

Recent Trends in Photocatalytic Materials for Reduction of Carbon Dioxide to Methanol

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Abstract

One of the promising approaches to alleviate the problems associated with energy crisis and global warming is through photocatalytic reduction of CO₂ to hydrocarbon fuels. Ultimately, photocatalytic processes utilize solar energy to convert CO₂ into hydrocarbon fuels by deploying effective photocatalysts. Among the solar fuels produced from CO₂ photoconversion, methanol is a versatile feedstock for producing numerous chemicals in the industry. The success of a photocatalytic conversion process hinges on the type of photocatalyst material. Although TiO₂ is considered a very viable candidate due to its availability, non-toxicity, ease of synthesis and affordability, its large band gap and inability to absorb in the visible region has necessitated research into other materials. For several years researchers have reported different viable materials for this process leading to improvements in the catalytic activity. However, actualizing the conversion efficiency desired from the solar energy to produce fuels still requires modification of existing materials and discovery of new ones. The objective of this review is to provide an in-depth systematic information on different photocatalysts that have been used over the years and discuss factors that

influence their effectiveness. Various modification methods for tuning the properties and improving the performance of photocatalysts are discussed. Composites or heterostructures synthesized through these modification methods are also evaluated. Comparative analysis of the performance of these composites or heterostructures with that of TiO₂ is presented in this review followed by useful, applicable suggestions and recommendations for future progress.

Keyword: Photocatalyst, Carbon dioxide, Photocatalytic reduction, Methanol.

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1. Introduction

Although industrialization and technological advancement is a major booster to the global economy, many of the activities attributed to this improvement have contributed to the gradual destruction of our ecosystem. Hazardous effluents and by-products have cut short the life expectancy of human beings, adversely affected the growth and development of plants and animals and polluted air, land and water [1]. Global warming has been identified as a root cause of several problems threatening the existence of humankind, animals and the earth itself. Global warming contributes little or no positive effects to the earth and its adverse effects trickles down to every sphere of life (our communities, health and climate). Irregular/extreme heat, rising sea level resulting in coastal flooding, extensive and damaging wildfires, dangerous hurricanes, worsening air pollution, prevalent diseases, destruction of marine life,

extensive drought seasons, disrupted food supplies and abrupt climate change are just the beginning. The future of our planet as we know it is very bleak because of the culminating effect of global warming; the slightest changes in the temperature of the earth is resulting in drastic changes to our ecosystem [2]. The 2018 report of the Lancet Countdown on health and climate change shows that we are more vulnerable to extreme weather changes, vector and water borne diseases, financial losses from climate-related events such as hurricanes and storms all due to global warming [3].

While governments and international organizations claim to be making efforts to develop and improve existing health and climate change monitoring systems, they continue to fund/support industries and activities which encourage global warming. Although the Paris agreement was signed by 187 countries who committed to reduce greenhouse emissions at their national level, many still fail to meet the agreement leaving the possibility of achieving the aims of the agreement at limbo [4]. Several countries still focus on the use of fossil fuels for power generation though they claim to have embarked on a low-carbon path, industries and activities which contributes to carbon footprint must be fully eradicated for significant progress to be achieved [5]. Flue gas emitted from industries mostly contains: carbon monoxide (CO), sulphur dioxide (SO₂), nitrogen dioxides (NO_x), other hydrocarbons and carbon dioxide (CO₂) are collectively known as greenhouse gases and are responsible for the greenhouse effect associated with global warming.

Although CO₂ can generally be considered harmless (at least physiologically to plants and animals – including humans), the quantities of about 6 billion tons released annually into the atmosphere has led to climate and health altering effects. In humans, extreme heat due to global warming has led to heat stroke, triggered existing heart failure, frequent cases of acute kidney injury due to dehydration, chronic cardiovascular and renal diseases in old and young, drug resistant bacteria and vectors with diseases such as dengue, diarrhoeal and malaria

becoming more prevalent. Animals such as polar bears are losing their homes while aquatic life and coral reefs are being lost due to a combination of extreme heat, air pollution and water pollution [3]. Of all the greenhouse gases, CO₂ is identified as the primary source with methane (CH₄), nitrous oxide (N₂O) and fluorinated gases (hydrofluorocarbons, perfluorocarbons and sulphur hexafluorides) as the other contributors. Greenhouse gases are predominantly generated by the following activities: electricity and heat generation, industrial activities, agricultural activities, transportation, onsite energy generation such as burning fuels for heating in homes and other energy production processes. These activities are all prevalent in our society it is therefore obvious that human activities are fundamental to solving the issue of greenhouse gas emissions and global warming [6, 7].

On the other hand, another issue of concern in the world today is clean energy generation and its sustainability. The need for energy cuts across every aspect of our life and it indicates the level of industrialization and economic expansion of any nation [8]. This need for greater sustainable and clean energy supply has led to the movement for a “*transition from fossil fuels*” [9]. The “*transition*” from fossil fuel energy is evident in different countries because there has been an increase in energy generated from renewables. For example, the United States of America sourced up to 17% of its electricity from renewables in 2018 according to the US Energy information Administration [10] In fact, the addition of renewable energy sources saw the United States reduce its CO₂ emissions per capita from 16.5 in 2014 to 15.56 in 2016 as it generated up to 17.64% from renewable sources in 2016 (but only 13.39% in 2014) [11]. However, despite the progress made in the US it is important to take a global perspective, the CO₂ emissions per capita of oil producing countries (such as Saudi Arabia, Kuwait, Qatar and United Arab Emirates) continue to rise [12, 13]. Most of these countries rely on fossil fuels because they have it in abundance and make a lot of money from trading it. Also, the cost of establishing renewable energy sources such as wind farms, solar

farms, hydro-electric power and geothermal energy systems are still too high for developing countries, so they rely on fossil fuels. Therefore, there is still a need for more sustainable and clean sources of energy. Another perspective is the depletion of existing resources, according to the US Energy Information Administration, as at January 2018 the world reserve of natural gas was estimated at about 7,124 trillion cubic feet (Tcf) and majority of the proved reserves were in the Middle East and in Russia [14]. This has a significant impact on the world's energy balance. As per estimation, at the current rate of use, the reserves are expected to last for about 50 years only [15]. Hence, an alternative source of energy that cannot be monopolized, that is sustainable and can provide a simpler and cleaner fuel is of importance.

Considering nuclear, geothermal, wind, hydroelectric, and solar sources of energy, although they do not emit a considerably large amount of CO₂ or other greenhouses gases, the cost, safety and life cycle of these energy sources are of concern. For example, people living near wind turbines are often at the risk of Chronic sleep disturbance, absorption of infrasound which causes wind syndrome associated with symptoms such as tinnitus [16]. Some countries still use nuclear energy as a source of clean energy as there are no emissions although when there is an accident like the case of Chernobyl, the effects are catastrophic. Apart from the cost of establishment, the level of trust in safety of using nuclear reactors for energy generation varies, some people believe it is safe while others have a different perspective and this is based on different criteria such as gender etc. [17]. Some reports suggest that shading caused by PV panels for solar energy generation will lead to changes to wind flow, and could alter temperature, change rainfall distribution (which affects soil moisture) and disrupts wind flow over the land [18]. Hydroelectric [19] and Geothermal [20] energy generation are not entirely clean energy processes because their plants still generate some greenhouse gases and they are quite expensive to set up. For every alternative there is a problem attributed to it, perhaps there is no silver bullet to address the issue of renewable energy or global warming. To this

end, a multidisciplinary approach might be the most reliable way – a combination of different technologies to solve the major issue facing humankind [21]. Transforming energy from one form to another can be achieved through different routes and the use of solar energy can be regarded as a sustainable alternative considering it is primarily sourced from the sun. One application of solar energy to solve the problem of global warming and increasing clean energy demand is the conversion of CO₂ to hydrocarbon fuels [22, 23].

The conversion of CO₂ into useful hydrocarbon fuels (e.g., methanol) is a viable route for clean energy generation as it tackles two of the issues facing mankind. [24]. Known also as artificial photosynthesis, photocatalytic conversion of CO₂ using solar energy is considered as a feasible approach for the transformation of CO₂ to hydrocarbon fuels [25]. The interest in this field has been aroused dramatically after several demonstrations on photocatalytic reduction of CO₂ to organic compounds debuted in 1970s [25]. The pace has recently increased enormously, because of the focus on advanced technologies (e.g. nanotechnology and in-situ advanced characterization) for development of novel photocatalysts [26]. Various methods exist for harvesting solar energy and the use of photocatalysts provides a viable option because of the reversible oxidation-reduction capabilities. Photocatalytic CO₂ reduction is a two-way process which involves; CO₂ recycling and production of useful chemical fuels. The process involves the use of a photocatalytic material to deploy solar energy and its reaction with CO₂ in either aqueous or gas phase system [27]. The properties of the photocatalytic materials through photo-oxidation reactions could reduce carbon dioxide to different hydrocarbon fuels such as methanol, formic acid, formaldehyde, methane and hydrogen. These hydrocarbon fuels can then be used as a fuel and a raw material for different applications [24].

The type of photocatalyst materials for photoreduction of CO₂ is a critical factor in a photocatalytic process as it determines several key details of the process. Some of these key

details include: the reaction pathway, the type of light that would be absorbed and used for the process, the likely products obtainable from the process and ultimately the effectiveness and yield of the process [28]. Therefore, the choice of photocatalyst material is very crucial and therefore it has been the focus of research in this field. Various material categories ranging from metal oxide semiconductors to sulphides, nitrides, and carbides to carbonaceous materials to quantum dots, dyes and enzymes have been reported as promising photocatalysts. Metal oxide semiconductors such as titanium oxide (TiO_2), tungsten oxide (WO_3), and zinc oxide (ZnO) etc. are widely used for photocatalytic conversion of CO_2 [29]. Amongst the metal oxide semiconductors, TiO_2 is a commonly used photocatalyst due to its attractive properties. These properties include; availability and affordability, good charge transfer potentials, safety and corrosion resistant, powerful oxidation properties and ease of tunability [30, 31]. Unfortunately, TiO_2 only possesses UV light (wavelength less than 380 nm) activity because it has a high band gap (3.20 eV for anatase) [30, 32]. This implies that under visible light (which is the largest part of the solar spectrum) TiO_2 is mostly inactive in this region of the spectrum. Overcoming this limitation is possible through different modification methods which will be discussed later in this review. Although it is possible to achieve VLR TiO_2 using modification methods, other photocatalysts which are VLR active have been reported for CO_2 photoreduction. The photocatalysts demonstrated higher photo-activity than TiO_2 in most cases especially under visible light irradiations. Most of these VLR photocatalysts are metal/non-metal oxides such as WO_3 , NiO_2 , In_2O_3 , TaO_4 , Fe_2O_3 , Bi_2O_3 etc [33]. Although VLR photocatalysts have reported higher photo-activity and product yield compared to UV sensitive TiO_2 , selecting/highlighting a material as the best is not accurate as most reported works are carried out under varying reaction and experimental conditions. Also, the accuracy and credibility of some reported photocatalytic systems is questionable because in some cases it is difficult to ascertain the origin of the electrons used for the photoreaction [34]. Thus, more

research is needed to further understand the process and to optimize existing materials as well as discover new viable photocatalytic materials.

Although the band gap of the photocatalyst material dictates its photo-activity, its efficiency as a material is also affected by other properties. These include ability to absorb CO₂, availability of interconnected porous network, easy migration of electrons through pathways and a large surface area. All these properties are related to its structure or morphology. Bulk materials are mostly non-porous; hence they are not able to accommodate enough adsorbate needed for optimum reaction efficiency. This limitation spurred research into nanostructured materials for optimum CO₂ photoreduction. Nano sized materials such as nanotubes, nanorods, and nanofibers have helped to improve the performance of photocatalytic materials due to several advantages including high surface to volume ratio, better adsorption rate, improved light absorption efficiency and rapid migration of electrons. These properties have improved the effectiveness of photocatalytic materials, increased product yield as a result of a boost in the overall efficiency of the process [35]. Material design is very critical in photocatalytic processes because as band engineering tunes band gap, material design restructure and optimize materials for effective performance. Design of materials with core-shell, yolk-shell, multi-shell, hollow structures have helped to improve performance by reducing the transport distance of holes and electrons. However, most of these unique morphologies are synthesized by multi-step complex methods which sometimes use toxic, expensive or non-sustainable materials. Also, during some of these synthesis methods, the photocatalytic property of the material such as its band gap could be altered. For example, it is possible to create oxygen vacancies on a nanostructured material during its synthesis. These oxygen vacancies can positively impact the reaction pathway but while they might improve a specific process, they might also facilitate the occurrence of side-reactions. Hence, it is important to consider the effect of synthesis method and structural modification on the

photocatalytic reaction [36-38]. The challenge with band gap engineering relates to having a photocatalyst material which possess a medium or low band gap suitable for the desired process and matching the band gap to thermodynamic reduction potential demands [32, 39]. Meanwhile, the challenge experienced with material design is the synthesis of a morphology or structure which provides a large surface area, interconnected network of pores available for easy transport of electrons while maintaining the band engineering of the material. Therefore, it is evident that more research work is needed in the design and tuning of materials for effective photocatalytic processes.

In terms of photocatalyst materials and hydrocarbon/solar fuels, there is a relationship between the two and the linkage between them is the band gap of the photocatalyst material and the redox potential of reaction between CO_2 and H_2O . As a general rule, for a photocatalyst material to effectively transfer electrons to the adsorbed CO_2 , the relative potential level of the acceptor is thermodynamically required to be more positive than the conduction band (CB) of the semiconductor [40]. This implies that for a photocatalyst to yield methanol as a product, it is required for its CB to be more negative than -0.38 eV, which is the reduction potential for half-cell reduction reaction of CO_2 to methanol in H_2O at pH 7 vs NHE. Aliwi et al. [41] demonstrated this by reducing CO_2 to formic acid and formaldehyde using CdS as a photocatalyst. CdS has a CB of -1.0 eV while the reduction potential for both hydrocarbon fuels are -6.1 and -5.2 eV. Based on the fulfilment of the thermodynamic criteria, the reaction was possible. Although this perspective is right and has been proven several times, the efficiency and selectivity of a photocatalyst material is dependent on more than the band gap, thermodynamic reduction potential or pH. An in-depth study of these factors is presented in this review. Photoreduction of CO_2 can yield several hydrocarbon fuels including carbon monoxide, methane, formaldehyde, formic acid, acetic acid, ethanol and methanol. Methanol serves as a major basic feedstock in the production of several organic compounds, a vital

intermediate for several chemicals used in everyday products such as silicone, paint, and plastics [42]. It could also serve as an alternative to gasoline in the future. Methanol is also currently used in an electrochemical device that converts chemical energy of fuels into electrical energy. The Direct Methanol Fuel Cell (DMFC) is rapidly developing as a prospective energy storage device and it is currently used to supply power to small electronic devices such as mobile phones and laptop and tablet computers [43]. Also, in liquid form it provides a safer and convenient way for storing energy unlike gasoline. Methanol is also used in the process of transesterification for the conversion of triglycerides to produce useful fuels known as biodiesel. Methanol is produced from synthesis gas (syn. gas), - a mixture of carbon monoxide, carbon dioxide and hydrogen, in large scale industrial plants for commercial purposes at millions of tons per year. [44, 45]. It can also be produced from the conversion of methane, e.g., selective oxidation of methane, catalytic gas phase oxidation of methane, liquid phase oxidation of methane, mono-halogenations of methane, and microbial or photochemical conversion of methane [44]. Reduction of carbon dioxide to produce methanol provides a highly attractive solution by recycling carbon dioxide into useful chemicals and sources of alternative energy simultaneously making the earth safer for mankind and animals to co-exist [42].

Considering the importance of solar assisted carbon dioxide conversion to hydrocarbon fuels and several synthetic hydrocarbons and chemicals which use methanol as a raw material, methanol can be regarded as a versatile and widely used hydrocarbon fuels from this process [46]. Therefore, we present one of the first reviews to exclusively discuss photoreduction of CO₂ to methanol focusing on materials. This review gives an overview of different materials explored for photoreduction of CO₂ to methanol. It highlights important criteria for an effective material for CO₂ photoreduction and how these affect the efficiency of the process and yield of products. Different methods for modifying and designing better

materials for photoreduction of CO₂ are provided. The discussion ends with an assessment of the “methanol economy” and a perspective on the way forward.

2. Basics of Heterogeneous Photocatalytic Processes

2.1. Principles of Photocatalysis

Heterogeneous photocatalytic process involves one or more reaction steps occurring by means of electron pairs photo-generated on the surface of a semi conducting material illuminated by light of suitable energy. This type of pathway is totally different from the usual thermal reaction sequence and leads to product selectivities different from those for thermal/catalysed reactions [47]. Unlike other reaction pathways, the absorption of irradiated light by a semiconductor of comparative band gap is the beginning of a photocatalytic reaction. This absorbed photonic energy is then used to activate the reductive process for which the system is designed which is mostly dye or pollutant degradation for water purification or photoreduction of CO₂ to renewable chemicals. Semiconductors are filled with clusters of electronic energy levels which results in two bands; the highly electron dominated valence band denoted VB and the high energy conduction band (CB) as shown schematically in Fig. 1. These bands are separated by a region known as the band gap through which electrons migrate from the populated VB to the vacant region of CB resulting in the creation of a positive charged hole (h^+) species in the VB of the photocatalyst. This migration of photoactivated electrons can only be accomplished if the band gap of the said photocatalyst is less than that of the incident light. Without this successful electron transport from the VB to the CB a photocatalytic reaction will not occur because the photogenerated electron and hole species facilitate photoreactions at the surface of the photocatalyst.

The design of photocatalytic materials with optimum efficiency and effectiveness is dependent on different parameters which are not limited to; suitable band gap which aligns

with the region (wavelength) of irradiated light in the spectrum and inhibition of electron-hole recombination by using appropriate photocatalyst modification method. Furthermore, the particle size and surface area, dispersal or deposition method (i.e. dispersed in reductant or coated on a substrate) of the photocatalyst and consideration of the NHE potential of the desired product as it relates to the band gap of the photocatalyst must be considered. To put things in perspective, without migration of photoactivated electrons from the VB of a photocatalyst to its CB a photoreaction cannot be initiated however the success of the photocatalytic reaction depends on several other factors with inhibition of recombination playing a key role [48]. In the absence of suitable adsorbates, electron-hole pair recombination occurs with release of thermal and/or light energy [49].

2.2. Thermodynamic barriers for methanol production

While the electron-hole pair exists, the photocatalyst can perform useful reduction and oxidation reactions by accepting electrons into its valence band or donating the promoted electrons in its conduction band. When an electron moves to the surface of the photocatalyst and has the correct potential, anion radicals are produced, while cation radicals are produced from electron holes at the surface. Generally, it is preferable that the redox potential of a donor species adsorbed on the photocatalyst surface be more negative (higher in energy) than the valence band position of the semiconductor in order to refill the electron vacancies. Likewise, acceptor molecules must have a redox potential more positive (lower in energy) than the conduction band [48, 50]. Therefore, the redox potential and band energy are two criterions for electron transfer in a photocatalytic process. If we consider the reduction potentials for half-cell reactions in aqueous solution in Table 1, the electrons from the semiconductor must have a more negative redox potential than that of water splitting for CO₂ photoreduction to hydrocarbons to occur [51]. For CO₂ to be converted to methanol the semiconductor to be

used must have a CB more negative than -0.38 eV otherwise the result will be a water splitting reaction instead of CO₂ photoreduction. Thus, for methanol production a suitable semiconductor to use is one with a CB less positive compared to 0.38 eV. e.g. considering TiO₂ with a CB of -0.50 eV, its CB is less positive than the required energy to convert CO₂ to methanol. Hence thermodynamically, using TiO₂ as a photocatalyst for reduction of CO₂ to obtain methanol would be feasible [52].

2.3. Selection of materials for methanol production

Choice of photocatalytic material used for CO₂ photoreduction an important factor that determines the effectiveness of the process. It dictates the band gap of the photocatalyst material. The band gap of the semiconductor is very important for an effective photocatalytic process to occur because the light absorption capacity and charge carrier generation of the semiconductor is dependent on the band gap. Likewise, it is preferable that the VB and CB be slightly greater than the redox potentials required for the process. However, most photocatalysts with wide-band gaps do not absorb great amount of light. For example, TiO₂ has a band gap of 3.2 eV (Fig. 2.) Which reduces its light absorption to less than 390 nm. Therefore, the conversion efficiency of the photocatalytic process is low. The first and second criterions (the redox potential of desired products and the band gap of the specific photocatalyst) are related and both determine the effectiveness of a photocatalyst for a specific process [53].

Fig. 2 shows the band gap of a group of photocatalysts with respect to the redox potential of different possible products at a pH of neutrality (7) [53]. The type of products that can be formed from the process depends on the relationship between the band engineering and the redox potential of the product of choice. The band energy of the top part of the CB dictates the reductive power of electrons in the photocatalyst. Conversely the oxidative strength of

holes in the photocatalyst is dependent on the energy of the lower part of the photocatalyst, VB. To this end, for a photocatalyst to yield a product, the band energy of the CB should be higher than the potential of producing that product. From Fig. 2, TiO_2 and CdS are shown to produce hydrogen and oxygen while WO_3 and Fe_2O_3 can only oxidize water (to give O_2) but cannot reduce it (to give H_2). The relationship between redox potential and band gap also relates to CO_2 for reduction to different hydrocarbon fuels e.g. H_2 , methanol, formic acid, methane etc.

Apart from mismatching between the absorption ability of semiconductor and the solar spectrum due to their wide band gap energy, there are other challenges. Poor charge carrier separation efficiency, low solubility of CO_2 molecule in water for aqueous processes (approximately 33 μmol in 1 ml of water at 100 kPa and room temperature), reversed reactions during reduction of CO_2 and water splitting are some of the challenges [27]. Over the years several strategies have been employed to increase the process efficiency. The efficiency of any photocatalytic process is largely dependent on the choice of photocatalytic material used, the nature of the system and the operating parameters or conditions that ensure optimal performance. Of all the factors listed, the choice of photocatalytic material plays a major role because it dictates the pathway of the photoreaction. Therefore, our first focus in this review highlights the developments in photocatalytic materials used for photoreduction of CO_2 .

3.0. Advancements in Photocatalytic Material for CO_2 Reduction

3.1. TiO_2 - Based Photocatalysts

Amongst the semiconductors widely used for CO_2 photoreduction Titanium dioxide (TiO_2) is a widely investigated for photocatalytic reactions. This is because of its properties e.g. high photo-activity, suitable optical/electronic qualities, low cost and availability, low toxicity and earnest chemical and thermal stability [54]. It provides enough negative and

positive redox potentials for the photocatalytic process. It exists in three different polymorph structures - anatase, rutile and brookite. Of the three crystalline configurations, anatase has the highest level of photoconductivity with a band gap of 3.2 eV. Rutile is the least photo reactive of the three due to its more proficient recombination of the electron hole pair and smaller surface area [55]. Several researches have been carried out using pure TiO_2 for photoreduction of CO_2 to methanol, but despite the numerous studies using bare TiO_2 for photocatalytic conversion of CO_2 , it is still limited in its efficiency. Relatively poor charge transport property and, fast recombination rate of its photo-induced electron-hole pairs, low oxygen production after absorption of UV photons and wide band gap of approximately 3.2 eV are its main limitations [56].

The other concern is the light used for photocatalysis. UV photosensitive catalysts are limited because UV light that reaches the earth is only 3-5% of the solar irradiation. Thus, it is important for photocatalyst to be sensitive to visible light. Taking TiO_2 as an example, high energy input is required for it to be activated, but the high energy photons that exists in the UV region is only 4% of the total energy. Therefore, the efficiency of TiO_2 is minimized. In order to overcome these limitations various surface modification techniques have been employed such as doping, dye sensitization [57] and combination with Quantum Dots (QDs) [58], synthesis of composite semiconductors [59], and formation of heterostructures [60] and nanostructures [61]. The different technologies for CO_2 photoreduction and different modification methods for photocatalysts are exhibited in Fig. 3.

3.1.1. Doping

One of the most common and perhaps oldest methods of modifying the properties or aligning the band engineering of a semiconductor is by doping it. One advantage of doping is that most of the metal dopants (especially transition metals having plasmonic properties) can

act as electron trapping agent thereby, enhancing charge separation and improving the efficiency of the photocatalyst [62]. Also, doping has been reported to create a strong imaginary electric field at the interface of the metal-semiconductor. The presence of this electric field leads to an increase in the number of charge carrier species at the interface of the metal-semiconductor. The charge carrier species are then able to migrate to the surface where they are used in redox reactions [63]. Modification of a semiconductor by doping has proven to be a successful approach to improving the efficiency of a photocatalyst.

3.1.1.1. Metal Doping

The purpose of doping a semiconductor is to introduce impurities into its pure structure for adjusting its electrical properties. Pure TiO_2 with its 3.2 eV large band gap is unable to absorb high photon energy but doping helps to decrease its band gap energy. In metal -doped TiO_2 photocatalysts the electrons are transferred from the CB to the metal dopant. Doping has been researched with metals, non-metals, noble metals, transition metals and rare-earth metals. Doping process has been carried out using several methods such as impregnation method [64], sol-gel method [65], co-precipitation [66], metal-ion implantation [67] and RF magnetron sputtering method [68]. Common metals used to dope TiO_2 include Cu, Ag, Fe, Cr, Pt, and Rh. A transition metal is used to modify the band gap of TiO_2 by doping it into its structure. In this type of heteroatom doped photocatalyst, photoconversion of CO_2 takes place on the doped metal atom. When photo-excitation occurs and electrons are transferred from the VB to CB, these electrons are further transferred to the metal heteroatom upon which conversion of CO_2 occurs. Doping of the heteroatom on TiO_2 causes an alteration in its band gap thereby shortening it to < 3.2 eV. Most transition metals such as Au and Ag possess additional effect known as the localized surface Plasmon resonance (LSPR). Fig. 4 shows the photocatalytic mechanism and LSPR effect of Ag/TiO_2 (a), comparison of photocatalytic

activity of pure TiO₂ and Ag modified TiO₂ under UV (b) and visible light (c). This effect contributes to a strong absorption of the visible light [69]. Therefore, they can improve the photo-activity of the photocatalyst material hence its performance under the visible light illumination. When combined with UV sensitive photocatalysts such as TiO₂, metals which possess the LSPR effect such as gold nanoparticles can efficiently transfer electrons to the conduction band (CB) of TiO₂ under visible light irradiation. Through this transfer from the gold nanoparticles, UV light sensitive TiO₂ can function as a VLR photocatalyst because provided by doping it with Au. This can then result in prolonged recombination time, instant charge separation and an enhanced photocatalytic behaviour in the photocatalyst which could be attributed to the SPR effect of Au nanoparticles. Due to the LSPR effect of the metal, the photocatalyst can accept electrons from external donors and use this for reduction of CO₂ to CO, CH₄ and methanol after faster rate than usual. This is similar to the report given by Tahir et al [70]

When a metal is doped into an n-type semiconductor e.g. TiO₂ if the work function of the metal W_m is greater than that of the semiconductor W_s (i.e. $W_m > W_s$) holes from the semiconductor cannot easily migrate to the metal. This is because a Schottky barrier forms at the interface of the metal-semiconductor. Conversely, when $W_m < W_s$ a charge accumulation layer is formed at the interface and this prevents formation of the Schottky barrier hence electrons are free to move in any direction [71]. However, for a p-type semiconductor e.g. Cu₂O doped with a metal e.g., Pd, if $W_s > W_m$ the migration of holes from the semiconductor to the metal is made easy by migration of charge carriers. This would ensure the chances of recombination is reduced [63]. These shows that the choice of dopant is very crucial to the pathway and the mechanism of the photocatalyst determines the type of reactions and the products obtained. For example, using Pt as a dopant for TiO₂ produces higher methane yield than methanol from CO₂ photoreduction. This is because since $W_{Pt} > W_{TiO_2}$ photo-generated

electrons can be transmitted through the metal atom thereby fostering charge separation and inhibiting recombination [72].

Amongst all the metals used for CO₂ photoreduction (Pt, Au, Ag, Pd, Ru, Rh, Cu, and Zn etc.), copper (Cu) and silver (Ag) have been mostly used to improve the photo-activity of TiO₂ and selectivity of methanol production during photoreduction of CO₂. Fig.. 4. Shows the photocatalytic Mechanism of Ag/TiO₂ (a) and a comparison of photocatalytic activity of pure TiO₂ and Ag modified TiO₂ under UV (b) and visible light (c). Several reports have shown that Cu doped TiO₂ photocatalysts are very efficient to convert CO₂ and H₂O to methanol (-0.38 V) and this can possibly be traced to the reduction potential of Cu ($\text{Cu}^{2+}/\text{Cu} = + 0.337$ V). Although the oxidation state of Cu determines its reaction pathway, using Cu₂O as an example, its VB and CB are located above that of TiO₂ facilitating the photo-generated electrons to migrate from Cu₂O to TiO₂. This simultaneously create holes in the VB of Cu₂O thereby ensuring separation of electron-hole pairs. The migration enables rapid conversion of CO₂ to methanol and the separation inhibits occurrence of recombination [73-78]. In some cases, Cu is mostly re-oxidized either from Cu (metal) to Cu⁺ or from Cu²⁺ to Cu⁺ after the photocatalytic reaction and this is usually obvious in the colour changes of the Cu doped photocatalysts by (usually to a darker colour) [74]. It has been proven from different reports that doping of Cu on TiO₂ improves the photo-activity of TiO₂ as the Cu metal acts as an electron trapping agent whilst maintaining the mobility of photoelectrons in the photocatalyst. Also, doping of Cu into TiO₂ could lower its band gap due to the lower redox potential of copper ions thus improving its light absorption efficiency [32, 79]. Li et al 2016 reported that the impregnation of copper could improve the photo-efficiency and selectivity to produce methanol and ethanol. The increased photo-activity of Cu/TiO₂ is since the Cu ions act as electron trapping sites, improving interfacial charge transfer, enhancing charge separation at the Schottky barrier whilst maintaining the mobility of the photoelectrons. Na₂SO₃ was used

as a hole scavenger in this report and stated that its presence facilitated the production of ethanol. One drawback with excess copper loading is reduced surface area and decreased photo-excitation capacity. Therefore, doping most noble metals into a semiconductor photocatalyst results in a reduction in its band gap, improvement in the visible light absorption and increase in the charge transfer rate hence boosting the photo-activity. However, due to the relationship between band gap engineering and reduction potential of the semiconductor and metal dopant two main metals (Cu and Ag) perform better for photoreduction of CO₂ to methanol.

3.1.1.2. Non-metal doping

Another type of TiO₂ modified system is photocatalyst systems based on semiconductors doped with anions (C, N, S, P, B etc.). The least reported non-metal doped with TiO₂ for CO₂ photoreduction is phosphorus however Wang et al 2016 reported the use of phosphorus doped TiO₂ nanotubes. A high methanol yield of up to 860.4 µmolg/cat was achieved from this work, Fig. 5. details results obtained from this work [80]. Anionic (non-metal) doping introduces substitution of lattice oxygen of TiO₂, transfer of occupied orbitals above the VB energy and narrowing the band gap energy hence fostering absorption of visible light. Anionic doping of nitrogen from previous research is seen to have the highest influence in narrowing band gap possibly due to its similarity in atomic size with oxygen, high stability and low ionization energy [81].

Nitrogen is a commonly used non-metal for semiconductor doping in diverse applications including photoreduction of CO₂. Tsai et al demonstrated the importance of nitrogen doping in their work where they reported N-doped InTaO₄. In this work nitrogen doping was used to improve the light absorption of the photocatalyst by shifting its absorption band. It also helped to inhibit recombination of electron-hole pairs. They reported that doping

with nitrogen resulted in a red shift in absorption wavelength of the material. Also, the band gap was narrowed allowing for parallel movements of absorption edges. It was possible to shorten the band gap by nitrogen doping because the energy of N^{2p} is higher than that of O^{2p} . Hence, annealing the material in NH_3 to achieve N-doping was able to shift the absorption band and shorten the band gap. The yield of methanol was doubled when $InTaO_4$ was doped with N compared to without it, this indicated the importance of nitrogen doping in the photocatalyst material [82]. Kumar et al also reported the photoreduction of CO_2 to methanol under visible light using nitrogen doped graphene supported on copper complex. In this work the researchers also reported that N-doping helped to reduce recombination during the photocatalytic process. When nitrogen was doped with graphene it was able to bind effectively with three carbon atoms by sp^2 hybridization hence it was able to influence the distribution of charges within the carbon atoms. By combining its π -bonds with those from graphene, a very rich electron cloud was created. This caused a shift in the Fermi level resulting in a break of the graphene symmetry resulting in the creation of a CB and VB. Due to this, the N-doped graphene functioned as a semiconductor material. Another major advantage of N-doping in this work is the creation of multiple electron transfer through its π -bond interaction with graphene thereby providing multiple electrons for generation of methanol [83]. Although anionic (non-metal) doping of TiO_2 can improve its photo-activity, some reports focus on its application for other processes. More reports can be gathered on its application in dye degradation, dye sensitized solar cells, oxygen/hydrogen evolution reaction (OER/HER), CO_2 reduction to methane, hydrogen and other hydrocarbons. Different methods have been used for synthesis of N-doped semiconductor photocatalysts. Fig. 6. Exhibits different synthesis methods previously reported [84].

3.1.1.3. Co-Metal doping

Co-doping involves the doping of more than one metal on a semiconductor and this is useful for tuning the selectivity of reduction products from the process. As an example, common co-catalysts used for the CO₂ photoreduction process are Ag and Cu whereas Pt and Au are more favourable for hydrogen production. Fig. 5 exhibits the photocatalytic reduction mechanism of CO₂ to methanol using TiO₂ modified with two different metal dopants. As depicted in Fig. 5, compared to Fig. 4 both reduction (CO₂ to hydrocarbon fuels) and oxidation reaction take place on two different doped metal atoms. This means photo-generated electrons are transferred from the VB of TiO₂ to its CB then to the CB of the heteroatom while holes are transferred to the VB.

Different metals have been reported as viable co-catalysts for two main purposes; to extend the VLR efficiency of TiO₂ and accomplish improved quantum efficiency and yield by decreasing recombination of electron-hole species[85]. The choice of co-dopants and their percentage is of outmost importance because co-doping of metals leads to competition for functionality. Kavil et al recently showed the effect of co-doping by using Cu-C as co-dopants for TiO₂ [86]. Fig. 7. Shows the mechanism of CO₂ photoreduction for Cu-C/TiO₂ under UV light (a) Time dependence study of methanol yield for TiO₂ and Cu-C/TiO₂ photocatalysts under UV light (b). It is common knowledge that carbon and nitrogen are highly conductive and electron rich hence they are used for modification of materials in applications such as energy storage materials e.g. batteries and energy releasing reactions such as oxygen and hydrogen evolution reactions. However, carbon is seldom used for modifying photocatalyst materials. In this work they synthesized the Cu-C/TiO₂ photocatalysts by sol-gel method, used NaOH as the reductant and a UV lamp of 365 nm wavelength and natural sunlight were used as the light source. A high methanol yield of 2593 $\mu\text{mol/g}$ was obtained after 5 h reaction and the Cu-C/TiO₂ photocatalyst performed better than TiO₂ (P25) and C/TiO₂ though that of the

latter was higher than the former. Each constituent of the photocatalyst provided different benefits to the overall system. Recombination of holes and electrons was suppressed by Cu due to its property as an electron trapping agent, C helped to reduce the optical band gap energy of TiO₂ while TiO₂ served as the basic semiconductor photocatalyst. Contact between TiO₂ and Cu encouraged charge redistribution through the photocatalyst. Therefore, separation of electron-hole species was enhanced due to rapid migration of photo-generated electrons. It is noteworthy to mention that Cu²⁺ was used in this work and it is known to be a very good oxidation state of Cu to function as a dopant. Its unfilled 3d shell electrons can be easily trapped onto surface of TiO₂. The photo-energized conduction band electrons (e_{cb}^-) will be attracted by Cu²⁺ and reduced to Cu species. Electrons on the Cu⁺ species can then be consumed as a result of the decline in hydrogen radical H• production by H⁺ therefore Cu⁺ can be re-oxidized back to Cu²⁺. Repetition of this cycle during photoreaction can hence inhibit recombination in the reaction. Based on the mechanism of methanol production from CO₂ proposed by Kakumoto, the Authors suggested a sequence of reactions to form methanol. Firstly, adsorption of CO₂ on Cu, attack of CO₂ by H atom adsorbed on Cu resulting in formate intermediate formation. Further attack of C-O bond of formate species by H atom resulted in HCOH intermediate formation on Cu and, attack of HCOH intermediate specie by H atoms on TiO₂ to yield CH₃O intermediate and finally methanol formation.

3.1.2. Modification using Metal Oxides

Metal oxides have also been used for doping pure TiO₂ to obtain photocatalysts of superior photo-activity due to the improved charge separation [87-89], light absorption [88-90], structural properties [89, 90] and surface chemistry [87, 88, 90]. At the heterojunction of the MO and TiO₂ charge separation is achieved and this creates a separation of redox reactions which prevents back and side reactions benefiting the yield of the product from the

photoreduction of CO₂. This is because if the MO doped has a smaller band gap compared to TiO₂ it improves the light absorption capacity of the composite formed. However, the improved light absorption is dependent on whether or not the VBs and CBs are well matched for simultaneous charge separation[91]. A very good example is Slamet et. al., 2005's work on photocatalytic reduction of CO₂ on copper doped TiO₂. They synthesized different species of copper (Cu⁰, Cu^I, Cu^{II}) by improved impregnation method. CuO was the most active dopant compared with other copper species synthesized. Since the band gap of the synthesized copper-loaded catalysts were smaller than that of TiO₂ the photon energy needed to excite electrons and holes would not be too high. Furthermore, it can increase the activity of TiO₂. They reported methanol as the product of the photoreduction process and CuO gave the highest yield although Cu₂O showed very promising result [92]. Cu₂O is one of the most reported MO dopants due to its band gap of 2.0-2.2 eV which effectively absorbs visible light and its VB and CB well matched to shorten distance from the bulk to surface when using TiO₂ and Cu₂O nanoparticles [85]. Nasution et al also researched on photoreduction of CO₂ to methanol using 3% CuO doped TiO₂ synthesized by improved impregnation method [93]. In the research, CO₂ saturated KHCO₃ (1M 300 mL solution) was used and a 10 W UV black light lamp with a wavelength of 415 – 700 nm and 2.45 mW cm² was the light source. The slurry type photocatalytic reactor consisted of a horizontal stainless-steel vessel with an inner diameter and height of the vessel 140 and 50 mm, respectively having a plate cover at the top of the vessel made of Pyrex. They reported methanol product of 442.5 and 19.23 μmolh⁻¹ per g catalyst [93].

3.1.3. Modification by formation of nanomaterials

The nanostructured composites have been widely researched due to their viable benefits. Nano-structured photocatalysts offer various advantages such as high adsorption

surface area, faster diffusion rate, inhibition of electron-hole pair recombination and higher surface to volume ratios [94]. Several materials have been synthesized in nanosizes such as nano-rods, nanofibers, nanotubes, nanowires and nano-strings and ribbons. Unique nanostructured composite and heterostructured materials have also been synthesized e.g. core-shell, hollow, multi-shell and yolk-shell structures. These different nanostructured materials can provide features which are able to improve the efficiency of the photocatalyst material. These features cause the photocatalyst to experience; greater adsorption capacity, higher surface to volume ratios, fast diffusion rate and inhibition of electron-pair recombination. As a result of their unique morphology electron pathways are well-defined and interconnected hence their transport is rapid and wider. Also, the unique structures allow for effective separation of electron-hole pairs and this means they help to inhibit recombination in these materials.

In the investigation of Wang et al on Pt-TiO₂ nanowires, they reported nanowires with graphene-like properties were more effective for separation of electron hole pairs hence they showed enhanced photo-activity. [95]. Carbon nanotubes and 1D nanowires demonstrated outstanding results due to their spatial electronic configuration. Single walled and multi walled carbon nanotubes doped with TiO₂ also recorded enhanced photocatalytic activity [35]. The large surface areas and inhibition of recombination boosted the yield in the photoreduction of CO₂ to methanol. Despite the advantages of these unique structures only a few literatures exist on the design of unique structures like hollow, core-shell, yolk-shell and multi-shell morphologies for CO₂ photoreduction. However, a few works exist which demonstrate the importance of these unique nanostructured materials for CO₂ photoreduction. Examples include; Dai et al (flower-like), Hefeng et al (hollow structure) Tsai et al (core-shell structure), Junior et al and Ijaz et al (rod-like structure) [78, 82, 96-98].

One of the outstanding works on CO₂ photoreduction using core-shell structure is that of Tsai et al, a methanol yield of over 300 mol/g. cat. was obtained [82]. These unique structures particularly core-shell structures provide several advantages in photocatalysis. As an example, encapsulating a metal (Cu) into a semiconductor like TiO₂ provides the semiconductor with stability inhibiting aggregation, corrosion and damage of its structure. Likewise, the low-lying fermi energy level of the metal provides an electron sink/reservoir thereby extending the lifetime of photo-generated charge carriers, boosting product yield and efficiency of the process. Also, the unique core/yolk shell structure avails close metal-semiconductor contact thereby improving the process of interfacial charge transfer [99]. It is obvious that more work needs to be done in the design and synthesis of nanostructured materials with unique morphologies for improved CO₂ photoreduction. Two limitations affect this approach: complexity of synthesis and use of toxic/dangerous chemicals. However, simpler and green chemicals for effective synthesis can be sourced.

Particles size is an important property which dictates the reaction pathway of materials. By a phenomenon known as quantum size effect, nanosized TiO₂ particles showed an increase in its CB with a corresponding decrease in VB [100]. The understanding of this phenomenon came with the knowledge that decreasing particle size resulted in changes in the recombination rates at the surface. A decrease in particle size leads to a decrease in volume recombination which in turn leads to improved photonic efficiency as a result of improved interfacial charge transfer rate. Since particle size affects the adsorption rate of CO₂ and these affected the band gap and recombination rate, it is evident that synthesis of nanostructured materials with unique morphology is one way to achieve better product yield in photoreduction of CO₂ [101].

The importance of crystallite size to performance and photo-activity of photocatalysts was long demonstrated by the work of Koci and Obalova where they studied the effect of TiO₂

particle size on the band gap and yield of methanol. In this work they concluded that higher methanol and methane yield was obtained as particle size reduced. The optimal particle size reported was 14 nm and below this size photo-activity of the photocatalyst began to decline. They highlighted that competition for surface area, light absorption efficiency and charge-carrier dynamics accounted for the observed optimum particle size [100]. From this work it was established that particle indeed affects the photo-activity of a photocatalyst material. Therefore, keeping the morphology and structure of the material in mind, particle size is also a very important part of the material used for CO₂ photoreduction. Fig. 8. Shows the effect of TiO₂ particle size on band gap and product yield obtained from this work. Nanostructured materials are the way forward for photocatalytic reactions and particularly photoreduction of CO₂.

3.1.4. Modification by Sensitization

Surface sensitization increases the efficiency of the excitation processes and expands the usable light wavelength of the photocatalyst by excitation. The sensitizers can enhance the visible light absorption of a semiconductor [102]. The semiconductor serves primarily as the charge carrier, rather than the source of electrons and holes photo generated electrons and is very fast. Dye sensitizers are one of the most widely employed sensitizers. Fig. 9. Illustrates the photoreduction scheme of CO₂ to methanol using dye sensitized TiO₂ photocatalyst. In this system the dye and semiconductor (TiO₂) assume different responsibilities in that TiO₂ serves as the electron acceptor while the dye bears the role of light harvester. In a typical situation, like other photocatalytic systems it begins with photo-excitation of electrons from the highest occupied molecular orbital (HOMO) of the dye to its lowest unoccupied molecular orbital (LUMO) followed by transference of photo-generated electrons from the LUMO of the dye to the CB of TiO₂ and this is then used up by the reactant CO₂ for reductive conversion

of CO₂ to hydrocarbon fuels. A benefit of this process is the possibility of recycling the oxidized dye through oxidation of H₂O. Photoelectrons are provided by a photosensitive dye that is in contact with the semiconductor material and charge separation occurs at the surfaces between the dye, semiconductor, and an electrolyte. Surface sensitization through chemisorbed or physisorbed dyes increase the excitation process and expands the usable light wavelength through excitation. In dye photosensitization, if the oxidative energy level of the excited dye is more electronegative than the CB of the semiconductor e.g. TiO₂, electrons produced in CB of the dye sensitizer are transferred to the CB of TiO₂ during visible light irradiation. The efficiency of this electron transfer process is dependent upon the lower unoccupied molecular orbital and the conduction band edge of the TiO₂ or other semiconductor used [103].

Several research works have used dye sensitizers for CO₂ reduction [104]. They have been mostly used for CO₂ reduction to methane and other hydrocarbon fuels, but the efficiency and conversion are minimal. Thus, further research is required. Other types of sensitizers include coupling semiconductors e.g. AgBr/TiO₂, quantum dots e.g. CdSe QDs and phthalocyanine oxide derived photocatalysts and novel sensitizers [105]. The quantum dots sensitized photocatalysts have been researched in the photoreduction of CO₂ to methanol with commendable results. QDs possess outstanding electronic as well as optical properties which distinguish them from others. The QDs exhibit high absorption capacity for light [106], their band gaps can be corrected easily by simply modifying their size [107]. This makes it easy to align their band gap to that of the solar spectrum. The structure of their electrons can be easily tuned and used to prepare heterostructures having specific band alignment. Thus, electron-hole pairs which causes recombination [108] are maximally separated. Also, optimizing their energetics for optimum light absorption will be made easy and their redox chemistry will be better. Another advantage QDs have is that if synthesized with highly advanced method,

materials whose structures and properties can be controlled for specific applications can be obtained. The QDs are also nanometre in measurement meaning they naturally possess large surface area which is key for effective adsorption and uptake in catalysis. It is possible that multiple electron generation can efficiently take place in QDs and this means enhanced photocatalysis is possible [109]. QDs which have band gaps in the near infrared region (PbS and PbSe) [106] demonstrate strong electronic interaction with catalytically active TiO_2 under visible light [110]. The unique size of the quantum dots which influences characteristics such as intrinsic optical and electrical behaviour distinguishes the dye sensitized TiO_2 from the normal TiO_2 . Generally chalcogenide metals inclusive of CdS and ZnS are used with semiconductors like TiO_2 to propagate photon transformation of CO_2 to hydrocarbon fuels. Small sized QDs inject electrons swiftly to the conduction band edge of TiO_2 and large-sized QDs cover the visible region [111]. The metal phthalocyanines possess an unusual semi-conductivity and chemical stability which makes them relevant in the application of photoreduction of CO_2 . Just like the quantum dots, when photo-excited under visible light they can emit electrons to the conduction band of TiO_2 . This improves the electron hole separation and reducing band gap for photocatalytic efficiency, selectivity and higher yield of specific hydrocarbon fuels [112].

3.1.5. Modification by Formation of Heterostructures

The formation of heterostructures is arguably the most effective method of modifying the properties of a photocatalyst. When properly matched, the individual semiconductors demonstrate a mutualistic relationship in that the heterostructure combines the individual properties of each semiconductor which results in a material with a photo-activity that is greater than that of each photocatalyst. A schematic diagram illustrating photoreduction of CO_2 to methanol through a heterojunction in a composite catalyst is depicted in Fig. 10 [113].

Heterostructure is formed by the combination of two semiconductors which have complementary properties of making the heterostructure perform better than the individual materials. Like all pure photocatalysts, the photoreaction in an heterostructure begins with photo-activation and excitation of the individual materials forming the heterostructure. When irradiated and photo-activation occurs, photo-generated electrons move from the CB of semiconductor B and transfer to that of A. The determination of origin and destination of photo-generated electrons depends on the band engineering of the heterostructure [27]. As a principle, photo-generated electrons generally move from a semiconductor with a higher CB to that with lower CB as the energy requirement for such a transition is not as high as that required for the opposite. The photo-generated electrons transferred to A can then be used at the surface for reduction reaction (CO_2 to methanol). Simultaneously, as this process occurs, photo-generated holes migrate from the VB of A to that of B i.e. in the opposite of the electrons. The photo-generated holes which are transferred are likewise used for reactions at the surface but in this case a water reaction [30].

Formation of heterostructures generally improve light absorption capacity, enhance textural and morphological properties, foster separation of electron-hole pairs and increase efficiency of CO_2 photoreduction. Separation of charges is usually accomplished by transference of photo-generated electrons from the semiconductor with higher CB to that with lower CB and migration of holes from semiconductor with lower VB to higher VB. This was observed by Wang et al., when $\text{Cu}_2\text{O}/\text{TiO}_2$ nanotube was used to photo-reduce CO_2 to methanol under UV-visible light. Since TiO_2 had a lower CB of -0.5 while Cu_2O had a CB of about -1.5, flow of electrons was from the CB of Cu_2O to that of TiO_2 while flow of holes was from the VB of TiO_2 to that of Cu_2O . This was the reason for improved photo-activity and stability since charge separation was facilitated [30, 114]. The choice of individual semiconductors used for a heterostructure dictates its photo-activity and effectiveness. For

example, using a VLR photocatalyst like CeF_3 with TiO_2 can produce an heterostructure that is active both in the UV and visible region [115]. Similarly, the use of materials with d- π or π - π overlapping such as CNTs, nanostructured polymeric materials can improve charge separation as these π interactions create a passage for photo-generated electrons [116-118].

Another modification method employed to improve the effectiveness of TiO_2 as a photocatalyst for CO_2 photoreduction is by creating defects in the structure. Defect chemistry is a very effective way to modify the intrinsic properties of a material thereby improving the rate of electron and ion transport within its structure [119]. Particularly, the research into engineering defects in metal oxides have gained massive attention over the years [120]. Anatase TiO_2 is highly susceptible to defect e.g. oxygen vacancies [121] or formation of amorphous layers at the surface [122]. These defects can be created by; calcination [123], high energy ball milling [124], microwave/ultrasonic irradiation [125], doping [126], hydrogenation process [127], plasma treatment [128], the use of strong reducing agents such as sodium borohydride [129] and electrochemical reduction [130]. The effect and study of defects on the structure of the material can be observed by analysing the surface chemistry of the material using high powered microscope [131] or by density functional theory (DFT) prediction. This was reported by Liu et al., who studied the mechanism of CO_2 photoreduction of CH_3OH on the (101) surface of Anatase TiO_2 . In their study they created defects via oxygen vacancy on the surface of the TiO_2 structure and they investigated the reaction pathway for a one-electron CO_2 photoreduction process to generate CH_4 and CH_3OH using DFT. This study proved that oxygen vacancies facilitated the reaction rapidly when compared to pristine/bulk TiO_2 because the adsorption energy of CO_2 molecules on the surface of the defected structure was greater. Furthermore, the common problem of reaction intermediates hindering production of desired products was limited on the defected structure. Since CO_2 photoreduction is often a multi-directional pathway reaction, they reported that the feasible

progression from this work was; through the CO species on the surface, to CHO, CHOH, CH₂OH or CHO, CH₂O and CH₃O which leads to production of CH₄ and CH₃OH [132]. Despite the successful results obtained, they however identified that the energy barrier to be overcome for each step of the reaction pathway were very high and there was a need to decrease the activation energies which would further accelerate the reaction rate and improve product yield.

3.1.6. Metal-Ligand Charge Transfer

The focus of research in photocatalysis and photoelectrochemical systems have been development of different ways to circumvent the obstacle of recombination. Two approaches have been used over the years and these are: - band engineering and synthesis of nanomaterials [133]. The first approach has been discussed so far. The second approach focuses on material design through synthesis of 1D, 2D and 3D materials, sub-1 nm ultrathin material, different morphologies (rod, sphere, single, multi, hollow and core-shell structures, carbon nanodots etc). This approach changes or modifies the pore size, surface area, mass transport and the pathway excitons use in approaching the surface of the semiconductor hence its interfacial charge transfer can be improved [134, 135]. Interfacial charge transfer can be regarded as the effective and efficient transport of excitons through the interfaces in a semiconductor. The interfacial charge transfer can be considered for a semiconductor-heteroatom (doped material), a semiconductor-semiconductor (composite and heterostructured materials), and Ligand-semiconductor material. Throughout this review the first two (doped material and composite/heterostructured material) have been extensively discussed because several works have been reported on their application for CO₂ photoreduction. This section provides a brief discussion on the principle behind reduction of CO₂ to useful fuels using homogeneous catalytic systems with focus Metal-Ligand Charge Transfer (MLCT) [71].

Photoreduction of CO₂ have been explored using either of two categories of catalytic systems; heterogeneous catalytic systems (involving nanoparticles of semiconductors) and homogeneous metal complexes also known as molecular or ligand metal complexes. The interfacial charge transfer in the molecular or ligand metal complexes are the focus of this section. The use of molecular or ligand metal complexes for catalytic reactions provide a mechanistic edge over the heterogeneous catalytic systems because they are able to effectively reduce/convert CO₂ to useful chemicals by a multi-electron process due to the transition metal in their complexes [136, 137]. Their ability to store electrons in vacant π^* orbitals make it possible for them to execute multi-electron reduction of an acceptor (CO₂). This network of π systems also make it possible for such ligands to shift their light absorption to regions of lower energy thereby improving their absorption of light. Also, some complexes can generate bimetallic systems due to the presence of their bidentate ligand which possess additional binding sites. This bimetallic system means their transition metal can function as extra light absorbers and the extra binding sites can allow for interaction with more acceptors [138]. The most commonly used complexes (in no particular order) contain transition metals such as Co [139], Ni [140], Re [141], Ru [142], Fe [136], Mn [143], Pt, Pd etc. Though most of these noble metal complexes have been deployed for CO production from CO₂ [136, 140, 141], some of them have been reported to work successfully in production of methanol and formate e.g. Ru and Re. The homogeneous catalytic systems would usually consist of a photosensitizer (light harvester) and the catalytic sites (one for reduction and the other for oxidation).

Typically, the process for photocatalytic systems begin with irradiation of light, absorption of photons by the photosensitizer and photo-excitation. Photo-excited electron migrates from the orbitals of the transition metal ion to the empty orbital of the ligand hence formation of a singlet metal to ligand charge transfer (¹MLCT) occurs [144]. Migration of the photo-excited electron creates a vacuum (hole), if a sacrificial electron donor such as TEOA

(triethanolamine) or ascorbate is used in the system this hole can be rapidly filled by electron-transfer from them. This process is known as reductive quenching of the photo-excited state. This leads to inter-system crossing (ISC) and transfer of the electrons to the triplet excited state ($^3\text{MLCT}$). This triplet excited state represents the reductive site and compared to the ground state it possesses several redox properties. The reduced complex at this $^3\text{MLCT}$ state will possess a reduction potential close to that of an aromatic radical say about 1.02V vs NHE as the case of $[\text{Ru}(\text{bpy})_3]^+$. Having such a potential the complex is more suited to reduce protons to hydrocarbon products such as CO and methanol. In most cases the $^3\text{MLCT}$ is only stable for microseconds and interaction with the electron produced by the oxidative site causes the ground state of the one-electron reduced specie to be formed. With the production of one-electron reduced specie an electron can then be transferred to the reductive site so that the d^6 neutral ground state of the photosensitizer is recovered [71, 140]. Fig. 11. Illustrates the basic principle of photo-redox reactions in homogeneous catalytic systems.

In a nutshell, the process occurs as a cycle which begins with photo-excitation and absorption, electron-transfer and redox reaction then deactivation and returning to the initial state. Deactivation or decay of the excited state generally occurs by one of two non-reactive pathways; emission of a photon or vibrational relaxation. The former is a slow radiative process known as luminescence while the latter is a faster non-radiative decay process. The pivotal issue in catalytic systems involving Ligand-Metal Complexes is ways to extend the lifetime of the excited state as this means more time for interaction with the acceptor (CO_2) and the more products that can be formed. Fig. 12. Shows the electronic pathway of interfacial charge transfer in the redox reaction of a ligand based photocatalytic system.

Though several factors dictate the lifetime of the excited state, the type of photosensitizer or chromophores used is crucial as they all absorb at different region of the solar spectrum. Some of them are better absorbers in the visible light spectrum while others

are more active in the UV spectrum. Transition metal complexes of ruthenium polypyridyl are an example of chromophores which absorb very well in the visible region hence they are preferable for photo-redox reactions. A number of reports have been made on photoreduction of CO₂ to methanol using Ruthenium complex and the first reported work was by MacDonnell et al [145]. They reported photoreduction of CO₂ to methanol and formate using a pyridine-based complex with [Ru (phen)₃]²⁺ as the chromophore while the sacrificial electron donor was ascorbate. The turnover for formate and methanol after 1 hr. were 0.025 and 1.1 x 10⁻⁴ respectively, due to degradation of the chromophore the system became inactive after 6 hr.

Contrary to previous reports on pyridine based systems they reported addition of Pt yielded no methanol in their system [145]. In 2014, MacDonnell et al [142] used a system combining [Ru(phen)₃]²⁺ and pyridine for photoreduction of CO₂ to methanol, formate and formaldehyde using a mixed solvent of water and DMF and with TEA as the sacrificial reductant. They synthesized two forms of the Ruthenium complex chromophore; ([Ru(phen)₂(ptpbα)]²⁺ (Ruα) and [Ru(phen)₂(ptpbβ)]²⁺ (Ruβ) which functioned as electrocatalysts and photocatalysts for CO₂ photoreduction. The selectivity and choice of product obtained using the chromophore (Ruβ) was different for different solvents [142]. The higher solubility of CO₂ in DMF and the fact that the photo-excited state of the complexes can be improved in mixed solvent systems of water and aprotic solvent also contributed to the efficiency of the system. In aqueous solvents, the complexes tend to lose their photochemical activity which is why water is seldom used as a medium for this systems though several researchers have tried to use water with no success [139]. These [Ru(phen)₃]²⁺ based complexes showed better methanol selectivity than formate and their activity was higher than previously reported but the use of DMF was a concern hence the search for better aqueous systems was pertinent.

One of the limitations of homogeneous systems is the fact that as the name implies, the catalysts are homogeneous and are mostly rare-earth metals. This means; unlike heterostructures they would lack some sort of thermal and mechanical support and stability, sustainability would be difficult because they are expensive, recovery of the catalyst will be a challenge hence releasing it to the environment will be harmful. Suman et al approached this problem by attaching the complex to graphene due to its excellent properties. They reported the photoreduction of CO₂ to methanol in a water-DMF solution using TEA as the reductive quencher but using ruthenium trinuclear polyazine complex immobilized on graphene in phenanthroline (Ru-phen-GO) as the chromophore. This work reported one of the highest yield of methanol (3977.57 μmolcat^{-1} after 48 hr. irradiation) from a homogeneous catalytic system [146]. Methanol is a very functional chemical that can be obtained from photoreduction of CO₂ [147]. Formic acid is another resourceful product from CO₂ photoreduction due to the variety of functions it serves in the chemical industry. There are several reports on the successful photoconversion of CO₂ to formic acid using homogeneous catalytic systems though majority of them deal with metal organic frameworks (MOFs). One of the notable works on the application of homogeneous catalyst system particularly ruthenium complex is that of Osamu et al.[148]. They reported the use of Ru (II) multinuclear complexes for CO₂ photoreduction however the high turnover frequency (671) obtained is what distinguished the work. Two different Ru(II) complexes $[\text{Ru}(\text{dmb})_n(\text{BL})_{3-n}]^{2+}$ and $[\text{Ru}(\text{dmb})_m(\text{BL})_{2-m}(\text{CO})_2]^{2+}$ were used as photosensitizer and catalyst, respectively. As one of the first works to report the successful photoreduction of CO₂ to formic acid using molecular photocatalysts, the principle behind the success of this work is sets the tone for several other works in this field. The first important finding was the excited electron of Ru (II) in its ³MLCT was inserted in the bridging ligand. Another breakthrough for this work was instead of using a conjugated bridging ligand as previous works did, a non-conjugated bridging ligand was

used. The reason for this was because the use of a conjugated bridging ligand would lead to a decrease in the reducing power of the catalyst.

The photoreduction process occurred via two important steps: reduction of the $[\text{Ru}(\text{dmb})_n(\text{BL})_{3-n}]^{2+}$ by a NADH modelled compound and transfer of electrons to $[\text{Ru}(\text{dmb})_m(\text{BL})_{2-m}(\text{CO})_2]^{2+}$ [148]. In 2015 Seth et al also successfully reduced CO_2 to formic acid using a MOF (UiO-66 UiO – University of Oslo) having Cr (III) and Ga (III) metal sites with 1-benzyl-1,4-dihydronicotinamide (BNAH - $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$) and TEA as sacrificial reductants. The synthesis pathway for this photocatalyst is represented in Fig. 13. In this synthesis, a post synthetic method was used along with (catbdc, 2, 3-dihydroxyterephthalic acid (an organic linker) was used to synthesize the actual ligand to be used (UiO-66-CAT). Finally, the metals (Ga (III) and Cr (III) were incorporated into the MOF in order to foster electron transfer while the organic linker was responsible for the visible light absorption of the complex. Their report shows Cr (III) gave a much better TON than using Ga (III) owing to the structure of the former [149]. They also reported the use of a mixed metal and mixed ligand MOF - UiO-66-derivative $(\text{Zr}_{4.3}\text{Ti}_{1.7}\text{O}_4(\text{OH})_4(\text{C}_8\text{H}_7\text{O}_4\text{N})_{5.17}(\text{C}_8\text{H}_8\text{O}_4\text{N}_2)_{0.83}$ and $^1(\text{Zr}/\text{Ti})$) for CO_2 photoreduction to formic acid. Like their first report, post synthetic exchange (PSE) was used for synthesis of the complex and BNAH and TEOA were used as sacrificial reductant and sacrificial base. After 13 hours of irradiation, several other products ($^{13}\text{CO}_2$, $^{13}\text{CO}_3^{2-}$, $\text{H}^{13}\text{COO}^-$, $\text{H}^{13}\text{CO}_3^{2-}$) were detected by NMR and the major product was formic acid [137]. In summary, ligand based catalytic systems have proven to be an alternative route to photoreduction of CO_2 to useful hydrocarbon fuels such as carbon monoxide, methanol and formic acid with high TON and good selectivity. However more research is still required for it to be up to par with conventional heterogeneous semiconductor based catalytic systems and obviously a long way before practical application can be achieved. Table 2. Lists previous researches on photoreduction of CO_2 to methanol using TiO_2 based photocatalysts.

3.2. Substitutes for TiO₂ based photocatalysts for CO₂ photoreduction

Although TiO₂ is a widely researched photocatalyst which possesses several properties that makes it a viable photocatalyst for commercial application, it is still limited by its wide band-gap. Hence, several alternative photocatalysts have been researched and are still been discovered by scientists. These include metal oxides, mixed metal oxides, graphene-based composites, sulphides, nitrides, and Metal Organic Frameworks (MOF) [167]. These photocatalysts possess enhanced properties better or equivalent to that of TiO₂ complimenting the limitations of TiO₂. Most of these photocatalytic materials have smaller band gap, matching valence and or conductance band, excellent physical, structural, crystallographic properties and better surface chemistry potentials. Although the materials still have some limitations, it is still increasingly being researched and used for CO₂ photoreduction. Some of these non-TiO₂ based catalysts have shown positive results in the photoreduction of CO₂ to methanol specifically and the results are quite commendable compared to TiO₂. For example, a methanol yield rate of 162, 127.5 and 63.5 $\mu\text{mol g}^{-1}\text{h}^{-1}$ was obtained for Ni-NiO/InTaO₄-N and InTaO₄, respectively when Tsai et. al., investigated the efficiency of solar driven Ni and modified N doped InTaO₄ using a visible light xenon lamp as light source with PE3OBF filters [82, 108]. Pan et al. converted CO₂ into methanol using NiO_x/InTaO₄ as the photocatalyst. The only product of the process - methanol had a yield of 1.394 $\mu\text{mol g}^{-1}\text{h}^{-1}$ recorded [168]. NiO_x/InTaO₄ was used to attract electrons and to provide active reaction sites. The relationship between the nanostructure composite and the different structures as well as their photo-activities are explained by a reaction mechanism (See Fig.. 14.). Liou et al. also reported photoreduction of CO₂ to methanol using NiO doped InTaO₄ as photocatalyst illuminated under solar spectrum of 400 nm. The methanol yield was 0.16 $\mu\text{mol g}^{-1}\text{h}^{-1}$ [169]. Wang et al. used NiO doped InTaO₂ in optical fibre photoreactor with a light intensity of 327 mWcm^{-2} and room temperature to reduce CO₂ to methanol. A methanol rate of 11.1 $\mu\text{mol g}^{-1}\text{h}^{-1}$ was recorded, but when the temperature was

increased to 75 °C the yield rate was 21.0 $\mu\text{mol g}^{-1}\text{h}^{-1}$ [170]. All these works confirm that these substitute photocatalysts performed better based on the yield of products obtained.

Several photocatalysts other than TiO_2 have been used for photoreduction of CO_2 . The non - TiO_2 catalysts can be classified into five different categories namely the metal oxides and hydroxides, metal organic frameworks (MOF) and, Oxysalts, metal chalcogenides and nitrides and polymeric materials. Table 3. Shows a list of selected non- TiO_2 based materials used for photoreduction of CO_2 to methanol. This table shows photocatalysts which consisted of more than one photocatalyst or heteroatom combined together in order to obtain optimum performance. Although these photocatalysts gave equal or better results compared to that obtained from using TiO_2 based photocatalysts, there are also some drawbacks such as poor stability, complicated synthesis method which produce toxic by-products and difficulty or expensive in scaling up for industrial application. For example, the germanium and gallium-based materials (ZnGa_2O_4 , Zn_2GeO_4 etc.) possess high CB positions and able to facilitate CO_2 photoreduction. However, these materials have wide band gaps (4.5 eV and 4.65 eV) and less light absorption capacity than TiO_2 [171].

3.2.1. Metal oxides and hydroxides

Metal, mixed oxides and hydroxides of different elements such as Cu (I) & Cu (II), Ni (II), Si (II), Zn (II), Ga (III), Ge (III), Ce (IV) and layered double hydroxides have been used for photoreduction of CO_2 to methanol. Copper has always been identified as a suitable dopant and co-dopant for photoreduction of CO_2 to methanol since, , it is able to serve as an electron trapping agent during photoreduction of CO_2 [172]. When used as a dopant or co-dopant it also creates a Schottky barrier which helps to foster charge separation and inhibit recombination. Oxides in the Cu^{2+} and Cu^+ states have been used for photoreduction of CO_2 with the Cu^+ state able to effectively trap visible light and function as an efficient VLR

photocatalyst. Zinc oxide has been used for photoreduction of CO₂ to, over nitrogen-doped zinc CO₂ converted to methanol under an 8 W fluorescent tube with water vapour as the reductant. The gas phase process produced a methanol of $2 \times 10^{-4} \mu\text{molg.cat.h}^{-1}$ alongside H₂, CH₄ and CO as by-products [83]. Graphitic carbon nitride (g-C₃N₄) was modified by ZnO nanoparticles to produce a superior photocatalyst for CO₂ photoreduction. Even though there was little or no improvement to the light absorptivity of the nanocomposite, interaction between ZnO and g-C₃N₄ produced a photocatalyst with enhanced charge separation, high inhibition to recombination and superior performance. Methane, ethanol and carbon monoxide were also obtained and the rate of CO₂ conversion was up to $45.6 \mu\text{molg.cat.h}^{-1}$ [173]. Meanwhile, photoreduction of CO₂ to methanol using germanium oxide, produced $1\text{--}10 \mu\text{mol h}^{-1}\text{gcat}^{-1}$ methanol and methane using promoted Zn₂GeO₄ [85].

The oxides of cerium can be used for photocatalytic reduction of CO₂ to methanol and modification with other metals or semiconductors boosts its photo-activity. Huang et al., co-doped Co₃O₄ and CeO₄ using a combustion method for photoreduction of CO₂ to methanol and C₂H₅OH under visible light. It was obvious from the research that modification with Co₃O₄ was the sole reason for improvement in the photo-activity because neither methanol nor C₂H₅OH was detected when using pure Co₃O₄. The optimum yield of methanol and C₂H₅OH were 1.52 and $4.75 \mu\text{molg.cat.h}^{-1}$ respectively [96]. Just like most d¹⁰ configuration metal oxides (Ge⁴⁺, Sn⁴⁺, In³⁺) gallium oxide possess highly mobile photo-generated electrons since their CB contains hybridized s and p orbitals to increase photo-activity. However, only few works exist on CO₂ conversion to methanol using gallium oxide or hydroxide even though it has been used to obtain other products such as CH₄ [174] and CO [175]. Morikawa et al., reported photoreduction of CO₂ to CO and methanol using Ga, Cu and Zn modified double hydroxides under UV-visible light [176]. Jiang et al., also reported photoreduction of CO₂ using ordered layered double hydroxides modified with Cu₂O [177]. UV-visible light was used,

hydrogen was the reductant and CO was produced alongside methanol. They reported product selectivity was dictated by the choice of metal dopant where modification with zinc produced optimum yield of CO ($620 \mu\text{mol.g.cat.h}^{-1}$) while using Cu gave optimal yield of methanol. Modification with Cu increased selectivity up to 68% and enabled photo-coupling of protons and photo-generated electrons to produce methanol

3.2.2. Metal organic frameworks and mesoporous materials

Metal organic frameworks (MOFs) and mesoporous materials are another class of photocatalytic materials evolving in the research of CO₂ to methanol. These materials are used in almost all fields of research primarily because of large surface area, pore structure and porous nature of their morphology. Combining two catalysts or materials together often increase the surface area of the resultant photocatalyst material, but what distinguishes these set of materials is the feasibility of accurately controlling the textural properties of the material enabling high adsorption rate for CO₂ for improved photo-activity, easy access of reactants to pores in the catalyst and better selectivity [178-181].

Different types of mesoporous materials have been used for photoconversion of CO₂ to hydrocarbon fuels from Ti-MCM-41, TUD-1 silica matrix, TiO₂/mesoporous silica (KIT-6) [181]. Most of these mesoporous materials are hardly used alone as photocatalysts, but as co-catalysts for forming heterostructures especially with Ti. Metal organic frameworks (MOFs) have also been extensively used as photocatalysts due to their 3D crystalline structure which gives them their very large surface area, porosity and higher flexibility. Surface area and porosity are very pertinent characteristics of a viable photocatalyst for both water splitting and CO₂ photoreduction therefore the MOFs have great prospects for these processes. The mesoporous materials also have organic linkers allowing migration of photo-generated electrons to metal centre easy and rapid. Unfortunately, they experience weak thermal and

hydrothermal stability. Triethanolamine (TEA/TEOA) sacrificial reagent could improve its stability by reversal of electron deficiency [182].

For an effective CO₂ photoreduction process to take place, the chosen catalyst must be soluble in water for the reaction to occur. However, this is not so for MOF as they lack connection between metal-organic linkers. The MOF can be said to be water intolerant [183-186]. The intolerance of MOFs affects the photo-activity because the metal clusters will be starved of photo-generated electrons if the organic linkers are not photo-excited effectively. The choice of organic linker, metal cluster and modification for a MOF also affects the selectivity and yield of products. The use of MOFs for photoreduction of CO₂ has not been fully explored. Liu et al., captured and photo-reduced CO₂ to methanol using a copper modified porphyrin-based MOF. With the Cu-porphyrin based MOF, they reported a methanol production activity seven times higher than porphyrin-based MOF highlighting adsorption of CO₂ onto the surface of Cu²⁺. The improved photo-activity is attributed to superior efficiency [187]. More research work is still needed on the application of mesoporous and MOFs for selective photoreduction of CO₂ to methanol. It is expected that because of the unique properties that MOFs possess, when combined with other semiconductor materials, superior textural and morphological properties of composites or heterostructures would be produced. These composites or heterostructures should demonstrate better photo-activity due to the presence of MOFs.

3.2.3. Oxysalts

Oxysalts are another category of photocatalysts researched for photoreduction of CO₂ to methanol. Common members of this group are the titanates and tantalates. Other members of this category are the tungsten-based materials, niobium based, vanadium based, and bismuth based. Though there are few or no works on using oxysalts directly, the alkaline earth titanates

and layered titanates have been explored. Alkaline earth titanates and tantalates such as SrTiO_3 [188], NaTaO_3 [189], KTaO_3 [190] etc. and layered titanates and perovskite tantalates like $\text{Sr}_3\text{Ti}_2\text{O}_7$ [180], $\text{La}_2\text{Ti}_2\text{O}_7$ [191], and $\text{K}_2\text{Ti}_6\text{O}_{13}$ [192] have been explored. Just like the famous TiO_2 , TiO_3 has also been used for photoreduction of CO_2 to hydrocarbon fuels and particularly to methanol. Many of these oxysalts were used to photo-reduce CO_2 to other hydrocarbon fuels such as CH_4 [193], H_2 [194] and also CO [195]. However, some have been used to obtain methanol especially after Halmann et al., converted CO_2 to methanol using SrTiO_3 [196]. It was noticed that because SrTiO_3 had a higher CB than the oxidation potential of $\text{CH}_3\text{OH}/\text{H}_2\text{CO}_3$, photoconversion to a range of aqueous products (including methanol) was possible. Kato et al., identified that the type of metal dopant on layered perovskites affected photo-activity and product selectivity. From their research it was confirmed the Na doped tantalate oxide was the most active among the alkali –metal- modified tantalate oxide used [194]. Coupling tantalate and titanate oxides with other semiconductors has also been shown to be a good way to improve photo-activity and efficiency for CO_2 photoreduction.

Xiang et al., recently produced methanol from the photoreduction of CO_2 using CuO loaded NaTaO_3 [76] with isopropanol ($\text{C}_3\text{H}_8\text{O}$) as the reductant. A high-pressure mercury lamp was used as the light source. Optimum yield of 137.48 and 335.93 $\mu\text{mol.g}^{-1}\text{h}^{-1}$ was obtained for methanol and $\text{C}_3\text{H}_6\text{O}$, respectively. Improvement in product yield was traced to the choice of dopant used, its properties and the choice of reductant. $\text{C}_3\text{H}_8\text{O}$ functioned as an electron donor and could absorb CO_2 very well. The reaction mechanism for the UV light photoreduction process is depicted in Fig. 15. The mechanism begins with the production of electron-hole pairs via photo-irradiation of the photocatalyst (NaTaO_3). Unmodified NaTaO_3 has a CB of -0.92 V vs NHE while CuO has a CB of -0.78 V vs NHE [117]. Based on the principle that electrons move from a photocatalyst with higher CB to that of lower CB, therefore it is evident that electrons from NaTaO_3 could easily recombine with holes in VB of

CuO. This migration would further enhance electron-hole separation and hence prolong their life span [118]. Since the movement of electrons occurred in the manner described earlier it is expected that the reduction reaction (reaction of CO_2 with electrons to produce methanol) would occur at the CB of CuO. This was confirmed as no methanol was observed when only NaTaO_3 was used as a photocatalyst [117]. The thermodynamics of the process further establishes these results because NaTaO_3 has a VB of 3.13 V while the potential for oxidizing the reaction media (isopropanol) to acetone is 0.47 V [119]. This explains why a high yield of acetone instead of methanol was observed – it was easier for the reaction media to be oxidized to Acetone.

Despite the fact most titanates are often active in the UV region of the spectra, modification with metals (e.g. C, N, Fe, Ni, Co etc.) can shift their optical absorption to the visible range [197, 198]. Tungsten-based materials on the other hand are visible light responsive materials. In fact, all oxo-metalates (V, Mo and Bi) are. WO_3 is limited by low conduction band which does not allow it to directly facilitate CO_2 reduction. WO_3 exhibits visible light absorption and photo-activity. The fact that it is a (visible light responsive) VLR catalyst makes it useful for CO_2 photoreduction once it is modified. For example, Ohno et al., photo-reduced CO_2 to methanol using $\text{Au/Ag-g-C}_3\text{N}_4/\text{WO}_3$ under visible light via a Z-scheme. Optimum yields of 2500 and 1750 nmol/ghr were obtained for the Au and Ag modified samples, respectively. Loading the metal nanoparticles affected the photo-activity of the composites and the yield of products because it aided multi-electron photoreduction of CO_2 . The bare composites were 1.7 times less active compared to the metal modified ones [199]. Lais et al also reported the synthesis of pure and silver loaded NaNbO_3 for photoreduction of CO_2 to methanol with high selectivity owing to the multi-electron transfer facilitated by the presence of Ag as a cocatalyst [200]. A commonly used tungsten-based material is Bi_2WO_6 and it has also been used in photoreduction of CO_2 . Cheng et al. reduced CO_2 to methanol

under visible light energy and the maximum yield of methanol reported was $17 \mu\text{mole g cat}^{-1} \text{h}^{-1}$ using Bi_2WO_6 hollow microsphere [97] (See Fig. 16.).

Niobium based materials have attracted some attention in photocatalysis and photoreduction of CO_2 . Even though limited by wide band-gap, which limits access to the UV region of the spectra, when modified Nb materials can perform well enough. As an example, Lee et al., synthesized NiO modified InNbO_4 for photoreduction of CO_2 to methanol using halogen lamp. A solution of KHCO_3 was used as the reductant and 1 wt.% of NiO gave the optimum yield of methanol – $1.4 \mu\text{mole g cat}^{-1} \text{h}^{-1}$ [201]. The Nb-based materials might not be very exceptional for photoreduction of CO_2 to methanol at the moment, but are effective for other hydrocarbon fuels e.g. CH_4 [202-204]. More work can be done to improve the methanol selectivity and to enhance their performance for CO_2 photoreduction generally.

Like all other oxo-metalates, vanadium-based catalysts especially InVO_4 are all visible light active. It can also experience sub-band gap absorption because the depletion layer of InVO_4 has vacant donor states being a transition metal-based material with d^0 configuration. Comparing the band gap structure of InVO_4 with other oxo-metalates (InTaO_4 and InNbO_4), it is reasonable to say it would be almost impossible for (InVO_4 to convert CO_2 to methanol. Considering Fig. 14, InTaO_4 and InNbO_4 are better considering their band structure and the redox potential of $\text{CO}_2/\text{CH}_3\text{OH}$. This perspective is rather myopic because a critical look at Fig. 14 indicates that InVO_4 will photo-reduce CO_2 to methanol if the reaction medium used for the process is KHCO_3 . This is because when CO_2 dissolves in KHCO_3 it forms carbonate ions and considering Fig. 17. It will be possible and easier to convert to methanol with carbonate instead of gaseous CO_2 . The nature of the photocatalyst (InVO_4), reductant to be used (KHCO_3) and the desired product (methanol) will now dictate the choice of light to be used. Since the CB of InVO_4 has a more negative potential than $\text{CO}_2/\text{CH}_3\text{OH}$ (-0.38 eV), $\text{H}_2\text{CO}_3/\text{CH}_3\text{OH}$ (0.044 eV) and $\text{CO}_3^{2-}/\text{CH}_3\text{OH}$ (0.209 eV) in water, visible light will be suitable

[205]. Choice of reductant affects the rate of feed adsorption on the photocatalyst, the performance of the photocatalyst and the efficiency of the process.

In order to improve the efficiency of the process however, modification with other metal oxides is advisable. When modified with metals or other semiconductors e.g. NiO, sub-band gaps are formed in its valence band due to f multiple defect sites. Lee et al., used NiO and NiO/InVO₄ for photoreduction of CO₂ to methanol. Distribution of photo-generated electrons through the composite as a result of accurate NiO loading made the yield of products higher than e bare InVO₄. The pin holes created in the NiO₄ loaded InVO₄ created more active sites on the composite [205]. Vanadium based materials have also been used for photoreduction of CO₂ to other hydrocarbon fuels e.g. the use of rGO/BiVO₄ for photoreduction of CO₂ to CH₄ etc. Bismuth based materials are functional for visible light photoreduction of CO₂. The materials are largely coupled with other semiconductors for improved photo-activity. Photoreduction of CO₂ to methanol using Bi₂WO₆ hollow microspheres without co-catalyst was one of the major research reported [206]. The strategy used for the work involved anion exchange hinged on the microscale Kirkendall effect. A methanol yield of over 50 $\mu\text{mole g cat}^{-1} \text{h}^{-1}$ was obtained. The improved photo-activity and yield was attributed to more CO₂ being adsorbed on the microspheres and the visible light utilization capacity of the photocatalyst [206]. Sodium bismuthate – an inorganic compound of bismuth has also been used as a photocatalyst for photoreduction of CO₂ to methanol. A xenon lamp ($\lambda < 400 \text{ nm}$) was used as the irradiation source, a solution of water and sodium hydrogen carbonate was used as the reductant and the reaction time was 9 hr. The sodium bismuthate nanorods formed were highly photoactive and were efficient for CO₂ photoreduction. Maximum yield of methanol obtained was about 0.85 $\mu\text{mole g cat}^{-1} \text{h}^{-1}$ and the photocatalyst remained active after 5 cycles [207]. Bismuth based materials remain prospective photocatalysts for CO₂ photoreduction provided necessary modifications are made.

3.2.4. Metal chalcogenides and nitrides

All sulphides, selenides and tellurides are known as chalcogenides. Owing to their unique properties, metal sulphides are often used as photocatalysts for CO₂ photoreduction. Relatively, chalcogenides have a higher CB than many of the metal oxide semiconductors to militate unique light absorption ability. Therefore, chalcogenides are suitable for photocatalysis and photoreduction of CO₂ to hydrocarbon fuels. Xiaofeng et al., reported the use of pulsed laser for photoreduction of CO₂ to methanol over a ZnS nanoparticle catalyst. A 355 nm laser was used as the radiation source while 100 ml of water as the reductant. Optimum methanol yield of about 90 $\mu\text{mole g cat}^{-1} \text{h}^{-1}$ [208] was obtained when 100 mg of ZnS was used. . In 2012, Dibenedetto et al., demonstrated conversion of CO₂ to methanol by a photocatalytic-enzymatic process using Ru modified ZnS as the photocatalyst. The coenzyme regeneration process was a multi-electron process involving photo-coupling of an organic radical and CO₂•⁻. ZnS has two limitations: one being low photo-stability and the other is the tendency to favour production of H₂ instead of CO₂ photoreduction. The former limitation can be overcome by selection of appropriate sacrificial agent e.g. (methanol [209] or C₃H₈O [210]) which would act as electron scavengers and prevent photo-corrosion [211]. Modification of ZnS with suitable co-dopants and or semiconductor can tune the band gap so that it becomes suitable for CO₂ photoreduction instead of water splitting and H₂ production [212].

Another commonly used chalcogenide is Bi₂S₃. Having a wide absorption range in the spectra as a result of narrow band gap and the moderate ability to convert irradiated light to electrons, it is indeed a worthy photocatalyst. Pure Bi₂S₃ is still a prospective photocatalyst because there exist only few works on CO₂ photoreduction using it has not been fully explored for CO₂ photoreduction due to the wide band-gap but it has been deployed for water treatment and dye photosensitization. This is why several 1D nanomaterials and modified forms of Bi₂S₃

are been synthesized as this can adjust or tune the band gap [213]. Even though it has not been extensively used for CO₂ photoreduction, Prasad et al., used Bi₂S₃/CdS to photo-reduce CO₂ to methanol under visible light. The optimum yield of methanol obtained after 6 hr was 20 $\mu\text{mole g cat}^{-1} \text{ h}^{-1}$. It was noted that increase in product yield was a function of co-dopant loading though up to 45 wt% of CdS was loaded. There are little or no report on photoreduction of CO₂ to methanol using of the chalcogenides probably because of certain limitations in their band engineering or morphology. However, many of them have been used to convert CO₂ to other hydrocarbon fuels like ZnTe, CoTe, CuS and Cu₂S for CH₄ [214], ZnS for HCOOH [210], CdInS₄ for HCOOCH₃ [209, 213], and ZnS for CO [210, 212]. Most of the chalcogenide were not used bare but modified with different co-catalysts and semiconductors. This confirms that most of the chalcogenides are not suitable for CO₂ photoreduction but given the appropriate modification method promising results could be obtained.

3.2.5. Polymeric materials

The latest trend in photocatalysis and CO₂ photoreduction is the use of carbon-based catalysts – polymers such as graphene, graphene oxide (GO), carbon nitride (C₃N₄) and conjugated polymers. These compounds are increasingly been employed for photoreduction of CO₂ due to well-developed surface area, unique optical and electronic properties. Graphene as a material is a very good conductor because of its properties and this explains why in some photocatalytic and other systems it is often used as an electron donator. It is often used in place of some metals because its comparable conductivity [215]. Its oxide - GO is a unique material with similar properties like that of a semiconductor. It can and has often been used as an affordable photocatalyst especially in CO₂ photoreduction. The optical properties of GO could effectively trap solar energy. It can adsorb a lot of CO₂ because it has a large surface area which is highly porous.

In terms of band gap, unlike inorganic semiconductors the band gap of GO is dictated by the C-O ratio and this can be altered during synthesis [215]. This was achieved by Hsu et al., when they synthesized GO of different oxygen content for photoreduction of CO₂ using the Hummer's method. They reported the obtained GO photocatalysts had different band gap with the least having a band gap of 2.9 eV and the widest band gap was 4.4 eV. When the three different GO samples were used to photo-reduce CO₂, only methanol was obtained as the product and compared to the reference (TiO₂ P25), the different GO samples gave higher product yield [216]. Shown et al., also used GO to photo-reduce CO₂ to methanol under visible light. Water vapour was used as the reductant and CH₃CHO was obtained as the major product while methanol was also produced. The maximum yield of methanol was 0.294 $\mu\text{mole g cat}^{-1} \text{h}^{-1}$ when 10 wt. % Cu was decorated on GO. The product yield was 60 times greater when Cu/GO was used.

Another property of GO beneficial to CO₂ photoreduction and photocatalysis in general is the fact that formation of heterostructures with other semiconductors or metals is relatively easy. This is because, the presence of several oxygenated functional groups that reside on the basal plane means that incoming noble metals or semiconductors can easily cling/attach to it and this forms a heterostructure layer at that junction. This junction can serve as an effective way to separate electron and hole pairs and this would further improve the photo-activity and reduce the rate of recombination. A good example is the photoreduction of CO₂ to methanol using hexa-molybdenum cluster compounds (See Fig. 18.). In this work the authors tried to solve the problem of non-recyclable catalysts by anchoring them to photoactive supports such that they can receive support from their host and be recovered for recycle. In this case cluster-based compounds of Mo₆ - Cs₂Mo₆Br₈Br^a₆ and (TBA)₂Mo₆Br₈Br^a₆ were clamped on graphene oxide (GO) sheets such that by recovering GO they were also collected back. This work reported one of the highest methanol yields in literature (1644 $\mu\text{mol/gcat.}$). Each of the

constituents functioned differently; Mo₆ boosted the visible light absorption due to its lower band gap hence its immobilization on GO. This means after photo-excitation electrons migrated from the LUMO of Mo₆ to the CB of GO where photoreduction of CO₂ occurred while water splitting occurred at its VB. GO provided better charge mobility and reaction area due to its large surface area [217].

Gusain et al. also reported reduction of CO₂ to methanol using GO (rGO) modified with CuO nanorods (See Fig. 19.). As shown below, due to the lower band gap of CuO and its localized surface Plasmon resonance (LSPR) from the presence of Cu, the 1D CuO were trapped into 2D graphene sheet. By so doing the whole heterostructure can benefit from the large surface area of rGO which provides more active sites for reaction. Reductive conversion of CO₂ takes place at the CB of CuO and oxidation occurs at its VB. When CuO nanorods were used for the photoreduction process, only a low yield of 175 $\mu\text{mole g cat}^{-1} \text{h}^{-1}$ was obtained because the rate of recombination was very rapid. However, the yield of methanol over rGO/Cu₂O and rGO/CuO drastically improved to 862 μmolg^{-1} and 1228 μmolg^{-1} respectively. Slower recombination of electron hole pairs and better transfer of photo-generated electrons in the nanocomposite were mentioned as the reasons for improved photo-activity and increase in product yield [218]. Graphene and graphene oxide (GO) remain viable materials for photoreduction of CO₂ to methanol and other hydrocarbon fuels. Another unique and prospective photocatalyst is graphitic carbon nitride (g-C₃N₄) based materials. Graphitic carbon nitride as a metal free photocatalyst has the following benefits; low cost, effectiveness, sustainable and less toxic, low band gap of 2.7 eV, high chemical and thermal stability, and suitable redox potential to efficiently catalyse reactions. Graphitic carbon-based materials have produced some promising results for CO₂ photoreduction to methanol. It has also been employed for oxygen evolution and overall water splitting. Mao et al used g-C₃N₄ synthesized from two different precursors (urea and melamine) for CO₂ photoreduction with NaOH as the

reductant. From the research, the products were methanol and $\text{C}_2\text{H}_5\text{OH}$ although the selectivity was different for the two. The main product for u-g- C_3N_4 was methanol while that of m-g- C_3N_4 was ethanol [219]. The yield over m-g- C_3N_4 was only 8.7 mmol for 12 h visible-light irradiation, while the methanol and $\text{C}_2\text{H}_5\text{OH}$ yields over u-g- C_3N_4 are calculated to be 15.1 mmol and 10.8 mmol, respectively. Shi et al., reported the application of Cerium oxide (CeO_2) with reduced graphene oxide/CuO as a cocatalyst for photoreduction of CO_2 to methanol with a high yield of $135.6 \mu\text{mol g}^{-1} \text{ cat h}^{-1}$ after 5 hours of reaction. In this work they report that the presence of reduced graphene oxide (rGO) in the composite was instrumental to the achievement of such a high product yield because it facilitated the separation of photogenerated electron and hole pairs while the selectivity of the system could be attributed to the CuO cocatalyst [220].

Although graphitic carbon nitride possesses exceptional properties, it has high recombination rate of the photo-generated electron-hole pair. This draw-back is minimized by doping and other enhancement methods. Pt/g- C_3N_4 has been used for CO_2 photoreduction under UV-vis light and the products were methane, methanol and formaldehyde [51]. G- C_3N_4 composites and nanomaterials have also been researched due to their large surface. For example, TiO_2 was modified with Cu and created a nanocomposite of g- C_3N_4 , Cu and TiO_2 (See Fig. 20.). Though g- C_3N_4 has a lower band gap of 2.7 eV, when Cu was doped into its structure it did not perform as effective as when it was combined with TiO_2 . Cu was added as a heteroatom dopant because of its affinity for methanol during photoreduction reactions as reported from previous reports. From the results obtained, addition of Cu to carbon nitride reduced the band gap, recombination rate of electron and hole pairs and ultimately increased the yield of methanol from the process. The nanocomposite formed from the combination of carbon nitride, copper and titanium dioxide brought about a synergistic interaction between TiO_2 and g- C_3N_4 . This interaction between the two catalysts helped the composite remunerate

the unique properties of each constituent to overcome their individual set-backs [221]. The role of the copper metal doped on TiO_2 in the composite included: (1) increased active sites for CO_2 adsorption, (2) increased photo-activity of TiO_2 to absorb and utilize visible light and (3) development of Schottky barrier to promote separation of electron and hole pairs hence inhibiting recombination. $\text{g-C}_3\text{N}_4$ as a metal free visible light sensitive photocatalyst was responsible for the increased absorption of visible light by the composite [221]. This combined effect from each constituent in the composite was responsible for the optimal yield of methanol during CO_2 photoreduction. Thus, $\text{g-C}_3\text{N}_4$ can also be considered an effective photocatalyst for photoreduction of CO_2 to methanol provided appropriate co-dopant is used.

Considering the reported existing works on photoreduction of CO_2 using the substitute (non- TiO_2) photocatalysts, it is obvious that though higher product yield has been reported, some draw-backs still exist. In some cases, the materials are rare or limited in the earth crust hence they are not sustainable, are synthesized by expensive multi-step processes, synthesized at extreme temperatures, not photo-stable and/or must be modified with another compound or heteroatom which maybe toxic or produce toxic wastes. This concludes our material review and brings us to a perspective. TiO_2 is a viable, stable and sustainable of all photocatalysts though other photocatalysts have also proved to be promising but they are either too expensive, toxic, complicated in synthesis or limited in application. This does not necessarily mean that TiO_2 is the best or further research should not be envisioned instead the contrary is the case in that extensive and rewarding researches should be pursued. Photocatalysts with better yield and higher selectivity should be the focus as these determines the possibility of industrial application for large scale production of methanol from solar energy as this is a very promising and sustainable solution to the dilemma of continual rising energy demand and reduction of CO_2 emission.

4. Challenges and Recommendations

From this review, a solution to the challenges of greenhouse gases and increasing demand for energy in the world today has been discussed from a photochemical point of view. The process essentially involves the use of a suitable semiconductor which possess a narrow band gap amidst other requirements. Considering the fact, the process of CO₂ photoreduction is kinetically and thermodynamically complex, the process achieved since inception can be deemed commendable even though it is not yet industrially feasible. Over the years progressive results have been obtained using different photocatalyst materials. However, there is need to do a critical assessment of the field in general and to focus in particularly on the photoreduction of CO₂ to methanol as it is a versatile and useful product from CO₂ photoreduction. Methanol can be used for several purposes ranging from prospects as a future fuel to be a precursor to synthesis of several important chemicals therefore it is important to do an evaluation of the progress made so far. This review has achieved this using a systematic approach, but more importantly projected and given probable solutions to the problems encountered so far.

One major problem in the field of photocatalysis and specifically CO₂ photoreduction is the fact that existing materials have several limitations. Although TiO₂ is widely researched, its wide band gap and poor light absorption capacity has been a draw-back over the years and though several modification methods have been employed, the desired yield and selectivity level has not been attained. Techniques such as doping, sensitization, formation of nanocomposites and heterostructures etc. have shown positive results in boosting the capabilities of TiO₂. On the other hand, non-TiO₂ based semiconductors with narrower band gaps have also been used for this process though many of them are expensive when compared to TiO₂. Though these substitutes showed better result due to their band engineering, textural properties and characteristics, their cost, stability and toxicity (especially the toxicity of the precursors used in preparing them) remain a cause for concern.

TiO₂ is more environment friendly, stable and reusable compared to other semiconductors but is less photoactive. Due to this dilemma, there is a need for continuous search for more novel photoactive, stable and selective photocatalysts for photoreduction of CO₂. These photocatalysts will have to be VLR photocatalysts that can deploy the visible range of the solar spectrum and can reduce the rate of recombination, enhance charge separation and selectively photo-reduce CO₂ to specific products. The existent substitute non-TiO₂ based photocatalysts have shown prospects so far e.g. g-C₃N₄, graphene, graphene oxide etc. Therefore, improvements and modifications can be made to tune the photo-activity of these materials using the same methods used to modify TiO₂. Also, the use of heterostructures (especially type II) have proven rewarding considering recent researches and efforts should be intensified in this direction. Heterostructures can effectively deploy the strong points of each constituent, improve the visible light absorption capacity and improve and increase the textural properties (surface area, pore structure etc.) of the material.

Similarly, the properties (textural, morphological and photocatalytic) of a photocatalyst are often determined by their preparative or synthesis method. The crystal facet, shape, surface area, pore structure, integration of modifiers, dopants or sensitizers etc. can be engineered during the preparation process. The calcination time, temperatures, inhibition of interfering organic materials, method of agitation etc. all determine the nature and properties of the photocatalytic material synthesized. To this end there is a need to discover/develop new, advanced methods for synthesis of photocatalysts used for CO₂ photoreduction. In-depth understanding of the surface chemistry, atomic interactions and reactions taking place during the synthesis of photocatalytic materials will help to design process specific materials functional for production of desired products. The photocatalytic material used in CO₂ photoreduction determines the rate of reactant (CO₂) adsorption to the surface of photocatalyst, rate of desorption of products from the bulk catalyst, the flow of electrons and holes, the rate

of recombination and in fact the yield and selectivity. It is therefore imperative to research more into new synthesis methods or improve existing ones so that photocatalysts with better performance are obtained.

Furthermore, the knowledge of reaction mechanisms, reaction pathways, kinetic and thermodynamic analysis of the CO₂ photoreduction process on a general note is still minimal. One of the uniqueness and complexities of the CO₂ photoreduction process is that it is a multistep and multi electron process. Also, it is thermodynamically uphill in that, since CO₂ has a very negative adiabatic electron affinity, transfer of a single electron to it is very endergonic. Also, recombination of electrons and holes take place at a rate that is two to three orders faster than that of electron transfer. Photoreduction of CO₂ to methanol is specifically difficult because kinetically, it requires 6 electrons unlike HCOOH requiring only 2 electrons. The kinetics of CO₂ photoreduction also depends on factors such as intensity of incident light and fraction absorbed etc. Considering all these, it is evident photoreduction of CO₂ to methanol is a challenging task and we can say progress has been made so far. However, the only way to effectively improve the efficiency of photocatalytic materials is to have better understanding of the mechanism by which photoreaction takes place on the surface, how recombination takes place and how to tune the product selectivity. More research in the area of photochemistry and surface chemistry will produce deeper understanding of the activities at the surface of the photocatalyst and this will improve the utilization of photocatalytic materials. The use of computer simulations and advanced material characterization techniques can broaden knowledge in this aspect.

Semiconductors such as TiO₂ have been extensively used for photoreduction of CO₂ with commendable results. Despite the achievements recorded, most semiconductor photocatalysts still suffer from lack of chemical, thermal and photo-stability, low efficiency under certain condition and susceptibility to agglomeration. Conversely, polymeric materials

exhibit properties such as relatively low/no toxicity, earth abundant element based and inexpensive, easy to synthesize, lightweight, flexible and easy tuneable properties [229]. Many of the polymeric photocatalysts are able to function effectively even without the presence of a noble metal e.g. g-C₃N₄. The tunability of polymers give them certain properties such as ability to absorb light in the visible region, variable band gaps, and inherently porous. Other advantages include bi-continuous donor–acceptor architectures due to their synthetic framework, longer life time of excited charges and high charge carrier mobilities [229, 230]. Also, after photo-excitation of a photocatalyst, photo-excited e^-h^+ could separate into polaron pairs which must migrate rapidly to the surface of the photocatalyst where the actual CO₂ photoreduction takes place. In the case of polymers this e^-h^+ can take place faster than in inorganic semiconductors because of the presence of stacked π bonds present in 2D polymers such as g-C₃N₄ etc. [231]. These assembled π bonds are able to facilitate the rapid transfer of charges from the photocatalyst to the co-catalyst or dopant. Different types of polymeric photocatalysts such as the linear, porous polymers, the covalent triazine frameworks, covalent organic frameworks and the carbon nitrides all have distinct properties that makes them suitable for application in CO₂ photoreduction. Any material that has delocalized π orbitals (double and triple bonds in organic molecules) can absorb the sunlight, creating charge carriers, which are subjected to transport the material [231, 232]. All these classes of polymeric photocatalysts except the linear polymers have the stacked π bonds in their framework unfortunately, research in π -conjugated polymeric materials for solar fuel generation is still in its infancy [229]. It is expected that intensifying research in the use of carbon-based polymeric materials for CO₂ photoreduction could produce better result than most existing semiconductors. Although these materials have shown promising results, modification and band engineering are essential for optimal performance.

Finally, away from the photocatalyst material design and photoreactor engineering, another major area of solar driven energy generation and conversion is the efficiency of the process and its sustainability. The thermodynamic, economic and environmental impacts of an energy generation or conversion process cannot be determined by determining the yield of products obtained (which is what most publications focus on). Considering the fact that a life cycle approach is a more accurate perspective when comparing emissions associated with any type of energy generation and conversion technology, there is a need for in-depth and detailed study of photocatalytic photoreduction reactions using advanced sustainability assessment tools such as Life Cycle Assessment (LCA) software, Exergy and preferably a combination of both software [233]. This type of approach will give a holistic and sustainability focused assessment of photocatalytic reduction of CO₂ to renewable fuels and its prospects as a future approach to solving greenhouse gas emissions and energy generation.

5. Concluding remarks

From the discussions in this review, it has been established that photocatalysis and photoreduction of CO₂ to hydrocarbon fuels provides a win-win solution to the problems of global warming and the need for alternative source of energy. A systematic record of previously used photocatalysts and recently designed ones have been discussed in this review. Likewise, the conditions which favour optimum yield and selectivity have been discussed. Challenges and limitations experienced in photoreduction of CO₂ have also been discussed with useful recommendations and suggestions provided. It can be concluded from the critical review of different photocatalytic materials used for CO₂ photoreduction that carbon-based materials specifically graphene based photocatalysts mostly produce the highest yield of methanol. The properties of graphene-based materials such as the surface and textural properties are responsible for this superior performance it exhibits. Since the method of preparation and

modification affects the photo-activity of a photocatalyst, new and advanced synthesis methods should be discovered, or existing ones should be improved on. Most of the organic and polymeric compounds lose their photo-activity during preparation especially upon exposure to strong rays of light, extreme temperature and pressure. Therefore, novel polymeric materials with better photo-stability, photo-activity, band engineering and light trapping capacity should be explored.

Based on the reported yield of methanol it can be proven that polymeric and organic materials can effectively photo-reduce CO₂ to methanol, but, clear details of how this process takes place is still far-fetched. Deeper understanding of the surface chemistry, atomic interactions, textural and morphological changes occurring during material synthesis is imperative. In-depth understanding of the reaction mechanisms, pathways and photo transformations during CO₂ photoreduction is pivotal to development and advancement of this field of research. Of all metal atoms doped on photocatalyst materials, copper modified photocatalysts produce higher yield of methanol. The light trapping ability of copper, LSPR effect and the ease of band energy modification (especially with TiO₂) make it preferable for photoconversion of CO₂ to methanol. However, the method of modification determines how atoms of the metal will be distributed over or into the photocatalyst material. Therefore, methods or procedures with which accurate positioning and dispersion of metal dopants on a photocatalyst will help maximize the photocatalytic properties of the dopant atoms.

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