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Review

Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond

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ABSTRACT

Photocatalytic reduction of carbon dioxide to fuels using solar energy is an attractive option for simultaneously capturing this major greenhouse gas and solving the shortage of sustainable energy. Efforts to demonstrate the photocatalytic reduction of CO₂ are reviewed herein. Although the photocatalytic results depended on the reaction conditions, such as the incident/absorbing light intensity from the sun or a simulated solar light source, the performance of different systems is compared. When the reactants included CO₂ and water, it was necessary to determine whether the products were derived from CO₂ and not from impurities that accumulated on/in the catalysts as a result of washing, calcination, or pretreatment in a moist environment. Isotope labeling of ¹³CO₂ was effective for this evaluation using Fourier-transform infrared (FTIR) spectroscopy and mass spectrometry (MS). Comparisons are limited to reports in which the reaction route was verified spectroscopically, the C source was traced isotopically, or sufficient kinetic analyses were performed to verify the photocatalytic events. TiO₂ photocatalytically produced methane at the rate of $\sim 0.1 \,\mu$ mol h⁻¹ g_{cat}⁻¹. In aqueous solutions, formic acid, formaldehyde, and methanol were also produced. When TiO₂ was atomically dispersed in zeolites or ordered mesoporous SiO₂ and doped with Pt, Cu, N, I, CdSe, or PbS, the methane and CO formation rates were greater, reaching $1-10 \,\mu$ mol $h^{-1} \,g_{cat}^{-1}$. As for semiconductors other than TiO₂, CdS, SiC, InNbO₄, HNb₃O₈, Bi₂WO₆, promoted NaNbO₃, and promoted $Zn_2GeO_4\ produced\ methane\ or\ methanol\ at\ rates\ of\ 1-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}, and\ promoted\ A^{II}La_4Ti_4O_{15}\ pro-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}, and\ promoted\ A^{II}La_4Ti_4O_{15}\ pro-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}, and\ promoted\ A^{II}La_4Ti_4O_{15}\ pro-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}, and\ promoted\ A^{II}La_4Ti_4O_{15}\ pro-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}, and\ promoted\ A^{II}La_4Ti_4O_{15}\ pro-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}, and\ promoted\ A^{II}La_4Ti_4O_{15}\ pro-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}, and\ promoted\ A^{II}La_4Ti_4O_{15}\ pro-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}, and\ promoted\ A^{II}La_4Ti_4O_{15}\ pro-10\ \mu mol\ h^{-1}\ g_{cat}\ ^{-1}\ pro-10\ \mu mol\ h^{-1}\ pro-10\$ duced CO at a rate greater than $10 \,\mu mol \,h^{-1} \,g_{cat}^{-1}$, in addition to the historically known ZnO and GaP (formaldehyde and methanol formation). The photocatalytic reduction of CO₂ was also surveyed with hydrogen, because hydrogen can be obtained from water photosplitting by utilizing natural light. CO was formed at a rate of ${\sim}1\,\mu\text{mol}\,h^{-1}\,g_{cat}{}^{-1}$ using TiO_2, ZrO_2, MgO, and Ga_2O_3, whereas both CO and methanol were formed at a rate of $0.1-1 \,\mu$ mol h⁻¹ g_{cat}⁻¹ using layered-double hydroxides consisting of Zn, Cu, Al,

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and Ga. When hydrogen is used, in addition to identifying the origin of the carbon, it is critical to confirm that the products are photocatalytically formed, not thermally produced via CO_2 hydrogenation. The feasibility of the strategy involving the recycling of a sacrificial electron donor and the direct supply of protons and electrons released from water oxidation catalysts to photocatalysts for the reduction of CO_2 to fuels has been demonstrated. However, based on the results obtained to date, it is clear that the practical use of the photocatalytic reduction of CO_2 as one possible solution for global warming and the world's energy problems requires the development of more efficient photocatalysts.

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1. Background

Owing to the limited amount of energy sources and the recent effects of fossil fuel use on the global environment, the paradigm of energy supply is changing from one based on the use of carbon-rich rocks, peat, and liquid found in the Earth to one based on renewable sources, such as energy crops, sunlight, and wind [1]. According to the Intergovernmental Panel on Climate Change (IPCC), oil (34.6%), coal (28.4%), gas (22.1%), and nuclear energy (2.0%) were major worldwide energy sources in 2008 (Fig. 1). The percentage of renewable energy was 12.9%; however, if the traditional simple burning of biomass (6.3%) is excluded, renewable energy accounted for only 6.6% of total consumption.

Carbon dioxide is one of the major greenhouse gases and is formed as a result of the consumption of fossil fuels [2]. In the CO₂ emission scenarios described for 2050, bioenergy $(1.6 \times 10^{20} \text{ J y}^{-1})$, direct solar energy $(3 \times 10^{19} \text{ J y}^{-1})$, and wind energy $(2.5 \times 10^{19} \text{ J y}^{-1})$ are the top three renewable technologies that must be adopted in order to realize the ambitious target that calls for the decrease in the atmospheric CO₂ concentration to less than 440 ppm. Thus, renewable energy must be investigated intensively, because modern biomass, direct solar energy, and wind energy supply only 1.9×10^{19} , 0.5×10^{18} , and $1 \times 10^{18} \text{ J y}^{-1}$, respectively [1], and the application of renewable energy is increasing very slowly.

Several methods for reducing the CO_2 concentration in the atmosphere and preventing CO_2 emissions due to human activity have been investigated, such as investigating the sorption of CO_2 into new/functionalized materials; increasing the quantity of green carbon sinks (plants, phytoplankton, and algae containing chloroplasts); increasing the level of dissolved carbonate and its salts in sea water; or capturing CO_2 and transferring it to the bottom of the sea in a supercritical state [3].

It would be advantageous to capture CO_2 from the atmosphere or the exhaust of factories/power stations and convert it to fuel by using a sustainable source of energy such as sunlight. This option solves the problems of global warming and the sustainable energy shortage simultaneously [3–6]. It is an enormously difficult task



Fig. 1. 2008 distribution of world energy consumption by source [1].

to combine water splitting and carbon dioxide reduction [3,7,8]. Water oxidation and the subsequent reduction of CO_2 are required. This review mainly discusses the photocatalytic conversion of CO_2 to fuels (Sections 3–5) using semiconductors, but also presents a comparison of the related thermochemical conversion of CO_2 to fuels (Section 2) via the reduction–oxidation of metal oxides.

2. Thermochemical conversion of CO₂ to fuels

The energy from the sun that reaches the Earth in 1 h is 9200 times $(4.3 \times 10^{20} \, J \, h^{-1})$ the energy consumed on the Earth in 1 h in 2001 $(4.7 \times 10^{16} \, J \, h^{-1})$ [9]. In other words, all the energy consumed on the Earth in one year can be supplied from solar energy in only 1 h. To utilize the enormous energy provided by the sun, two-step thermochemical cycles to dissociate CO₂ and H₂O using metal oxide redox reactions have been proposed [10]. Nonstoichiometric oxides such as cerium oxide are partially reduced at higher temperatures (1873 K for cerium oxide), releasing O₂ under concentrated solar radiation, and then are oxidized again by reacting with CO₂ and H₂O at lower temperatures:

$$2MO_2 \rightarrow 2MO_{2-\delta} + \delta O_2(g)$$

$$\delta H_2 O + MO_{2-\delta} \rightarrow \delta H_2(g) + MO_2$$

 $\delta \text{CO}_2 + \text{MO}_{2-\delta} \rightarrow \delta \text{CO}(g) \,+\, \text{MO}_2,$

where M is Ce, Zn, or Fe, and the above stoichiometry represents an example for the case when M is Ce.

Compared to the redox systems consisting of $Zn^{II}O-Zn^{0}$ and $Fe^{II}Fe^{III}{}_{2}O_{4}$ - $Fe^{II}O$, cerium oxide is attracting attention because CeO_{2} is partially reduced via the formation of an oxygen vacancy without significant reorganization of the crystal lattice, and therefore, it reversibly stores and releases lattice oxygen atoms. Furthermore, CeO_{2} has a high melting point (2220 K), thermal stability, and is less susceptible to crystal-reordering phase transitions [11]. Above 1173 K under a solar flux with a density of 150 W cm⁻², the average evolution rate of O_{2} was $0.049 \, \text{mLmin}^{-1} \, \text{g}_{cat}^{-1}$ from cerium oxide, and the obtained partially reduced $CeO_{2-\delta}$ transformed CO_{2} to CO at 1173 K at an average rate of 1.8 mLmin⁻¹ $\, \text{g}_{cat}^{-1}$ and transformed $H_{2}O$ to H_{2} at 1173 K at an average rate of 0.95 mLmin⁻¹ $\, \text{g}_{cat}^{-1}$ [10].

These thermochemical conversion rates are higher than the photocatalytic rates discussed below, but focusing lenses for sunlight and high-temperature reactors incur high initial investment costs.

3. Photon energy conversion of CO₂ to fuels with water

3.1. TiO₂ photocatalysts

The photon energy of sunlight can be converted to electric energy using solar cells [12] and to chemical energy using photocatalysts. The development of photocatalysts to convert solar energy to chemical energy is an indispensable option for storing energy and for mobile use, especially when using sustainable, cheaper

1 F	Fable 1A Reported CO ₂ photo	oreduction cata	alysts, reaction condition	is, and the formation rate	es in water/	with moisture using TiO ₂ .	
	Photocatalyst		Reactants		T (K)	Light source	Major product {formation rate
	Brand name	Amount (g)	CO ₂	H ₂ O			$(\mu mol h^{-1} g_{cat}^{-1})$
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Brand name	Amount (g)	CO ₂	H ₂ O			$(\mu mol h^{-1} g_{cat}^{-1})$	
TiO ₂	1	Saturated	Liq (100 mL)		500 W Xe/HP Hg	Formaldehyde (16) Methanol (3.3)	[14]
TiO ₂	0.3	Saturated	Liq (120 mL)	333	500 W HP Xe	Formaldehyde (2.0 ^a)	[19]
TiO ₂	0.15	Saturated	100 mL, 0.1N NaOH		500 W W-halogen	Formic acid (22 ^a)	[40]
TiO ₂ (P25)	0.15	Saturated	Liq (1.5 mL)	278	500 W HP Hg arc (>310 nm)	CO (0.35)	[39]
Anatase TiO ₂	0.05	9.0 MPa (sc)	Liq (5 mL, added later)	308	990 W Xe (>340 nm)	Formic acid (1.8)	[18]
TiO ₂ (JRC-TIO-4)	-	111 kPa (gas total)	Saturated gas		UV (254 nm)	Methane (0.014)	[15]
Anatase TiO ₂	-	Gas (0.04-0.15 mmol)	Gas (0.04-0.25 mmol)	323	75 W HP Hg (>280 nm)	Methane (0.17)	[16]
TiO ₂ (P25)	-	Gas (17%)	Gas (83%)		UV (365 nm)	Methane (15ª)	[45]
TiO ₂ pellet	-	111 kPa (gas total)	Saturated gas		UV (254 nm)	Methane (0.0021)	[15]
Ti-PVG	-	111 kPa (gas total)	Saturated gas		UV (254 nm)	Methane (0.0025)	[15]
Ti-PVG	-	Gas (0.04-0.15 mmol)	Gas (0.04-0.25 mmol)	323	75 W HP Hg (>280 nm)	Methane (0.020)	[16]

^a Spectroscopic verification of reaction route, isotope tracing to identify the C source, or sufficient control kinetic tests to verify the photocatalytic event is required.

semiconductors [3,5,9,13]. Photocatalytic conversions of CO₂ to fuels with water using semiconductors are summarized in Table 1.

In a pioneering paper in 1979, the photoreduction of CO_2 to formaldehyde and methanol in purified water using the semiconductors TiO_2 , ZnO, CdS, GaP, SiC, and WO_3 was reported [14]. Based on the correlation between the conduction band energy potential and the yield of methanol, it was suggested that the photoreduction of CO_2 proceeded by the photoexcited electrons in the conduction band moved to CO_2 . The conduction band energy minimum was higher than that for CO_2 photoreductions.

$$CO_3^{2-} + 6H^+ + 4e^- \rightarrow H_2CO(aq) + 2H_2O, \quad E^{\circ}(298 \text{ K}) = +0.197 \text{ V}$$

$$CO_3^{2-} + 8H^+ + 6e^- \rightarrow CH_3OH(aq) + 2H_2O, E^{\circ}(298 \text{ K}) = +0.209 \text{ V},$$

in which the electric potentials are referenced to a standard hydrogen electrode (SHE). The photocatalytic results in this review are explained on the basis of this band gap electron excitation mechanism.

The photoreduction of CO₂ using TiO₂ has been most extensively investigated (Table 1A). The CO₂ photoreduction in water-saturated CO₂ gas was compared at 111 kPa using TiO₂ powder (reference catalyst JRC-TIO-4, Catalysis Society of Japan), anchored Ti oxide on porous Vycor glass (PVG), and 4-mm pelletized TiO₂ under UV (ultraviolet) light for 48 h. The methane formation rates were 14 nmol h⁻¹ g_{cat}⁻¹, 2.5 nmol h⁻¹ g_{cat}⁻¹, and 2.1 nmol h⁻¹ g_{cat}⁻¹, respectively [15], suggesting that the specific surface area of the catalyst was of prime importance. CO and H₂ were minor products.

The photocatalytic performance was also compared on a single crystal surface of rutile-type $TiO_2(100)$ (Ti terminating) and $TiO_2(110)$ (O terminating) (Fig. 2). Careful kinetic measurements were performed, because the surface area of a single crystal surface is limited in comparison to that of porous powders. The $TiO_2(100)$



Fig. 2. Comparison of the (100) and (110) crystal faces in the crystal structure of rutile TiO₂ and their performance in photocatalytic CO₂ reduction [16].

surface was more photocatalytically active than the $TiO_2(110)$ surface by a factor of 7.4, suggesting that a reductive Ti-terminating surface is favorable for reducing CO_2 [16].

The reactant CO₂ was condensed to a supercritical (sc) condition ($T_{critical}$ = 304.1 K, $P_{critical}$ = 7.375 MPa) [17] to boost the reaction frequency. When anatase-type TiO₂ powder was set in supercritical CO₂ (308 K, 9.0 MPa) and irradiated under UV–visible light (>340 nm) followed by the addition of water, formic acid was formed at a rate of 1.8 µmol h⁻¹ g_{cat}⁻¹ [18]. The two-step synthesis of formic acid starting from CO₂ was accelerated by the addition of phosphoric, nitric, or hydrochloric acid in the second step. In particular, an H₃PO₄ solution worked best for protonation to form formic acid at a pH of 2.2 and a rate of 2.9 µmol h⁻¹ g_{cat}⁻¹.

This result reported in Ref. [18] is one of the best rates in Table 1A for conditions where the photocatalytic reaction route was supported by spectroscopy. The reaction mechanism was proposed to proceed through a one-electron reduced radical intermediate species (\cdot CO₂⁻) whose presence was confirmed by electron spin resonance (ESR) measurements:

$$TiO_{2} \xrightarrow{h\nu} e^{-} (as Ti_{3}^{+}) + h^{+}$$
$$Ti^{4+} - O^{2-} \xrightarrow{h\nu} Ti^{3+} - O^{-}$$
$$CO_{2} + e^{-} \rightarrow \bullet CO_{2}^{-}$$

 ${}^{\bullet}\text{CO}_2{}^- + 2\text{H}^+(\text{of water or acid}) + e^- \rightarrow \text{HCO}_2\text{H}$

 $\bullet CO_2^- + \bullet CO_2^- + 2H^+$ (of water or acid) $\rightarrow HCO_2H + CO_2$

3.2. Metal-loaded TiO₂ photocatalysts

Various studies on the use of an added metal to enhance the photocatalytic activity of TiO₂ have also been reported. An aqueous suspension of TiO₂, Rh/TiO₂, or Rh/WO₃–TiO₂ at 333 K was bubbled with a CO₂ flow and illuminated by a xenon lamp, and the exit gas was trapped at 273 K and analyzed [19]. The major product when using the TiO₂ suspension was formaldehyde, which was formed at a rate of 2.0 μ mol h⁻¹ g_{cat}⁻¹ (Table 1A). A minor amount of formic acid was also detected. However, the major product detected when using the air-calcined Rh/WO₃–TiO₂ suspension was formic acid, which formed at a rate of 1.6 μ mol h⁻¹ g_{cat}⁻¹ (Table 1B). Minor amounts of methanol and formaldehyde were also detected. Furthermore, the product distribution clearly changed again when H₂-reduced (473 K) Rh/WO₃–TiO₂ was used. In this case, methanol was synthesized exclusively at a rate greater than 4.0 μ mol h⁻¹ g_{cat}⁻¹.

Reference

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Table 1B

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Reported CO₂ photoreduction catalysts, reaction conditions, and the formation rates in water/with moisture using metal-loaded, highly-dispersed, and modified TiO₂.

Photocatalyst		Reactants		<i>T</i> (K)	Light source	Major product {formation	Reference
Brand name	Amount (g)	CO ₂	H ₂ O			rate $(\mu mol h^{-1} g_{cat}^{-1})$	
TiO ₂ -MWCNT	-	Gas (17%)	Gas (83%)		UV (365 nm)	Ethanol (30ª) formic acid (19ª), methane (12ª)	[45]
Ti-Y-zeolite	0.15	$Gas(24\mu mol)$	Gas (120 µmol)	328	HP Hg (>280 nm)	Methane (0.046), methanol (0.031)	[28]
Pt—Ti-Y-zeolite	0.15	Gas (24 µmol)	Gas (120 µmol)	328	HP Hg (>280 nm)	Methane (0.080)	[28]
Ti-MCM-48 (Si/Ti = 80)	-	$Gas(24\mu mol)$	Gas (120 µmol)	328	HP Hg (>280 nm)	Methane (7.5), methanol (3.1)	[29]
Pt—Ti-MCM-48 (1.0 wt% Pt, Si/Ti = 80)	-	$Gas(24\mu mol)$	Gas (120 µmol)	328	HP Hg (>280 nm)	Methane (12)	[29]
Ti-SBA-15 (0.29 wt% Ti, Si/Ti = 270)	0.05	Gas (36 µmol)	Gas (180 µmol)	323	100 W HP Hg (>250 nm)	Methane (0.31), methanol (0.081)	[30]
Ti-SBA-15 (0.05 wt% Ti)	0.05	Gas (38 µmol)	Gas (76 µmol)	313	120 W HP Hg	Ethane (0.020), methane (0.016), ethene (0.007)	[31]
CdSe-Pt/TiO ₂	0.3	Gas (40 Pa)	Gas (400 Pa)		300 W Xe (>420 nm)	Methane, methanol	[26]
PbS-Cu/TiO ₂		Gas	Saturated gas		300 W Xe (UV cut)	CO (0.82), methane (0.58)	[27]
Rh(1 wt%)/WO3 (2 wt%)-TiO2	0.3	Saturated	Liq (120 mL)	333	500 W HP Xe	Formic acid (1.6 ^a)	[19]
Rh/WO ₃ -TiO ₂ -reduced	0.3	Saturated	Liq (120 mL)	333	500 W HP Xe	Methanol (4.0 ^a)	[19]
Co ^{II} -Pc(0.7 wt%)/TiO ₂	0.15	Saturated	100 mL, 0.1N NaOH		500 W W-halogen	Formic acid (150 ^a)	[40]
Zn ^{II} -Pc(1 wt%)/TiO ₂	0.15	Saturated (2.3 g)	100 mL, 0.1N NaOH		500 W W-halogen	Formic acid (98 ^a)	[41]
Nd ^{III} (0.2 wt%)/TiO ₂	-	Saturated	Liq		UV	Methanol (23 ^a)	[44]
Pd(1 wt%)-TiO ₂	0.15	Saturated	Liq (1.5 mL)	278	500 W HP Hg arc (>310 nm)	Methane (0.37)	[39]
Cu-TiO ₂	0.15-0.6	Saturated	300 mL, 0.2 N NaOH	323	Hg (254 nm)	Methanol (20 ^a)	[42,43]
Cu-N-TiO ₂ NT	-	108 kPa (gas total)	Saturated	317	Sun	Methane (4.4)	[13]
Cu-N-TiO ₂ NT	-	108 kPa (gas total)	Saturated	317	No light	Methane (0.13 ^a)	[13]
Pt—N-TiO ₂ NT	-	108 kPa (gas total)	Saturated	317	Sun	Methane (2.9)	[13]
No catalyst	0	108 kPa (gas total)	Saturated	317	Sun	Methane (0.10 ^a)	[13]
I-TiO ₂	0.2	99 kPa	2.3 kPa		Xe	CO (2.4 ^a)	[37]

^a Spectroscopic verification of reaction route, isotope tracing to identify the C source, or sufficient control kinetic tests to verify the photocatalytic event is required.

The following reaction mechanism, which again includes a oneelectron reduced species ($^{\circ}CO_2^{-}$), was proposed [19] and is based on a probable photo-assisted thermal methanol synthesis at 333 K, starting from CO₂ and H₂O. oxidation of the CdSe quantum dots, the photocatalyst was deactivated. PbS quantum dots (4 nm) were also effective for boosting the photocatalytic conversion of CO₂ to CO and methane (Table 1B) [27].

3.3. Highly dispersed TiO₂ photocatalysts

The photocatalytic enhancement of TiO_2 was also attempted using highly dispersed active Ti ion species. The performance of



Fig. 3. Energy diagram for bulk and nano CdSe with TiO_2 , and the redox potentials for the CO_2 reduction and water oxidation reaction steps.

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 $CO_2 + e^- \rightarrow \ ^{\bullet}CO_2^-$

 $\bullet \mathrm{CO}_2^- + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{HC}(\mathrm{O})\mathrm{O}^{\bullet} + \mathrm{OH}^-$

 $\text{HC(0)O}^{\bullet} \,+\, e^- \rightarrow \,\,\text{HCO}_2{}^-$

 $\text{HCO}_2^- + \text{H}^+ \rightarrow \text{HCO}_2\text{H}$

It is also plausible that water photosplitting first occurred photocatalytically, and then the thermal reaction of CO_2 with H_2 (or a H species present on the Rh surface) proceeded, because Rh/WO₃-TiO₂ is a typical thermal catalyst for CO/CO₂ hydrogenation [20–24].

The addition of Cu⁺ to TiO₂ powder photocatalysts was reported to lead to the formation of methanol [16]. The effects of doped- d^{10} configuration Cu⁺, Ag⁺, and Pb²⁺ ions on d⁰-configuration metals, such as Ti, Nb, and Ta oxides, have been discussed for photocatalytic water splitting reactions, and hopefully can be applied also to the carbon dioxide photoreduction [25].

CdSe quantum dots (2.5 and 6.0 nm) were mixed with a Pt/TiO₂ photocatalyst, and the photocatalyst was sensitized for the photoreduction of CO₂ (40 Pa) with moisture (400 Pa) under visible light exposure [26]. The photoexcitation of the electrons between the band gap of TiO₂ by visible light (>420 nm) is hardly possible, but the photoexcitation of electrons between the band gap of the CdSe quantum dots is possible using visible light, and the excited electrons would be injected to the conduction band of TiO₂ (Fig. 3). With this system, the conversion of CO₂ to methane (major) and methanol (minor) was observed for 4–6 h, but because of the

Ti species anchored on PVG prepared from TiCl₄ and highly dispersed TiO₂ powder in the photocatalytic reduction of CO₂ was compared [16]. The Ti sites of Ti-PVG were surface-isolated tetrahedral TiO₄ based on the intense Ti 1s-3d electronic transition peak and a weaker signal ascribed to Ti-O-Ti (or Ti-O-Si) bonding in the Ti K-edge extended X-ray absorption fine structure (EXAFS) compared to highly dispersed anatase-type TiO₂.

Under CO₂ gas and water vapor, the photocatalysts were irradiated with UV light through water and a cut-off filter (λ > 280 nm) at 323 K. The anatase-type TiO₂ exclusively produced methane with a formation rate of $0.17\,\mu mol\,h^{-1}\,g_{cat}{}^{-1},$ in contrast to the Ti-PVG, which led to the formation of methane, methanol, and CO. The methane formation rates for the Ti-PVG photocatalyst increased from 1.6 nmol $h^{-1}\,g_{cat}{}^{-1}$ to 5.0 nmol $h^{-1}\,g_{cat}{}^{-1}$ when the molar ratio of H_2O and CO_2 increased from 0 to 3 and then to increased to 20 nmol h^{-1} g_{cat}^{-1} when the molar ratio of H_2O and CO₂ increased to 5.

In addition, the total yield increased when this UV irradiation test was conducted at 323 K compared to that conducted at 275 K. Based on the temperature dependence, the thermal assist mechanism may be applicable in Ref. [16], but the charge separation between Ti and O in the Ti³⁺-O⁻ bond was monitored by ESR spectroscopy, and the quenching of photoluminescence in the presence of CO₂ was also shown. Essentially, the charge separation between Ti and O in the Ti³⁺–O⁻ bond played both reductive and oxidative photocatalytic roles [16].

The photocatalytic reduction of CO_2 (24 μ mol, 0.73 kPa) by atomically dispersed Ti sites in Y-zeolite and its derivatives in the presence of water (120 µmol, 3.7 kPa) using UV light from a high-pressure Hg lamp (>280 nm) at 328 K [28,29] was also reported. Atomically dispersed Ti sites in Y-zeolite prepared via an ion-exchange method produced both methane $(46 \text{ nmol } h^{-1} \text{ g}_{\text{cat}}^{-1})$ and methanol $(31 \text{ nmol } h^{-1} \text{ g}_{\text{cat}}^{-1})$, whereas a Pt-loaded ion-exchanged Ti-Y-zeolite selectively formed methane $(80 \text{ nmol } h^{-1} \text{ g}_{cat}^{-1})$. Impregnated Ti oxide species in Y-zeolite exclusively formed methane.

The selectivity difference was explained as follows. The Ti sites in the ion-exchanged Y-zeolite are atomically dispersed on the basis of X-ray absorption near-edge structure (XANES) and EXAFS analyses. The charge separation between Ti and O in the Ti³⁺–O⁻ bond was evaluated on the basis of the photoluminescence spectra. The lifetime of the excited $Ti^{3+}-O^-$ was determined to be $54\,\mu s$, which is substantially higher than that for TiO₂ powders (nanosecond order). Owing to quantum size effects, the dispersed Ti³⁺ sites were more negative, and accordingly exhibited a greater reducing potential for the CO₂ substrate, enabling methanol formation based on the band-gap values given from the UV-visible spectra. The E° values were -0.32 and -0.244 V for methanol and methane formation, respectively (Fig. 3). CO seemed to be an intermediate for the reduction of CO2, but H2 was not an intermediate. The water could have been oxidized to OH and H⁺, and the Pt sites probably worked to suppress charge recombination [28].

Ti-MCM-48 produced methane Similarly, both $(7.5 \,\mu mol \, h^{-1} \, g_{cat}^{-1})$ and methanol $(3.1 \,\mu mol \,h^{-1} \,g_{cat}^{-1}),$ while Pt-Ti-MCM-48 was the most active and selectively formed methane $(12 \,\mu mol \,h^{-1} \,g_{cat}^{-1})$ [29]. Ti-SBA-15 also produced methane and methanol with formation rates of 0.31 and 0.081 μ mol h⁻¹ g_{cat}⁻¹, respectively (Table 1B) [30]. In contrast, when the Ti-SBA-15 was illuminated in humid helium to remove any C residues, the rates of photoreduction of CO₂ to ethane, methane, and ethylene were quite small $(0.020-0.007 \,\mu\text{mol}\,h^{-1}\,g_{cat}^{-1})$ [31]. Minor carbonaceous impurities in the Ti-MCM-41 were detected by Fourier-transform infrared (FTIR) spectroscopy using isotopes [32]. Based on these results, it is possible that the C residues remaining from the original organic

1500 1000 2.30 PM 2:14 PM 500 3:14PM 3:52PM 0 300 400 500 600 700 800 Wavelength (nm)

Fig. 4. (a) Photograph of the reaction chambers set in the sunlight during summer in Pennsylvania, USA for photocatalytic CO_2 conversion under CO_2 saturated with moisture (total pressure <108 kPa). (b) Spectral irradiation for the photocatalytic tests.

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template compounds used in the syntheses of Y-zeolite, MCM-48, and SBA-15 were the (partial) source of the products reported in Refs. [28-30], but the very low Ti loading level in Ref. [31] may be related to the lower photocatalytic activity.

Exclusive formation of CO and O2 was reported for Ti-MCM-41 under CO_2 and H_2O [32]. The light intensity from a 266-nm pulsed Nd:Yag laser was varied between 80 and 160 mW cm⁻², and a proportional increase in CO production was observed, which indicated a single photon process accompanying the charge separation between Ti and O in the Ti³⁺-O⁻ bond. The difference in the major product (CO) compared to that formed in Refs. [29–31] (methane) is due to the different light source: a UV-pulsed laser versus a Hg lamp.

3.4. Modified/doped TiO₂ photocatalysts

Nitrogen-doped TiO₂ nanotube arrays were synthesized by the anodization of Ti metal in an ethylene glycol aqueous solution (2vol%) with 0.3 M ammonium fluoride as a the N source. The Cu- or Pt-loaded N-doped TiO₂ nanotube photocatalysts were set outside on a sunny summer day in Pennsylvania, USA under water-vapor-saturated CO₂ (total pressure <108 kPa) for 2.5-3.5 h at 317 K (Fig. 4) [13]. The major product using the Cu- and Pt-loaded





N-doped TiO₂ nanotubes was methane, which was produced at a rate of 4.4 μ mol h⁻¹ g_{cat}⁻¹ and 2.9 μ mol h⁻¹ g_{cat}⁻¹, respectively, in addition to minor amounts of CO, ethane, propane, butane, pentane, and hexane. The major advantages of using N-doped TiO₂ nanotubes for the CO₂ photoreduction were considered to be (1) a minimum thickness of the N-doped TiO₂ nanotubes of ~10 nm versus a hole diffusion length of ~10 nm [33] and an electron diffusion length of ~10 μ m in TiO₂; [34] and (2) the electron trap at the Cu or Pt to donate electrons to CO₂. A later paper on the CO₂ photoreduction using Pt-TiO₂ nanotubes reported the exclusive formation of methane in addition to trace amounts of ethane [35]. Based on a comparison of the two studies, it is possible to conclude that (at least part of) the hydrocarbons produced in Ref. [13] originated from the tape used in the reactor.

When the fraction of sunlight with wavelengths shorter than 400 nm was removed, the photocatalytic activity of CO₂ reduction was reduced to 3% of that under the entire solar spectrum. The control reaction in the dark (using the Cu-loaded N-doped TiO₂ nanotubes) and in the absence of catalyst produced methane at rates of 0.13 μ mol h⁻¹ g_{cat}⁻¹ and 0.10 μ mol h⁻¹ g_{cat}⁻¹, respectively. The reaction mechanism operating in response to the UV light was proposed as follows [13].

 $\mathrm{H_2O}\,+\,h^+\!\rightarrow\,{}^{\bullet}\mathrm{OH}\,+\,\mathrm{H^+}$

 $H^+ + e^- \rightarrow \ ^\bullet H$

 ${}^{\bullet}H + {}^{\bullet}H \rightarrow H_2$

 $2CO_2 + 4e^- \to \ 2CO \ + \ O_2$

 $CO~+~6e^-+6H^+\rightarrow~CH_4+H_2O$

lodine-doped TiO₂ is known as a visible-light-responsive photocatalyst, typically for photooxidation [36]. Essentially, doped I⁻ anions form impurity energy levels above the valence band of TiO₂ and extend the availability of the visible light. This strategy was applied to the CO₂ photoreduction in the gas phase. The CO formation rate ($2.4 \,\mu$ mol h⁻¹ g_{cat}⁻¹; Table 1B) [37] is comparable to verified methane formation rates using other dispersed or doped TiO₂ photocatalysts. Linear O₂ formation was also monitored, but to further discuss the following proposed mechanism compared to competitive H₂ formation, quantitative kinetic data are needed.

 $\text{TiO}_2 \rightarrow \ h^+ + e^-$

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2$$

 $\mathrm{CO}_2 + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \ \mathrm{CO} \ + \ \mathrm{H}_2\mathrm{O}$

To summarize Sections 3.2–3.4, when TiO₂ was atomically dispersed on zeolites or ordered mesoporous SiO₂ or doped with Pt, Cu, N, I, CdSe, or PbS, photocatalytic methane or CO formation rates increased to $1-10 \,\mu$ mol $h^{-1} \,g_{cat}^{-1}$.

3.5. Historical low conversion rates and misunderstandings when using TiO₂-based photocatalysts

The reaction routes for the CO_2 reduction with water should be carefully checked to determine whether the carbon source was actually the CO_2 reactant. The major obstacle for the reduction of CO_2 is the thermodynamic limitation [3]:

$$\begin{split} \text{CO}_2(\textbf{g}) &+ 2\text{H}_2\text{O}(\textbf{g}) \rightarrow \text{CH}_3\text{OH}(\textbf{g}) + 1.5\text{O}_2(\textbf{g}), \\ \Delta G_{\textbf{r}}^\circ &= +689\,\text{kJ}\,\text{mol}^{-1} \end{split}$$

This significant up-hill free-energy change is due to the greater enthalpies for CO_2 and H_2O . The free-energy change for water splitting is lesser by 34%.

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g), \quad \Delta G_r^{\circ} = +457.2 \text{ kJ mol}^{-1}$$

Therefore, in view of the free-energy change, the CO_2 conversion is extremely unfavorable, and the reduction of impurity carbon to methanol could be misinterpreted as the reaction of CO_2 [38,39].

In one example, TiO₂ was synthesized by a sol-gel route starting from titanium(IV) *n*-butoxide and polyethylene glycol (PEG) [38] or *n*-butanol plus acetic acid [40–43]. Methanol (20 μ mol h⁻¹ g_{cat}⁻¹) [42,43] and formic acid formation (150–98 μ mol h⁻¹ g_{cat}⁻¹) [40,41] were reported using a suspended, Cu-loaded, sol-gel-derived TiO₂ in NaOH solution saturated with CO₂ under UV light from a mercury lamp [42,43] or using Co^{II}-phthalocyanine(Pc)/TiO₂ and Zn^{II}-Pc/TiO₂ under a W halogen lamp [40,41]. In an aqueous solution saturated with CO₂ using Nd^{III}/TiO₂ under UV irradiation, the formation rate of methanol was as much as 23 μ mol h⁻¹ g_{cat}⁻¹ [44]. The TiO₂ powder used in this study was also prepared via a sol-gel route.

TiO₂ has also been synthesized via a sol-gel route starting from Ti(IV) tetrachloride and hydrochloric acid, followed by the addition of ammonia until the pH reached 7. Nanocomposites of TiO₂ and multi-walled carbon nanotubes (MWCNTs) produced ethanol, formic acid, and methane with formation rates of 30, 19, and $12 \,\mu mol \, h^{-1} \, g_{cat}{}^{-1}$, respectively, (Table 1B) in H₂O and CO₂ (molar ratio 5:1) under a UV lamp (365 nm) for 5 h [45]. In this study, TiO₂ (P25, Degussa) and TiO₂ synthesized by a sol-gel method were also tested for the CO₂ photoreduction. Unmodified TiO_2 (P25) produced ethanol, formic acid, and methane with formation rates of 1.0, 19, and $15 \,\mu$ mol h⁻¹ g_{cat}⁻¹, respectively, and the sol-gel-derived TiO₂ was even more active. These results were in contradiction to those reported in Refs. [15,16] in which anatase-type (or anatase-type major) TiO₂ produced only methane at rates of $0.014-0.17 \,\mu mol \,h^{-1} \,g_{cat}^{-1}$ under similar reaction conditions (Table 1A).

To investigate the surface reaction mechanism starting from CO₂ to fuels, the isotope distribution of adsorbed CO (12 CO at 2115 cm⁻¹ and 13 CO at 2069 cm⁻¹) over Cu¹/TiO₂ was monitored using diffuse reflectance infrared Fourier-transform spectroscopy in 13 CO₂ gas (Fig. 5) [38]. Adsorbed 12 CO species were the primary products, indicating that a reverse disproportionation reaction of impurity carbon with CO₂ proceeded to form CO.

 $^{12}C(impurityin/oncatalyst) + {}^{13}CO_2 \rightarrow {}^{12}CO + {}^{13}CO$

If the carbon residues deposited/buried on the catalyst surface during the catalyst synthesis were involved in reactions with photocatalytically activated surface-adsorbed water via

$$\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{O}_2, \quad \Delta G_r^{\circ} = +432 \text{ kJ mol}^{-1}$$

in which the free-energy change is lesser by 37% compared to the reduction of CO_2 to methanol, the thermodynamic limitation can be partially compensated for by the impurity carbon.

Recently, based on detailed gas chromatography (GC) and GC–MS (Mass spectrometry) analyses, the C source was carefully investigated with respect to the production of CO, methane, ethane, acetic acid, formic acid, and methanol from CO_2 [39]. The tests were conducted in CO_2 -saturated water using TiO_2 (P25) at 278 K under UV–visible light (>310 nm). Using as-received TiO_2 , methane was formed at a rate 150 nmol h⁻¹ g_{cat}⁻¹, but the molar amount corresponded well to that of acetic acid desorbed by calcination at 623 K. The reaction was not considered to be CO_2 photoreduction, but the photo-Kolbe reaction [46]:

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Fig. 5. Isotope distribution of the adsorbed CO (¹²CO at 2115 cm⁻¹ and ¹³CO at 2069 cm⁻¹) over Cu¹/TiO₂ monitored by diffuse reflectance infrared Fourier-transform spectroscopy in ¹³CO.

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$$CH_3CO_2H + h^+ \rightarrow {}^{\bullet}CH_3 + CO_2 + H^+$$

${}^{\bullet}\text{CH}_3 + \text{CH}_3\text{CO}_2\text{H} \ \rightarrow \ \text{CH}_4 + {}^{\bullet}\text{CH}_2\text{CO}_2\text{H}$

After calcination at 623 K and further thorough washing of the TiO₂ with deionized water, the reaction was repeated, and the organics were not detected; the actual CO and methane formation rates under UV–visible light were 350 and 25 nmol h⁻¹ g_{cat}⁻¹, respectively. Similarly, photochemically deposited Pd–TiO₂ was washed several times and set in CO₂saturated water under UV–visible light. Methane was the major product (370 nmol h⁻¹ g_{cat}⁻¹), and ethane and CO were formed in minor amounts. The methane source was tested using ¹³CO₂, and the GC–MS peak at m/e = 17 confirmed the formation of ¹³CH₄ directly from ¹³CO₂ [39].

In summary, based on the studies presented in Refs. [38,39], it is essential to verify the C source for the products reported in Refs. [40–45]. The products were very likely derived from an alkyl group of the catalyst precursor compounds or the organic solvent.

3.6. Semiconductor photocatalysts other than TiO₂

In the pioneering report in 1979, the photoreduction of CO_2 to formaldehyde and methanol in water was reported using TiO₂, ZnO, CdS, GaP, SiC, and WO₃ (Table 1C). The rates of formaldehyde production were in the order:

$CdS \ > \ ZnO \,{\sim}\, TiO_2 \,{>}\ GaP \,{\sim}\, SiC$

However, the rates of methanol formation followed quite a different order [14]:

$$SiC \gg CdS \sim GaP > ZnO > TiO_2$$

CdS nanoparticles were supported on montmorillonite, and the photoreduction of CO₂ was tested in an alkaline solution under UV light (254 nm) [47]. Although water photosplitting proceeded predominantly (H₂ formation rate: $8.7 \,\mu$ mol h⁻¹ g_{cat}⁻¹), the secondary hydrogenation of CO₂ was suggested with a formation rate of 0.93 μ mol h⁻¹ g_{cat}⁻¹. p-SiC powder and copper powder were dispersed in a potassium hydrogen carbonate solution saturated with CO₂ at a pH of 5 at 313 K. When the suspension was illuminated with UV light from a mercury lamp (7 mW cm⁻² at 365 nm), methane was the major product, which had a formation rate of 0.63 μ mol h⁻¹ g_{cat}⁻¹, and ethylene and ethane were

minor products [48]. The Cu site was suggested to be an acceptor of photogenerated electrons, but the Cu-p-SiC photocatalyst deactivated in 1–2 h.

InTaO₄ that was previously synthesized by solid-state synthesis starting from In₂O₃ and Ta₂O₅ was impregnated with 0–1.0 wt% NiO using an aqueous nickel nitrate solution [49], calcined at 623 K, reduced at 773 K, oxidized at 473 K, and then used as a catalyst for the photcatalytic reduction of CO₂. After the photocatalytic test in a CO₂-saturated potassium bicarbonate solution was complete, the aqueous phase was analyzed, and methanol was formed at a maximum rate of 1.4 μ mol h⁻¹ g_{cat}⁻¹ using NiO/InTaO₄. Unfortunately, control reactions (in the dark, in the absence of catalyst, in the absence of CO₂ and/or KHCO₃) and other product information, including analysis of the gas phase were not reported. The NiO/InTaO₄ photocatalysts were also tested for the gas-phase CO₂ reduction using a monolith reactor [50]. The major product was acetaldehyde, which was formed at a rate of 0.21 μ mol h⁻¹ g_{cat}⁻¹ (Table 1C), rather than minor methanol formation.

InNbO₄ was synthesized by solid-state reactions and then tested for the CO₂ photoreduction in a KHCO₃ solution [51]. Based on the control tests and the fact that the catalyst was prepared via a carbon-free synthetic method, the methanol formation, which occurred at a rate of $1.3 \,\mu$ mol h⁻¹ g_{cat}⁻¹ under UV-visible light, should be photocatalytic. Hydrothermally synthesized HNb₃O₈ nanobelts and Bi₂WO₆ nanoplates also underwent the photoreduction of CO₂ to methane with rates of 3.6 and 1.1 μ mol h⁻¹ g_{cat}⁻¹, respectively, (Table 1C) [52,53] which are comparable to TiO₂based photocatalysts. The [001] face of the nanoplates was suggested to be responsible. Pt-promoted perovskite NaNbO₃ was reported to produce methane from CO₂ + H₂O at a rate comparable to the levels of the other best semiconductor photocatalysts: 4.9 μ mol h⁻¹ g_{cat}⁻¹ [54].

BiVO₄ was synthesized by a hydrothermal method starting from acidic bismuth nitrate and alkaline ammonium vanadate solutions [55]. Cetyltrimethyl ammonium (CTMA) bromide (to obtain monoclinic BiVO₄ crystals) or PEG (to obtain tetragonal BiVO₄ crystals) was added to both solutions, and the two solutions were mixed. The mixed solution was heated at 473 K in an autoclave under microwave irradiation. In the cooled water saturated with CO₂ gas, the monoclinic BiVO₄ was reported to produce ethanol with rates of 2000 and 110 μ mol h⁻¹ g_{cat}⁻¹ under UV-visible and visible light, respectively.

A control reaction was performed in nitrogen gas instead of CO_2 , and no ethanol production was detected. However, this fact did not

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Table 1C

Reported CO₂ photoreduction catalysts, reaction conditions, and the formation rates in water/with moisture using semiconductor photoatalysts other than TiO₂.

Photocatalyst		Reactants		<i>T</i> (K)	Light source	Major product {formation rate (µmol h ⁻¹ g _{cat} ⁻¹)}	Reference
Brand name	Amount (g)	CO ₂	H ₂ O				
ZnO	1	Saturated	Liq (100 mL)		500 W Xe/HP Hg	Formaldehyde (17), methanol (5.0)	[14]
CdS	1	Saturated	Liq (100 mL)		500 W Xe/HP Hg	Formaldehyde (29), methanol (17)	[14]
GaP	1	Saturated	Liq (100 mL)		500 W Xe/HP Hg	Formaldehyde (14), methanol (16)	[14]
SiC	1	Saturated	Liq (100 mL)		500 W Xe/HP Hg	Formaldehyde (14), methanol (76)	[14]
CdS-montmorillonite	1 g/L	Saturated	0.2 mM NaOH		8 W Hg	Methane (0.93)	[47]
Cu-p-SiC	0.10	Saturated	0.5 M KHCO ₃	313	Hg (>275 nm)	Methane (0.63)	[48]
NiO(1.0 wt%)/InTaO ₄	0.14	Saturated	0.2 M KHCO3		500 W halogen	Methanol (1.4 ^a)	[49]
NiO(2.6 wt%)/InTaO ₄		Gas	Gas	303	300 W Xe	Acetaldehyde (0.21 ^a)	[50]
BiWO ₆	0.1	Saturated	1 mL		300 W Xe arc (>420 nm)	Methane (1.1)	[53]
BiVO ₄ , monoclinic	0.20	Saturated	100 mL	273	300 W Xe arc	Ethanol (2000 ^a)	[55]
BiVO ₄ , monoclinic	0.20	Saturated	100 mL	273	300 W Xe arc (>400 nm)	Ethanol (110 ^a)	[55]
InNbO ₄	0.14	Saturated	0.2 M KHCO3		500 W halogen	Methanol (1.3)	[51]
HNb ₃ O ₈	0.1	Gas (94 kPa)	Gas (7 kPa)	318	350 W Xe	Methane (3.6)	[52]
Pt-NaNbO3	0.1	Gas (80 kPa)	3 mL		300 W Xe arc	Methane (4.9)	[54]
Zn_2GeO_4	-	Gas	Gas		Light	Methane (0.41)	[57]
RuO ₂ -Zn ₂ GeO ₄	-	Gas	Gas		Light	Methane (1.9)	[57]
RuO ₂ -Pt-Zn ₂ GeO ₄	-	Gas	Gas		Light	Methane (6.5)	[57]
Cu-BaLa4Ti4O15 b	0.3	Saturated	360 mL		400 W HP Hg	CO (2)	[60]
Ag-BaLa ₄ Ti ₄ O ₁₅ ^b	0.3	Saturated	360 mL		400 W HP Hg	CO (14)	[60]
Ag-CaLa ₄ Ti ₄ O ₁₅ ^b	0.3	Saturated	360 mL		400 W HP Hg	CO (7.7), formic acid (4.3)	[60]
Ag-SrLa ₄ Ti ₄ O ₁₅ ^b	0.3	Saturated	360 mL		400 W HP Hg	CO (6.0), formic acid (1.7)	[60]
Ag-BaLa4Ti4O15 ^c	0.3	Saturated	360 mL		400 W HP Hg	CO (73), formic acid (2.3)	[60]
Ag-CaLa4Ti4O15 ^c	0.3	Saturated	360 mL		400 W HP Hg	CO (31)	[60]
Ag-SrLa ₄ Ti ₄ O ₁₅ ^c	0.3	Saturated	360 mL		400 W HP Hg	CO (24), formic acid (2.7)	[60]
[Re ^l (CO) ₃ (dcbpy)Cl]-Zr ₆ O ₄ (OH) ₄ (bpdc)	~0.02	Saturated	Acetonitrile (2 mL), TEA (0.1 mL)		450 W Xe (>300 nm)	CO (42)	[61]

^a Spectroscopic verification of reaction route, isotope tracing to identify the C source, or sufficient control kinetic tests to verify the photocatalytic event is required.

^b Cu or Ag was photodeposited during catalyst preparation.

^c Ag was reduced in liquid phase during catalyst preparation.

rule out the presence of carbon impurity intermediates derived from CTMA⁺ cations. In the FTIR spectrum for the as-prepared monoclinic BiVO₄, very weak peaks appear in the 3000–2900 cm⁻¹ region [55], which are likely due to the presence of C—H bonds derived from CTMA⁺ or PEG used during the catalyst preparation.

Delafossite $CuGa_{1-x}Fe_xO_2$ (x=0.15) was tested in an ambient pressure of CO_2 -saturated H_2O under a Xe arc lamp. The formation rate of the major product CO was reported to the 19% of the corresponding rate to form methane obtained with CdSe-Pt/TiO₂ under visible light [26,56], indicating the superiority of TiO₂-based photocatalysts.

Single crystalline Zn_2GeO_4 nanoribbons with a thickness as small as 7 nm, a width of 20–50 nm, and a length of hundreds of micrometers were applied in the photoreduction of CO_2 in the presence of water [57]. The band-gap value of the nanoribbons was estimated to 4.5 eV, and their specific surface area was $28 \text{ m}^2 \text{ g}^{-1}$. The methane formation rate (0.41 µmol h⁻¹ g_{cat}⁻¹) for 13–16 h under light using the Zn_2GeO_4 nanoribbons increased to $1.9 \,\mu\text{mol} \text{ h}^{-1} \text{ g}_{cat}^{-1}$ with the addition of 1 wt% RuO₂, and further to $6.5 \,\mu\text{mol} \text{ h}^{-1} \text{ g}_{cat}^{-1}$ with the further addition of 1 wt% Pt (Table 1C). The crystalline nanoribbons were suggested to suppress charge recombination and facilitate charge transport from the bulk to the surface-active sites. Zinc germanium oxynitride was prepared from Zn_2GeO₄ with ammonia at 1073 K [58]. The band gap increased to 2.70 eV, and the rate of CO₂ photoreduction to methane increased. The positive shift of the top of the valence band was considered to enhance water photooxidation and effectively supply the produced protons to the CO₂.

Layered-perovskite photocatalysts $A^{II}La_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) that have been reported for complete water splitting [59] were recently applied to the CO₂ photoreduction [60]. In a series of photocatalytic tests in CO₂-saturated water under a 400-W Hg lamp, CO was formed in a competitive reaction to produce H₂ and a minor amount of formic acid. The reactivity order to form CO was

Ag(2 wt%)-BaLa₄Ti₄O₁₅-LPR(73)

- $> \text{Ag}(1 \text{ wt\%})\text{-CaLa}_4\text{Ti}_4\text{O}_{15}\text{-LPR}(31)$
- $> Ag(1 wt\%)-SrLa_4Ti_4O_{15}-LPR(24)$
- $> Ag(1 wt\%)-BaLa_4Ti_4O_{15}-PD(14)$
- $> Ag(1 wt\%)-CaLa_4Ti_4O_{15}-PD(7.7)$
- $> Ag(1 wt\%)-SrLa_4Ti_4O_{15}-PD(6.0),$

where LPR and PD indicate Ag doping to photocatalysts by liquidphase reduction and photodeposition, respectively, and the values in the parentheses are the CO formation rates in the unit of μ mol h⁻¹ g_{cat}⁻¹ (Table 1C). The formation rates of the by-product formic acid were 4.3–1.0 μ mol h⁻¹ g_{cat}⁻¹. Silver nanoparticles of ${\sim}10\,\text{nm}$ on the edge sites of the layered BaLa_4Ti_4O_{15} were suggested to be favorable for the reduction of CO_2 to CO.

$$2H_2O + 4h^+$$
 (basal plane of BaLa₄Ti₄O₁₅) $\rightarrow 4H^+ + O_2$,

$$E^{\circ}(298\,\mathrm{K}) = +1.229\,\mathrm{V}$$

 $CO_2 + 2H^+ + 2e^-$ (Ag nanoparticles on the edge)

$$\rightarrow$$
 CO + H₂O, $E^{\circ}(298 \text{ K}) = -0.11 \text{ V}$

It was also discussed that the spatial separation of the oxidation and reduction sites suppressed the reverse reaction of CO to CO₂.

The chemistry of metal-organic frameworks (MOFs) has recently attracted attention owing to the freedom of element choice and the size of the micro/mesopore for realizing designed chemical functions, such as sorption and catalysis. The immobilization of homogeneous photocatalysts for the CO₂ photoreduction to an MOF [61] can be compared to the semiconductor-type photocatalysts in this review. Among the various homogeneous photocatalysts for the CO₂ photoreduction, including cobalt, nickel, iron, and rhenium complexes [6], Re^l(CO)₃(dcbpy)Cl (4.2 wt%; dcbpy=2,2'-bipyridine-5,5'-dicarboxylic acid) was incorporated to a $Zr_6O_4(OH)_4(bpdc)$ (bpdc = para-biphenyl-dicarboxylic acid) framework. When the catalyst was placed in CO2-saturated acetonitrile including triethylamine as a sacrificial electron donor under UV-visible light from a 450-W xenon lamp (>300 nm), the turnover number to CO was 10.9 in 20 h, corresponding to $42 \,\mu mol \, g_{cat}^{-1} \, h^{-1}$. The amount of catalyst includes both the Re complex and the MOF. After the 20-h reaction, 43.6% of the Re leached into the supernatant, indicating the detachment of the Re carbonyl species from the MOF.

When $\text{Re}^{1}(\text{CO})_{3}(\text{dcbpy})\text{Cl}$ was used as a homogeneous photocatalyst under similar conditions, the turnover number to CO was 3.5 (corresponding to 760 μ mol g_{cat}⁻¹ h⁻¹) in 6 h, but the catalyst deactivated after 6 h, even when triethylamine was added to the reaction system at 6 h. Control reactions were also reported in the absence of CO₂, in the dark, and in solvent labeled with isotopic CD₃CN, and the lack of formic acid/methanol formation was confirmed by proton nuclear magnetic resonance (¹H NMR) spectroscopy. These results strongly suggested the photocatalytic formation of CO, but recyclability tests indicated that catalyst deactivation occurred after two 6-h reaction runs [61].

If the scope of this review is widened to include photocatalysts that require a sacrificial electron donor in order to reduce the CO₂, colloidal ZnS [62,63] and CdS [64,65] nanoparticles should be considered. These catalysts formed formic acid and CO with high quantum yields when excited under UV–visible light [62,63,65] or visible light only (>400 nm) [64].

In summary, CdS, SiC, InNbO₄, HNb₃O₈, BiWO₆, promoted NaNbO₃, and promoted Zn₂GeO₄ produced methane or methanol with rates of 1–10 μ mol h⁻¹ g_{cat}⁻¹, and promoted A^{II}La₄Ti₄O₁₅ produced CO with a rate greater than 10 μ mol h⁻¹ g_{cat}⁻¹. The more negative conduction band energy for CdS, SiC, Nb, and Ta seems to be one of the key factors for effective CO₂ photoreduction [14,59,66]. A homogeneous Re complex supported on an MOF improved the life of the homogeneous photocatalyst.

3.7. Carbon-based photocatalysts

Small carbon nanoparticles of less than 10 nm can be covalently functionalized, e.g., with PEG, to give them strong absorption and emission properties in the visible light region. Gold was photoreduced onto functionalized C nanoparticles, and the photocatalytic conversion of CO_2 to formic acid in an aqueous solution was reported with a quantum yield of 0.3% based on ¹H NMR analysis [67], but detailed quantitative kinetic data were not shown in the paper. Semiconductor-like charge separation was suggested, and the advantage of the Au-functionalized C was claimed due to the aqueous solubility. Separately, efficient CO formation was reported using graphitic carbon nitride under visible light (>420 nm); however, it is essential to verify whether the CO was derived from CO₂, and not from the surface functional groups or the carbon nitride itself, before any further discussion is warranted [68].

A solvent-exfoliated graphene (SEG) dispersion, obtained via the ultrasonic treatment and centrifugation of natural graphite in *N*,*N*-dimethylformamide, was mixed with TiO₂ (P25) and ethyl cellulose to form films that were calcined at 673 K [69]. The rate of photoreduction of CO₂ to methane using the SEG (0.27 wt%)–TiO₂ (8.3 μ mol h⁻¹ m⁻²) was 4.5 times greater than that using TiO₂ (P25) under UV light. The less-defective SEG was a better photocatalytic promoter than reduced graphene oxide, demonstrating an electric diffusion effect, rather than the presence of reactive defect sites.

A disorder-engineered black TiO₂ photocatalyst prepared by hydrogenation at 473 K was reported to be effective for the water reduction reaction with the use of a sacrificial electron donor. A mid-gap electronic state resulting from the introduction of the structural disorder was assumed to change the powder color and shorten the band gap. The color was stable for more than a year [70]. Unfortunately, the black color was later reported to be due to the presence of ${\sim}0.6\,\mu\text{mol}$ of chromium contained per unit gram of the TiO₂ nanotubes, which originated from the passivating Cr oxide layer of the stainless steel autoclave [71]. The visible light response using metal-cation-doped TiO₂ photocatalysts has already been established as being due to the impurity energy level below the conduction band [36,72-74]. Although dark blue TiO₂ with structural disorder that was free from Cr was instantly oxidized back to white TiO₂ at room temperature in air, the application of TiO₂ with structural disorder to the CO₂ photoreduction is expected.

4. Photon energy conversion of CO₂ to fuels using hydrogen

4.1. Photocatalytic conversion of CO_2 to methane or CO using hydrogen

The reduction of CO₂ with hydrogen is thermodynamically favorable compared to the reduction with water $(\Delta G_{\rm r}^{\circ} = +689 \text{ kJ mol}^{-1}; \text{ Section 3.5})$ as follows.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g), \quad \Delta G_r^{\circ} = +2.9 \text{ kJ mol}^{-1}$$

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g), \quad \Delta G_r^{\circ} = -113.6 \text{ kJ mol}^{-1}$$

In this case, we assume that hydrogen is supplied via sustainable ways, e.g., photocatalytic water reduction utilizing sunlight [59,75,76].

The reduction of CO₂ to methane with H₂ gas was first reported using Ru/RuO_x/TiO₂ [77]. The initial formation rate of methane was 49 μ mol h⁻¹ g_{cat}⁻¹ at 319 K using light from a solar simulator with a total intensity of 80 mW cm⁻² (Table 2). The CO₂ conversion was believed to be due to thermal and UV light effects. However, a later report concluded that it was solely a thermal effect [78]. Comparable or slower methane formation to that reported in Ref. [77] was reproduced at 295 and 373 K in the dark. The enhancement of methane formation by light was completely suppressed by placing a 25-mm water filter on the 150-W xenon lamp. Even when the irradiation power was varied between 2 and 350 mW cm⁻², no change in the kinetic results was observed as long as the water filter was used.

The photoreduction of CO₂ using hydrogen as a reductant has also been reported to produce carbon monoxide using Rh/TiO₂ (5.1 μ mol h⁻¹ g_{cat}⁻¹) [79], ZrO₂ (0.56 μ mol h⁻¹ g_{cat}⁻¹) [80], and

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Reported CO³ photoreduction catalysts. reaction conditions, and the formation rates with hydrogen [and moist

Photocatalyst		Reactants (gas)		T (K)	Light source	Major product {formation rate $(\mu mol h^{-1} g_{cat}^{-1})$ }	Reference
Brand name	Amount (g)	CO ₂	H ₂ O H ₂				
Ru/RuO _x /TiO ₂	0.1	5.1 kPa	61 kPa	319	Solar simulator	Methane (49)	[77] ^a
Rh/TiO2	0.3	150 µmol	50 µmol		500 W HP Hg	CO (5.1)	[79]
ZrO ₂	0.3	150 µmol	50 µmol		500 W HP Hg	CO (0.56)	[80]
MgO	0.3	150 µmol	50 µmol		500 W HP Hg	CO (1.6)	[81]
β-Ga ₂ O ₃	1.0	150 µmol	50 µmol		200 W Hg-Xe	CO (0.76)	[82]
TiO2	0.25	5.6 kPa	5.6 kPa 100 kPa		UV (365 nm)	Methane (4.1)	[83]
ZrO ₂	0.25	5.6 kPa	106 kPa		UV (254 nm)	CO (0.62)	[83]
Ti-SBA-15 (0.05 wt% Ti)	0.05	38 μmol	76 µmol	313	120 W HP Hg	Methane (0.012), ethene	[31]
						(0.008), ethane (0.005)	
$[Zn_3Al(OH)_8]^+_2(CO_3)^{2-}.mH_2O$	0.10	2.3 kPa	22 kPa(1.7 mmol)	305-313	$500\mathrm{W}$ Xe arc (42 mW cm $^{-2}$)	CO (0.62), methanol (0.039)	[3]
		(0.18 mmol)					
$[Zn_{1.5}Cu_{1.5}Al(OH)_8]^+2(CO_3)^2mH_2O$	0.10	2.3 kPa	22 kPa	305-313	500 W Xe arc (42 mW cm ⁻²)	CO (0.37), methanol (0.13)	[3]
$[Zn_{1.5}Cu_{1.5}Al(OH)_8]^+_2(CO_3)^2 - mH_2O$	0.10	2.3 kPa	22 kPa	305-313	500 W Xe arc (106 mW cm ⁻²)	CO (0.58), methanol (0.20)	[3]
[Zn ₃ Ga(OH) ₈] ⁺ 2(CO ₃) ²⁻ mH ₂ O	0.10	2.3 kPa	22 kPa	305-313	500 W Xe arc (42 mW cm ⁻²)	CO (0.080), methanol (0.051)	[3]
$[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2(CO_3)^{2mH_2}O$	0.10	2.3 kPa	22 kPa	305-313	500 W Xe arc (42 mW cm ⁻²)	Methanol (0.17), CO (0.079)	[3]
[Zn ₃ Ga(OH) ₈] ⁺ 2[Cu(OH) ₄] ²⁻ ·mH ₂ O	0.10	2.3 kPa	22 kPa	305-313	500 W Xe arc (42 mW cm ⁻²)	Methanol (0.30), CO (0.13)	[4]
[Zn _{1.5} Cu _{1.5} Ga(OH) ₈] ⁺ 2[Cu(OH) ₄] ²⁻ · <i>m</i> H ₂ O	0.10	2.3 kPa	22 kPa	305-313	500 W Xe arc (42 mW cm ⁻²)	Methanol (0.49), CO (0.070)	[4]
Cu-ZnO	0.10	2.3 kPa	22 kPa	305-313	500 W Xe arc (42 mW cm ⁻²)	CO (0.030)	[3]
α -Ga ₂ O ₃	0.10	2.3 kPa	22 kPa	305-313	500 W Xe arc (42 mW cm ⁻²)	CO (0.047)	[3]
^a Sufficient control kinetic tests to deny the	e photocatalytic e	vent were reported	in Ref. [78].				

MgO (1.6 μ mol h⁻¹ g_{cat}⁻¹) [81] under CO₂ + H₂ (total 25 kPa) illuminated with a Hg lamp and β -Ga₂O₃ (0.76 μ mol h⁻¹ g_{cat}⁻¹) under CO₂ + H₂ (total 3.2 kPa) illuminated with a Hg–Xe lamp [82] (Table 2). When TiO₂ and ZrO₂ in CO₂ + H₂ + H₂O and CO₂ + H₂ were illuminated with UV light of 365 and 254 nm from a near-UV fluorescent black lamp, methane and CO were produced at rates of 4.1 μ mol h⁻¹ g_{cat}⁻¹ and 0.62 μ mol h⁻¹ g_{cat}⁻¹, respectively [83].

In summary, rhodium was an effective additive, but only simple metal (Ti, Zr, Mg, and Ga) oxide semiconductors photoreduced CO₂ with molecular H₂ at a rate of ~1 μ mol h⁻¹ g_{cat}⁻¹.

4.2. Photocatalytic conversion of CO_2 to methanol using hydrogen

Layered-double hydroxide (LDH) compounds are a family of clays, but their layers are positively charged in contrast to more general clays, in which the layers are negatively charged, e.g., the smectite and vermiculite families [3,84–86]. LDHs are materials based on the layered structure of brucite (Mg(OH)₂), which has a hexagonal crystal structure in which the MgO₆ octahedra are linked at the edge to form sheets. One of the naturally occurring LDH compounds is hydrotalcite. The charge of cationic sheets formulated as [$M^{II}_{1-x}M^{III}_{x}(OH)_{2}$]^{x+} is compensated with an intercalated anion group, e.g., CO_{3}^{2-} , SO_{4}^{2-} , NO_{3}^{-} , CI^{-} , or OH^{-} . The M^{II} site can be Mg, Mn, Fe, Co, Ni, Cu, or Zn, and the M^{III} site can be Al, Cr, Mn, Fe, or Ga. The value of the variable *x* is normally within the range 0.17–0.33. The molar amount of structural water intercalated between the cationic layers is about half of the total molar amount of metal cations.

LDH compounds have already been applied to photocatalytic water oxidation [87,88]. $Zn_4Ti^{IV}_x$, $Zn_4Ce^{III}_x$, and $Zn_4Cr^{III}_x$ (0.25 < *x* < 2) LDH compounds exhibited good quantum yields for photocatalytic water oxidation in the presence of silver nitrate as a sacrificial oxidizing reagent under visible light (>400 nm) [87]. The LDH compound [$Zn_{0.69}Cr^{III}_{0.31}(OH)_2$]^{0.31+}0.31NO₃⁻⁻0.6H₂O and the nanohybrid material Zn—Cr LDH and layered titanate were also effective for photocatalytic water oxidation in the presence of 0.01 M AgNO₃ as a sacrificial oxidizing reagent under visible light (>420 nm) [88].

Ordered LDHs consisting of zinc and/or copper hydroxides combined with aluminum have been reported to be good photocatalysts for the conversion of gaseous CO₂ to methanol or CO under UV–visible light using hydrogen [3]. The LDH compound $[Zn_3Al^{III}(OH)_8]^+_2(CO_3)^{2-}\cdot mH_2O$ (band gap: 5.7 eV) was the most active for the CO₂ photoreduction, and the major product was CO, which formed at a rate of 0.62 µmol h⁻¹ g_{cat}⁻¹, along with minor amounts of methanol (Table 2). The methanol selectivity (5.9 mol%) modestly increased to 26%, but the total photoactivity decreased, when Cu sites were introduced in the LDH, i.e., $[Zn_{1.5}Cu_{1.5}Al(OH)_8]^+_2(CO_3)^{2-}\cdot mH_2O$ (band gap: 4.1 eV). The CO₂ conversion was 0.16–0.11% using $[Zn_{3-x}Cu_xAl(OH)_8]^+_2(CO_3)^{2-}\cdot mH_2O$ ($0 \le x \le 1.5$) photocatalysts.

Ordered LDHs consisting of zinc and/or copper hydroxides combined with gallium were synthesized, and the methanol formation rate and selectivity using $[Zn_{1.5}Cu_{1.5}Ga^{III}(OH)_8]^+_2(CO_3)^{2-} \cdot mH_2O$ LDH (band gap: 3.5 eV) were 0.17 µmol h⁻¹ g_{cat}⁻¹ and 68 mol%, respectively. The CO₂ conversion was 0.03–0.02% using $[Zn_{3-x}Cu_xGa(OH)_8]^+_2(CO_3)^{2-} \cdot mH_2O$ ($0 \le x \le 1.5$) photocatalysts. The specific interaction of the Cu sites with CO₂ was spectroscopically suggested (based on XANES analysis) to enable coupling with protons and photogenerated electrons to form the methanol. The participation of Cu sites in the redox process in the CO₂ photoreduction was also suggested [5].

The rate of photoconversion of CO₂ to methanol was improved to $0.49 \,\mu\text{mol}\,h^{-1}\,g_{cat}^{-1}$ by replacing the interlayer carbonate anions of $[\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}(\text{OH})_8]^+_2(\text{CO}_3)^{2-}\cdot\text{mH}_2\text{O}$ with $[\text{Cu}(\text{OH})_4]^{2-}$,

and the methanol selectivity increased to 88 mol% [4]. The band-gap value of the improved LDH catalyst was 3.0 eV. A direct electronic transition from the O 2p to the metal 3d, 4s, or 4p was suggested for the photocatalysis excited largely by UV.

No chemicals containing carbon atoms were used of the LDH throughout the synthesis compounds $[Zn_{3-x}Cu_{x}A(OH)_{8}]^{+}_{2}X^{2-} \cdot mH_{2}O$ (A = Al, Ga; X = CO₃, Cu(OH)₄; $0 \le x \le 1.5$) except for sodium carbonate, or during the pretreatment prior to the catalytic tests. After the synthesis of the LDH, the powder was thoroughly washed using deionized water $(<1.0 \,\mu\text{S}\,\text{cm}^{-1})$ before drying. The sodium carbonate was the source of the interlayer anions, and the products produced in the reaction were essentially identical with the species derived from the photoconversion of gas-phase CO₂. Furthermore, no products were detected when the $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2(CO_3)^{2-} mH_2O$ compound was suspended in deionized water under UV-visible light for 5 h [3]. Thus, the possibility [38,39] that carbon impurities that accumulated during the LDH catalyst preparation and/or activation before the kinetic tests were conducted was converted rather than CO₂ is not plausible in Refs. [3,4].

possibility However, the of a thermal reaction should also be seriously considered [77,78]. The inprocess spectra for $[Zn_3Ga(OH)_8]^+_2(CO_3)^{2-} mH_2O$ and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2(CO_3)^{2-} mH_2O$ during the photoreaction in $CO_2 + H_2$ were reported (Fig. 6). The formation of both CO and methanol reached a maximum at a wavelength of 400 nm both for $[Zn_3Ga(OH)_8]^+_2(CO_3)^{2-} mH_2O$ and $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2(CO_3)^{2-} mH_2O$ (Fig. 6, inset).

This trend is in clear contrast to methane formation using Ru/RuO_x/TiO₂. At fixed temperature (319K) in CO₂+H₂, the methane formation rate increased by 2.8 times when the reaction mixture was irradiated with light from a solar simulator [77], but a second study found that the light effect was due to an increase in the temperature from 298 to 314 K and suggested the temperature control in Ref. [77] was not exact. When a water filter was inserted between the catalyst and a 150-W xenon lamp, no effect of the light was observed [78]. In contrast, when a water filter was inserted for the [Zn_{1.5}Cu_{1.5}Al(OH)₈]⁺₂(CO₃)^{2–}·mH₂O catalyst (Fig. 7B), the methanol and CO formation rates increased (Table 2) owing to an increase in the UV + visible light intensity from 42 mW cm⁻²



Fig. 6. Dependence of the formation rates of methanol and CO on the cutoff wavelength for photoreactions in CO₂ (2.3 kPa)+H₂ (22 kPa) using 0.10g of $[Zn_3Ga(OH)_8]^+_2(CO_3)^{2-}.mH_2O$ or $[Zn_{1.5}Cu_{1.5}Ga(OH)_8]^+_2(CO_3)^{2-}.mH_2O$. Sharp cutoff filters UV-32, L-37, L-42, or Y-48 were used at the exit of the Xe arc lamp. (Inset) In-process spectrum of product formation rates versus wavelength [3].

(Fig. 7A) to 106 mW cm⁻² (Fig. 7B). The maximum temperature during these photocatalytic reactions was 313 K, but a control reaction using $[Zn_{1.5}Cu_{1.5}Al(OH)_8]^+_2(CO_3)^{2-} \cdot mH_2O$ in the dark at 296–313 K [3,89] under CO₂ + H₂ exhibited no conversion above the detection limit of the GC. Thus, the catalysis using LDH compounds under CO₂ + H₂ proceeded photocatalytically.

In summary, using LDH photocatalysts consisting of Zn, Cu, Al, and Ga, both CO and methanol were formed at rates of $0.1-1 \,\mu$ mol h⁻¹ g_{cat}⁻¹.

5. Photon energy conversion of $\mbox{\rm CO}_2$ to fuels using a new reaction system

5.1. Recycling of sacrificial electron donors

The regeneration of a sacrificial electron donor in the photoreduction of CO_2 was reported [8,90] to make the overall catalytic reaction system cyclic. The tricyclic tertiary amine 10-*endo-anti*-11-aza-10-methoxy-11-methyltricyclo [4.3.1.1^{2,5}] undecane was



Fig. 7. Quartz photocatalytic reactor illuminated using a Xe arc lamp Model UI-502Q, Ushio (a) and Model SX-UID502XAM, Ushio (b) used in Refs. [3,4].

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Fig. 8. Recyclable photocatalytic CO₂ reduction to formic acid using a sacrificial electron donor amine that can be regenerated by hydrogenation using a Pd catalyst. Reprinted by permission from Macmillan Publishers Ltd: Michl [8]. Copyright (2011).

selected as the sacrificial electron donor (Fig. 8). An electron, a proton, and a hydrogen atom were donated by the amine, and the CO₂ was converted to formic acid using a *p*-terphenyl photocatalyst under irradiation from a Hg lamp at 254 nm. The amine was transformed to the stable alkene 10-*endo-anti*-11-aza-10-methoxy-11-methyltricyclo [$4.3.1.1^{2,5}$] undec-7-ene. The alkene was successfully hydrogenated back to the original alkane using a Pd/C catalyst. In Ref. [90], the hydrogen was assumed to be generated from the photosplitting of water, similar to the photocatalytic CO₂ reduction using H₂ in Refs. [3,4].

5.2. Photoconversion of CO_2 to fuels utilizing anode oxidation and cathode reduction compartments

Various photocatalysts for the photooxidation of water have been reported [59,75,91,92]. The idea of an artificial dark reaction following water photooxidation was also proposed [7,9,93].

In 2006, a solar fuel cell was proposed on the basis of the concept of a polymer electrolyte fuel cell (PEFC) and a phosphoric acid fuel cell consisting of an electrolyte for the transfer of protons from the anode side to the cathode side. A solar photovoltaic assembly was proposed to separate the holes and electrons, an anode catalyst to oxidize water using the holes, and a cathode catalyst to reduce the protons to hydrogen using the electrons (Fig. 9). In photosynthesis, protons are reduced by Photosystem I to hydrogen equivalents. In other words, electrons are stored through the conversion of NADP to NADPH. Thus, if the photon conversion device is based on a single-bandgap absorber consisting of a semiconductor, the theoretical thermodynamic conversion efficiency is 32% in unconcentrated sunlight [9].

A dye-sensitized solar cell utilizing a polymer membrane and a manganese catalyst was proposed in 2009 [93]. Inspired by Photosystem II, in which a cube-shaped Ca—Mn oxide catalyst oxidizes water to O_2 , protons, and electrons, the synthetic model Mn oxide cluster complex Mn_4O_4 was incorporated into a proton-conducting membrane, e.g., Nafion. The complex and an H⁺-conducting membrane were integrated into a solar cell (Fig. 10). An organic ruthenium dye captured sunlight, and the excited electrons were injected into the neighboring TiO₂ nanoparticles. The manganese catalyst also captured sunlight and oxidized water. The grabbed



Fig. 9. Concept of a fuel cell supplied with hydrogen and oxygen (or air) that converts chemical energy to electricity. The solar fuel cell uses light to separate holes and electrons that oxidize water and reduce protons, respectively.

Source: Lewis and Nocera [9]. Copyright (2007) National Academy of Sciences, USA.

electrons from the water were passed from the Mn catalyst to the dye molecules. The electrons were transmitted to the cathode via an external circuit, while the protons transmitted through the H^+ -conducting membrane were reduced to H_2 on the cathode catalyst with the electrons. A solar cell (or solar fuel cell using water as the fuel) integrating an H^+ -conducting membrane and an iridium oxide catalyst was also reported.

The concept of the combined photocatalytic reduction of CO_2 was also proposed in 2010 [7]. In this system, a water oxidation catalyst releases protons and electrons, followed by competitive reduction reactions of the protons to form H_2 and react with CO_2 to form fuel(s) (Fig. 11). If good ligands are chosen for the homogeneous water oxidation catalyst complexes, O_2 molecule formation is synchronized with the removal of the H⁺ and the electrons. However, the drawback of rapid deactivation often exists because of the decomposition of the finely tuned ligands, e.g., heterocyclic organic compounds. Heterogeneous catalysts for water oxidation may be more stable and self-reparable.

The feasibility of using methanol oxidation as a source of H₂ in a PEFC [94] was also investigated. The fuel cell catalysts consisted of a TiO₂ photocatalyst for the oxidation of methanol to CO₂ and a Pt catalyst to reduce the protons to H₂. The two catalysts were separated by an H⁺-conducting polymer (Fig. 12). The amount of TiO₂ was optimized to 3.0 mg cm⁻² on carbon paper, and the Pt–C at 0.2 mg cm⁻² on C paper, depending on the catalytic rate of each. Under UV–visible light illumination (100 mW cm⁻²) using a Cu sulfate filter for the anode (TiO₂) in a 1 M methanol solution, 0.1 M H₂SO₄ as the electrolyte, and (Pt–C) as the cathode in a



Fig. 10. Dye-sensitized solar cell utilizing a polymer membrane and a manganese catalyst [93].

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Fig. 11. Combination of water oxidation catalyst and the reduction of protons to H₂ or CO₂ to fuels. The reduction is promoted as a result of charge separation under light irradiation. The reduction catalyst might be assembled on an electrode, a suspension of nanoparticles, or conducting organic or inorganic membranes capable of directing charge transport.

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Fig. 12. Feasibility test of a fuel cell consisting of a TiO₂ photocatalyst for methanol oxidation, a Pt catalyst for the production of H₂, and an H⁺-conducting polymer between them.

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0.1 M H₂SO₄ solution, a short circuit current of 0.34 mA cm⁻² was obtained. Under similar reaction conditions, hydrogen was produced at a rate of $3.5 \,\mu mol \, h^{-1} \, cm^{-2}$ (1.2 mmol $h^{-1} \, g_{TiO2}^{-1}$). The photocatalytic reaction at the anode was proposed to proceed as follows.

$$TiO_2 \xrightarrow{hv} h^+ + e^-$$

 $CH_3OH + h^+ \rightarrow {}^{\bullet}CH_3O + H^+$

 ${}^{\bullet}CH_{3}O \,+\, H_{2}O \,\rightarrow\, CO_{2} + 5H^{+} + 5e^{-}$

 $2H^+ + 2e^- \rightarrow \ H_2$

In total, hydrogen was produced by the photocatalytic decomposition of methanol, and a stoichiometric electric current was obtained for the overall reaction: $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$. This study described the reverse reaction of the photocatalytic

Fig. 13. Proposed reaction mechanism using a PEFC starting from H₂ and CO₂ (a) and from H₂O and CO₂ (b) [100].

conversion of CO₂, but also utilized a Pt electrocatalyst to reduce protons to H₂ using a PEFC.

It is well known that plants and cyanobacteria use the reducing power generated by light-driven water oxidation in Photosystem II to produce NADPH by reducing the protons in Photosystem I [95].

 $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (Photosystem II), $E^{\circ}(pH7) = +0.815V$

 $NADP^+ + H^+ + 2e^-$

 \rightarrow NADPH(Photosystem I), $E^{\circ}(pH7) = -0.320V$

The weak reductant formed by light energy in Photosystem II reduces the weak oxidant formed by different light energy in Photosystem I. This linked mechanistic model is called the Z-scheme. In 1982, artificial H₂ formation starting from water was reported using a photodiode consisting of a Mg-doped p-type iron oxide and a Si-doped n-type iron oxide [96]. Using the combination of Pt-WO₃ for water oxidation and Pt-SrTiO₃ for water reduction, the stoichiometric H_2 and O_2 photocatalytic formation from water was also reported by applying the Z-scheme [97]. Furthermore, the separation of a TiO₂ catalyst for water oxidation and a Pt-TiO₂ catalyst for proton reduction by Nafion was reported to separately form O₂ and H_2 gas [98].

The concept of the Z-scheme was also applied to the photoreduction of CO₂ using semiconductor catalysts for the water oxidation and homogeneous metal complex catalysts for the CO₂ reduction. These studies have been previously reviewed as an extension of homogeneous photocatalysts of the photoreduction of CO₂ [99].

The direct transfer of protons and electrons released from water oxidation catalysts to photocatalysts for the reduction of CO₂ must be advantageous for achieving efficient rates for the photoconversion of CO₂ to fuels. A Pt–C catalyst and an LDH photocatalyst $[Zn_{1.5}Cu_{1.5}Ga^{III}(OH)_8]^+_2(CO_3)^{2-} \cdot mH_2O$ (see Section 4.2) were directly attached to a 50-µm-thick proton-conducting membrane. The CO₂ and water, supplied separately to each catalyst in the PEFC cell (Fig. 13B), were converted to methanol at a rate of 5.1 $\mu mol\,h^{-1}\,g_{cat(LDH)}{}^{-1}.$ It has also been found that heating at 413 K makes the membranes used in Refs. [4,100] more H⁺-conductive. The development of a total photocatalytic system consisting of WO3 and Zn-Cu-Ga LDH photocatalysts for the direct transfer of protons and electrons is underway [100].

6. Concluding remarks

The dramatic growth of renewable solar energy is needed. The initial investigation of the renewable energy options utilizing the thermochemical and photocatalytic conversion of CO₂ to fuels has been reviewed. Semiconductor photocatalysts are advantageous if they are cheap and sustainable. Starting from CO₂ and water, TiO₂ photocatalytically produced methane at a rate of ${\sim}0.1\,\mu\text{mol}\,h^{-1}\,g_{cat}{}^{-1}.$ When TiO_2 was atomically dispersed in Y-zeolite, MCM-48, or SBA-15, or doped TiO₂ was used, the rate of methane or CO formation increased to $1-10 \,\mu\text{mol}\,h^{-1}\,g_{cat}^{-1}$. CdS, SiC, InNbO₄, HNb₃O₈, Bi₂WO₆, Pt-NaNbO₃, and RuO₂-Pt-Zn₂GeO₄ produced methane or methanol at rates greater than $1 \,\mu mol \,h^{-1} \,g_{cat}{}^{-1}$, and Ag-BaLa₄Ti₄O₁₅ produced CO at a rate of $73 \,\mu mol \, h^{-1} \, g_{cat}^{-1}$.

The photocatalytic reduction of CO₂ with molecular hydrogen was also surveyed. CO was formed at a rate of $\sim 1 \,\mu$ mol h⁻¹ g_{cat}⁻¹ using TiO₂, ZrO₂, MgO, and Ga₂O₃, while CO and methanol were formed at rates of 0.62 μ mol h⁻¹ g_{cat}⁻¹ and 0.49 μ mol h⁻¹ g_{cat}⁻¹, respectively, using LDHs consisting of Zn, Cu, Al, and Ga.

Spectroscopic monitoring using ESR, EXAFS, XANES, photoluminescence, diffuse reflectance UV-visible, FTIR, and NMR techniques, and isotope monitoring using GC-MS and electron microscopy are essential for the verification of photocatalytic events and the source of C used to produce the fuels. The reaction mechanism of photocatalysis is still not well understood; e.g., the preferable formation of methane from $CO_2 + H_2O$ using TiO₂ has not been explained. It should be more complex than the consecutive reduction from CO₂ to formic acid (or CO), the formyl group, formaldehyde, methoxy, methanol, and then methane [3] based on recent reports using ESR, which suggest formyl dimerization to glyoxal (OHC-CHO) as an intermediate of an efficient electron acceptor [101]. Theoretical understanding based on the comparison between band energy and the red-ox potential is in progress, but not enough to explain the product selectivity using TiO₂ [102].

Further efficiency improvements for the CO₂ conversion are highly expected by the combination of different photocatalysts (Section 4) and the use of new reaction systems (Section 5). In particular, the combination of water photosplitting to form hydrogen (or protons and electrons) and CO₂ photoreduction with the formed hydrogen (or the formed protons and electrons) can potentially boost the efficiency of CO₂ conversion.

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