

Review

Advances in Photocatalytic CO₂ Reduction with Water: A Review

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Abstract: In recent years, the increasing level of CO₂ in the atmosphere has not only contributed to global warming but has also triggered considerable interest in photocatalytic reduction of CO₂. The reduction of CO₂ with H₂O using sunlight is an innovative way to solve the current growing environmental challenges. This paper reviews the basic principles of photocatalysis and photocatalytic CO₂ reduction, discusses the measures of the photocatalytic efficiency and summarizes current advances in the exploration of this technology using different types of semiconductor photocatalysts, such as TiO₂ and modified TiO₂, layered-perovskite Ag/ALa₄Ti₄O₁₅ (A = Ca, Ba, Sr), ferroelectric LiNbO₃, and plasmonic photocatalysts. Visible light harvesting, novel plasmonic photocatalysts offer potential solutions for some of the main drawbacks in this reduction process. Effective plasmonic photocatalysts that have shown reduction activities towards CO₂ with H₂O are highlighted here. Although this technology is still at an embryonic stage, further studies with standard theoretical and comprehensive format are suggested to develop photocatalysts with high production rates and selectivity. Based on the collected results, the immense prospects and opportunities that exist in this technique are also reviewed here.

Keywords: photocatalysis; CO₂ reduction; visible light irradiation; plasmonic photocatalyst; surface plasmon resonance (SPR)

1. Introduction

Global warming is viewed to be one of the vital environmental concerns that humankind is dealing with [1]. CO₂ contributes mostly to the worldwide climate change because it is more than 64% effective than other greenhouse gasses in the atmosphere [2]. This chemically stable gas contributes to the increase in global temperature through absorption and re-emission of infrared radiation. In the past century, the temperature of the Earth's surface increased by roughly 0.6 K; the warming trend reveals more significant changes in last 20 years, according to the Intergovernmental Panel on Climate Change (IPCC) [3]. The consequences of the greenhouse effect are global and severe, such as ice melting at the Earth's poles, the quick rising of sea level, and growing precipitation across the globe [4]. To deal with these issues, numerous studies have been conducted over the last few decades applying various strategies to control CO₂ emission or convert it into other products.

There are at least three routes of lowering the amount of CO₂ in the atmosphere: (i) direct reduction of CO₂ emission; (ii) CO₂ capture and storage (CCS); and (iii) CO₂ utilization [5–7]. Lowering the CO₂ emission may seem quite unrealistic because of the present human lifestyle and emergent use of fossil fuel. The potential of CCS technology can be restrained because of the environmental risk of leakage and the energy requirement for fuel compression and transportation. Among the renewable resources, solar energy is the most exploitable one by making available more energy to the Earth for every hour than the total amount of energy humans consume in a year [8].

Harvesting this abundant sunlight in solving environmental problems is a promising approach and one of the ultimate goals for sustainability of global development. In the long term, photocatalytic conversion of CO₂ utilizing solar energy is the most appealing route for CO₂ reduction [9,10]. In addition, CO₂ reduction advances recycling of carbon source [8]. The interest in this field of research has begun with the work of Fujishima and Honda in 1972 [11]. The advancements in nanotechnology, particularly the synthesis of nanomaterials with different structures and morphologies [12,13], and the most recent approach of using noble metals, such as Au or Ag, with surface plasmon resonance (SPR) to enhance the photocatalytic efficiency of TiO₂ or other semiconductors [14–16] have facilitated the progress.

For real life application, a photocatalytic system must be capable of working under daylight even when the sun is not directly overhead and show both long-time consistency and efficiency. The reduction process has to be promoted while suppressing any side reaction that can occur during the reaction, and H₂O should be used as an electron source [17]. Unfortunately, a photocatalyst that satisfies all these requirements has not been reported yet. A considerable number of review papers on this emerging topic have already been published. Some papers focus on the advances in developing novel photocatalysts with high photocatalytic activity [18–22], while others on studying the enhancement mechanisms and the influences of co-catalysts [23], the applications by highlighting on the reaction conditions, reactor design and analysis methods [18,24] and comprehensive discussion on general considerations that apply specifically to CO₂ reduction [25,26]. Furthermore, extensive studies on TiO₂-based photocatalysts [27–29] and noble metal nanoparticles dispersed plasmonic photocatalysts have been published as well [30–32]. Nevertheless, the basic insight of photocatalytic CO₂ reduction in presence of H₂O and comparison among the photocatalytic efficiency of different photocatalysts in this reaction has not been clearly documented to date. This review paper covers the basic aspects of photocatalytic CO₂ reduction process with H₂O, concentrating on recently reported semiconductor photocatalysts with high photoactivity, particularly on plasmonic photocatalysts.

2. Photocatalysis and Photocatalytic Reduction of CO₂ with H₂O

The word photocatalysis consists of two parts: photo and catalysis, “photo” means light and “catalysis” is the performance of a substance during the chemical transformation of the reactants to modify the reaction rate without being changed ultimately [33]. In practice, the word photocatalysis refers to the acceleration of a photoreaction in the presence of a catalyst [34]. In photocatalytic CO₂ reduction system with water, both photo-reduction of CO₂ and photo-oxidation of H₂O occur simultaneously under sunlight irradiation using a suitable photocatalyst. A variety of reaction conditions intensely affects the product distribution of this reaction, such as reactor geometry, catalyst type, sacrificial reagents, and even illumination type. Thus, predicting the product distribution of a particular photocatalytic reaction is very challenging [35].

The photocatalytic CO₂ reduction is a very effective method considering that no additional energy is needed and no negative effect on the environment is produced. The use of cheap and abundant sunlight to transform this major greenhouse gas into other carbon containing products is also an ideal approach because of its low cost. Here, the high activation energy to break very stable CO₂ molecule is provided by solar energy [35]. To date, many photocatalysts, including oxides and non-oxides, e.g., TiO₂, ZnO, Fe₂O₃, ZrO₂, SnO₂, BiWO₃, Ti-MCM-41, CdS, TNTs, ZnS, GaN, and SiC, have been studied for the photocatalytic reduction of CO₂ with H₂O. A summary of different photocatalytic systems employed in this technology since 2010 are given in Table 1.

Table 1. Advances in photocatalytic systems for CO₂ reduction with water since the year 2010.

Photocatalyst	Radiation Source	Major Products	Comments	References
0.5 wt % Cu/TiO ₂ -SiO ₂	Xe lamp (2.4 mW cm ⁻² , 250–400 nm)	CO and CH ₄	The synergistic combination of Cu deposition and high surface area of SiO ₂ support enhanced CO ₂ photoreduction rates.	[36]
ZnGa ₂ O ₄	300 W Xe arc lamp	CH ₄	Strong gas adsorption and large specific surface area of the mesoporous ZnGa ₂ O ₄ photocatalyst contribute to its high photocatalytic activity for converting CO ₂ into CH ₄ .	[37]
(RuO + Pt)-Zn ₂ GeO ₄	300 W Xe arc lamp	CH ₄	In the presence of water, ultra-long and ultrathin geometry of the Zn ₂ GeO ₄ nano-ribbon promotes CO ₂ photo-reduction, which was significantly enhanced by loading of Pt or RuO ₂ .	[38]
Ag/AlA ₄ Ti ₄ O ₁₅ (A = Ca, Ba and Sr)	400 W Hg lamp	CO, HCOOH, and H ₂	On the optimized Ag/BaLa ₄ Ti ₄ O ₁₅ photocatalyst, CO was the reported as the main product. The molar ratio of O ₂ production (H ₂ + CO:O ₂ = 2:1) demonstrated that water was consumed as a reducing reagent in the photocatalytic process.	[39]
I-TiO ₂ nanoparticles	450 W Xe lamp	CO	High photocatalytic activity was observed under visible light and the efficiency of CO ₂ photoreaction was much greater than undoped TiO ₂ due to the extension in the absorption spectra of TiO ₂ to the visible light region and facilitated charge separation.	[40]
LiNbO ₃	Natural sunlight or Hg lamp (64.2 mW cm ⁻²)	HCOOH	The MgO-doped LiNbO ₃ showed an energy conversion efficiency rate of 0.72% which was lower than that for the gas–solid catalytic reaction of LiNbO ₃ (2.2%).	[41]
G-Ti _{0.91} O ₂ hollow spheres	300 W Xe arc lamp	CH ₄ , CO	The presence of G nanosheets compactly stacking with Ti _{0.91} O ₂ nanosheets allows the rapid migration of photo-generated electrons from Ti _{0.91} O ₂ nanosheets into G and improves the efficiency of the photocatalytic process.	[42]
Graphene oxides (GOs)	300 W commercial halogen lamp	CH ₃ OH	Among all GOs, GO-3 exhibited the highest efficiency as a photocatalyst for CO ₂ reduction under visible light, and the conversion rate of CO ₂ to CH ₃ OH on modified GO (GO-3) was 0.172 mmol g ⁻¹ cat h ⁻¹ , which is six-fold higher than that of pure TiO ₂ .	[43]
W ₁₈ O ₄₉	300 W Xe lamp	CH ₄	The oxygen-vacancy-rich ultrathin W ₁₈ O ₄₉ nanowires can be used to design materials with extraordinary photochemical activity because it displayed high CO ₂ reduction capability in presence of water.	[44]
Zn _{1.7} GeN _{1.8} O	300 W Xe arc lamp	CH ₄	Zn _{1.7} GeN _{1.8} O loaded with co-catalysts showed significantly higher conversion rate of CO ₂ into CH ₄ .	[45]
Pt-, Au-, or Ag-loaded mesoporous TiO ₂	350 W Xe lamp	CH ₄	The mesoporous TiO ₂ showed higher efficiency towards CO ₂ reduction when loaded with noble metal particles, and the order of enhanced photocatalytic activity was Pt > Au > Ag. The optimum loading amount of Pt was 0.2 wt %.	[16]
0.5 wt % Pt loaded ZnAl ₂ O ₄ -modified mesoporous ZnGaNO	300 W Xe lamp ($\lambda = 420$ nm)	CH ₄	The high photocatalytic activity of this photocatalyst was attributed to the improved gas adsorption of the mesoporous structure, the chemisorption of CO ₂ on the photocatalyst and the narrow bandgap of ZnAl ₂ O ₄ -modified ZnGaNO to extend the light absorption.	[46]

Table 1. Cont.

Photocatalyst	Radiation Source	Major Products	Comments	References
Ga ₂ O ₃ with mesopores and macropores	300 W Xe lamp (500 mW cm ⁻²)	CH ₄	Ga ₂ O ₃ with mesopores and macropores showed high photocatalytic activity due to its higher CO ₂ adsorption capacity (300%) and increased surface area (200%) compared to the bulk nanoparticles.	[47]
Pt-TiO ₂ thin nanostructured films	400 W Xe lamp	CO and CH ₄	The catalyst can be produced at an industrial scale for commercial application and showed high efficiency for selective CH ₄ formation.	[48]
HNb ₃ O ₈	350 W Xe lamp	CH ₄	KNb ₃ O ₈ and HNb ₃ O ₈ were synthesized by the conventional solid-state reaction and performed more effectively in photocatalytic CO ₂ reduction than commercial TiO ₂ .	[49]
ZnO-based materials	8 W fluorescent tube (average intensity 7 mW cm ⁻²)	CO, CH ₄ , CH ₃ OH, H ₂	N-doping did not show any important influence on the photocatalytic behavior of ZnO-based photocatalysts. The mesoporous structure of ZnO favored CO and H ₂ production, but catalysts with Cu showed an enhancement in the hydrocarbon production, mainly CH ₃ OH.	[50]
Ag, Pt, bimetallic Ag-Pt and core-shell Ag@silica (SiO ₂) nanoparticles with TiO ₂	100 W Hg lamp (330 nm)	CH ₄	The use of a reactor with three optical windows, a combination of both bimetallic co-catalysts, and Ag@SiO ₂ nanoparticles increased the product formation significantly compared to bare TiO ₂ .	[51]
Carbon nanotubes Ni/TiO ₂ Nano-composites	75 W visible daylight lamp ($\lambda > 400$ nm)	CH ₄	Compared to Ni/TiO ₂ and pure anatase TiO ₂ , Ni/TiO ₂ incorporated with carbon nanotubes demonstrated maximum CH ₄ product yield of 0.145 mmol h ⁻¹ g ⁻¹ catalysts after 4.5 h of irradiation under visible light.	[52]
Pt/Cu/TiO ₂	200 W Xe lamp	CH ₄ , CO, H ₂	The addition of co-catalyst Pt decreases the selectivity for CO ₂ photo-reduction; however, loading Cu onto TiO ₂ increases the selectivity from 60 to 80%.	[53]
Au/Pt/TiO ₂	500 W Xe lamp	CH ₄ , CO	Plasmonic photocatalyst Au/Pt/TiO ₂ provided a more effective way to harvest solar energy by consuming a high-energy photon in the solar spectrum (UV region) and using it for charge carrier generation. Moreover, it also utilized visible light to enhance the photocatalytic activity.	[54]
20 wt % montmorillonite modified TiO ₂	500 W Hg lamp (365 nm)	CH ₄	Loading of montmorillonite on TiO ₂ enhanced the surface area and reduced particle size, thus improving charge separation, resulting in maximum yield for CH ₄ (441.5 mmol·g·cat ⁻¹ h ⁻¹).	[55]
0.5 wt % Pt/NaNbO ₃	300 W Xe lamp ($\lambda > 300$ nm)	CH ₄ , CO, H ₂	The cubic-orthorhombic surface-junctions of mixed-phase NaNbO ₃ enhanced the charge separation, thereby improving its photoactivity.	[56]
Ag supported on AgIO ₃ (Ag/AgIO ₃ particles)	500 W Xe arc lamp	CH ₄ and CO	In the conversion of CO ₂ to CH ₄ and CO using water vapor, Ag/AgIO ₃ particles showed high and stable activity because of the surface plasmon resonance effect of Ag particles.	[57]
g-C ₃ N ₄ /NaNbO ₃ nanowires	300 W Xe arc lamp	CH ₄	An intimate interface formation was suggested between the C ₃ N ₄ and NaNbO ₃ nanowires in g-C ₃ N ₄ /NaNbO ₃ heterojunction photocatalyst, resulting in almost eight-fold higher CO ₂ reduction than individual C ₃ N ₄ under visible light irradiation.	[58]

Table 1. *Cont.*

Photocatalyst	Radiation Source	Major Products	Comments	References
In ₂ O ₃ /g-C ₃ N ₄	500 W Xe lamp	CH ₄	The addition of In ₂ O ₃ nanocrystals onto g-C ₃ N ₄ surface improved the photocatalytic CO ₂ reduction process significantly due to the interfacial transfer of photo-generated electrons and holes between g-C ₃ N ₄ and In ₂ O ₃ .	[59]
SnO _{2-x} /g-C ₃ N ₄ composite	500 W Xe lamp	CO, CH ₃ OH, and CH ₄	Enhancement in the surface area of g-C ₃ N ₄ was observed by introducing SnO _{2-x} . Improve photocatalytic performance was attributed to the increased light absorption and accelerated the separation of electron-hole pairs.	[60]
AgX/g-C ₃ N ₄ (X = Cl and Br) nanocomposites	15 W energy-saving daylight bulb.	CH ₄	Under ambient condition and low-power energy-saving lamps, the optimal 30 AgBr/pCN (protonated graphitic carbon nitride photocatalyst) sample showed highest photocatalytic activity with significant enhancement in CH ₄ formation compared to individual AgBr and pCN photocatalyst.	[61]
Ag supported on Ag ₂ SO ₃ (Ag/Ag ₂ SO ₃)	500 W Xe lamp	CH ₄ and CO	Plasmonic photocatalyst Ag/Ag ₂ SO ₃ was stable towards CO ₂ photoreduction after 10 repetitive catalytic cycles with high efficiency under visible light irradiation.	[62]

One of the major obstacles to this research progress is that most of the CO₂ reducing photocatalysts are not visible light responsive [63]. In this context, numerous types of photocatalysts have been developed. A few of these catalysts performed under visible light irradiation with high conversion rate and selectivity, whereas other catalysts were weakly responsive under visible light and showed a low rate of reaction yield [64]. The introduction of plasmonic metal onto semiconductor materials to enhance photocatalytic activity has been demonstrated to be very attractive in the visible region.

In the following sections, the basic mechanisms and principles of measuring the efficiency of a photocatalyst in photocatalytic CO₂ reduction with H₂O are discussed.

2.1. Theoretical Approach

Photocatalysis means activating a semiconductor using sunlight or artificial light. When a semiconductor material absorbs photons of sufficient energy, its electrons are excited from the valence band (VB) to the conduction band (CB), creating electron–hole pairs. VB is the highest energy band occupied by electrons and CB is the lowest energy band in which there is no electron at the ground state [65]. These photo-generated electrons can move to the surface of a semiconductor and react with the adsorbed species on the surface. Meanwhile, electron–hole recombination is also possible [66]. The efficiency of the photocatalytic reaction depends on the competition between these two processes [67].

The basic photocatalytic process can be summarized as follows:

- (i) Absorption of photons with suitable energy and generation of electron–hole pairs;
- (ii) Separation and transportation of electron–hole pairs (charge carriers); and
- (iii) The chemical reaction of surface species with charge carriers [68,69].

This process is illustrated in Figure 1. As the charge recombination process ($\sim 10^{-9}$ s) is usually much faster than the reaction process ($\sim 10^{-3}$ – 10^{-8} s), acceleration of the electron–hole separation step remarkably affects the reaction yield [22].

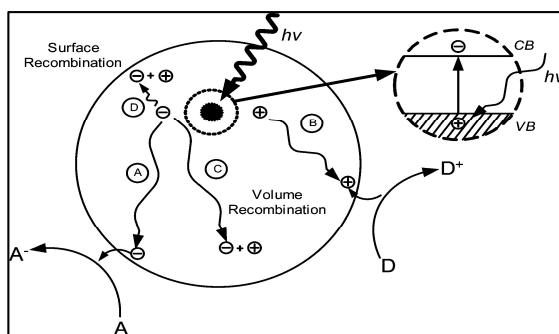


Figure 1. Schematic diagram of photo-excitation and electron transfer process (adapted from [63]).

Apart from the direct photon-excited charge carrier generation process in semiconductors Figure 1, collisions, photon-electron interaction [70–72] or electron transfer from the SPR-excited metal nanoparticle [73,74] can also generate electron–hole pairs. However, all of the photo-excited electrons reaching the surface cannot reduce thermodynamically inert and very stable CO₂ compound. This reduction reaction is endergonic and requires both hydrogen and energy [19]. Thus, photocatalytic CO₂ reduction using sunlight and water has the potential to be the most feasible means to remove atmospheric CO₂.

The reduction potential for the various products of CO₂ reduction at pH 7 is presented in Table 2. On the one hand, single-electron CO₂ reduction reaction requires a highly negative potential of -1.9 eV , which makes the one-electron reduction process very unfavorable. On the other hand, the proton assisted multi-electron CO₂ reduction reaction requires comparatively low redox potential (Table 2) and are more favorable. Photocatalysts can facilitate these reduction processes with lower potential. For this purpose, an ideal photocatalyst generally requires two characteristics: (i) the redox potential of the photo-excited VB hole must be sufficiently positive so that the hole can act as an electron acceptor; and (ii) the redox potentials of the photo-excited CB electron must be more negative than that of the CO₂/reduced-product redox couple.

Upon absorbing radiation from the light source, photo-generated holes in the VB of the photocatalyst oxidize H₂O. In addition, the photo-generated electrons in its CB form products such as HCOOH, HCHO, CH₃OH, and CH₄, by reducing CO₂. Here, the relation between the energy levels of the photocatalyst and the redox agent determines the type of reaction that takes place. Figure 2 shows the CB, VB potentials, and bandgap energies of various semiconductor photocatalysts and relative redox potentials of compounds involved in CO₂ reduction. The final carbon containing products are determined by the specific mechanism to conduct the reaction. The number and rate of transferred electrons from the photo-generated carriers to the reaction species in the reaction system also contribute in this process [26].

Table 2. Reduction potentials for the CO₂ reduction process. E⁰: Standard reduction potential.

Reactions	E ⁰ /eV
CO ₂ + e ⁻ → CO ₂	≥ -1.9
CO ₂ + 2e ⁻ + 2H ⁺ → HCOOH	-0.61
CO ₂ + 2e ⁻ + 2H ⁺ → CO + H ₂ O	-0.53
CO ₂ + 4e ⁻ + 4H ⁺ → HCHO + H ₂ O	-0.48
CO ₂ + 6e ⁻ + 6H ⁺ → CH ₃ OH + H ₂ O	-0.38
CO ₂ + 8e ⁻ + 8H ⁺ → CH ₄ + 2H ₂ O	-0.24

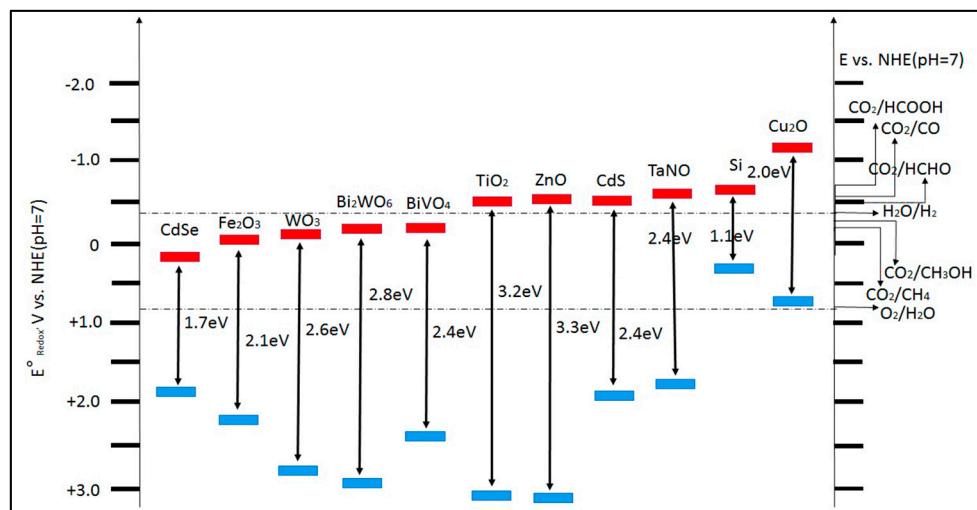


Figure 2. Schematic representation of conduction band, valence band potentials, and band gap energies of various semiconductor photocatalysts and relative redox potentials of the compounds involved in CO₂ reduction at pH 7 (Adapted from [22]).

The most commonly used light source for photocatalysis is ultraviolet (UV) light. The high energy content of UV light can effectively excite most photocatalysts. Thus, the majority of publications on photocatalytic CO₂ reduction processes are still based on using artificial UV light from high-power lamp [75–77]. Only about 4% of solar energy is used by UV light where 43% of solar energy is occupied by visible light; thus, a photocatalyst with a narrow bandgap that can use visible light is in high demand [65,78]. At present, a significant number of studies focus on the direct use of visible light both from artificial and natural sources. Using visible light is more favorable than using UV light because visible light is readily available from sunlight. However, the energy content of visible light is less competitive compared to UV light. Thus, in photocatalytic reduction, the visible light might not provide for an adequate amount of energy for photo-excitation of the catalysts. As such, photocatalysis using visible light and sunlight faces a great challenge [79].

2.2. Measures of Photocatalytic Efficiency

The photocatalytic CO₂ reduction efficiency is generally measured by the yield of the product. Here, the general unit for R is mol·h⁻¹·g⁻¹ of catalyst and for the product either in molar units (μmol) or in concentration units (ppm).

$$R = \frac{n(\text{Product})}{\text{Time} \times m(\text{Catalysts})} \quad (1)$$

In the catalyst-based measurements, the efficiency of the photocatalyst usually depends on the amount of photocatalyst, the intensity of the light, lighting area, etc., so under the irradiation of light, the amount of product formed by per gram of photocatalyst within a certain time period can be measured by its apparent quantum yield. It is calculated by using the amount of product and the incident photon number as shown in the following equations [19,26]. When the photocatalytic reduction reaction gives complex products, then the number of reacted electrons in the equation denotes the sum of the reacted electron to form each product [80,81]. Thus, in light-based measurements, the quantum yield of CO₂ photo-reduction into different products can be calculated using following equations:

$$\text{Overall quantum yield}(\%) = \frac{\text{Number of reacted electrons}}{\text{Number of absorbed photons}} \times 100\% \quad (2)$$

$$\text{Apparent quantum yield(QY, \%) = } \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \quad (3)$$

$$(\text{Apparent}) \text{ quantum yield of CO(\%) = } \frac{2 \times \text{Number of CO molecules}}{\text{Number of incident photons}} \times 100\% \quad (4)$$

$$(\text{Apparent}) \text{ quantum yield of HCOOH(\%) = } \frac{2 \times \text{Number of HCOOH molecules}}{\text{Number of incident photons}} \times 100\% \quad (5)$$

$$(\text{Apparent}) \text{ quantum yield of HCHO(\%) = } \frac{4 \times \text{Number of HCHO molecules}}{\text{Number of incident photons}} \times 100\% \quad (6)$$

$$(\text{Apparent}) \text{ quantum yield of CH}_3\text{OH(\%) = } \frac{6 \times \text{Number of CH}_3\text{OH molecules}}{\text{Number of incident photons}} \times 100\% \quad (7)$$

$$(\text{Apparent}) \text{ quantum yield of CH}_4(\%) = \frac{8 \times \text{Number of CH}_4 \text{ molecules}}{\text{Number of incident photons}} \times 100\% \quad (8)$$

3. Recent Photocatalysts for CO₂ Reduction with H₂O

The first step towards enhancing the photocatalytic activity is the selection of a proper photocatalyst. It is a subject of considerable importance both for practical application of photocatalysts and understanding their mechanism. Photocatalysts could be categorized into two basic groups based on their structures: homogeneous and heterogeneous photocatalysts.

The seminal work by Lehn et al. demonstrated the selective CO₂ reduction into CO by using Re(I) diimine complexes [82]; since then, the use of metal complexes in photocatalysis has been greatly studied for both CO₂ reduction [83–86] and H₂O oxidation [87–89]. CO₂ is efficiently reduced to form CO when homogeneous photocatalysts, such as Re complexes, are used in the presence of electron donors, such as triethanolamine [80,90,91]. However, CO₂ reduction and H₂O oxidation processes require distinct reaction conditions.

As a result, carrying out both of the reaction simultaneously using a metal complex catalyst in a single system is a very difficult task. Reverse oxidation of organic products generated from the reduction of CO₂ and the reverse reduction of O₂ generated from the oxidation of H₂O terminate the continuity of the reaction. Figure 3 summarizes these cases briefly [8]. Figure 3a shows the advantages of H₂O oxidation of a metal complex catalyst (H₂O oxidation site) with a sacrificial electron acceptor (SA). Figure 3b shows the advantages of CO₂ reduction for a metal complex catalyst (CO₂ reduction site) with a sacrificial electron donor (SD). Figure 3c shows the problems encountered when combining H₂O oxidation site and CO₂ reduction site: (I) reverse oxidation of products such as organic compounds; (II) electron transfer from H₂O oxidation site to CO₂ reduction site; (III) need to be electron storage; (IV) need to be active in H₂O; (V) easier reduction of O₂ than CO₂; and (VI) stability in H₂O [8]. A number of challenges are encountered in constructing a homogeneous metal complex system for CO₂ reduction along with H₂O oxidation. The inefficient electron transport between reduction and oxidation catalysts is one of the major difficulties in this process. Another drawback is the short lifetimes of the one-electron-reduced species and the photo-excited state in the presence of O₂ generated by H₂O oxidation.

Since the pioneering work of Fujishima, Honda, and their co-workers, where they reported the photocatalytic reduction of CO₂ to organic compounds, such as HCOOH, CH₃OH, and HCHO, in the presence of various semiconductor photocatalysts, such as TiO₂, ZnO, CdS, SiC, and WO₃ [92], many heterogeneous semiconductor compounds, including metal oxides, oxynitrides, sulfides, and phosphides, had been investigated for this purpose [10,20]. TiO₂, BaLa₄Ti₄O₁₅, SrTiO₃, WO₃ nanosheet, NaNbO₄, KNbO₄, Sr₂Nb₂O₇, Zn₂GeO₄, and Zn₂SnO₄ are the leading compounds in this list of photocatalysts and the list is increasing enormously in the last five years [1,9,10,18–20,28,64,65,93–98]. Activation of an inert molecule such as CO₂ requires contributions of both incident photons and effectively excited electrons. Thus, the presence of reducing agents can assist the CO₂ activation process. It takes advantage of H₂O oxidation and CO₂ fixation when H₂O is used as the reducing

agent. Appropriate incident light and suitable semiconductor materials have an important role in attaining this process. Moreover, intensified processing and sensibly engineered strong catalyst with great accessibility are essential to activate the very small molecules under ambient conditions [99]. Some of the desirable properties of an efficient heterogeneous photocatalyst are a high surface area, single site structure, light absorption, an efficient and long lifetime of charge separation, the high mobility of charge carriers, and product selectivity [25].

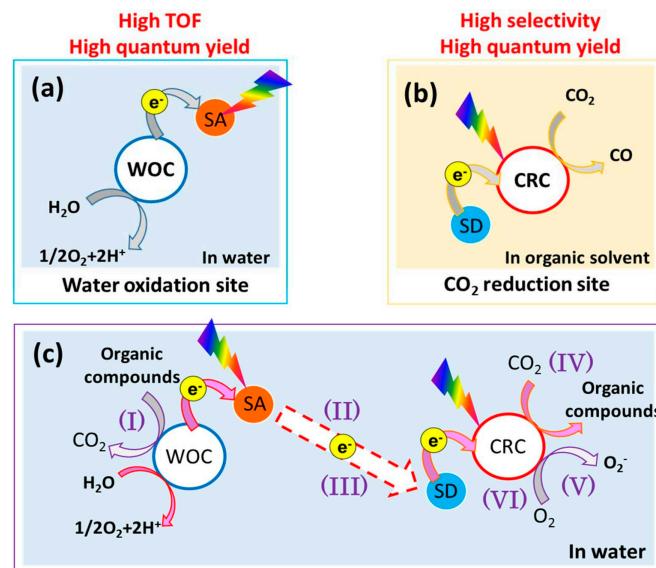


Figure 3. Advantages and disadvantages of metal complex catalysts for CO₂ reduction with H₂O oxidation (adapted from [8]). (a) The advantages of H₂O oxidation of a metal complex catalyst (H₂O oxidation site) with a sacrificial electron acceptor (SA); (b) the advantages of CO₂ reduction for a metal complex catalyst (CO₂ reduction site) with a sacrificial electron donor (SD); (c) the problems encountered when combining H₂O oxidation site and CO₂ reduction site.

Table 1 shows the studies on photocatalytic CO₂ reduction with H₂O to obtain good efficiency and selectivity for specific products. However, this approach is still far from practical implementation. Application of photocatalysis in the environmental and energy industries on a large scale is still limited. Among several difficulties in the heterogeneous photocatalysis, the two major ones are low photocatalytic efficiency and the lack of suitable visible-light-responsive photocatalyst [100, 101]. The first one is mostly because of the recombination of photo-generated electrons and holes. For example, the most widely used semiconductor photocatalyst, i.e., TiO₂, is well known for its low cost, nontoxicity, and stability with outstanding optical and electronic properties [102,103], but the high recombination rate of photoexcited electron–hole pairs in TiO₂ hinders its advanced application [104, 105]. Another difficulty is that most of the commonly used photocatalysts like TiO₂ and ZnO have large band-gaps, so they can only absorb sunlight in the near UV region. Thus, only a small percent of the solar spectrum is utilized, where many low-bandgap photocatalysts, such as CdS and Fe₂O₃, show low stability [30]. To resolve these drawbacks, new and more efficient visible-light-active photocatalysts have been studied to satisfy the necessity of future environmental and energy technologies driven by solar power [106]. The development of latest technological advances [82], application of modern synthesis methods to form high-surface-area catalyst nanostructures [83], studies on new co-catalysts to coupled with existing photocatalysts, and investigation on the visible-light-responsive plasmonic photocatalysts are some of the progressing ways of enhancing the photocatalytic activity.

In this section, we present a brief and necessary description on several recently reported semiconductor photocatalysts that exhibit high catalytic activity towards CO₂ reduction with H₂O. We limit our discussion here to extensively studied TiO₂ and modified TiO₂ photocatalysts,

layered-perovskite photocatalyst $\text{ALa}_4\text{Ti}_4\text{O}_5$, and ferroelectric photocatalyst LiNbO_3 and presented an overview of visible-light-active novel plasmonic photocatalysts in the next section.

3.1. TiO_2 and Modified TiO_2

TiO_2 and modified TiO_2 composites are the most commonly used photocatalysts worldwide. In TiO_2 -based materials CO_2 reduction with H_2O involves these basic six steps: (i) adsorption of the reactants on the photocatalyst; (ii) activation of the adsorbed reactants by photo-generated charge carriers; (iii) surface intermediates formation; (iv) intermediates to products conversion; (v) desorption of the products from the catalyst surface; and (vi) catalyst regeneration. The dynamics of the reaction process and final products from CO_2 reduction are determined by each of these steps. Previous literature has demonstrated that activation and dissociation process of CO_2 on TiO_2 surface can be increased by creating defect on the catalyst surface (e.g., Ti^{3+} and oxygen vacancy). By tailoring the crystal phase of TiO_2 (e.g., a mixture of anatase/brookite or anatase/rutile), engineering the defects in TiO_2 and incorporating modifiers with TiO_2 (e.g., metals, metal oxides, graphene, quantum dot sensitizers); the rate of charge separation and transfer can be enhanced [29].

Most studies in this field adopted a solid–liquid interface reaction mode. In such case, particles of a photocatalyst are dispersed or suspended in the aqueous solution, which dissolves CO_2 . A limited reduction of CO_2 and preferential adsorption of H_2O on catalyst surface could occur due to limited solubility of CO_2 in H_2O and direct contact of liquid H_2O with the photocatalyst [22]. These limitations could be overcome by using solid–gas or solid–vapor mode of reaction, which can also increase the reduction of CO_2 . For example, Xie et al. showed that the rate of hydrocarbon product formation increases by more than three times along with decreasing H_2 production from H_2O when TiO_2 (P25) or Pt-TiO₂ photocatalyst is placed on a holder surrounded by gaseous CO_2 and H_2O instead of dispersing the photocatalyst in liquid water (Table 3) [107]. The CO_2 reduction selectivity increased pronouncedly from 11–19% to 40–56%. Thus, the solid–vapor reaction mode is better for preferential reduction of CO_2 in the presence of H_2O . The microstructure of the photocatalysts and the ratio of gaseous CO_2 and H_2O in gas mode reaction influence the photoactivity and selectivity. For example, Zhang and co-workers found an increased CH_4 formation on Pt-loaded TiO_2 nanotubes with increasing concentration of H_2O molecules surrounding the TiO_2 nanotubes, as well as a high concentration of –OH groups on the surface. However, the ratio of gaseous $\text{CO}_2/\text{H}_2\text{O}$ displayed little effect on product formation over Pt-TiO₂ nanoparticles [108]. These results indicated that the adsorption of H_2O molecules on the photocatalyst surface can affect the photoreduction in gas mode. Optimizing and modulating the microstructure and surface property of the semiconductor is a very effective way to improve the activity and selectivity of photocatalytic CO_2 reduction in gas mode [19].

Table 3. Influence of reaction phase on photocatalytic reduction ^a of CO_2 with H_2O using TiO_2 and 0.5 wt % Pt-TiO₂ photocatalyst [107].

Reaction Mode	Photocatalyst	Formation Rate ($\mu\text{mol}\cdot\text{g}^{-1}\text{h}^{-1}$)			R (Electron) ($\mu\text{mol}\cdot\text{g}^{-1}\text{h}^{-1}$)	Selectivity for CO_2 Reduction (%)
		CO	CH_4	H_2		
Solid-gas	TiO_2	1.2	0.38	2.1	10	56
solid-liquid	TiO_2	0.80	0.11	5.3	13	19
solid-gas	Pt-TiO ₂	1.1	5.2	33	110	40
solid-liquid	Pt-TiO ₂	0.76	1.4	55	123	11

^a Reaction conditions: catalyst, 0.020 g; CO_2 pressure, 0.2 MPa; H_2O , 4.0 mL; irradiation time, 10 h.

The light source also has a strong impact on this reduction process. Varghese et al. reported that the rate of product formation from CO_2 reduction is at least 20 times higher under outdoor sunlight than previously published reports, where photocatalytic reductions were carried out using UV illumination [109]. Even though TiO_2 is the most widely studied and used photocatalyst, in spite of its high conversion rate, the overall quantum yield is considerably low for the reactions that have

been studied. Certainly as low as 10% for most processes [110]. Pure TiO₂ shows a lower efficiency towards the reduction reaction due to its high rate of charge-carriers recombination and a shorter lifetime of photo-generated charges. So far, many efforts are been made to utilize this photocatalyst more efficiently including nanostructured TiO₂ synthesis, single crystal TiO₂, metal or non-metal doped TiO₂, dye-sensitized TiO₂ etc. The majority of these techniques are expensive at the same time very complex.

3.2. Ag co-Catalyst Loaded ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba)

In recent years, a new set of materials unrelated to TiO₂ emerged in the photocatalysis study. Layered-perovskite ALa₄Ti₅O₁₅ (A = Ca, Sr, and Ba) photocatalysts with 3.79–3.85 eV of bandgaps, had been previously reported for effective water splitting [111] and later on also employed for the CO₂ reduction by Iizuka et al. In this process, HO⁻ was used as a reducing reagent. They also discussed the factors affecting the photoactivity on the basis of the examination and characterization of the co-catalysts [39]. They found that Ag co-catalyst-loaded ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba) reduces CO₂ into CO using H₂O as an electron donor. For this purpose, Ag co-catalyst-loaded BaLa₄Ti₄O₁₅ was the most effective photocatalyst.

Although large amounts of reacted electrons and holes are present (in the order of Au > Cu > Ru > NiO_x > Ag), Ag is the most active co-catalyst for CO₂ reduction, and its photocatalytic activity showed dependence on the loading methods (Tables 4 and 5). In addition to the size of Ag particles, the unique location of Ag nanoparticles on the working photocatalyst is also important. By a chemical reduction method, Ag particles could be loaded both on the edge and the basal planes of BaLa₄Ti₄O₁₅, which had a plate morphology with ~100 nm thickness and ~1 μm width. This liquid-phase chemical reduction method is the best for loading fine Ag particles, where the condition of the Ag co-catalysts is changed at the beginning stage of the photocatalytic reaction.

Table 4. CO₂ reduction over ALa₄Ti₄O₁₅ (A = Ca, Sr and Ba) photocatalysts with various co-catalysts^a [39].

Photo-Catalyst	Band Gap/eV	Co-Catalyst (wt %)	Loading Method	Activity/μmol·h ⁻¹			
				H ₂	O ₂	CO	HCOOH
BaLa ₄ Ti ₄ O ₁₅	3.9	none	-	5.3	2.4	0	0
BaLa ₄ Ti ₄ O ₁₅	3.9	NiOx ^b (0.5)	impregnation	58	29	0.02	0
BaLa ₄ Ti ₄ O ₁₅	3.9	Ru (0.5)	photodeposition	84	41	0	0
BaLa ₄ Ti ₄ O ₁₅	3.9	Cu (0.5)	photodeposition	96	45	0.6	0
BaLa ₄ Ti ₄ O ₁₅	3.9	Au (0.5)	photodeposition	110	51	0	0
BaLa ₄ Ti ₄ O ₁₅	3.9	Ag (1.0)	photodeposition	10 ^c	7.0 ^c	4.3 ^c	0.3 ^c
CaLa ₄ Ti ₄ O ₁₅	3.9	none	-	1.3	0.6	0.07	0
CaLa ₄ Ti ₄ O ₁₅	3.9	Ag (1.0)	photodeposition	5.6	2.1	2.3	1.3
SrLa ₄ Ti ₄ O ₁₅	3.8	none	-	0.8	0.5	0.06	0
SrLa ₄ Ti ₄ O ₁₅	3.8	Ag (1.0)	photodeposition	2.7	1.8	1.8	0.5

^a Catalyst 0.3 g, water 360 mL, CO₂ flow system (15 mL·min⁻¹), a 400 W high-pressure mercury lamp, an inner irradiation quartz cell. ^b Pretreatment: Reduced at 673 K and subsequently oxidized at 473 K after impregnation (543 K for 1 h). ^c Initial activity.

In the photo-deposition process, Ag particles of 30–40 nm size are loaded on the edge of the plate predominantly. The photo-generated holes could dissolve the Ag particles on the basal plane, which are then re-photo-deposited on the edge during the photocatalytic reaction. In this case, the re-photo-deposited Ag particles on the edge are smaller than 10 nm and more uniform than the direct photo-deposited Ag particles [39]. The Ag-loaded BaLa₄Ti₄O₁₅ prepared by impregnation followed by H₂ reduction also shows the re-photo-deposition, and the sizes of the re-photo-deposited Ag particles are within 10–20 nm. The CO formation rate in BaLa₄Ti₄O₁₅ under working conditions shows a change in an opposite sequence of the order of Ag particles size on its edge plane. Thus, smaller Ag particles on the photocatalyst result in higher activity of CO formation. The CO₂ reduction mainly occurred on the Ag nanoparticle loaded edge of the BaLa₄Ti₄O₁₅ plate, whereas H₂O oxidation

occurred on the basal plane. The unique location of Ag nanoparticles on the photocatalyst can separate the plane of oxidation and reduction reaction, thus increasing the activity of photocatalytic CO₂ reduction [107]. This Ag-doped system shows high selectivity for CO₂ reduction as indicated by the ratio of CO/H₂ (~2.0), but solar energy conversion rate is very low due to the large bandgap of this catalyst [8].

Table 5. Effect of loading method of Ag co-catalyst on the photocatalytic activity for CO₂ reduction over ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba) ^a [39].

Photocatalyst	Loading Amount/wt %	Loading Method	Activity/ $\mu\text{mol}\cdot\text{h}^{-1}$			
			H ₂	O ₂	CO	HCOOH
BaLa ₄ Ti ₄ O ₁₅	1.0	Impregnation ^b	8.2	5.7	5.2	0.2
BaLa ₄ Ti ₄ O ₁₅	1.0	Impregnation ^b + H ₂ red ^c	5.6	8.7	8.9	0.3
BaLa ₄ Ti ₄ O ₁₅	0.5	Liquid-phase reduction	4.5	6.8	11	0.03
BaLa ₄ Ti ₄ O ₁₅	1.0	Liquid-phase reduction	5.6	12	19	0.4
BaLa ₄ Ti ₄ O ₁₅	2.0	Liquid-phase reduction	10	16	22	0.7
BaLa ₄ Ti ₄ O ₁₅	3.0	Liquid-phase reduction	9.7	14	19	0.1
BaLa ₄ Ti ₄ O ₁₅	5.0	Liquid-phase reduction	4.8	6.6	12	0.02
BaLa ₄ Ti ₄ O ₁₅	1.0	Liquid-phase reduction	20 ^d	11 ^d	0 ^d	0 ^d
SrLa ₄ Ti ₄ O ₁₅	1.0	Liquid-phase reduction	4.8	5.8	7.1	0.8
CaLa ₄ Ti ₄ O ₁₅	1.0	Liquid-phase reduction	3.2	6.6	9.3	0.4

^a Catalyst 0.3 g, water 360 mL, CO₂ flow system (15 mL·min⁻¹), a 400 W high-pressure mercury lamp, an inner irradiation quartz cell. ^b 723 K for 1 h, ^c 473 K for 2 h, ^d Ar flow.

3.3. Ferroelectric LiNbO₃

The use of substances with a dipole, which separates the photogenerated electrons and holes, is an important part of surface photochemistry that has not been largely addressed. These substances are ferroelectric materials. The selective oxidation and reduction reactions, which take place on the surface of BaTiO₃, was demonstrated by an early work of Giocondi and Rohrer [112]. Subsequent work on the ferroelectric methods PbZr_{0.3}Ti_{0.7}O₃ [113,114] and LiNbO₃ [115] indicated that the dipole in the ferroelectric material determines the space charge layer structure because of the spontaneous polarization associated with lattice distortions. Ferroelectric LiNbO₃ is a promising photocatalyst for CO₂ reduction due to its comparatively strong remnant polarization of 70 μC/cm² [116] than other materials, such as KNbO₃ (30 μC/cm²) [117] and lead zirconate titanate [Pb(Zr_xTi_{1-x})O₃ (PZT)] (25 μC/cm²) [118]. In spite of the wide bandgap of LiNbO₃, which is 3.78 eV, its high remnant polarization was exploited to achieve products from CO₂ conversion either under high-pressure mercury lamp illumination or natural sunlight [119]. In the case of solid–liquid reactions, LiNbO₃ shows low efficiency in CO₂ reduction [120] but in a solid–gas reaction scheme, this ferroelectric material produces seven times the product formed by TiO₂ under UV light; under visible light, 36 times more product are produced compared with that by TiO₂. This high rate of product formation by LiNbO₃ in CO₂ reduction with H₂O can be explained by its strong remnant polarization, which is absent in TiO₂.

Remnant polarization creates an electric field in ferroelectric materials, like LiNbO₃, which is similar to usual p–n junction electric field. This electric field separates the photo-excited electrons and holes, leading to an enhanced lifetime of carriers. Thus, photo-excited carriers participate more in redox reactions because there is less chance of charge recombination [121]. In LiNbO₃, the decay time of polaron photo-luminescence is very high (9 μs) [122], thus confirming the controlled charge recombination and longer lifetime of carriers. Remnant polarization also causes a charge experienced at the interface of LiNbO₃, which interacts with the species in contact with the surface, thereby creating a strongly bound layer [123] and altering the bonding nature in physisorbed materials. Matt et al. suggested that in previous liquid–solid reaction schemes, particularly this tightly bound layer hinders high level of product formation. Another reason of high product formation rate by LiNbO₃ could be the

more energetically favorable reaction pathway availability than those from lower-energy photo-excited electrons of semiconductors [121]. For these characteristics, LiNbO₃ is considered as a promising photocatalyst in concrete construction to improve air quality [124]. An experimental demonstration of this effect was carried out by Nath et al., in which the addition of LiNbO₃ to concrete materials reduces CO₂ in the presence of water and forms O₂ [125]. This relatively new compound has already been used in electronic instruments in place of TiO₂ to achieve artificial photosynthesis [126]. These studies clearly showed that ferroelectric LiNbO₃ is effective even under weak solar energy in the ambient atmosphere for CO₂ reduction with H₂O. Further studies are required for the large-scale use of this water-insoluble, chemically inert photocatalyst.

4. Plasmonic Photocatalyst

For highly efficient photocatalysis process, plasmonic photocatalysts have become a topic of increasing interest, in recent years [101,103,127–131]. Nanoparticles of noble metals like Au, Ag, Pt exhibit strong absorption in the UV-visible region due to their surface plasmon resonance (SPR) [132]. SPR simply means the collective oscillations of conduction band electrons in a metal particle and it is driven by the electromagnetic field of incident light [133,134]. It is also known as localized surface plasmon resonance (LSPR).

Dispersal of noble metal nanoparticles of size 10 to 100 nm into semiconductor photocatalyst shows significant enhancement in photocatalytic activity under UV and visible range irradiation. In a conducting material, plasmons are the collective oscillation of the free charge (Figure 4). The oscillations confined to the surfaces of conducting materials are called surface plasmons, which strongly interact with light. When the real part of the dielectric function goes to zero at the plasmon frequency, a resonance in the absorption occurs.

The strong interaction with the resonant photons through an excitation of SPR is the characteristic of plasmonic metal nanoparticles. As such, SPR can be defined as the collective oscillation of valence electrons induced by the resonant photon. Au, Ag and Cu nanoparticles show resonant behavior when irradiated by UV and visible photons. As a large fraction of the solar energy consist of UV-vis photons, these noble materials become more promising [103]. This resonance frequency can be turned by manipulating the size, shape, material, and proximity of the nanoparticles [135–137].

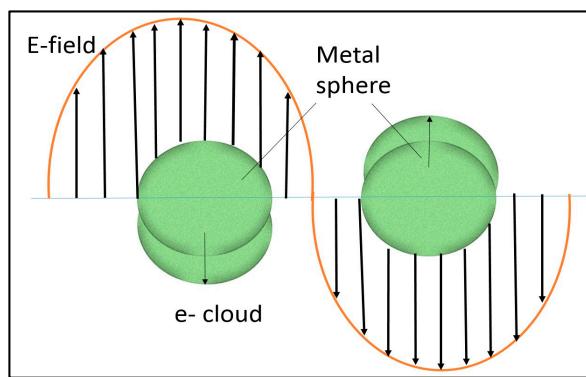


Figure 4. The schematic diagram is representing surface plasmon resonance in a spherical metal particle induced by the electric field component of incident light (adapted from [138]).

For example, the plasmon resonance of silver lies in the UV range but can be shifted to the visible range by minimizing the size of its nanoparticles; in the case of the gold, a smaller size of the nanoparticle can shift the plasmon resonance from the visible range to the infrared range [31]. Plasmonic metal nanoparticles exhibit the exceptional capability of concentrating electromagnetic fields, scattering electromagnetic radiation, and converting the energy of photons into heat, which is useful for different applications [103].

4.1. Fundamental of Plasmonic Photocatalyst

The photocatalytic reaction itself is a very complex process; the addition of the plasmonic resonance of noble metal nanoparticles makes it more complicated. The understanding of the physical mechanism of plasmonic photocatalysis is progressing steadily but has not reached unanimity. It is generally accepted that the vital role is played by the energy transferred from the metal nanoparticles to the semiconductors. However, the difference lies in the detailed approach of energy transfer in exciting more number of electrons and holes [30].

The presence of noble metal nanoparticles benefits photocatalysis in different ways. The two very distinct characteristics of plasmonic photocatalysts are SPR or LSPR and a Schottky junction. Even though Schottky junction is not a plasmonic or resonance effect but it is considered as an intrinsic feature while discussing plasmonic photocatalysts. When noble metal nanoparticles come in contact with the semiconductor photocatalysts, it results in the Schottky junction, which builds an internal electric field in a region (space-charge region) inside the photocatalyst, closer to the metal–semiconductor interface. Once the electrons and holes are generated near the Schottky junction, this internal electric field would force them to move in a different direction [128]. Moreover, a fast lane for charge transfer is provided by the metal part [139]; its surface also acts as a charge trap center and can host more active sites for the light-induced reaction. Both the Schottky junction and the fast-lane charge transfer help to minimize the electron–hole recombination process [30].

The surface plasmon resonance (SPR) of the noble metal nanoparticles in response to the incident light is the major attribute of the plasmonic photocatalyst. It brings enhancement in the photocatalytic activity. Depending on the size, the shape, and the surrounding environment, the resonance frequency of noble metal nanoparticles (like Au/Ag) can be tuned to fall in the visible or near UV range [138]. When it falls in the visible light range, the large bandgap photocatalyst such as TiO₂ becomes visible-light responsive. Again, for low-bandgap photocatalysts like Fe₂O₃ [140], SPR can significantly enhance the visible light absorption and UV absorption for large bandgap photocatalysts [127]. This feature is very useful for weakly absorbing materials. Due to the strong absorption, the larger portion of the incident light is absorbed by the photocatalyst surface in a thin layer (~10 nm) providing a shorter distance between the photo-generated electrons and/or holes and the surface, thus making it comparable to shorter carrier diffusion length [73,103,140]. This effect helps materials with poor electron transport. It also contributes in exciting more number of electrons and holes [70–72], increasing the rate of redox reaction and the mass transfer by heating up the surrounding environment [141–143] and enhancing adsorption by polarizing non-polar materials [142].

In general, the photocatalysis process consists of five individual steps [144,145], starts with reactants transfer to the photo-reactant surface, adsorption of the reactants, followed by redox reaction in this adsorbed phase, then product desorption from the surface, and finally, transfer of product away from the surface. Plasmonic photocatalysts contribute to all these steps. The enhancement in the creation and separation of excited electrons and holes increases the redox reaction rate, the SPR, the Schottky junction, the metal's fast transfer, charge carrier trapping, and large contact surface has a significant influence here [127,139,140,146–149]. The heating effect also increases the redox reaction rate [141–143,150,151], and benefits the reactant transfer, product desorption and enhancing fluid mixing by product boosting. The polarization enhances the adsorption of reactants [142]. These are the major impacts of plasmonic photocatalysts that had been identified and verified so far [30], which explain how plasmonic photocatalysts mostly show great enhancement in the photocatalytic activity.

4.2. Reduction of CO₂ with H₂O by Plasmonic Photocatalyst

Noble metal nanoparticles in plasmonic photocatalysts generally coupled with substrates having a larger surface area and active sites. Thus in a co-operative way both the noble metal nanoparticle and the substrate work to enhance the photocatalytic activity [32]. The size, shape, and distribution of noble metal nanoparticles do have an effect on the plasmonic oscillation [152–154]. In this section, some of

the recently studied plasmonic photocatalysts (Au/Ag), that demonstrate a significant enhancement in the photocatalytic CO₂ reduction with H₂O are being discussed.

4.2.1. Au Deposited TiO₂

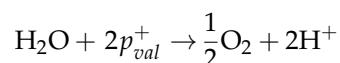
In a comprehensive study of photocatalytic CO₂ reduction with water, Hou et al. found that depositing Au nanoparticles on top of TiO₂ results in plasmonic enhancement [155]. In the visible range (532 nm) of light, the photon energy matches the plasmon resonance of the Au nanoparticles; at this wavelength, a 24-fold enhanced photocatalytic activity was reported.

The strong electric fields created by SPR of the Au nanoparticles locally excite the electron–hole pairs in the TiO₂ at a rate several times higher than that by usual incident light; this phenomenon is considered to be responsible for this plasmonic enhancement. The mechanisms of photocatalytic CO₂ reduction by Au nanoparticle/TiO₂ were investigated under two visible and two UV range wavelengths to separate the contribution of plasmon resonance from the effect of electronic transitions in Au on the overall process. Three basic types of sample were used in this study: (1) bare TiO₂; (2) Au nanoparticles deposited on top of TiO₂; and (3) bare Au nanoparticles. A quantitative study of the reaction products was conducted to determine the mechanism behind the higher photocatalytic activity. Hou et al. suggested an interband transition hypothesis for the contribution of Au nanoparticles in TiO₂ for the increase in photoactivity. This hypothesis was based on the comparative energies of the electrons and holes of the solid material with the redox potentials of the reaction product. Figure 5b shows that for all the three types of sample, CH₄ is the only detected product. The product formation in photocatalytic CO₂ reduction with H₂O under visible light (532 nm) irradiation on Au/TiO₂ is significantly high.

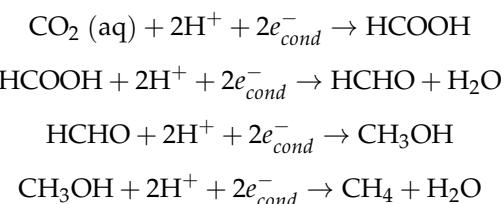
The explanation for this reaction is obtained by comparing the reduction potentials of the possible products from CO₂ reduction with the energies of VB and CB of TiO₂ [92,156], as shown in Figure 5c. The reduction potential of CO₂/CH₄ lies under the CB of TiO₂ [157], but for other possible products, i.e., HCOH and CH₃OH, it lies above the CB potential of TiO₂ [92,156]. This fact indicates the CH₄ formation is energetically favorable for photocatalytic reduction of CO₂ by TiO₂. The reaction scheme for this photocatalytic process is as follows, where e_{cond}^- symbolizes an electron in the CB and p_{val}^+ symbolizes a hole in the valence band (VB) [92]:



Oxidation reaction



Reduction reaction



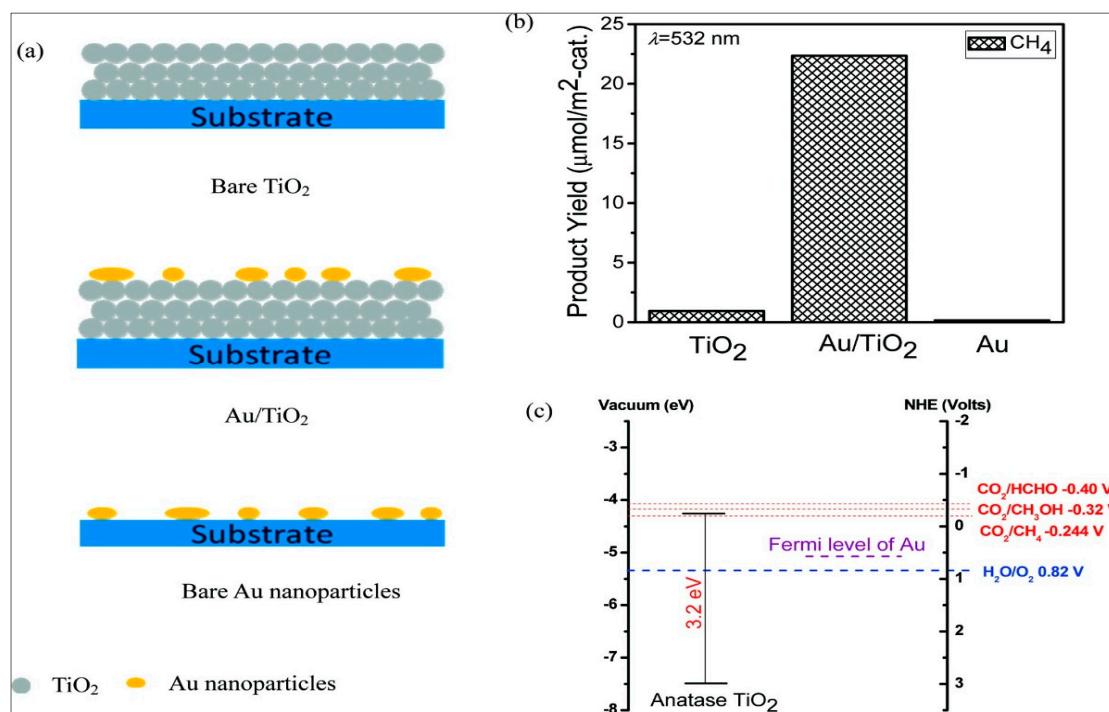


Figure 5. (a) Schematic diagrams of bare Au, Au/TiO_2 and the bare TiO_2 photocatalysts, (b) amount of CH_4 formed on these photocatalyst surfaces after 15 h and (c) the relevant redox potentials of CO_2 and H_2O under visible light and energy band positions of anatase TiO_2 and Au (Adapted from [155]).

To initiate the reduction process for CH_4 formation, electrons from the CB of TiO_2 are transferred to CO_2 [158]. In the case of bare TiO_2 -photocatalyzed CO_2 reduction, the product yield is very low because the energy of 532 nm wavelength light (2.41 eV) is considerably lower than the band-gap of TiO_2 (3.2 eV). For the third type of sample (i.e., bare Au), the amount of product formation is almost negligible, thus suggesting the importance of photocatalytic TiO_2 surface in this reduction process. These results correlate with their previous publications [159,160]. Under visible-light irradiation, the sub-bandgap transitions in TiO_2 generate electron–hole pairs not that in Au. When the photon energy is sufficiently high to excite d-band electrons of Au to its CB, which lies above the CB of TiO_2 in the UV range (254 nm), a different mechanism takes place, resulting in the formation of additional products, including C_2H_6 , CH_3OH , and HCHO . As the energy of d-band excited electrons lies above the redox potentials of $\text{CO}_2/\text{C}_2\text{H}_6$, $\text{CO}_2/\text{CH}_3\text{OH}$, and CO_2/HCHO , these additional products are formed [155].

4.2.2. Ag Supported on AgIO_3

In the photocatalytic conversion of CO_2 using H_2O , the plasmonic photocatalyst Ag supported on AgIO_3 (Ag/AgIO_3 particles) displays high activity and stability. In a longitudinal study, He et al. reported the synthesis, characteristics, and application of this plasmonic photocatalyst in CO_2 reduction with H_2O , where CH_4 and CO are produced under visible-light irradiation (>400 nm wavelength) [57]. It was found that Ag plasma induced photo-excited electrons in AgIO_3 facilitate the reduction reaction. The comparative photocatalytic activities towards the CO_2 reduction of a different photocatalyst in the presence of water under visible light were evaluated by the amount of carbon containing products. Figure 6 shows the increasing amount of CH_4 and CO formation with time under visible light range.

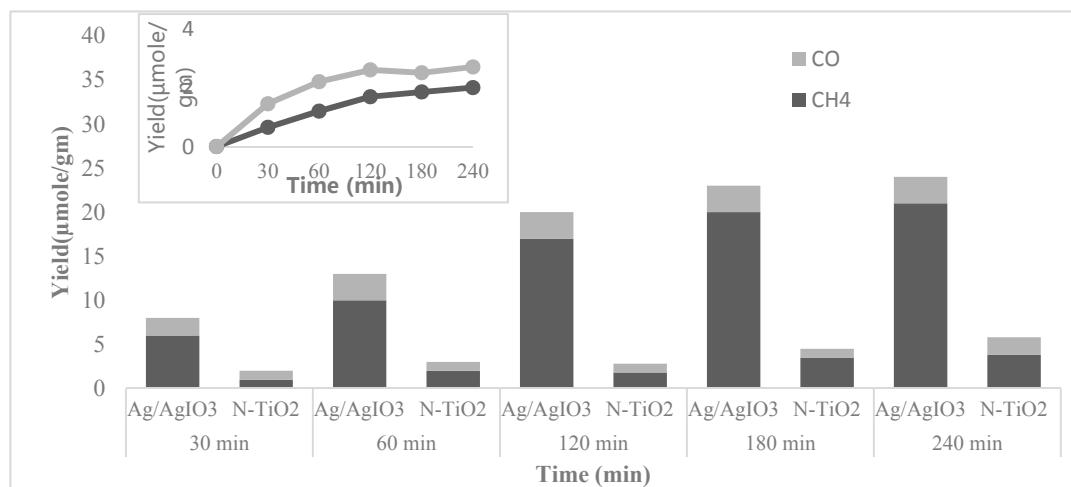


Figure 6. Schematic diagram showing time dependence yields of CH₄ and CO yields under visible light irradiation over Ag/AgIO₃ particles and over N doped-TiO₂. The inset shows the time dependence of CH₄ and CO yields over AgIO₃ under UV-vis light (Reproduced from [57]).

In comparison to N-TiO₂, Ag/AgIO₃ particles display higher photocatalytic reaction rate for CH₄ and CO production. The result of this 240 min reaction indicates the significance of Ag nanoparticles on AgIO₃ in photocatalytic CO₂ reduction. Under visible light irradiation, the estimated quantum yield is 0.19% for CO₂ reduction on Ag/AgIO₃ catalysts. The turnover number (TON) are 1367 and 167, respectively, for CH₄ and CO formation at 240 min. This information leads to the assumption that each Ag atom exposed to visible light is a potential active site. In photocatalytic CO₂ reduction, photoexcitation of Ag electrons to higher energy state is the initial step as AgIO₃ itself cannot be excited by visible light. The free electrons in Ag are either promoted by the intraband transitions from the half-filled s band below the Fermi level via surface plasmon excitation to unfilled s band states above the Fermi level or by the interband transition from the d-band to unfilled s-band states [57]. The first interband excitation occurs in Ag nearly at 3.8 eV energy band [161]. However, the energy of light in the visible range (400 nm wavelength) is 3.1 eV, which is less than the required amount of energy for interband transition in Ag; thus, electrons cannot be excited to the ECB (the CB edge potential) from the d band. Thus, the interband transition is not possible. This signifies that the SPR of Ag nanoparticles is the cause of photocatalytic reduction of CO₂ in this process. The plasmonic electrons and holes cannot drive the oxidation and reduction half-reactions because the plasmonic charges exist in the Fermi energy of the metal [31]. Therefore, in this process, both oxidation and reduction half-reactions occur on the AgIO₃ surface.

The contribution of SPR in CO₂ reduction by using Ag/AgIO₃ under visible light irradiation was established by studying the wavelength dependence quantum yield. When the light-excited plasmon produced energy or charge was transferred to AgIO₃ to drive the photocatalysis, only at that time photocatalytic activity at the SPR wavelength was reported [162]. In AgIO₃ the electron–hole pairs are generated by dipole-dipole interaction during resonant energy transfer from Ag to AgIO₃ and direct electron transfer between Ag (donor) and AgIO₃ (acceptor) [162,163]. These photo-excited electrons lead to the formation of CO by photocatalytic reduction of CO₂, where the photo-excited holes lead to the formation of O₂ by reacting with H₂O. He et al. also ran 10 repeated reaction cycle under visible light irradiation with Ag/AgIO₃ plasmonic photocatalyst to examine its stability, where the catalyst showed almost constant photocatalytic activity each time [45]. Their study demonstrated that “Ag/AgIO₃ particles manifest high and stable photocatalytic activity in the conversion of CO₂ to CH₄ and CO using water vapor.”

4.2.3. Ag Supported on Ag_2SO_3

The plasmonic-semiconductor structure of Ag supported on Ag_2SO_3 was also mentioned as an effective photocatalyst for photocatalytic reduction of CO_2 with water vapor under visible light irradiation by the seminal work of Wang et al. [62]. The major carbon-containing product from this CO_2 reduction is CH_4 , with a small amount of CO. The quantum yield is 0.126%, with an energy returned on energy invested of 0.156%. The study suggested that the energy conversion from incident photons to SPR oscillations of Ag nanoparticles initiates the photocatalytic activity of the catalysts. Ag_2SO_3 obtained this plasmonic energy by either one or both direct electron transfer and resonant energy transfer. The energy transfer results in separation of photogenerated electron–hole pairs, thereby increasing electron density and transferring the SPR electrons from Ag to the CB of Ag_2SO_3 by a direct electron transfer process as it lifts the Fermi level of Ag. Moreover, by dipole–dipole interaction, resonant energy transfer from Ag could also generate electron–hole pairs in the Ag_2SO_3 . Thus, for the photocatalytic CO_2 reduction, the light-induced sites are provided by Ag nanoparticles and the reaction sites are provided by Ag_2SO_3 .

Figure 7 reveals the yield of products (CH_4 and CO) in the presence of Ag_2SO_3 , 1-Ag/ Ag_2SO_3 , 5-Ag/ Ag_2SO_3 , and 10-Ag/ Ag_2SO_3 as a function of time. The CO yield on 1-Ag/ Ag_2SO_3 , 5-Ag/ Ag_2SO_3 , and 10-Ag/ Ag_2SO_3 reached 3.06, 4.94, and 2.44 $\mu\text{mol/g}$, respectively, and the amount of CH_4 formation reached 10.55, 12.05, and 7.42 $\mu\text{mol/g}$, respectively. Therefore, the optimal catalyst is 5-Ag/ Ag_2SO_3 . This result can be explained in terms of surface coverage of Ag_2SO_3 by Ag nanoparticles, where more Ag nanoparticles provide more light-induced sites, whereas fewer reaction sites result in a decrease in the rate of CO_2 reduction. For practical applications, evaluating the stability of photocatalyst is an important concern. In this case, Ag/ Ag_2SO_3 is considered as a stable photocatalyst for CO_2 reduction because it performed consistently under visible light irradiation even after 10 repeated catalytic cycles. The XRD patterns and surface atomic compositions of new and used catalyst are also quite indistinguishable [62], thus confirming its stability

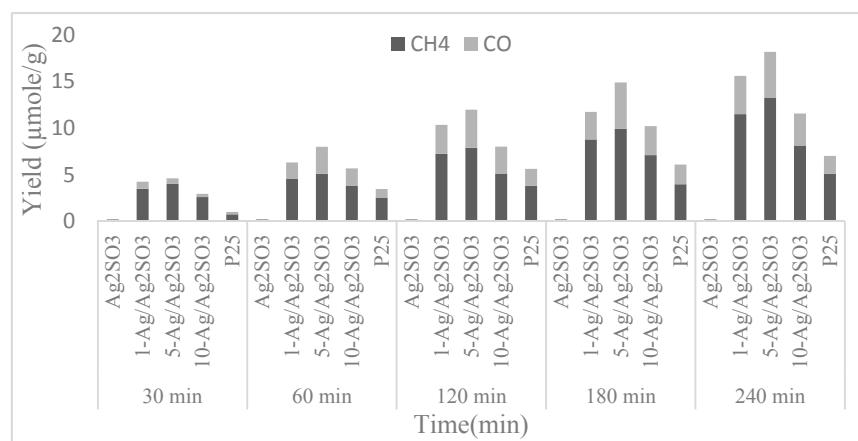


Figure 7. Formation of the product over TiO_2 (P25), Ag_2SO_3 , and Ag/ Ag_2SO_3 photocatalysts under visible light irradiation as a function of time (Reproduced from [62]).

5. Conclusions

From this review, it can be concluded that the environmental challenges are no longer confined issues but become global problems involving climate changes. To solve these problems, we are still far from having a scientific as well as a cost-effective photocatalyst for photocatalytic CO_2 reduction with H_2O . As previously mentioned, both physical mechanism and product distribution in photocatalytic reactions are very complicated which confines its applicability. The present situation in this area of research is quite confusing, and comparing the efficiency of the different photocatalysts is also difficult due to the high variability of influencing factors and reaction conditions. Details such as

mass balance (moles of CO₂ converted into the specific product), product distribution, and the amount of reducing agent, time requirement, solution pH, temperature, CO₂ pressure, light power, and activity decay over time were not discussed in many of the studies. Comprehensive studies on this process for further movement towards its practical implementation are necessary. An all-in-one standard format that will be unified and widely accepted should be established.

The low photocatalytic efficiency, low response to sunlight, inefficient electron transport between reduction and oxidation catalysts, and high recombination rate of photogenerated species are the major difficulties responsible for the current considerably low rate of average productivity in photocatalytic reduction of CO₂ with H₂O. Another drawback is the short lifetimes of one-electron-reduced species and the photo-excited state in the presence of O₂ generated by H₂O oxidation. Despite the fact that UV light can supply more energy than visible light, the availability of visible light from the abundant natural sunlight makes visible-light-harvesting photocatalysts the most desired ones for this process. In its infancy, plasmonic photocatalysts already showed promising performance to overcome the first two shortcomings of the above list. The boundaries of these highly efficient noble-metal photocatalysts are expanding rapidly that it is realistic to expect that plasmonic photocatalysts will contribute significantly in future environmental remedies. Further research should focus on the fabrication of optimal structured visible-light-responsive photocatalysts with a wide bandgap, high rate of photogenerated electron–hole transport, and low rate of recombination, to increase the possibility for practical application of photocatalytic CO₂ reduction with H₂O.

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