Recent Progress in the Photocatalytic Reduction of Carbon Dioxide

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ABSTRACT: Elimination or reduction of CO₂ in the atmosphere is a serious problem faced by humankind, and it has become imperative for chemists to find ways of transforming undesirable CO₂ to useful chemicals. One of the best means is the use of solar energy for the photochemical reduction of CO₂. In spite of considerable efforts, discovery of stable photocatalysts which work in the absence of scavengers has remained a challenge although encouraging results have been obtained in the photocatalytic reduction of CO₂ in both gas and liquid phases. Semiconductor-based catalysts, multicomponent semiconductors, metal–organic frameworks (MOFs), and dyes as well as composites involving novel composite materials containing C₃N₄ and MoS₂ have been employed for the photoreduction process. Semiconductor heterostructures, especially those containing bimetallic alloys as well as chemical modification of oxides and other materials with aliovalent anion substitution (N₃⁻ and F⁻ in place of O²⁻), remain worthwhile efforts. In this article, we provide a brief perspective of the present status of photocatalytic reduction of CO₂ in both liquid and gas phases.

1. INTRODUCTION

Nearly 80% of the energy supply of the world is based on fossil fuels, and humankind is expected to face a serious crisis because of the fast depletion of fossil fuels and increasing levels of CO₂ in the atmosphere. The present global energy consumption rate of 16.3 TW (2012) will be reaching nearly 40 TW by 2050 and nearly 60 TW by 2100.¹ The Intergovernmental Panel on Climate Change (IPCC) predicts that by the year 2100 the CO₂ levels may rise up to 590 ppm, and the average global temperature may rise by 1.9 °C.² As per the fifth assessment report (2014) of the IPCC, the levels of green house gases (GHGs) are increasing drastically. The steady increase of +1.3% per year (1970–2000) has taken a steep rise of +2.2% per year (2000 onward).³ Increasing atmospheric levels of CO₂ can adversely affect the world, causing an increase in average sea levels and average global temperature.³ Either developing alternative fuels or converting CO₂ back to the fuel forms would balance the CO₂ levels in the atmosphere. Sun’s energy reaching the earth’s surface (1.3 × 10²ª TW) is 10 000 times higher than the present rate of consumption or demand. Researchers are, therefore, attempting to develop photocatalysts for splitting water or reducing CO₂ to fuels (H₂, CO, HCOOH, HCHO, CH₄, OH, CH₃) using solar energy.

Natural photosynthesis involves both the oxidation of water and the reduction of CO₂ wherein three processes, light harvesting, generation of carriers, and separation and catalytic reactions, occur. Artificial photosynthesis attempts are being conducted to accomplish these by a two- or one-step process, the former being akin to the Z-scheme in natural photosynthesis.⁴ The photocatalytic agents in artificial photosynthesis can be semiconductors or dyes. In this perspective, we discuss the present status of the approaches to reduce CO₂ to the production of alternative fuels based on the recent literature as well as some of our own findings.

2. BASICS

Photocatalytic CO₂ reduction with water is akin to natural photosynthesis, a process wherein plants convert CO₂ and H₂O to oxygen and carbohydrates in the presence of sunlight. In this process solar energy is being converted and stored in the form of chemical bonds (carbohydrates). It is a combination of water oxidation and carbon dioxide reduction (or CO₂ fixation) reactions and involves both light and dark reactions.

The process of photocatalytic CO₂ reduction on a semiconductor photocatalyst is illustrated in Figure 1. Similar to photocatalytic water splitting,⁵ this process also involves three steps. They are

(i) Absorption of light (hν > E_g) by the semiconductor;
(ii) Separation of charge carriers (electron−hole);
(iii) Redox reactions at the surface

Upon illumination of light the photocatalyst absorbs light, and electrons in the VB get excited to the CB, leaving behind holes in the VB. Reduction of CO₂ is an uphill reaction, and in order to enable these uphill reactions, CB and VB of the photocatalyst should straddle the reduction potential of CO₂ and the oxidation potential of water (Figure 1). A negative CB edge relative to the reduction potential CO₂ facilitates the

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transfer of electrons from the CB to CO₂. A positive VB edge relative to the water oxidation potential facilitates the transfer of holes from the VB to water. Therefore, under the irradiation of light, transfer of electrons from the CB to CO₂ as well as from water to the VB are thermodynamically favorable, whereas direct reduction of CO₂ using water is an uphill reaction. Electrons in the CB reduce CO₂, whereas holes in the VB oxidize water to oxygen (Figure 1).

The formal reduction potentials of the reactions associated with the photoreduction of CO₂ and H₂O are given in eqs 1–8 (at pH 7). One-electron reduction reactions of CO₂ such as formation of CO₂⁻ are not feasible due to their large negative reduction potentials (\(E(\text{CO}_2/\text{CO}_2^-) = -1.85 \text{ V vs SHE}\)) relative to the conduction band (CB) edges of many of the semiconductors. Highly negative reduction potential arises from the change in hybridization of C from sp² to sp³. Reduction potentials for the formation of HCOOH, HCHO, CH₃OH, and CH₄ are small (−0.665, −0.485, −0.399, and −0.246 V) and positive relative to CB edges of several of the semiconductors. It is therefore preferable to undergo proton-coupled electron transfer (PCET) wherein electron transfer to CO₂ is associated with proton transfer.

\[
\text{CO}_2 + e^- \rightarrow \text{CO}_2^- = 1.850 \text{ V (vs SHE)} \tag{1}
\]

\[
\text{CO}_2(g) + \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{HCOO}^-_{(aq)} + \text{OH}^-_{(aq)} = 0.665 \text{ V (vs SHE)} \tag{2}
\]

\[
\text{CO}_2(g) + \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{CO}(g) + 2\text{OH}^-_{(aq)} = 0.521 \text{ V (vs SHE)} \tag{3}
\]

\[
\text{CO}_2(g) + 3\text{H}_2\text{O}(l) + 4e^- \rightarrow \text{HCHO}(g) + 4\text{OH}^-_{(aq)} = 0.485 \text{ V (vs SHE)} \tag{4}
\]

\[
\text{CO}_2(g) + 5\text{H}_2\text{O}(l) + 6e^- \rightarrow \text{CH}_3\text{OH} + 6\text{OH}^-_{(aq)} = 0.399 \text{ V (vs SHE)} \tag{5}
\]

\[
\text{CO}_2(g) + 6\text{H}_2\text{O} + 8e^- \rightarrow \text{CH}_4 + 8\text{OH}^-_{(aq)} = 0.246 \text{ V (vs SHE)} \tag{6}
\]

\[
2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-_{(aq)} = 0.414 \text{ V (vs SHE)} \tag{7}
\]

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+_{(aq)} + 4e^- + 0.816 \text{ V (vs SHE)} \tag{8}
\]

The ΔG values of the reactions are obtained from the equation, \(\Delta G = -nFE_{cell}\). The ΔG values of the above reactions are positive (nonspontaneous), being the least for the formation of HCOOH and maximum for the formation of CH₄ (HCOOH < CO < HCHO < CH₃OH < CH₄). However, they are also more positive compared to the ΔG of splitting of water.

The mechanism of reduction of CO₂ on metallic surfaces has been widely discussed. Here, we briefly discuss the mechanism of CO₂ reduction on the TiO₂ surface. There are several possible configurations for CO₂ adsorbed on the photocatalyst as shown in Figure 2. Spectroscopic studies have revealed the presence of bent CO₂ on the TiO₂ surface under illumination. Surface Ti⁴⁺ adsorbs CO₂ and forms bent CO₂⁻ by transferring an electron, and Ti⁴⁺ gets oxidized back to Ti⁵⁺. The H atom present on the surface assists in the further reduction of CO₂⁻. Gaseous CO₂ is a linear molecule, whereas the surface-bound carbon species have a bent structure. The adsorbed carbonate or CO₂⁻ species are active in the photoreduction of CO₂. LUMO of the surface chemisorbed CO₂ species (carbonate or CO₂⁻) is lower compared to that of gaseous CO₂, thereby making it easier to accept excited electrons form the semiconductors. CO₂ is an acidic molecule; therefore, basic metal oxides have greater tendency for CO₂ adsorption.

The reduction potentials for the PCET reactions are within the range of −0.7 to −0.2 V and are close to the reduction potential of water (−0.414 V at pH 7). The reduction products of CO₂ (HCHO, CH₃OH, and CH₄) require multielectron transfer, whereas the reduction of water is a two-electron process. Reduction of water therefore competes with the reduction of CO₂. Because of this, the extent of hydrogen generation is greater in liquid-phase reactions compared to vapor-phase reactions. Yields of photocatalytic processes are often much lower than the amount of photocatalysts. It is
possible to obtain the products from stoichiometric reactions involved with unstable photocatalysts. It is, therefore, necessary to present the activities in terms of TON and TOF (TON per unit time) in order to distinguish from stoichiometric reactions. Generally, for catalytic reactions TON is $\gg 1$.

3. METHODS OF REDUCING CO2
Reduction of CO2 can be carried out in the liquid phase or gas phase. In the liquid-phase reaction, reduction of CO2 is carried out with a saturated aqueous solution of CO2. Limited solubility of CO2 in water is the crucial problem to drive photocatalytic reduction of CO2 efficiently.9 The solubility of CO2 in water can be improved by using additives such as NaOH, NaHCO3, or Na2CO3. These additives enhance the CO2 solubility, though the reduction of bicarbonate and carbonate species is more difficult. Surface adsorption of H2O is more preferable over CO2 in the liquid phase, and thus the reduction of water is favorable. On the other hand, gas-phase reactions were carried out with humidified CO2. In order to explore the effect of the method of evaluation on activities, Xie et al.10 have employed TiO2 and Pt-TiO2 as photocatalysts and studied the reduction of CO2 in both the liquid phase and gas phase. CH4 production activity is nearly 3 times more, whereas hydrogen production is less in gas-phase compared to liquid-phase reactions. Nearly 3–4 times more selectivity in CO2 reduction over water reduction is observed in the gas phase.

Quantum dot photocatalysts have gained importance due to their high surface area and shorter charge transfer pathways.11 In addition, they possess enlarged band gaps and shifted band positions because of quantum confinement that provides more potential energy for photochemical reactions.12 In a recent study, CsPbBr3 quantum dots were employed for photocatalytic reduction of CO2. The QDs are more active than the bulk compound, giving CO 49.5 $\mu$mol g$^{-1}$ and CH4 22.9 $\mu$mol g$^{-1}$ after 12 h (100 W Xe lamp with an AM 1.5G filter).13

The efficiency of photocatalysts depends on the morphology, exposed facets, size and surface vacancies, etc. The activity in the liquid phase is also affected by the pH of the reaction medium, surface hydroxyl groups, solvent, and additives. The increase in pH increases the rate of the reaction

$$\text{CO}_2(\text{aq}) + \text{OH}^- \rightarrow \text{HCO}_3^-$$

This leads to different concentrations of species (CO2$,^2-$, HCO$^-_3$, and CO2) at different values of pH.14 The different chemical species get adsorbed to different extents on the catalyst surface and have different reduction potentials.15 Thus, addition of NaOH could improve the dissolution of CO2 thereby increasing the efficiency of photoreduction of CO2 on TiO2-supported Cu catalysts.16 In the gas phase, photocatalytic activity is affected by the surface properties of the photocatalysts, CO2–H2O ratio, and feed pressure, temperature, etc.

It is often customary to use sacrificial reagents to consume the holes. The addition of a sacrificial reagent to the reaction mixture enhances photocatalytic reduction, but in most of the cases the reagent would contribute to the yield of products. For example, methanol is used as a sacrificial hole acceptor. The reaction mechanism for the oxidation of methanol involves a step in which an electron is injected into the conduction band of the photocatalyst. This implies that part of the CO2 reduction products are formed through the action of holes and not that of the electrons.17 The presence of organic adsorbents (CH3CO2H, CH3OH, HCO2H, etc.) on the surface of the photocatalyst plays an important role in the photocatalytic reduction of CO2. The presence of CH3CO2H on the photocatalyst surface leads to the formation of CH4. This can occur by the conversion of CH3CO2H to CH4 via the photocatalytic reaction.18 Photocatalysis without any organic adsorbents shows a negligible amount of CH4 production.19

4. SEMICONDUCTOR-BASED PHOTO CATALYSTS
TiO2 has been employed extensively as a photocatalyst since the early report by Fujishima et al.20 for the photochemical reduction of CO2. A systematic study on photocatalytic as well as photoelectrochemical reduction of CO2 was carried out in aqueous suspensions of semiconductor powders such as TiO2, ZnO, CdS, SiC, etc.20 The yields of methanol are well correlated with the CB edge position of the semiconductors, indicating the necessary requirement of a negative CB edge relative to the CO2/CH4 and OH reduction potential. Anpo et al.21 have shown the necessity of the presence of H2O for the photoreduction of CO2 by employing titanium oxides anchored within the micro pores on zeolites.

4.1. Use of Cocatalyst. Deposition of metals such as Pt, Au, Pd, Ag, and Cu on the photocatalysts affects the photochemical reduction of CO2. The metals catalyze the reduction reactions upon receiving electrons from the photocatalyst. Ag shows superior activity for CO2 reduction due to weak binding with the CO, whereas Pt gets poisoned by CO. Pt is also highly selective to the reduction of water.6 Iizuka et al.22 have reported photocatalytic reduction of CO2 over Ag catalyst-loaded anisotropic Al$_3$Ti$_2$O$_{15}$ (A = Ca, Sr, and Ba) using water as a reducing reagent. Here, the Ag cocatalyst efficiently reduces CO2, the high yields of CO arising from the separate reaction sites for reduction and oxidation. Thus, coupling of semiconductors with bimetallic systems also shows promising results. Thus, Cu–Pt bimetallic photocatalysts loaded on TiO2 (Cu–Pt/TiO2) nanotubes reduce CO2 to CH2, CH4, C2H6, etc., with 4-fold improvement in the conversion in the presence of H2O under solar irradiation.23 Codoping of oxidation and reduction cocatalysts such as RuO2 (1 wt %) and Pt (1 wt %) on Zn$_3$GeO$_4$ causes significant improvement in CH4 production.24

4.2. Doping or Codoping. Since the UV component in the sunlight is limited (~4%), researchers have mainly explored visible-light (~43%) sensitive photocatalysts. The electronic band structure of the wide-band-gap semiconductors is altered by the incorporation of foreign elements into the lattice of the semiconductors. For example, N doping or Ce doping in TiO2 shows a red-shift in the absorption onset with visible absorption and superior activity compared to undoped TiO2.25 N doping in TiO2 as in CuO/TiO2–N$_x$ enhances the conversion of CO2 to CH4 under solar irradiation.26 Nakanishi et al.27 have employed metal-doped NaTaO3 (NaTaO3:A, where A = Ca, Mg, Sr, Ba, or La) with Ag cocatalysts under UV–visible irradiation (Figure 3) for the reduction of CO2 to CO. Ag deposited NaTaO3:Ba exhibits superior activity among all cation-doped NaTaO3, in the absence of any additives. Addition of NaHCO3 enhances CO production activity with NaTaO3:Ba being superior in the reduction of CO2 with nearly 90% selectivity toward the reduction of CO2. However, a considerable fraction of electrons is utilized in the reduction of water. Herein, water acts as a reducing agent and gets oxidized to oxygen.

4.3. Solid Solutions. Electronic band structures of wide-band-gap semiconductors can be tailored by forming solid solutions. Liu et al.28 have employed (Zn1–xGe)$_x$(N$_2$O$_5$) nanostructures for the reduction of CO2 to CH4 under
visible-light irradiation. Figure 4 shows the electronic absorption spectra of the nitridation product of Zn$_2$GeO$_4$ (band gap 4.53 eV) with varying duration of nitridation at 700 °C. The absorption onset is gradually red-shifted with the increase in nitridation period, and samples turn yellow in color. Superior CO$_2$ reduction activity under visible-light irradiation is obtained with the product having a band gap of ∼2.4 eV, obtained after a nitridation period of 6 h (Zn 26.4%, Ge 19.6%, N 40.8%, and O 13.2%) with CH$_4$ yield of 1.63 μmol h$^{-1}$ with O$_2$:CH$_4$ ratio of 2:1 since the CH$_4$ is an eight-electron reduction production and O$_2$ is a four-electron oxidation production.

5. MULTICOMPONENT PHOTOCATALYSTS

5.1. TiO$_2$–RuH. Huang et al.$^{28}$ have developed a mononuclear C$_5$H$_5$–RuH complex oxo-bridged with TiO$_2$ for photoreduction of CO$_2$ to CH$_4$ under visible-light irradiation with a quantum efficiency of 0.56%. In this system, C$_5$H$_5$–RuH serves as the photon harvester and water-oxidation site, whereas TiO$_2$ acts as the electron collector and site of CO$_2$ reduction (Figure 5). The amount of CH$_4$ increases linearly under visible-light irradiation with time, whereas under dark conditions, no CH$_4$ is detected. The photocatalytic activity is maximum at Ru loading of 0.5 wt % on TiO$_2$. The superior efficiency of the catalyst for CO$_2$ reduction is attributed to the long-lived D$^+$–C$^-$–A$^-$ charge-separated state.

5.2. Semiconductor MOFs. Metal–organic frameworks have gained importance as photocatalysts in recent years since many of them possess high surface areas and good gas-adsorption properties. MOFs with a high CO$_2$ uptake can be considered as potential candidates for the CO$_2$ reduction. Here, we discuss a study based on a combination of TiO$_2$ with MOFs. Li et al.$^{29}$ have developed Cu$_3$(BTC)$_2$@TiO$_2$ (BTC-benzene-1,3,5-tricarboxylate) core–shell photocatalysts for the reduction of CO$_2$. Figure 6 shows a schematic diagram as well as TEM and SEM images of the corresponding nanostructures. There is a shell of TiO$_2$ over the Cu$_3$(BTC)$_2$ microcrystals, and the BET surface areas of Cu$_3$(BTC)$_2$ and Cu$_3$(BTC)$_2$@TiO$_2$ are 1183 m$^2$ g$^{-1}$ and 756 m$^2$ g$^{-1}$, respectively. The decrease in the surface area of the core–shell structure is attributed to the presence of a TiO$_2$ shell which does not have a large surface area. CO$_2$ adsorption based on the weight of the Cu$_3$(BTC)$_2$ component (80.75 cm$^3$ g$^{-1}$) of the core–shell structure is comparable to the bare Cu$_3$(BTC)$_2$ (49.17 cm$^3$ g$^{-1}$). This observation implies that the CO$_2$ molecules can easily go through the macroporous TiO$_2$ shells and get adsorbed at the microporous Cu$_3$(BTC)$_2$ cores. The photocatalytic activities of the TiO$_2$ and

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Figure 3. Photocatalytic CO$_2$ reduction on (a) Ag-NaTaO$_3$:Ca, (b) Ag-NaTaO$_3$:Sr, and (c) Ag-NaTaO$_3$:Ba in the liquid phase under UV irradiation. Figure legends: hydrogen (open circle), oxygen (solid circle), and CO (triangle). Reproduced with permission from ref 26.

Figure 4. (a) Electronic absorption spectra of nitridation products of Zn$_2$GeO$_4$ and (b) corresponding photocatalytic methane product activities. (c) Curve depicting the recyclability and stability of the photocatalyst. Reproduced with permission from ref 27.
Cu₃(BTC)₂@TiO₂ core–shell structure are given in Figure 6. The CH₄ production rate of the MOF is higher than that for TiO₂, and the MOF does not generate H₂. Note that the Cu₃(BTC)₂ itself is inactive.

5.3. Composites of Graphitic C₃N₄. Graphitic C₃N₄ has been used as a photocatalyst due to its high stability and visible response (E_g = 2.7 eV). Due to the fast recombination of the excited electron–hole pair, C₃N₄ is employed in combination with other materials. Loading of noble metals on the surface of g-C₃N₄ facilitates the interfacial transfer of electrons from g-C₃N₄ to the metal particles. For example, loading of Pt on g-C₃N₄ increases the rate of reduction of CO₂. The selectivity depends on the amount of Pt. An increase in Pt content from 0 to 1 wt % increases the yields of CH₄ and CH₃OH, and a Pt content of 0–0.75 wt % favors formation of HCOOH.

g-C₃N₄ is also used to form heterojunctions to suppress the recombination of electrons and holes. The introduction of g-C₃N₄ in NaNbO₃ nanowires increases the photocatalytic performance considerably (8-fold higher activity than naked C₃N₄). Similarly, deposition of Ag₃PO₄ on g-C₃N₄ enhances the photocatalytic performance. Ong et al. have demonstrated a robust method to synthesize proton-functionalized/protonated g-C₃N₄ (pCN). The positively charged g-C₃N₄ can form a hybrid nanostructure with the negatively charged GO sheets, forming rGO/pCN which is more active than the g-C₃N₄ itself. Addition of rGO has a substantial effect on the photocatalytic performance of the g-C₃N₄ which increases with the increase in rGO content. The highest CH₄ production occurs for the 15 wt % rGO/pCN (13.93 µmol g⁻¹, 5.4 times higher than C₃N₄). The higher activity by the addition of rGO is due to its lower Fermi level relative to the conduction band of C₃N₄. The formation of this heterojunction suppresses the charge recombination.

5.4. Semiconductor Homojunctions. The dependence of the photocatalytic activity of TiO₂ on the facet and shape of the catalyst particles is known. Yu et al. have carried out photocatalytic CO₂ reduction on TiO₂ with coexposed facets of (001) and (101). DFT electronic structure calculations show that the CB and the VB of the (101) facets of TiO₂ are positioned slightly below the CB and the VB of the (001) facets of TiO₂, respectively. This is similar to type II band alignment in semiconductor-based heterostructures. Apparently, exposure of the (001) facets increases the amount of CH₄. The facets help in the separation of charges with the electrons migrating to the (101) facet and the holes migrating to the (001) facet. A study based on TiO₂ with systematically varied ratios of (001) and (101) facets shows that the photocatalytic production of CH₄ increases with the increase in the fraction of (001) facets.
reaching a maximum of 1.35 \( \mu \text{mol h}^{-1} \text{ g}^{-1} \) at 58\% of (001) facets (Figure 7). Further increase in the (001) facet fraction decreases the photocatalytic activity. Similarly, facet-derived heterostructures formed by ZnSn(OH)\(_6\) also give rise to superior photocatalytic activity and longer charge carrier lifetimes.\(^{36}\)

Cosubstitution of aliovalent anions such as N\(^3^-\) and F\(^-\) for O\(^2^-\) in an oxide has a huge effect in altering the electronic band structure as well as optical and catalytic properties.\(^{37}\) N and F cosubstituted TiO\(_2\) (anatase) has a band gap of 2.6 eV and is yellow in color (Figure 8). N,F-TiO\(_2\) reduces CO\(_2\) to CO using water as the reducing agent under the irradiation of sunlight.\(^{37}\) Replacing Pt with Fe only resulted in the formation of H\(_2\) (>55 ppm g\(^{-1}\) h\(^{-1}\)) which indicates that Fe catalyzes photoreduction of water rather than of CO\(_2\).\(^{38}\)

5.5. Semiconductor Heterostructures. Type II band alignment in heterostructures causes effective charge separation.\(^{39,40}\) Kim et al.\(^{44}\) have employed Cu\(_2\)ZnSnS\(_4\)/TiO\(_2\) heterostructures with type II band alignment for the reduction of CO\(_2\) under solar irradiation (Figure 9). CH\(_4\) yield of 119 ppm h\(^{-1}\) g\(^{-1}\) is achieved with the heterostructure, which is nearly 12 times higher compared to TiO\(_2\) alone. The superior activity in heterostructures is attributed to the improved light absorption and surface area in addition to effective charge separation. Wang et al.\(^{45}\) have employed CdSe/Pt/TiO\(_2\) heterostructures for the visible-light-induced reduction of CO\(_2\). These heterostructures exhibited reduction of CO\(_2\) under visible-light irradiation, in the presence of H\(_2\)O, leading to the formation of CH\(_4\) (48 ppm g\(^{-1}\) h\(^{-1}\)) and methanol (3.3 ppm g\(^{-1}\) h\(^{-1}\)) and H\(_2\) (trace) and CO (trace). Replacing Pt with Fe only resulted in the formation of H\(_2\) (>55 ppm g\(^{-1}\) h\(^{-1}\)) which indicates that Fe catalyzes photoreduction of water rather than of CO\(_2\). Wang et al.\(^{46}\) have used PbS/Cu/TiO\(_2\) and CdSe/Pt/TiO\(_2\) heterostructures for the photoreduction of CO\(_2\). Both of them suffer from photodegradation due to the oxidation of CdSe and PbS quantum dots. CsPbBr\(_3\) QD/GO shows higher activity than CsPbBr\(_3\) QDs with CO and CH\(_4\) rates of 58.7 and 29.6 \( \mu \text{mol/g in 12 h} \).\(^{13}\) Roy in this laboratory has been able to reduce CO\(_2\) to CO by solar radiation using Cd\(_4\)P\(_2\)X\(_3\) (X = Cl, Br, or I) in the absence of any sacrificial agent.

ZnO/Pt/CdS heterostructures with type II band alignment and metal nanoparticles present on the oxide surface have shown excellent photocatalytic activity for hydrogen evolution.\(^{47}\) These heterostructures would be potential candidates for the efficient reduction of CO\(_2\) under visible-light irradiation. However, Pt is often poisoned by CO; therefore, it would be beneficial to use Ag in place of Pt. Cu is also effective for the reduction of CO\(_2\) but is unstable. In view of this, we have employed heterostructures containing bimetallic alloys and systematically evaluated the photocatalytic activities of ZnO/M/CdS (M = Ag, Au, Pt, Ag\(_{1-x}\)Au\(_x\), Ag\(_{1-x}\)Cu\(_x\)) heterostructures. ZnO/Ag/CdS and ZnO/Au/CdS exhibit significant CO\(_2\) reduction activity, whereas ZnO/Pt/CdS exhibits mainly reduction of water. Bimetallic Ag\(_{0.5}\)Au\(_{0.5}\) exhibits superior CO\(_2\) reduction activity compared to individual Ag and Au under...
visible-light irradiation. Photocatalytic reduction of CO$_2$ under visible-light irradiation on ZnO/Ag$_{1-x}$Cu$_x$/CdS heterostructures is presented in Figure 10. ZnO/Ag$_{0.75}$Cu$_{0.25}$/CdS heterostructures exhibit superior activity ($327 \mu$mol h$^{-1}$ g$^{-1}$) with the least hydrogen evolution activity among all the compositions. The ZnO/CdS interface causes effective separation of charge carriers, and the bimetallic alloy, Ag$_{0.75}$Cu$_{0.25}$, is a stable and efficient cocatalyst for the reduction of CO$_2$ (Table 2).

5.6. Z-Scheme Photocatalysts. Wang et al. 38 have recently developed an $\alpha$-Fe$_2$O$_3$/Cu$_2$O Z-scheme photocatalyst for the reduction of CO$_2$ using water as the reducing agent (Figure 11). $\alpha$-Fe$_2$O$_3$ is an n-type material, while Cu$_2$O is a p-type material. The photocatalytic activity under visible-light irradiation increases with the increasing Cu$_2$O content reaching a maximum yield of $5 \mu$mol g$^{-1}$ in 3 h with a Cu:Fe ratio of 0.5:1. Further increase in the Cu$_2$O content decreases the activity. Band positions estimated from electronic absorption, ultraviolet photoelectron, and X-ray photoemission spectroscopic studies show that $\alpha$-Fe$_2$O$_3$/Cu$_2$O forms a p–n junction. The observed photocatalytic activity arises because of the operation of the Z-scheme.

Takayama et al. 53 have employed CuGaS$_2$–RGO–TiO$_2$ for the liquid-phase reduction of CO$_2$ under UV–visible irradiation (Figure 12). CuGaS$_2$ acts as a reduction center, whereas TiO$_2$ acts as an O$_2$ evolution center. RGO facilitates the electron transfer from the CB of TiO$_2$ to the VB of the CuGaS$_2$. In the absence of RGO, the photocatalytic activities are negligible.

### Table 1. Photocatalytic CO$_2$ Reduction Yields Obtained by Various Photocatalysts in Gas-Phase Reactions Using Water as the Reducing Agent

| Photocatalyst                  | Light Source | Reaction Medium | Major Products       | Yields ($\mu$mol h$^{-1}$ g$^{-1}$) | References |
|-------------------------------|--------------|-----------------|----------------------|------------------------------------|------------|
| N,F-TiO$_2$:Ag                | Solar        | CO$_2$ and H$_2$O | CO                   | 8.7                                | Present study |
| TiO$_2$:N,F-TiO$_2$           | Solar        | CO$_2$ and H$_2$O | CO                   | 6.0                                | Present study |
| TiO$_2$ (anatase–brokite)     | Solar        | CO$_2$ and H$_2$O | CO                   | 2.1                                | 40         |
| P25 (anatase–rutile)          | Solar        | CO$_2$ and H$_2$O | CO                   | 1.3                                | 40         |
| CuO–TiO$_2$–N$_x$             | Solar        | CO$_2$ and H$_2$O | NO                   | 41 ppm h$^{-1}$ g$^{-1}$            | 41         |
| $\alpha$-Fe$_2$O$_3$/Cu$_2$O | Visible      | CO$_2$ and H$_2$O | CO                   | 1.67                               | 38         |
| Pt:TiO$_2$–doped TiO$_2$      | Visible      | CO$_2$ and H$_2$O | CH$_4$               | 1.6                                 | 42         |
| WO$_3$/Au/In$_2$Si            | Visible      | CO$_2$ and H$_2$O | CH$_4$               | 0.42                                | 39         |
| Pt:Zn$_2$Ge$_3$Ru$_2$O        | UV           | CO$_2$ and H$_2$O | CH$_4$               | 6.7                                 | 24         |
| anatase TiO$_2$ (010) facet   | UV           | CO$_2$ and H$_2$O | CH$_4$               | 1.2                                 | 43         |
| Cu$_x$ZnSnS$_y$–RGO–TiO$_2$   | UV           | CO$_2$ and H$_2$O | CH$_4$               | 120 ppm h$^{-1}$ g$^{-1}$           | 44         |
| Ag-loaded BaLa$_4$Ti$_4$O$_{15}$ | UV         | CO$_2$ and H$_2$O | CH$_4$               | 14.3                                | 22         |
| (Zn$_{1-x}$Ge$_x$)(N$_2$O$_y$) | Visible     | CO$_2$ and H$_2$O | CH$_4$               | 2.5                                 | 27         |
The photocatalytic production of hydrogen (28.8 μmol h⁻¹) is larger than that of CO (0.15 μmol h⁻¹).

6. OUTLOOK

While finding photocatalysts with viable photostability remains a great challenge for reducing CO₂ in the absence of any hole scavenger, chemists have no option but to discover the right catalysts. Considering the small UV fraction in solar irradiation, we need to concentrate on visible-light-sensitive photocatalysis. In this regard, N and F codoped systems such as ZnO₁₋ₓ(N,F)ₓ, TiO₂₋ₓ(N,F)ₓ, and SrTiO₃₋ₓ(N,F)ₓ could be potential candidates for both visible-light sensitization as well as photostability. Recent work suggests beneficial results by using bimetallic alloys in heterostructures. There may be new catalytic materials such as Cd₃P₂X₂ (X = Cl, Br, or I) with favorable characteristics. Recently it has been shown that cross-linked materials of C₃N₄ and others show remarkable properties. Exploring them for the reduction of CO₂ is also important.

Bipolar membranes are employed between anodic and cathodic compartments in order to avoid the migration of reactive species. Therefore, carrying out oxidation and reduction reactions in chambers separated with bipolar membranes would be a good strategy for beneficial conversion of CO₂. Since it is likely that CO will be the prominent product of photoreduction of CO₂, it would require further processing to generate methanol and other products. Direct photochemical conversion of CO₂ to methanol and other useful compounds continues to remain an important research target.

Table 2. Photocatalytic CO₂ Reduction Yields Obtained by Photocatalysts in Liquid-Phase Reactions

| photocatalyst | light source | reaction medium | products | yields (μmol h⁻¹ g⁻¹) | references |
|---------------|--------------|-----------------|----------|------------------------|------------|
| ZnO/Ag₀.5Cu₀.5/CdS | sunlight | 2-propanol·H₂O | CO, CH₄, H₂ | 162 (CO) | present work |
| ZnO/Ag₀.75Cu₀.25/CdS | visible | 2-propanol·H₂O | CO, CH₄, H₂ | 327 (CO) | present work |
| Pt/TiO₂ | UV | H₂O | H₂, CH₄, CO | 1.4 (CH₄) | 10 |
| ZnS:Cd | UV (Xe) | 2-propanol·H₂O | HCOOH, H₂ | 10 μmol h⁻¹ (HCOOH) | 48 |
| CdS | visible | 2-propanol·H₂O | HCOOH, CO, H₂ | 10 (HCOOH) | 49 |
| ZnFe₂O₄/TiO₂ | UV | cyclohexanol·H₂O | HCOO⁻ | 22 (HCOO⁻) | 50 |
| Ru(II)-complex/C₃N₄ | visible | methanol·DMA | CO | 5.7 (CO) | 51 |
| Ru(II)-complex/Ag/C₃N₄ | visible | K₂CO₃·EDTA·H₂O | HCOO⁻, H₂ | 83 (HCOO⁻) | 52 |

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