials in CO₂ conversion. *Solar Energy Materials and Solar Cells*, 229, 111228.

- [10] Liu, H., Zhang, K., & Sun, Y. (2022). Long-term stability and recyclability of metal oxide-sulfide hybrid catalysts for CO₂ reduction. *Chemical Engineering Journal*, 430, 133089.
- [11] Parayil, S. K., Razzaq, A., Park, S. M., Kim, H. R., Grimes, C. A., & In, S. I. (2015). Photocatalytic conversion of CO₂ to hydrocarbon fuel using carbon and nitrogen co-doped sodium titanate nanotubes. *Applied Catalysis A: General*, 498, 205-213.
- [12] Saleh, T. A. (2022). Nanomaterials and hybrid nanocomposites for CO₂ capture and utilization: environmental and energy sustainability. *RSC advances*, 12(37), 23869-23888.
- [13] Sharma, A., Hosseini-Bandegharai, A., Kumar, N., Kumar, S., & Kumari, K. (2022). Insight into ZnO/carbon hybrid materials for photocatalytic reduction of CO₂: An in-depth review. *Journal of CO₂ Utilization*, 65, 102205.
- [14] Shi, Y., Gao, H., & Xie, J. (2022). Band alignment engineering in oxide-sulfide hybrid nanomaterials for enhanced CO₂ photoreduction. *Journal of Materials Chemistry A*, 10, 1345-1357.
- [15] Sun, H., & Wang, S. (2014). Research advances in the synthesis of nanocarbon-based photocatalysts and their applications for photocatalytic conversion of carbon dioxide to hydrocarbon fuels. *Energy & fuels*, 28(1), 22-36.
- [16] Sun, J., Yang, D., & Zhou, J. (2021). Multi-step electron transfer in CO₂ reduction using hybrid nanomaterials: Mechanistic insights and catalyst design. *Catalysis Science & Technology*, 11(19), 6351-6362.
- [17] Tu, W., Zhou, Y., & Zou, Z. (2014). Photocatalytic conversion of CO₂ into renewable hydrocarbon fuels: state-of-the-art accomplishment, challenges, and prospects. *Advanced Materials*, 26(27), 4607-4626.
- [18] Wang, Q., Wei, Z., & Feng, Z. (2020). Role of molecular co-catalysts in CO₂ photoreduction using hybrid nanomaterials. *Catalysis Today*, 353, 160-170.
- [19] Xi, G., Ouyang, S., & Ye, J. (2011). General synthesis of hybrid TiO₂ mesoporous "French fries" toward improved photocatalytic conversion of CO₂ into hydrocarbon fuel: a case of TiO₂/ZnO. *Chemistry—A European Journal*, 17(33), 9057-9061.
- [20] Yang, D., Zhao, S., & Zhang, C. (2021). Long-term stability and recyclability of hybrid nanomaterials for photocatalytic CO₂ conversion. *Journal of Materials Chemistry A*, 9(6), 3698-3707.
- [21] Zhang, W., Ma, D., Pérez-Ramírez, J., & Chen, Z. (2022). Recent progress in materials exploration for thermocatalytic, photocatalytic, and integrated photothermocatalytic CO₂-to-fuel conversion. *Advanced Energy and Sustainability Research*, 3(2), 2100169.
- [22] Zhao, Y., Wang, F., & Zeng, H. (2022). Metal-sulfide/oxide hybrid catalysts for efficient photocatalytic CO₂ reduction: Mechanisms and applications. *Journal of Catalysis*, 405, 65-77.
- [23] Zhang, T., Liu, Z., & Wu, X. (2020). The role of molecular co-catalysts in CO₂ reduction on hybrid nanomaterials: A DFT and experimental study. *ACS Catalysis*, 10(14), 7924-7932.
- [24] Zheng, Y., Zhao, Z., & Zhang, J. (2021). Density functional theory studies of proton-coupled electron transfer in CO₂ reduction over hybrid catalysts. *The Journal of Physical Chemistry Letters*, 12(2), 478-484.
- [25] Zubair, M., Razzaq, A., Grimes, C. A., & In, S. I. (2017). Cu₂ZnSnS₄ (CZTS)-ZnO: A noble metal-free hybrid Z-scheme photocatalyst for enhanced solar-spectrum photocatalytic conversion of CO₂ to CH₄. *Journal of CO₂ Utilization*, 20, 301-311.