1. Introduction

1.1. Research Background

Since the first industrial revolution in the 18th century, human society has relied on fossil fuels such as coal, petroleum, and natural gas, all of which are limited resources that have accumulated inside the Earth. This reliance on fossil fuels has resulted in serious concerns worldwide regarding potential energy shortages. In addition, it is the general consensus of the scientific community that anthropogenic CO₂ emissions are the major cause of climate change, which may be related to recent extreme weather events. As a result, there is currently a search for clean, renewable, inexpensive, and practical alternatives to fossil fuels. Among the various methods and reaction schemes proposed, heterogeneous photocatalysis driven by sunlight is one of the most promising means of clean energy production because of its potential scalability and environmentally benign nature.⁴

Consequently, extensive efforts have been made to develop efficient photocatalysts for water splitting driven by visible light, the main component of the solar spectrum, over the past four decades.⁵ Some such studies have achieved solar-to-hydrogen energy conversion efficiencies of greater than 1%.⁶

In contrast to these significant advances in photocatalytic water splitting, heterogeneous photocatalysts for CO₂ fixation are still in the developmental stage. Nevertheless, the photocatalytic conversion of CO₂ into energy-rich chemicals using water as the electron source is very attractive from the viewpoints of both renewable energy production and CO₂ capture. The production of carbon feedstocks from CO₂ and water driven by light can be regarded as a sort of artificial photosynthetic process, and it is important to research such systems.

1.2. Key Features of Semiconductor Photocatalysis and CO₂ Reduction

Figure 1A shows the basic principle of a photocatalytic reaction on an illuminated semiconductor. In this process, the bandgap photoexcitation of the semiconductor generates electrons and holes in the conduction and valence bands, respectively. These photogenerated charge carriers are subsequently able to participate in surface redox reactions if the conduction band minimum (CBM) and the valence band maximum (VBM) of the material straddle the redox potentials of such reactions. The CBM and VBM potentials therefore determine the reactivity of photogenerated electrons and holes, and are thus very important parameters in semiconductor photocatalysis, as discussed herein. In the case of artificial photosynthetic reactions, including water splitting and CO₂ fixation, both thermodynamic and kinetic factors (e.g., photogenerated-charge-carrier dynamics and surface catalysis) must be carefully considered when designing a photocatalytic reaction that will proceed at a suitable rate (see Figure 1B). A highly crystalline semiconductor typically exhibits higher photocatalytic activity because the lifetimes of the photogenerated charge carriers are increased in such materials.⁷ In addition, cocatalysts consisting of metal or metal oxide nanoparticles (or molecular compounds) are often applied to the surfaces of semiconductor photocatalysts to enhance the charge-separation efficiency.
and/or surface chemical reactions during photocatalytic water splitting.

There are several challenges associated with the development of efficient heterogeneous photocatalysts for CO$_2$ reduction. The major obstacle is the fact that, because CO$_2$ is a very stable molecule, the reduction of CO$_2$ requires a high electrochemical potential [$E^° = -1.9$ V vs normal hydrogen electrode (NHE) at pH = 7, see Equation (1)]

$$\text{CO}_2 + e^- \rightarrow \text{CO}^-$ \hspace{1cm} (E° = -1.9 V) \hspace{1cm} (1)$$

Besides, the high reactivity of the one-electron-reduction product (CO$_2^-$) makes it difficult to control the product selectivity. Utilization of a multielectron process in conjunction with proton-coupled electron transfer significantly lowers the potential required for CO$_2$ reduction, and gives a variety of products that depend on the number of electrons involved. The potential reactions are summarized below

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH} \hspace{1cm} (E° = -0.61 \text{ V}) \hspace{1cm} (2)$$
$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2 \hspace{1cm} (E° = -0.53 \text{ V}) \hspace{1cm} (3)$$
$$\text{CO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{HCHO} + \text{H}_2 \hspace{1cm} (E° = -0.48 \text{ V}) \hspace{1cm} (4)$$
$$\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2 \hspace{1cm} (E° = -0.38 \text{ V}) \hspace{1cm} (5)$$
$$\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2 \hspace{1cm} (E° = -0.24 \text{ V}) \hspace{1cm} (6)$$

The two-electron-reduction products, HCOOH (formate) and CO, are both useful compounds. HCOOH has recently gained attention as a hydrogen carrier, because it is transportable and can be readily decomposed to H$_2$ and CO$_2$ in the presence of a suitable catalyst, even under mild conditions.$^{[15–17]}$ CO is an important raw material in the chemical industry, such as in the well-known Fischer–Tropsch process for the synthesis of hydrocarbon fuels.

The multielectron reduction of CO$_2$ is thus promising, but in turn requires a suitable catalyst (or cocatalyst) that selectively promotes a desired reaction while suppressing others. Numerous efforts have been made over the past several decades to develop photocatalytic systems that can induce multielectron CO$_2$ reduction. However, satisfactory results have not yet been obtained. A suitable photocatalytic CO$_2$-reduction system has to function in response to irradiation by visible and near-infrared light, because these comprise the majority of the sunlight spectrum. In addition, side reactions such as proton reduction to H$_2$ (see Equation (7)) should in principle be suppressed

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \hspace{1cm} (E° = -0.41 \text{ V}) \hspace{1cm} (7)$$

Finally, a weak electron donor (ideally water) must be present to construct a light-energy conversion scheme in which the change in the standard Gibbs energy is positive ($\Delta G^° > 0$). Because the potential associated with the water-oxidation reaction (see Equation (8)) is +0.82 V at pH 7, the minimum photon energy required to drive photocatalytic CO$_2$ reduction on a thermodynamic basis (to generate HCOOH, for example) and to oxidize water is 1.43 eV, which corresponds to a wavelength of $\approx 870$ nm.
O_2 + 4H^+ + 4e^- → 2H_2O \quad (E^\circ = +0.82 \text{ V}) \quad (8)

Therefore, the entire spectral range of visible light (400 < λ < 800 nm) can theoretically be utilized. However, a photon energy greater than the bandgap of the photocatalyst is usually required to drive the overall reaction at a reasonable rate.

Metal complexes and semiconductors are both promising photocatalysts toward CO_2 reduction to formate, CO, or various hydrocarbons. However, both these materials have strengths and weaknesses, and, to date, none have exhibited completely satisfactory performance. In the following sections, some representative examples of photocatalytic CO_2 reduction using metal complexes and semiconductors are introduced.

1.3. Metal-Complex Photocatalysts

Metal complexes can be designed on the molecular scale, which allows precise control of functionality, including photo-physical, electrochemical, and catalytic properties.\(^ {18–21}\) Lehn and co-workers reported the first demonstration of selective CO_2 reduction to CO using Re(I) complexes \([\text{fac-Re(bpy)(CO)Cl}_2]\) in a mixture of N,N-dimethylformamide (DMF) and triethanolamine (TEOA) under UV irradiation.\(^ {22–24}\) These metal-complex photocatalysts enabled efficient conversion of CO_2 to CO, partly due to the selective coordination of CO_2 molecules to the metal centers of the complexes.\(^ {25}\) Since that first report, metal complexes (in particular Ru(II) and Re(I) complexes) have been widely examined as photocatalysts from the excited state of the Ru unit, and also much more rapid than the reductive quenching of the excited Ru photosensitizer by an electron donor (such as BNAH or BIH).\(^ {30}\) This efficient intramolecular electron transfer explains the high performance of such supramolecular photocatalysts. A recent study also demonstrated that the Ru(II)–Re(I) supramolecular photocatalyst is capable of reducing CO_2 to CO with high selectivity, even in an aqueous solution that contains a suitable electron donor, providing a 13% quantum yield and a TON\(_{CO_2}\) of 130.\(^ {31}\)

One sophisticated approach to overcoming these issues is the use of molecular design to connect the photosensitizer and catalyst via a bridging ligand, producing a supramolecular metal complex that contains both units in one molecule (Figure 2B).\(^ {27}\) Supramolecular photocatalysts such as Ru(II)–Re(I) and Ru(II)–Ru(II) binuclear complexes have been shown to work efficiently with high selectivity to CO or formate in the presence of a sacrificial electron donor such as 1-benzyl-1,4-dihydroxytriphenylamine (BNAH) or 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH), and such systems are functional even under visible light.\(^ {28,29}\) Time-resolved infrared (TR-IR) spectroscopy has demonstrated that intramolecular electron transfer from the one-electron-reduced species of the Ru photosensitizer unit to the Re catalyst unit in this type of Ru(II)–Re(I) supramolecular photocatalyst is much faster \((\kappa_{ET} \approx 10^{-7}–10^{-6} \text{ s}^{-1})\) than that from the excited state of the Ru unit, and also much more rapid than the reductive quenching of the excited Ru photosensitizer by an electron donor (such as BNAH or BIH).\(^ {30}\) This efficient intramolecular electron transfer explains the high performance of such supramolecular photocatalysts. A recent study also demonstrated that the Ru(II)–Re(I) supramolecular photocatalyst is capable of reducing CO_2 to CO with high selectivity, even in an aqueous solution that contains a suitable electron donor, providing a 13% quantum yield and a TON\(_{CO_2}\) of 130.\(^ {31}\)

Unfortunately, the intrinsic photo-oxidation abilities of supramolecular photocatalysts and organic photosensitizers are generally low, so a strong electron donor such as BNAH or BIH is required to promote the photocatalytic CO_2-reduction reaction. However, as noted in Section 1.2, it is preferable to use water (a weak electron donor) because the goal of photocatalytic CO_2 reduction is to efficiently convert solar energy into useful carbon feedstocks.

1.4. Semiconductor Photocatalysts

Semiconductors have also been popular as photocatalysts that enable a wide variety of redox reactions, including CO_2...
CO$_2$ reduction, since the first demonstration of a rutile-TiO$_2$-based photoelectrochemical cell for water splitting in the 1970s by Honda and Fujishima.[13] Overall, semiconductors offer superior photo-oxidation activity, stability and recyclability relative to metal complexes. Following modification with nanoparticulate cocatalysts, certain semiconductor photocatalysts optimize overall water splitting even under visible light.[7,10] As an example, a solid solution of GaN and ZnO modified with an H$_2$ evolution cocatalyst is capable of splitting pure water stoichiometrically into H$_2$ and O$_2$ without any sacrificial reagent under visible light.[11,34]

CO$_2$ reduction combined with water oxidation has also been accomplished using several metal oxide semiconductors.[35–37] In one study, BaLa$_4$Ti$_4$O$_{15}$ photocatalyzed CO$_2$ reduction to CO with water as the electron donor under UV irradiation ($\lambda > 200$ nm) when modified with Ag nanoparticles as the CO$_2$-reduction cocatalyst.[35] In this case, the reduction products were CO, formate, and H$_2$, with a CO$_2$-reduction selectivity of $\approx$40%. The total amount of these products was consistent with that of the oxidation product (O$_2$), with an electron/hole ratio of unity. Highly selective CO$_2$ to CO conversion was also reported using Ag-loaded ZnGa$_2$O$_4$ and CaTiO$_3$.[36,37] In these metal oxide photocatalyst systems, the presence of the Ag cocatalyst was found to be indispensable for obtaining high photocatalytic CO$_2$-reduction activity and selectivity, because Ag functions as a good CO$_2$-reduction electrocatalyst, with a relatively large overpotential for proton reduction.[38] Unfortunately, the majority of metal oxide photocatalysts work only under UV irradiation (at wavelengths shorter than 400 nm) due to their larger bandgaps ($E_g > 3$ eV).

Recently, the use of two different semiconductors—p-type metal sulfides and CoO$_x$-loaded BiVO$_4$ working as reduction and oxidation photocatalysts, respectively—enabled CO$_2$ reduction to CO under visible light with water as the electron donor.[39] This system functioned based on the two-step photoexcitation of the two semiconductors (representing a so-called Z-scheme[4,6,10]), and allowed the efficient utilization of visible light. The primary drawback currently associated with visible-light Z-scheme CO$_2$ reduction is the low selectivity of these processes ($\approx$1%) because of the competition by proton reduction to give H$_2$.

1.5. Metal-Complex/Semiconductor Hybrid Photocatalysts

Considering the strengths and weaknesses of metal complexes and semiconductors as components of photocatalytic CO$_2$-reduction systems, it seems likely that a hybrid system comprising a metal complex and a semiconductor as the respective reduction and oxidation centers could work as an efficient visible-light photocatalyst for CO$_2$ reduction, using water as the electron source, with high selectivity. The performance of such metal-complex/semiconductor hybrid systems in aqueous environments could potentially be improved by anchoring water-insoluble metal-complex (photo)catalysts to solid surfaces to prevent undesirable aggregation. One of the best-known examples of a metal-complex/semiconductor hybrid intended for photochemical application is the dye-sensitized solar cell.[40] These devices have also been extended to photoinduced water splitting in recent years.[5,11,41] In contrast to dye-sensitized systems in which electron injection occurs from the excited state of the adsorbed photosensitizer to the conduction band of the semiconductor, electron transfer in these hybrid CO$_2$-reduction systems proceeds in the opposite direction. The excited dye-to-semiconductor electron-transfer process has been studied extensively, including by spectroscopy. However, research regarding electron transfer in the opposite direction has been very rare,[42] even though this mechanism is of interest from a scientific point of view.

Here, the focus is on published literature regarding metal-complex/semiconductor hybrid photocatalysts for CO$_2$ reduction. As discussed in detail below, proof-of-concept evidence for CO$_2$ reduction by metal-complex/semiconductor hybrid photocatalysts was first demonstrated in 2010. Since then, significant progress has been made in this research field. Because there have already been many review articles that deal with specific aspects of CO$_2$ photoreduction,[19–21,27,43–50] here, the development of metal-complex/semiconductor hybrid photocatalysts for CO$_2$ reduction is the main focus. In addition, hybrid photoelectrodes are addressed, with the aim of providing the first thorough review of metal-complex/semiconductor hybrid photosystems for visible-light CO$_2$ reduction.

Figure 3 summarizes the metal-complex/semiconductor hybrid systems for visible-light-driven photocatalytic and photoelectrochemical CO$_2$ reduction that have been established to date. The first system (Figure 3A) consists of a mononuclear metal-complex catalyst and a visible-light-absorbing semiconductor. The working mechanism for this type of hybrid photocatalyst can be explained based on a combination of semiconductor photocatalysis and catalysis by a metal complex. In such cases, the semiconductor works as a light absorber and hosts oxidation sites, while the adsorbed metal complex serves to provide active sites for CO$_2$ reduction. In the second system (Figure 3B), the key feature is the use of a supramolecular metal-complex photocatalyst. By combining this supramolecular photocatalyst with a suitable semiconductor photocatalyst that can absorb visible light, it is possible to obtain an artificial Z-scheme that functions via stepwise photoexcitation of the supramolecular metal complex and semiconductor by visible light. The Z-scheme principle can, at least theoretically, simultaneously address the low oxidation ability of metal-complex photocatalysts and the inferior reduction performance of semiconductor photocatalysts. With a Z-scheme system, it is also possible to utilize a wider range of visible light, because the energies required to drive CO$_2$ reduction and water oxidation can be lowered as compared to those needed for a one step photoexcitation system. In the case of such two-reaction schemes, the photocatalytic performance is strongly influenced by both the metal complex and the semiconductor components, as will be discussed in the following sections. Development of both metal complexes and semiconductors is therefore important.

The hybrid photocatalyst concept can be extended to photoelectrochemical systems. That is, the single-absorber system shown in Figure 3A can be applied as a photocathode in a photoelectrochemical cell (Figure 3C), where electrons are supplied from a (photo)anode through an external circuit. When an visible-light-responsive photoanode is employed, the overall system can be regarded as a photoelectrochemical Z-scheme...
system. Similarly, a supramolecular metal complex/semiconductor Z-scheme system (Figure 3B) can be used in a dual-absorber photoelectrochemical cell (Figure 3D). In this case, a p-type semiconductor (e.g., NiO) that may be transparent to visible light was employed as a scaffold to immobilize the supramolecular photocatalyst. Table 1 lists various semiconductors that are applicable to these hybrid CO$_2$ photoreduction systems, along with their bandgaps and CBM potentials as reported in the literature.[51–59]

Figure 3. Metal-complex/semiconductor hybrids for CO$_2$ photoreduction. A) Single-photon photocatalytic system with a metal-complex catalyst. B) Two-photon Z-scheme system with a supramolecular photocatalyst. C) Photoelectrochemical system with a metal-complex catalyst. D) Photoelectrochemical system with a supramolecular photocatalyst. In photoelectrochemical systems, the photoanode component may be replaced by an ordinary “dark” anode, such as a Pt wire.

1.6. Important Points in Evaluating Photocatalytic and Photoelectrochemical CO$_2$ Reduction

Prior to considering literature data, some important points regarding the evaluation of CO$_2$ photoreduction systems are addressed in this section.

1.6.1. Confirmation of the Carbon Source

The most important aspect of assessing these catalytic systems is confirming the source of the CO$_2$-reduction products. This is particularly vital when working with semiconductor-based photocatalysts, because the contributions of surface contaminants (mostly adventitious carbon species) to the reduction products cannot be neglected in such cases.[60] The established approach to this analysis is to use isotope tracer experiments with $^{13}$C-enriched CO$_2$, followed by spectroscopic/spectrometric analyses, including gas chromatography–mass spectrometry, nuclear magnetic resonance, and infrared spectroscopy. For the most part, publications that included isotope experiments are cited here.

1.6.2. Catalytic Turnover Number

The TON is an important indicator of whether or not a given reaction is catalytic, and is typically calculated as

$$\text{TON} = \frac{[\text{Product}]}{[\text{Catalyst}]}$$

where [Product] and [Catalyst] represent the amounts of the CO$_2$-reduction product and catalyst used (or, more specifically, the quantity of active sites), respectively. If a given reaction is truly catalytic, the TON should exceed 1, meaning that the amount of products obtained should exceed the quantity...
Table 1. Bandgaps and conduction band minimum potentials of representative semiconductors applicable to hybrid CO$_2$ photoreduction systems.

| Semiconductor (conduction type) | Bandgap [eV] | $E_{CBM}$ [V] vs NHE vs Ag/AgNO$_3$ | Application type (see Figure 3) | Remarks | Ref. |
|---------------------------------|--------------|------------------------------------|---------------------------------|--------|-----|
| Ta$_2$O$_5$:N (p)              | 2.4          | −1.3 (pH 0)                        | A, C                             |        | [61, 77, 169] |
| mpg-C$_3$N$_4$ (n)             | 2.7          | −1.3 ± 0.1 (pH 6.6)                | A, B                            |        | [64–68, 84, 90, 91, 95] |
| g-C$_3$N$_4$ nanosheet (n)     | 2.8          | −2.1 ± 0.1                         | A, B                            | Prepared by thermal heating of urea. | [69–71, 92, 94, 127] |
| Copolymerized g-C$_3$N$_4$ nanosheet (n) | 2.0 | −2.0 ± 0.1                         | A                               | Prepared by thermal heating of urea and phenylurea. The main absorption edge lies at ≈450 nm, with a shoulder extending to 600 nm. | [71] |
| CaTaO$_2$N (n)                 | 2.5          | −1.8 (pH 0)$^g$                    | −2.15$^h$                        | A, B   | [98] |
| ZnS:Ni (n)                     | 2.3          | −1.3 V (pH 0)                      | A                               |        | [99] |
| (CuGa)$_2$Zn$_{1-x}$S$_2$ (n)  | 2.2          | >−1.3 V (pH 0)                     | A                               |        | [99] |
| (AgIn)$_{2.22}$Zn$_{1.35}$S$_2$ (p) | 2.4 | >−1.3 V (pH 0)                     | A                               |        | [99] |
| CdS quantum dots (n)           | 2.74         | −0.84 (pH 6.7)                     | A                               |        | [100] |
| ZnSe quantum dots (n)          | >2.7         | −1.1 (pH 0)$^g$                    | A                               |        | [101] |
| CuInS$_2$ quantum dots (p)     | 2.3          | −2.16 (pH 0)                       | A                               | The bandgap of bulk CuInS$_2$ is ≈1.5 eV. | [102] |
| TaON (n)                       | 2.5          | −0.3 (pH 0)$^c$                    | −1.3$^d$                         | B      | [122, 124] |
| Y-Ta oxynitride (n)            | 2.1          | −0.84 (pH 7)                       | −1.40$^h$                        | B      | [126] |
| GaN:ZnO solid solution (n)     | 2.6–2.8      | −0.94 (pH 7)                       | −1.50$^h$                        | B      | The $E_{CBM}$ values are almost the same, regardless of the composition. | [128] |
| TiO$_2$:Ta,N (n)               | 2.3          | −0.2 (pH 0)$^i$                    | −1.2$^h$                         | B      | [128] |
| Ta$_2$N$_5$ (n)                | 2.1          | −0.4 (pH 0)$^c$                    | −1.4$^d$                         | B      | [129] |
| Li$_2$LaTa$_2$O$_6$N (n)       | 2.5          | −1.95                               | B                                |        | [140] |
| Pb$_2$TiO$_4$.S$_{1.12}$ (n)   | 2.4          | −1.6 ± 0.1                         | B                                |        | [143] |
| Si (p)                         | 1.1          | −0.6 (pH 1)$^e$                    | C                                |        | [157, 162, 163] |
| GaAs (p)                       | 1.4          | −0.75 (pH 1)$^e$                   | C                                |        | [159] |
| InP (p)                        | 1.3–1.35     | −0.1 (pH 1)$^e$                    | C                                | In some cases, Zn was doped into InP. | [158, 168] |
| GaP (p)                        | 2.3          | −1.2 (pH 1)$^e$                    | C                                |        | [159] |
| CdTe (p)                       | 1.47         | −0.2 (pH 1)$^e$                    | C                                | Doped with P. | [161] |
| Cu$_2$ZnSnS$_4$ (p)            | 1.5          | −1.3 (pH 0)                        | C                                |        | [170] |
| Cu$_2$O (p)                    | 2            | −0.7 (pH 0)$^c$                    | C                                | p/n junction formation with n-type ZnO:Al, followed by coating with TiO$_2$, protecting layer was needed. | [165, 167] |
| Fe$_2$O$_3$:Zn,N (p)           | 2.1–2.2      | −0.6 (pH 0)                        | −1.6 to −1.7                     | C      | A Cr$_2$O$_3$ underlayer and TiO$_2$ protecting layer was necessary to obtain high performance. | [172] |
| NiO (p)                        | 3.46         | −3.66                               | D                                | $E_{VBM} = −0.2$ V vs Ag/AgNO$_3$; See ref. [52]. | [176, 177, 181] |
| CuGaO$_2$ (p)                  | 3.6$^i$      | −3.64 to −3.74                     | D                                | $E_{VBM} = −0.04$ V vs Ag/AgNO$_3$; | [182] |
| ZnTe (p)                       | 2.26         | −1.63 (pH 0)                       | Without metal complex             |        | [174] |

$^a$[Ag/AgNO$_3$ at pH 7] = [NHE at pH 7] − 0.56; $^b$Corrected value; $^c$Ref. [57]; $^d$Ref. [58]; $^e$Ref. [59]; $^f$Ref. [43]; $^g$Ref. [51]; $^h$Ref. [52].
of catalyst employed. Although TONs may be reported with respect to the amount of photosensitizer, TONs as calculated according to Equation (9) are reported here.

1.6.3. Product Distribution, Selectivity, and Stoichiometry

As described in Section 1.2, the reduction of CO₂ via proton-coupled electron transfer gives a variety of products and inevitably competes with proton reduction. As a result, the CO₂-reduction selectivity may be reduced by competitive H₂ evolution, so it is important to determine the product distribution from the CO₂-reduction reaction while accounting for H₂ evolution.

All photocatalytic processes consist of reduction and oxidation reactions, and the reduction and oxidation products should be determined in stoichiometric proportions. Given that photocatalytic CO₂ reduction to formate can be accomplished with 100% selectivity using water as the electron source, the formate/O₂ molar ratio should be 2, because the CO₂ reduction to formate and water oxidation to O₂ involve two and four electrons, respectively. It is thus necessary to identify the oxidation products, especially when using water as the electron source, for the confirmation of energy-conversion scheme. This is also the case for photoelectrochemical systems, as some semiconductors (in particular, mixed-anion compounds such as oxynitrides) may undergo degradation during the water-oxidation reaction under certain conditions. Similarly, self-reduction of the semiconductor cathode component should be considered carefully; this will lower the CO₂-reduction selectivity. However, CO₂ reduction is a highly difficult reaction to achieve, requiring an energy-rich electron donor for efficient operation even when employing semiconductors, so the detection of oxidation product(s) may be omitted in such a case.

1.6.4. Quantum Yield and Solar Energy Conversion Efficiency

The performance of a photocatalytic system should ideally be evaluated on the basis of quantum yield. However, it is generally difficult to measure the internal quantum yield of a powder-based semiconductor photocatalyst suspension system, due to the lack of a suitable method for evaluating the loss of incident photons by scattering and reflection in the suspension. Therefore, the apparent (or external) quantum yield (AQY) is used, assuming that all the incident photons are absorbed by the photocatalyst suspension. The AQY can be estimated as

\[
\text{AQY(\%)} = \left( \frac{A \times R}{I} \right) \times 100
\]

where A, R, and I represent the number of electrons required for CO₂ reduction to form one product molecule, the rate of product formation, and the rate of incident photons at a given wavelength, respectively. The total number of incident photons can be measured using a power meter or chemical actinometry. It is also very important to generate an action spectrum (i.e., a plot of the AQY as a function of the wavelength of the incident light) for any photochemical reaction, to determine whether or not the reaction occurs via light absorption by a given photocatalyst.

In a photoelectrochemical system, the incident photon-to-current conversion efficiency (IPCE) is used as a performance indicator. This variable is calculated using Equation (11)

\[
\text{IPCE(\%)} = \frac{hc}{\lambda} \times \frac{I}{\lambda \Phi} \times 100
\]

where \( h \), \( c \), \( e \), \( I \), \( \lambda \), and \( \Phi \) indicate the Planck constant, the speed of light, the elementary charge, the photocurrent recorded under a given set of conditions (mA cm⁻²), the wavelength of the incident photon (nm), and the intensity of the incident light (mW cm⁻²), respectively. It should be noted that the observation of a photocurrent may not always reflect that the desired reaction is proceeding. Therefore, the Faradaic efficiencies of the cathodic and anodic reactions should also be determined by quantifying the reduction and oxidation products. This is also related to the stability issue mentioned above.

Because the ultimate goal of photocatalytic CO₂ reduction is to efficiently convert solar energy into chemical feedstocks, the solar energy conversion efficiency (η) is also a suitable, general means of evaluating efficiency. This value can be calculated as

\[
\eta(\%) = \left( \frac{\text{Output chemical energy}}{\text{Energy of incident sunlight}} \right) \times 100
\]

Taking CO₂ to CO conversion as an example, Equation (12) becomes

\[
\eta(\%) = \frac{R_{\text{CO}} \cdot \Delta G}{I_{\text{sun}} \cdot S} \times 100
\]

where \( R_{\text{CO}} \), \( I_{\text{sun}} \), and \( S \) represent the rate of CO formation (mol s⁻¹), the incident solar irradiance (W cm⁻²), and the irradiated area (cm²), respectively. The term \( \Delta G^\circ \) (J mol⁻¹) is the change in the standard Gibbs energy for the reaction

\[
\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2
\]

2. Hybrids of Metal-Complex Catalysts and Visible-Light-Absorbing Semiconductors

This section first focuses on hybrid materials consisting of a metal-complex catalyst and a visible-light-absorbing semiconductor (as shown in Figure 3A). The various combinations that have been reported to date are summarized in Table 2. In a typical synthesis of metal-complex/semiconductor hybrid materials, a semiconductor powder is dispersed in a solution containing a dissolved metal complex that possesses appropriate anchoring groups such as carboxylic (COOH) or phosphonic acid (PO₃H₂), followed by stirring at room temperature overnight to allow for adsorption/desorption equilibrium. The resulting solid is separated by filtration or centrifugation and is subject to drying at mild temperatures (typically <343 K).
Table 2. Hybrids consisting of a mononuclear metal complex and a semiconductor for visible-light-driven CO₂ reduction.

| Entry | Metal-complex catalyst | Semiconductor | Main product (selectivity [%]) | TON | Maximum AQY [%] | Reaction time | Reactant solution | Light source and other remarks. | Ref. |
|-------|------------------------|---------------|--------------------------------|------|-----------------|---------------|-------------------|-------------------------------|------|
| 1     | Ta₂O₅:N                | Formate (>75) | 89                             | 1.9 (405 nm) | 20 h | MeCN/TEOA (5:1 v/v) | A 500 W xenon lamp (410 ≤ λ ≤ 750 nm). | [61] |
| 2     | Ta₂O₅:N                | Formate (–)   | 118                            | –    | 60 h | MeCN/TEOA (5:1 v/v) | A 500 W xenon lamp (410 ≤ λ ≤ 750 nm). TONCO = 67. | [77] |
| 3     | mpg-C₃N₄               | Formate (80)  | 216                            | 1.5 (400 nm) | 20 h | MeCN/TEOA (4:1 v/v) | A 450 W high-pressure mercury lamp (λ > 400 nm). | [64] |
| 4     | mpg-C₃N₄               | Formate (80)  | 1061                           | 5.7 (400 nm) | 20 h | DMA/TEOA (4:1 v/v) | A 400 W high-pressure mercury lamp (λ > 400 nm). | [66] |
| 5     | mpg-C₃N₄               | Formate (74)  | 19                             | –    | 20 min | MeCN/TEOA (4:1 v/v) | A 400 W high-pressure mercury lamp (λ > 400 nm). | [67] |
| 6     | mpg-C₃N₄               | Formate (82)  | 35                             | –    | 20 min | MeCN/TEOA (4:1 v/v) | A 400 W high-pressure mercury lamp (λ > 400 nm). | [67] |
| 7     | Copolymerized g-C₃N₄ nanosheet | CO (82) | >68                           | –    | 4 h | MeCN/TEOA (5:1 v/v) | A 300 W xenon lamp (λ > 420 nm). The semiconductor was prepared from urea and barbituric acid. | [89] |
| 8     | Copolymerized g-C₃N₄ nanosheet | Formate (67) | >250                          | 1.1 (400 nm) | 5 h | MeCN/TEOA (4:1 v/v) | A 400 W high-pressure mercury lamp (λ > 400 nm). Formate selectivity was improved to 98% under >500 nm irradiation. | [71] |
| 9     | g-C₃N₄ nanosheet        | Formate (>90) | 5775                          | 4.2 (400 nm) | 48 h | DMA/TEOA (4:1 v/v) | A 400 W high-pressure mercury lamp (λ > 400 nm). 2.0 wt% Ag was loaded onto the semiconductor. | [70] |
| 10    | mpg-C₃N₄               | CO (80–90)   | 13                             | 0.25 (420 nm) | 2 h | MeCN/TEOA (2:1 v/v) | A 300 W xenon lamp (λ > 420 nm). Modification of mpg-C₃N₄ with CoOₓ improved the CO formation, but lowered the selectivity. Reaction temperature: 333 K. | [90] |
| 11    | Co-ZIF-9 + bpy         | mpg-C₃N₄     | CO (97)                        | 35   | 0.9 (420 nm) | MeCN/ H₂O/TEOA (3:2:1 v/v/v) | A 300 W xenon lamp (λ > 420 nm). | [91] |
| 12    | [Co(bpy)]²⁺             | g-C₃N₄ nanosheet | CO (>80) | >18  | 1.6 (400 nm) | MeCN/ H₂O/TEOA (3:1:1 v/v/v) | A light emitting diode (λ = 400 nm). | [92] |
| 13    | g-C₃N₄                 | CO (80)      | <1                            | 0.8 (420 nm) | MeCN/TEOA (4:1 v/v) | A 300 W xenon lamp (400 ≤ λ ≤ 800 nm). | [93] |
Table 2. Continued.

| Entry | Metal-complex catalyst | Semiconductor | Main product (selectivity [%]) | TON | Maximum AQY [%] | Reaction time | Reactant solution | Light source and other remarks | Ref. |
|-------|------------------------|---------------|-------------------------------|-----|-----------------|---------------|------------------|-------------------------------|------|
| 14    | g-C3N4 nanosheet        | CO (98)       | 5.7                           | –   | 6 h             | MeCN/H2O/TEOA (3:1:1 v/v) | A 300 W xenon lamp (420 ≤ λ ≤ 780 nm). | [94] |
| 15    | mpg-C3N4               | CO (97)       | 155                           | 4.2 (400 nm) | 17 h          | MeCN/TEOA (4:1 v/v)       | A 400 W high-pressure mercury lamp (λ > 400 nm). | [95] |
| 16    | CaTaO2N                | Formate (98)  | 11                            | –   | 15 h           | DMA/TEOA (4:1 v/v)       | A 400 W high-pressure mercury lamp (λ > 400 nm). 1.0 wt% Ag was loaded onto CaTaO2N. | [98] |
| 17    | ZnS:Ni                 | Formate (49)  | 104                           | –   | 16 h           | MeCN/TEOA (5:1 v/v)       | A 500 W xenon lamp (190 < λ < 750 nm). | [99] |
| 18    | (CuGa)12Zn0.8S2        | Formate (6)   | 12                            | –   | 16 h           | MeCN/TEOA (5:1 v/v)       | A 500 W xenon lamp (190 < λ < 750 nm). | [99] |
| 19    | (AgIn)0.22Zn1.56S2     | Formate (44)  | 126                           | –   | 16 h           | MeCN/TEOA (5:1 v/v)       | A 500 W xenon lamp (190 < λ < 750 nm). | [99] |
| 20    | CdS quantum dots       | CO (>90)      | 20                            | 0.28 ± 0.04 (400 nm) | 24 h | 0.1 m aqueous TEOA containing 0.5 vol% MeCN | A UV-filtered simulated solar light (λ > 420 nm, 100 mW cm⁻²). | [100] |
| 21    | ZnSe quantum dots      | CO (34 ± 2)   | 283 ± 23                      | 3.4 ± 0.3 (400 nm) | –   | –               | A UV-filtered simulated solar light (λ > 420 nm, 100 mW cm⁻²). Modification of ZnSe with 2-(dimethylamino)ethanethiol partially suppressed H₂ generation and enhanced the CO production. | [101] |
| 22    | CuInS₂/ZnS (core/shell)| CO (100)      | 450                           | 0.025 (450 nm) | 30 h | 5 × 10⁻³ M KCl + 15 × 10⁻³ M TEOA aqueous solution | A 450 nm laser pointer. | [103] |
| 23    | (CuGa)12Zn0.8S2        | CO (64)       | =100                          | 9 h | 0.1 m NaHCO₃ + 0.02 × 10⁻³ M [Co(tpy)]₂⁺ aqueous solution | A 300 W xenon lamp (λ > 420 nm). BiVO₄ was used as an O₂ evolution photocatalyst. | [109] |
| 24    | CO₂-reducing enzyme    | Dye-sensitized TiO₂ | CO (100) | >1200 | 4 h | 200 × 10⁻³ M 2-(N-morpholino)ethanesulfonic acid | A tungsten-halogen lamp (λ > 420 nm, 45 mW cm⁻²). TiO₂ = P25. | [113] |
2.1. Proof of Concept Using Nitrogen-Doped Ta$_2$O$_5$ and Ru(II) Complex Catalysts

In 2010, proof-of-concept evidence for the reduction of CO$_2$ to formate under visible light via a metal-complex/semiconductor hybrid-photocatalyst system was published. This system incorporated nitrogen-doped Ta$_2$O$_5$ (Ta$_2$O$_5$:N; energy gap $\approx 2.4$ eV) as a p-type semiconductor together with the Ru(II) complexes [Ru(bpy)$_2$(CO)$_2$]${^{2+}}$, [Ru(dcbpy)(bpy)(CO)$_2$]${^{2+}}$, or [Ru(dcbpy)$_2$(CO)$_2$]${^{2+}}$ (bpy: 2,2'-bipyridine; dcbpy: 4,4'-dicarboxy-2,2'-bipyridine) as catalysts.$^{[61]}$ These [Ru(bpy)$_2$(CO)$_2$]${^{2+}}$-type complexes have also been used as electrocatalysts for CO$_2$ reduction to formate.$^{[62]}$ Interestingly, neither the metal complex nor the Ta$_2$O$_5$:N alone showed any photocatalytic activity under the same reaction conditions. In contrast, irradiation of the hybrid photocatalyst with visible light in a mixed solution of acetonitrile (MeCN) and TEOA resulted in photoexcitation of the Ta$_2$O$_5$:N, generating electrons and holes in the conduction band. The excited-state dynamics of the [Ru(dcbpy)$_2$(CO)$_2$]${^{2+}}$ complex was found to occur with a time constant of 12 $\pm$ 1 ps.

Ta$_2$O$_5$:N is unable to oxidize water to O$_2$ because the VBM of the material has a sufficiently negative CBM for the reduction of water. However, depending on the preparation route and structural properties of the g-C$_3$N$_4$, it may exhibit an additional absorption band extending to 550 nm. This band is assigned to n–π* transitions of the heptazine rings. Another key feature of g-C$_3$N$_4$ is that it has several proposed allotropes, among which the graphitic phase is considered to be the most stable.$^{[73]}$ Recently, g-C$_3$N$_4$ has attracted considerable attention as an earth-abundant polymeric semiconductor photocatalyst for water splitting under visible light.$^{[74–76]}$ The bandgap of g-C$_3$N$_4$ is $\approx 2.7$ eV, corresponding to an absorption edge of $\approx 460$ nm. These reports, however, lack data from isotope tracer experiments using $^{13}$C-enriched CO$_2$ to be the CO$_2$ that was introduced as the reactant.

2.2. Graphitic Carbon Nitride Combined with a Mononuclear Ru Complex Catalyst

Graphitic carbon nitride (g-C$_3$N$_4$) and its variants have also been used as the semiconductor component of hybrid CO$_2$-reduction systems in conjunction with a similar Ru complex catalyst.$^{[64–71]}$ C$_3$N$_4$ is one of the oldest synthetic polymers$^{[72]}$ and has several proposed allotropes, among which the graphitic phase is considered to be the most stable.$^{[73]}$ Recently, g-C$_3$N$_4$ has attracted considerable attention as an earth-abundant polymeric semiconductor photocatalyst for water splitting under visible light.$^{[74–76]}$ The bandgap of g-C$_3$N$_4$ is $\approx 2.7$ eV, corresponding to an absorption edge of $\approx 460$ nm. However, depending on the preparation route and structural properties of the g-C$_3$N$_4$, it may exhibit an additional absorption band extending to 550 nm. This band is assigned to n–π* transitions involving lone pairs on the edge nitrogen atoms of the heptazine rings. Another key feature of g-C$_3$N$_4$ is that the material has a sufficiently negative CBM for the reduction of CO$_2$. Some early studies reported that g-C$_3$N$_4$ can photocatalytically reduce CO$_2$ to CO, CH$_3$OH, or C$_2$H$_5$OH.

These reports, however, lack data from isotope tracer experiments using $^{13}$CO$_2$ that show the origin of the CO$_2$-reduction products.

Photocatalytic $^{13}$CO$_2$ reduction over g-C$_3$N$_4$ was successfully demonstrated using mesoporous g-C$_3$N$_4$ (mpg-C$_3$N$_4$) having a specific surface area of 180–200 m$^2$ g$^{-1}$ and further
modified with trans(Cl)\(_2\)Ru\(\{(4,4\text{-trans}\text{Cl}_{2,2}\text{-bipyridine})\}\) \((\text{CO})_2\text{Cl}_2\) \((\text{RuCP})\) \((\text{Figure 4})\) as a molecular catalyst (or cocatalyst).\[^64\] RuCP is an active electrocatalyst for CO\(_2\) reduction, having an \(E_{\text{red}}\) value of \(-1.48\) V versus Ag/AgNO\(_3\) in a DMA/TEOA (4:1 v/v) mixed solvent (which is sufficiently positive to accept an electron from the conduction band of mpg-C\(_3\)N\(_4\)), while being almost transparent to visible light. When the RuCP-adsorbed mpg-C\(_3\)N\(_4\) hybrid was irradiated with visible light (\(\lambda > 400\) nm) in a CO\(_2\)-saturated MeCN/TEOA (4:1 v/v) solution, formate was produced as the major product with \(\approx 80\%\) selectivity and a maximum TON of 216 \((\text{Figure 5A})\), along with CO and H\(_2\) as minor products. Control experiments indicated no appreciable production of formate in the absence of RuCP, mpg-C\(_3\)N\(_4\), CO\(_2\), or visible light. It was also confirmed that the CO\(_2\)-to-formate conversion was driven by the light absorption of the mpg-C\(_3\)N\(_4\) by an action spectrum analysis,

\[\text{RuP} \quad E_{\text{red}} = -1.41\text{ V}\]

\[\text{RuC} \quad E_{\text{red}} = -1.41\text{ V}}^a\]
groups (i.e., COOH, PO₃H₂, and CH₂PO₃H₂) on the diimine ligands that were able to undergo hydrogen bonding with amino (NH₂) groups on the mpg-C₃N₄ surface. This result agrees with a suggestion by Thomas et al. that NH₂ groups on the g-C₃N₄ surface can serve as hydrogen-bonding motifs.[78] Interestingly, even the Ru complexes having anchoring groups were not supported very well by nonporous g-C₃N₄ (which has a low surface area).

The photocatalytic activities of mpg-C₃N₄ modified with the five different mononuclear Ru complexes during CO₂ reduction were examined under visible light (λ > 400 nm). Both the RuH and RuMe, neither of which could be adsorbed on the mpg-C₃N₄, were studied in a solution containing an appropriate amount of these complexes suspended along with mpg-C₃N₄. However, these mixed systems showed lower activity levels. Conversely, the adsorbed systems exhibited higher activity during CO₂ to formate conversion, with the level of activity depending on the structure of the Ru complex and decreasing in the order of RuC > RuP > RuCP ≈ RuH >> RuMe. These results clearly indicate that the adsorption of the Ru complexes on the mpg-C₃N₄, which enabled efficient electron transfer based on the energy difference between the CBM and Ered, was vital to obtaining higher photocatalytic activity. As an example, even though the Ered of RuP was similar to that of RuH, the RuP-adsorbed hybrid showed higher activity than the RuH analogue. In the case of the hybrids having adsorbed RuP or RuCP, the more positive Ered of the RuP presumably led to the higher performance exhibited by the former. A comparison of RuP and RuC is more interesting, because both these complexes could be adsorbed on mpg-C₃N₄ and had almost the same Ered but showed different activities.[67] Specifically, the RuC/mpg-C₃N₄ exhibited a higher initial rate of formate generation (as well as a superior TON value) compared to the RuP analogue, while the stability of the RuC/mpg-C₃N₄ (as reflected by its TON) was inferior.

Nonadiabatic molecular dynamics simulations of the systems in which RuC and RuP were attached to the Ta₂O₅:N surface indicated that electron transfer from the Ta₂O₅:N to the Ru complex was faster in the RuC system than in the RuP analogue, because of the greater degree of nonadiabatic coupling in the RuC system (Figure 6).[79] Electronic decoherence occurred more rapidly in the RuC system than in the RuP system, meaning that electronic transitions were less efficient in the former than in the latter, although the effect of this difference in decoherence was much weaker than that of the variation in nonadiabatic coupling. Calculation of the partial density of states for the RuC system indicated that both the LUMO and LUMO+1 contained obvious contributions from the central carbon atom of the COOH anchor, due to conjugation with the ligand π-system. In contrast, the RuP system showed little contribution of the anchor orbitals to the only acceptor state (the LUMO). This difference in the donor–acceptor orbital mixing accounts for the variations in the extent of nonadiabatic coupling. Thus, it was concluded that the COOH anchor is intrinsically superior to PO₃H₂ in terms of electron transfer, due to the greater degree of nonadiabatic coupling.

In summary, catalytic metal complexes with more positive Ered values and suitable anchoring groups show promise in terms of promoting electron injection from the conduction band of the semiconductor to the metal complex. This occurs
due to the larger driving force for the electron-injection process as well as the intimate interfacial contact between the two components. Although metal-complex catalysts with more negative $E_{\text{red}}$ appear to be advantageous over those having a positive $E_{\text{red}}$ because of the high potential difference between the CO$_2$-reduction potentials, experimental results indicate that enhancement of the electron-injection driving force from the semiconductor to the adsorbed metal complex is more important to the overall efficiency of the system. Thus, both thermodynamic aspects and the intrinsic nature of the bonding between the metal complex and semiconductor (i.e., nonadiabatic coupling and quantum coherence) are important factors that determine the overall efficiency.

The optimized RuP/mpg-C$_3$N$_4$ gave a TON formate of 1061 (over 20 h) in an $N,N$-dimethylacetamide (DMA)/TEOA (4:1 v/v) mixed solvent, along with an AQY of 5.7% at 400 nm and ≈80% selectivity.[66] This is the highest AQY yet reported for a hybrid photocatalyst using a mononuclear metal-complex catalyst and a visible-light-absorbing semiconductor. Although this reaction was sacrificial and had a negative Gibbs energy change ($\Delta G^o < 0$), the use of a DMA/methanol mixture (i.e., employing methanol as the electron donor) enabled the construction of a system for the conversion of light energy via CO$_2$ reduction to CO using mpg-C$_3$N$_4$.[68] In this case, nearly stoichiometric production of HCHO (the two-electron oxidation product of methanol) was confirmed. In this process, visible-light energy was stored as chemical energy in the form of CO and HCHO ($\Delta G^o$ = +67.6 kJ mol$^{-1}$) according to the reaction

$$\text{CO}_2 + \text{CH}_3\text{OH} \rightarrow \text{CO} + \text{H}_2\text{O} + \text{HCHO} \quad (\Delta G^0 = +67.6 \text{kJ mol}^{-1}) \hspace{1cm} (15)$$

This represents the first case of an energy-conversion scheme with the use of a carbon-nitride-type photocatalyst for CO$_2$ reduction.

The electron transfer from the conduction band of mpg-C$_3$N$_4$ to the best-performing recipient (RuP) was investigated by means of time-resolved visible-to-mid-IR absorption spectroscopy,[80] which allows an assessment of photogenerated charge carriers in a semiconductor.[13,81–83] Figure 7A shows a typical transient absorption spectrum acquired from mpg-C$_3$N$_4$ with excitation via a 355 nm laser pulse under vacuum.[84] Bandgap photoexcitation of the mpg-C$_3$N$_4$ generated broad absorption over the entire range of 20 000 to 1000 cm$^{-1}$. Absorption signals appearing in the visible-to-near-IR region (20 000–3000 cm$^{-1}$) can be assigned to deeply trapped electrons and/or holes at mid-gap states.[81,82] In contrast, the absorptions in the mid-IR region (3000–1000 cm$^{-1}$) are assignable to free or shallowly trapped electrons, which tend to be involved in reduction reactions.[83] The time courses of the photogenerated free and/or shallowly trapped electron populations in mpg-C$_3$N$_4$ and RuP/mpg-C$_3$N$_4$ are shown in Figure 7B. These data reflect changes in the transient absorption intensity at 1900 cm$^{-1}$ after photoexcitation. Note that these signals were evidently generated solely by the mpg-C$_3$N$_4$ and not the RuP because of the absence of peaks due to RuP at ≈1900 cm$^{-1}$. It is apparent that the signal decay was more rapid in the case of the RuP/mpg-C$_3$N$_4$. In contrast, there is no noticeable acceleration of decay in the time-course data recorded at a higher wavenumber of 6000 cm$^{-1}$ (Figure 7C).

These results strongly suggest that shallowly trapped and/or free electrons in the mpg-C$_3$N$_4$ were able to migrate to the adsorbed RuP on a timescale of several picoseconds, while deeply trapped electrons were not able to do so (Figure 7D). This timescale is comparable to that reported for $[\text{Ru(dcbpy)}_2(\text{CO})_2]^{2+}$/Ta$_2$O$_5$N.[63] Importantly, this spectroscopic study also indicated that emission from the photoexcited mpg-C$_3$N$_4$ was not quenched upon the addition of a hole scavenger (such as disodium dihydrogen ethylenediamine tetracetate dehydrate) and/or an electron acceptor (RuP). Therefore, it is likely that electron transfer from the mpg-C$_3$N$_4$ to RuP occurred through less luminescent or nonluminescent sites in the mpg-C$_3$N$_4$, in which mobile electrons existed with a certain lifetime.

### 2.4. Improvement in the Photocatalytic Activity of the Ru-Complex/C$_3$N$_4$ Hybrid System through Refinement of the Semiconductor Component

It is known that the performance of semiconductor-based photocatalytic systems is affected by the physicochemical properties of the semiconductor (e.g., crystallinity, particle size, and composition) as well as surface modifications (e.g., metal...
loading).

This is, of course, also the case for metal-complex/semiconductor hybrid photocatalyst systems. In this section, three different approaches to improving the photocatalytic performance of the Ru-complex/g-C\textsubscript{3}N\textsubscript{4} system are discussed.

### 2.4.1. Textural Engineering of g-C\textsubscript{3}N\textsubscript{4}

g-C\textsubscript{3}N\textsubscript{4} can be readily synthesized via the thermal condensation of a nitrogen-rich precursor (e.g., cyanamide or urea) in air or nitrogen.\(^\text{[78,85]}\) Several approaches to modifying the textural properties of g-C\textsubscript{3}N\textsubscript{4} have been proposed, based on this thermal condensation method. As an example, the pore-wall structure of g-C\textsubscript{3}N\textsubscript{4} can be modified using a mixture of cyanamide and colloidal silica having various particle sizes as a hard template.\(^\text{[75,86]}\) The pore volume can also be tuned by changing the ratio of silica to cyanamide during the synthesis. Thus, this hard-template method enables the synthesis of g-C\textsubscript{3}N\textsubscript{4} with controlled mesoporosity.

The photocatalytic activities of mpg-C\textsubscript{3}N\textsubscript{4} specimens having different pore-wall structures (i.e., different specific surface areas) in combination with RuP or RuCP have been investigated (Figure 8A).\(^\text{[65,84]}\) It was found that the introduction of mesopores into g-C\textsubscript{3}N\textsubscript{4} increased the specific surface area, leading to improved photocatalytic activity, while the pore size/volume did not greatly affect the activity. When RuP was employed, the optimal mpg-C\textsubscript{3}N\textsubscript{4} system showed \(\approx 15\) times higher activity than nonporous g-C\textsubscript{3}N\textsubscript{4}. During the CO\textsubscript{2}-reduction reaction, electrons photogenerated in the mpg-C\textsubscript{3}N\textsubscript{4} have to travel to the surface-bound Ru complex while undergoing minimal recombination with holes in the valence band. Simultaneously, the photogenerated holes must be consumed by an electron donor (here TEOA). It is believed that a decrease in the pore-wall thickness of mpg-C\textsubscript{3}N\textsubscript{4} and the resulting increase in specific surface area shortens the electron–hole migration distance and gives the photogenerated charge carriers a greater chance to participate in surface redox reactions, respectively. Therefore, the introduction of mesoporosity into g-C\textsubscript{3}N\textsubscript{4} is essential to realizing the full potential of this material as a semiconductor photocatalyst, even though g-C\textsubscript{3}N\textsubscript{4} (having a more negative CBM) might appear to be more suitable than mpg-C\textsubscript{3}N\textsubscript{4} in terms of electron injection into the Ru complex. However, an excessive increase in the specific surface area of mpg-C\textsubscript{3}N\textsubscript{4} resulted in an activity drop. This likely occurred because the increased surface area also increased the density of surface defect sites such as dangling bonds, which can act to promote the recombination of photogenerated electrons and holes. This hypothesis is also supported by the observation that the increase in specific surface area was not proportional to the activity increase. It should also be noted that employing RuCP, which is a less efficient catalyst than RuP,
resulted in little activity being exhibited by both the nonporous bulk g-C₃N₄ and the mpg-C₃N₄ having a higher surface area. This result again confirms that both the structural properties of the semiconductor and the intrinsic catalytic characteristics of the metal complex are important to maximizing the photocatalytic activity of metal-complex/semiconductor hybrids for visible-light-driven CO₂ reduction.

The effect of the specific surface area of g-C₃N₄ has also been confirmed by studies with g-C₃N₄ nanosheets (NS-C₃N₄) synthesized by heating urea in air at 773–923 K.[69] In this case, increasing the synthesis temperature (while remaining below the thermal decomposition temperature of g-C₃N₄) produced more highly crystallized NS-C₃N₄ with an increased specific surface area and more pronounced visible-light absorption. Each of these physicochemical characteristics tends to promote photocatalytic reactions.

Thus, there is a tradeoff between the specific surface area of the C₃N₄ and the photocatalytic activity obtained with the aid of a Ru-complex catalyst. An increased density of electron trapping sites has been reported to promote the degradation of organic pollutants using C₃N₄-based materials in the presence of O₂, because the trapped electrons can facilitate photoreduction in association with O₂.[87] However, it appears that trapped electrons located at such defects do not possess sufficient mobility to reach the surface-adsorbed Ru-complex catalyst, which is consistent with the results of time-resolved IR studies.[80]

2.4.2. Electronic Modification of C₃N₄ by Copolymerization

Ru-complex/g-C₃N₄ hybrids are evidently promising photocatalysts for CO₂-to-formate conversion under visible light. One of the drawbacks of g-C₃N₄ as a photocatalyst in artificial photosynthesis is its relatively wide bandgap (2.7–2.8 eV, corresponding to an absorption edge of ≈450–460 nm), which can utilize only a small portion of the solar spectrum.

A copolymerization approach has been proposed as a means of synthesizing C₃N₄-based materials that absorb longer-wavelength photons.[88] Compared to pristine C₃N₄ prepared by heating urea, copolymerized C₃N₄ obtained from a mixture of urea and barbituric acid showed enhanced activity (by a factor of 15) during CO₂ reduction with the aid of a Co(II) complex catalyst.[89] Unfortunately, this Co(II) complex/copolymer hybrid did not work efficiently at wavelengths longer than 500 nm, even though the copolymer had an absorption band extending to 600 nm.

Very recently, a follow-up study was performed, focusing on the RuP/NS-C₃N₄ hybrid system.[71] Copolymerization with urea and phenylurea in air at 823 K produced a brown-colored carbon nitride that absorbed visible light up to 650 nm. While a hybrid system constructed with pristine g-C₃N₄ showed no activity under longer-wavelength visible light (λ > 500 nm) due to its large bandgap, this copolymerized material was capable of photocatalytically reducing CO₂ to formate under the same conditions (Figure 8B). Importantly, the copolymerization altered not only the visible-light absorption of the g-C₃N₄ but also prolonged the lifetimes of photogenerated free and/or shallowly trapped electrons, as revealed by transient absorption spectroscopy. As a result, the copolymerized material exhibited higher activity than the pristine g-C₃N₄ even under shorter-wavelength visible light (λ > 400 nm) that resulted in the photoexcitation of both materials.
2.4.3. Surface Modification of C₃N₄ with Ag Nanoparticles

As discussed in the Introduction, the efficiency of semiconductor photocatalysis can be increased by introducing metal nanoparticles onto the semiconductor surface. This is possible because such nanoparticles can promote charge separation and/or reduce the activation energies for surface redox reactions. Nanoparticulate Ag is a particularly good promoter for photocatalytic CO₂ reduction using wide-gap metal oxide semiconductors.[35-37] Ag is also known to be a suitable electrocatalyst for CO₂ reduction, and has a relatively large overpotential for proton reduction, which improves the selectivity for CO₂ reduction.

The catalytic role of Ag in promoting photocatalytic CO₂ reduction was examined using mpg-C₃N₄.[84] Ag-loaded mpg-C₃N₄ (in this case, 5.0 wt% Ag with an average particle size of ≈7 nm) showed some degree of activity during CO₂ reduction to formate in a DMA/TEOA mixture under visible light (see Figure 8C), as confirmed by isotope tracer experiments with ^13CO₂. However, this activity was only ≈20% that of RuP/mpg-C₃N₄, and the Ag-loaded material also showed much lower selectivity for formate (36% vs 74% for RuP/mpg-C₃N₄). Time-resolved IR absorption spectroscopy indicated that the Ag nanoparticles on the mpg-C₃N₄ collected free and/or shallow-trapped electrons, although deeply trapped electrons were less mobile. The catalytic effect of the Ag nanoparticles on mpg-C₃N₄ was evidently not as effective as that of RuP, although electron transfer from the mpg-C₃N₄ to Ag would be expected. Interestingly, modification of Ag/mpg-C₃N₄ with RuP significantly enhanced the formate generation activity (by a factor of 16) compared to the results obtained using Ag/mpg-C₃N₄, together with a formate selectivity of 98%.

The structures of the nanoparticulate Ag species acting as promoters for the reaction were investigated in detail.[70] In this work, Ag particles were loaded on the surface of NS-C₃N₄ via impregnation from a AgNO₃ aqueous solution or using an in situ photodeposition method. Impregnation of NS-C₃N₄ with 2.0 wt% Ag followed by reduction with H₂ at 473 K resulted in the highest photocatalytic activity, in combination with RuP. The best-performing hybrid photocatalyst gave a TON of 5775 (based on RuP), which was the highest value yet reported for formate-generating hybrid systems constructed with a mononuclear complex. Furthermore, the rate of formate production remained almost unchanged during 48 h of visible-light irradiation. Physicochemical analyses indicated that the optimized photocatalyst contained highly dispersed Ag₂O-like nanoclusters as the major silver species. In addition, the experimental results suggested that the two main factors affected the activity: the size of the Ag species (with smaller particles giving better results) and the oxidation state of the Ag (with a metallic state being better).

2.5. Graphitic Carbon Nitride Combined with Other Mononuclear Metal-Complex Catalysts

Since the first report of Ru-complex/mpg-C₃N₄ hybrids for CO₂ reduction in 2013, C₃N₄-based hybrid systems using different metal complexes have been assessed, as listed in Table 2. Of particular interest is the use of metal complexes containing earth-abundant metals as catalysts, in place of expensive Ru-complex catalysts. As an example, the addition of both Co²⁺ ions and 2,2'-bipyridine to a reactant suspension along with mpg-C₃N₄ results in photocatalytic CO₂ reduction to CO with 80–90% selectivity in the presence of TEOA as an electron donor under visible light.[90] It has been suggested that a cobalt polypyridyl complex, most likely [Co(bpy)₃]²⁺, formed in situ serves as the reductive promoter for CO generation. Another interesting finding from this study was that the modification of mpg-C₃N₄ with nanoparticulate cobalt oxide, which is known to be a good oxidation promoter, further improved the CO formation rate, although selectivity was decreased from 91 to 79%. A follow-up study demonstrated that employing a zeolitic imidazolate framework containing cobalt (Co-ZIF-9) as a catalyst along with mpg-C₃N₄ resulted in enhanced activity, with an AQY of 0.9% at 420 nm.[91] In this case, the presence of 2,2'-bipyridine in the reactant solution was indispensable, likely due to the electron-mediating effect of this compound. It was proposed that the Co-ZIF-9 served to provide catalytically active sites for CO₂ reduction and as a CO₂ concentrator, both of which could contribute to enhanced activity. Combining urea-derived NS-C₃N₄ with the Co²⁺/2,2'-bipyridine system led to an improved AQY of 1.6% at 420 nm during CO generation, while maintaining a relatively high selectivity of ≈80%.[92] A covalently linked hybrid constructed with cobalt porphyrin and carbon nitride was reported to show photocatalytic activity during CO₂ reduction to CO in a mixture of MeCN and TEOA (4:1 v/v) under visible light.[93] However, careful investigations (including isotope tracer experiments using ^13CO₂) demonstrated that the TONCO with respect to cobalt porphyrin was very small (<1). An iron porphyrin/C₃N₄ hybrid showed an enhanced performance with a maximum TONCO of 5.7 and high selectivity of 98%.[94]

Despite these early studies, the development of a photocatalytic system that is efficient, selective and composed solely of earth-abundant elements remains challenging. Very recently, it was reported that a hybrid system consisting of mpg-C₃N₄ and [Fe(qpy)(H₂O)]²⁺ (qpy = 2,2'-6,2'-6'-quaterpyridine) worked as an efficient, selective photocatalyst for CO₂ to CO conversion under visible light (λ > 400 nm) in a MeCN/TEOA (4:1 v/v) mixture.[95] An iron quaterpyridine complex was also found to show good catalytic activity during CO₂ reduction to CO under photochemical conditions, with the aid of [Ru(bpy)]³⁺ as a photosensitizer and BHT as a sacrificial electron donor.[96] Electrochemical measurements indicated that the one-electron-reduced species Fe(qpy) produced upon the first reduction wave binds to CO₂ and the Fe(qpy)CO₂ adduct is then reduced at ca. –1.2 V versus SCE, with consequent formation of CO by C–O bond cleavage.[97] In this case, the CBM of mpg-C₃N₄ is sufficiently negative to reduce the Fe(qpy)CO₂ adduct, promoting the formation of CO. The [Fe(qpy)(H₂O)]²⁺/mpg-C₃N₄ hybrid exhibited high selectivity for CO (97%), a TONCO of 155 and an AQY of 4.2% under optimal conditions. These values were the highest yet reported for CO evolution by a hybrid photocatalyst. The superior selectivity and efficiency of this hybrid system during CO formation is attributable to the high reactivity of the Fe⁺ center toward CO₂.[97] This reaction does not involve more basic species containing Fe⁰ or an
extra electron on the ligand that could favor the competing H2-evolution reaction. Moreover, the reaction of CO2 with the Fe(qpy) allows activation of the substrate after the uptake of only one electron, thus increasing the efficiency of the process. The ability of Fe(qpy) to operate at a very low overpotential and its high selectivity toward CO make it a very suitable catalyst for CO2 reduction. This is especially so when this compound is combined with mpg-C3N4 (which has a sufficiently negative CBM), even in the absence of physical interaction between the Fe complex catalyst and mpg-C3N4.

2.6. Other Visible-Light-Absorbing Semiconductors

In addition to Ta2O5:N and C3N4, CaTaO2N has been found to be an active semiconductor in combination with RuCP.[98] Metal chalcogenides such as sulfides and selenides have been studied as effective building blocks for the fabrication of hybrid CO2-reduction systems in conjunction with suitable metal-complex catalysts.[99–104] Ni-doped ZnS, (CuGa)0.8Zn0.2S2, and (AgIn)0.2Zn1.56S2, which were originally developed as visible-light-driven photocatalysts for H2 evolution,[105,106] have been adopted as active semiconductor components for visible-light CO2 reduction to formate in MeCN/TEOA together with RuP.[99] Semiconductor quantum dots are also of interest as components of hybrid CO2 photoreduction systems with molecular catalysts, because of their significant reducing power that originates from quantum size effects. Certain chalcogenide quantum dots will function even in an aqueous environment,[100,101,103] although CO2 reduction is typically difficult under such conditions due to the high concentration of protons and low solubility of CO2.[107] In one example, CdS quantum dots modified with nickel terpyridine complex catalysts showed photocatalytic activity during CO2 reduction to CO under visible light (λ > 400 nm) in an aqueous 0.1 M TEOA solution.[100] Although the CdS component was unable to oxidize water due to its inherent instability,[108] and the observed TONCO was moderate (=20), a high CO selectivity of >90% was achieved without using a precious-metal component, even in aqueous solution. A material containing ZnSe quantum dots linked to a NiCycP catalyst (NiCycP) via a phosphonate anchor exhibited high activity during aqueous CO2 reduction to CO, with a TONCO greater than 120.[101] Surface modification of the ZnSe quantum dots with 2-(dimethylamino)ethanethiol partially suppressed H2 evolution and improved the CO evolution rate, resulting in a TONCO of more than 280 and a CO2-reduction selectivity of 33% after 20 h of visible-light irradiation (λ > 400 nm, AM1.5G, 1 Sun). An AQY of 3.4 ± 0.3% at 400 nm was recorded under the optimal conditions. Transient absorption spectroscopy showed that the bandgap excitation of the ZnSe quantum dots was followed by rapid hole scavenging and very fast electron trapping in the ZnSe, with subsequent electron transfer to the NiCycP on the picosecond timescale. CuInS2/ZnS (core/shell) quantum dots combined with a meso-tetrphenylporphin iron(III) chloride (FeTPP) cocatalyst produced a hybrid photocatalyst for CO2 to CO conversion with a TON of >50 (40 h) and 84% selectivity in dimethyl sulfoxide (DMSO) containing a trace amount of water under 450 nm light.[102] Electron transfer from the quantum dots to the FeTPP was reported to occur within 200 fs. Combining negatively charged colloidal CuInS2/ZnS quantum dots with positively charged trimethylamino-functionalized iron tetrphenylporphin molecules enabled the photocatalysis of CO2 to CO with a TON of 450 (30 h) and 99% selectivity in an aqueous solution containing 5 × 10⁻³ M KCl and 15 × 10⁻³ M TEOA.[103]

2.7. Z-Scheme CO2 Reduction Using Two Different Semiconductors Driven by Visible Light

The reaction mechanism associated with the one-step visible-light CO2-reduction system in Figure 3A is relatively simple, and so various semiconductors could potentially be employed to construct similar systems. However, the number of available semiconductors remains limited, especially visible-light-absorbing semiconductors that possess sufficient potential to oxidize water. This limited selection originates from the requirement for a one-step CO2-reduction semiconductor to have a CBM that is sufficiently more negative than the CO2-reduction potential, while possessing a valence band potential that is able to oxidize water. The data summarized in Tables 1 and 2 suggest that the application of a semiconductor having a relatively negative CBM is the most important aspect of achieving CO2 reduction in this type of hybrid system. This is because the CBM determines the driving force for electron transfer from the semiconductor to the adsorbed metal complex. Among the various semiconductor materials that have been assessed, g-C3N4 and CaTaO2N are very rare examples that meet these stringent requirements, although CO2 reduction combined with water oxidation has not yet been achieved, even with these compounds. Of course, the physicochemical properties of the semiconductor other than its CBM value are also very important, because they have a significant impact on the electron–hole lifetime in the illuminated semiconductor particles. This effect has been demonstrated by studies with mpg-C3N4 specimens having different pore-wall structures.[65]

Very recently, the so-called Z-scheme two-step photexcitation approach was employed to reduce CO2 using water as the electron source in a powder-based suspension system (Figure 9A).[105] In these systems, electron transfer between two semiconductors is promoted by a shuttle redox mediator. The semiconductor-based Z-scheme approach has become popular in research regarding photocatalytic water splitting because of various advantages.[6,6,7] These include utilization of a wider range of visible light as well as the potential to separate reduction/oxidation products. More importantly, semiconductors having a reduction potential suitable for either CO2 reduction or water oxidation can be applied to each side of the system.

Solid solutions between CuGaS2 and ZnS [(CuGa)1-xZn0.2S2] have been employed as components of CO2-reduction systems, in conjunction with RuP. These materials were previously developed as H2-evolution photocatalysts with applications to Z-scheme water splitting under visible light.[105] The CBM potentials of (CuGa)1-xZn0.2S2 solid solutions are largely determined by the hybridization of the Zn 4s/4p and Ga 4s/4p orbitals, which can be tuned by varying the compositional parameter, x. As a result, the bandgap energies can be controlled within the range of 2.24–2.54 eV.
The CO₂-reduction activities of unmodified (CuGa)₁₋ₓZnₓS₂ solid solutions (i.e., without RuP) have been examined in aqueous NaHCO₃ solutions containing dissolved [Co(tpy)]₃²⁺[2⁺] as the redox shuttle electron mediator. The [Co(tpy)]₃²⁺/²⁺ couple has been previously shown to be effective for Z-scheme water splitting in association with BiVO₄ as the water-oxidation photocatalyst. [110] [Co(tpy)₂]²⁺ (i.e., with one less terpyridine ligand) has also been reported to function as an electrocatalyst for CO₂ reduction to CO in a DMF/H₂O mixture (90:10 v/v). [111,112] However, this compound does not serve as a catalyst in a solid-solution system because the CBM potentials of (CuGa)₁₋ₓZnₓS₂ solid solutions are not sufficiently negative to reduce [Co(tpy)₂]²⁺. As shown in Figure 9B, the activities of such systems were greatly affected by the composition of the solid solution. The generation of CO, which was found to be the main CO₂-reduction product, increased as x was increased from 0 to 0.5, beyond which the CO production fell. A similar trend in activity was observed in the case of solid solutions on which RuP was adsorbed, although the highest activity was obtained with x = 0.7 [i.e., (CuGa)₀.₃Zn₁.₄S₂]. The increase in activity with increases in the x value can be explained by the trend to more negative CBM values, which resulted in more efficient electron transfer to RuP and thus a higher CO₂-reduction rate. The decrease in activity at higher x values is likely due to the formation of larger bandgaps in the (CuGa)₁₋ₓZnₓS₂ solid solutions, meaning inefficient visible-light absorption.

In contrast to the results obtained from unmodified solid solutions, both CO and formate were detected following the addition of RuP, and the origins of these CO₂-reduction products were confirmed by isotope tracer experiments with ¹³CO₂. The TON values associated with CO and formate generation were 214 and 70 after 16 h of reaction, respectively, providing confirmation of a catalytic cycle during the reaction.

Finally, CO₂ reduction combined with water oxidation was examined using the most active combination in a CO₂ flow system under visible light (λ > 420 nm). Under such conditions, O₂ detection is much easier than in a batch reactor. In this case, CO, formate, and H₂ were detected as the reduction products (Figure 9D), with TONs much greater than 1 after 9 h. The main CO₂-reduction product was CO, with 41% selectivity. This value was much greater than that provided by a Z-scheme system without a metal complex (<1%). More importantly, the oxidation product of O₂ was clearly obtained,

Figure 9. A) Schematic illustration of a visible-light-driven Z-scheme CO₂-reduction system consisting of a particulate RuP-modified (CuGa)₁₋ₓZnₓS₂ hybrid photocatalyst, a BiVO₄ photocatalyst, and [Co(tpy)]³²⁺ as the redox shuttle electron mediator. B) Effect of the (CuGa)₁₋ₓZnₓS₂ composition on photocatalytic activity under visible light (390 < λ ≤ 750 nm). C) Expected band structures of (CuGa)₁₋ₓZnₓS₂ solid solutions. D) Time courses of Z-scheme CO₂ reduction in an aqueous solution containing 0.1 M NaHCO₃ and 0.02 × 10⁻³ M [Co(tpy)]²⁺ under visible light (λ > 420 nm). A–D) Reproduced with permission.[109] Copyright 2018, Royal Society of Chemistry.
Another dye-sensitized CO2-reduction system was recently reported using a hybrid that consists of a catalyst, a wide-gap semiconductor, and a photosensitizer with a TON of 9 (vs [Co(tpy)]32+ after 9 h). The amount of O2 produced was less than that expected from the reaction stoichiometry, which can be attributed to the self-oxidation of the (CuGa)0.3Zn1.4S2, which competed with CO2 reduction to a small extent and supplied “excess” electrons. Nevertheless, this Z-scheme system clearly demonstrated that selective CO2 photoreduction is possible using a carefully designed metal-complex/semiconductor hybrid even in an aqueous environment.

2.8. Dye-Sensitized Semiconductors

The dye-sensitization of a wide-gap semiconductor is a conventional approach to developing a visible-light-responsive photocatalyst, in particular for H2 evolution from water.[5,11] This technique has also been applied to CO2-photoreduction systems. The principle of dye-sensitized CO2 reduction is summarized in Figure 10. Hybrid photocatalysts constructed with a catalytic metal complex and a dye-sensitized semiconductor do not completely conform to the basic concept of metal-complex/semiconductor hybrids, because such dye-based systems do not utilize the high oxidation ability of the semiconductor. Rather, they rely on another photosensitizer to activate a wide-gap semiconductor such as TiO2, with the aid of a strong electron donor (e.g., BIH). Nevertheless, it should be noted that some such systems have exhibited very high TOFs during CO2 reduction that cannot be attained using only a metal complex.

In 2010, it was reported that nanoparticulate TiO2 modified with a Ru(II) tri-diamine-type photosensitizer and a CO2-reducing enzyme (CODH I) from the anaerobic microbe Carboxydothermus hydrogenoformans photocatalyzed CO2 reduction to CO under visible light (λ > 420 nm) in the presence of 2-(N-morpholino)ethanesulfonic acid as a sacrificial electron donor.[113] Although this work did not report isotope labeling experiments to verify the origin of the CO, the TOF for CO reduction (which was assumed to be the CO2-reduction site) under optimal conditions was quite high (~530 h−1). Control experiments showed that negligible CO formation was observed when any one of the photosensitizer, TiO2, CODH I, or light was excluded. Thus, it is likely that catalytic CO2 reduction occurred in this hybrid system.

Another dye-sensitized CO2-reduction system was recently reported, based on the use of a highly robust hybrid system comprising a sensitizer, TiO2, and catalyst.[114,115] This system consisted of an organic dye sensitizer [5’-4-[bis-(4-methoxy-methyl)phenyl]amino]-phenyl-2,2’-dithio-phen-5-yI-(cyanoacrylic acid) and a [Re(bpy)(CO)3Cl]2+-type catalyst, both of which were anchored onto TiO2 particles. This structure enabled efficient visible-light-driven CO2 reduction to CO in DMF containing BIH as an electron donor, with a TON of >570 (30 h) under optimal conditions. An interesting feature of this hybrid is that substantial increases in the CO2-reduction activity can be achieved upon adding water or certain other species, such as Li+, Na+, and TEOA. Replacement of the organic dye with an Ir(III)-based photosensitizer gave essentially the same performance, with a TON of >300 (10 h).[116] In the absence of either the sensitizer, TiO2, or catalyst, the TON values became much lower. Although it would appear that the TiO2 CBM would be too positive to allow electron transfer to the Re(I) catalyst, electrochemical impedance spectroscopy indicated that the flat-band potential (i.e., the CBM) of TiO2 in dry DMF was considerably negative (~2.25 V vs SCE) but shifted positively upon the addition of water or Li+. This fact explains the positive effects of the additives on photocatalytic CO2 reduction, which evidently result from optimal alignment of the CBM of TiO2 with respect to the Edox of the sensitizer and the Ered of the catalyst in the ternary system. It was thus determined that the presence of the TiO2 semiconductor in this hybrid system was essential because this material functioned as an electron reservoir and electron-transporting mediator to promote continuous photocatalysis.

2.9. Heterogeneous Metal-Complex (Photo)Catalysts

Another interesting example of a metal-complex/semiconductor hybrid photocatalyst involves work with heterogeneous Re(I) complexes. As described in the Introduction, [Re(bpy)(CO)3X]2+-type complexes (X = Br, Cl) can function as either electrocatalysts or photocatalysts while exhibiting high quantum yields for CO2 to CO conversion. Immobilization of a phosphonated [Re(bpy)(CO)3Br]2+-type complex onto the surface of TiO2 was found to improve the rate of visible-light-driven CO2 reduction to CO in DMF containing TEOA as a sacrificial electron donor, as compared to the use of a Re(I) complex photocatalyst alone.[117] While [Re(bpy)(CO)3I]2+-type photocatalysts gave moderate TONCO values (typically around 10) under these reaction conditions, this heterogeneous system showed a TONCO that was increased by a factor of 5–6. Of course, TiO2 on its own did not undergo photocatalysis, giving no CO. Spectroscopic measurements also revealed the reaction mechanism by which CO was generated by the Re-complex/TiO2 system.[118] The first step involves electron injection from the excited state of the Re catalyst to the TiO2, followed by rapid and efficient regeneration of the Re5+ center by the attached TEOA ligand. A second electron transfer, from the TEOA radical cation, results in the formation of the singly reduced [Re(bpy)(CO)3]2+ species on a time scale of 35 ns. It was proposed that the increase in photocatalytic activity observed when the catalyst was bound to TiO2, as compared to the activity of a homogeneous system, was due to the slow charge recombination and high oxidative power of the Re5+ species after injection. These features were superior to those associated with the excited metal-to-ligand charge...

Figure 10. Dye-sensitized CO2 reduction using a hybrid that consists of a catalyst, a wide-gap semiconductor, and a photosensitizer.
transfer (MLCT) state in solution, resulting in a more efficient reaction with TEOA.

A follow-up study demonstrated that semiconducting hexaniobate nanoscrolls, prepared by chemical exfoliation of lamellar H₂K₂Nb₆O₁₇ and subsequent reassembly, showed the same functionality as TiO₂ but with a 20% higher TON. Transient absorption spectroscopy studies indicated that slow back electron transfer and the negative CBM of the nanoscrolls (which in turn increased the reducing power of electrons) both contributed to the improved CO₂ photoreduction.

The effectiveness of heterogenization of a metal-complex-based homogeneous photosystem with the use of a solid support was also reported. In this case, a phosphonic-acid-functionalized [Ru(bpy)₃]²⁺ sensitizer and a methyl-phosphonic-acid-functionalized [Ni(cyclam)]²⁺ catalyst were coinmobilized onto the surface of ZrO₂, which is a wide-gap insulator. The hybrid material could reduce CO₂ into CO in 0.1 M aqueous ascorbate solution with a TON of 4.8 and outperformed a homogeneous counterpart (without ZrO₂), although the selectivity to CO was relatively low due to competitive H₂ evolution (CO:H₂ = 4.15:1).

3. Artificial Z-Scheme Systems Constructed with a Supramolecular Metal-Complex Photocatalyst and a Visible-Light-Absorbing Semiconductor Photocatalyst

In this section, hybrid photocatalyst systems incorporating a supramolecular metal-complex photocatalyst (Figure 3B) are described. The majority have been constructed using a binuclear Ru(II) complex (Table 3).

| Entry | Semiconductor | Ag loaded [wt%] | RuRu' adsorbed [µmol g⁻¹] | Formate [µmol] | Selectivity [%] | TON Initial AQY at 400 nm [%] | Reaction time [h] | Reactant solution | Ref. |
|-------|---------------|-----------------|---------------------------|----------------|----------------|-----------------------------|-----------------|-----------------|-----------------|
| 1b)   | TaON          | 0.0             | 3.0                       | 0.07           | 27             | 3.1                     | 15              | Methanol         | [122]           |
| 2b)   | TaON          | 0.1             | 3.0                       | 0.97           | 57             | 41                       | 15              | Methanol         | [122]           |
| 3     | TaON          | 0.0             | 3.0                       | 1.2            | 19             | 103                       | 15              | 10⁻³ M EDTA·2Na aq. (pH 4.3) | [124]           |
| 4     | TaON          | 0.15            | 3.0                       | 7.0            | 37             | 600                       | 0.48            | 10⁻³ M EDTA·2Na aq. (pH 4.3) | [124]           |
| 5     | TaON          | 0.15            | 3.0                       | 8.5            | 37             | 750                       | 24              | 10⁻³ M EDTA·2Na aq. (pH 4.3) | [124]           |
| 6     | TaON          | 0.15            | 3.0                       | 4.0            | 85             | 340                       | 15              | 10⁻³ M EDTA·2Na aq. + 0.1 M Na₂CO₃ aq. (pH 7.0) | [124]           |
| 7     | TaON          | 0.15            | 3.0                       | 0.95           | 50             | 79                       | 15              | H₂O/methanol (4:1 v/v) | [124]           |
| 8     | CaTaO₂N       | 0.0             | 2.5                       | 0.09           | >99            | 9                         | 15              | DMA/TEOA (4:1 v/v) | [98]            |
| 9     | CaTaO₂N       | 0.10            | 2.5                       | 0.32           | >99            | 32                       | 15              | DMA/TEOA (4:1 v/v) | [98]            |
| 10    | Y-Ta oxynitride | 0.0            | 4.5                       | 0.16           | >99            | 5                         | 24              | DMA/TEOA (4:1 v/v) | [126]           |
| 11    | Y-Ta oxynitride | 0.15          | 4.5                       | 0.63           | >99            | 18                       | 24              | DMA/TEOA (4:1 v/v) | [126]           |
| 12    | mpg-C₂N₄      | 0.0             | 3.4                       | 0.6            | 52             | 43                       | 24              | DMA/TEOA (4:1 v/v) | [84]            |
| 13    | mpg-C₂N₄      | 0.50            | 3.4                       | 42.3           | >99            | 3110                     | 5.2             | DMA/TEOA (4:1 v/v) | [84]            |
| 14    | mpg-C₂N₄      | 0.50            | 0.5                       | 66.7           | 88             | 33 341                   | 48              | DMA/TEOA (4:1 v/v) | [84]            |
| 15    | g-C₃N₄nanosheet| 0.15            | 2.3                       | 5.0            | 98             | 2090[^d]                 | 0.2             | 10⁻³ M EDTA·2Na + 0.1 M K₂CO₃ aq. (pH 7.0) | [127]           |
| 16    | GaN:ZnO       | 0.15            | 3.0                       | 4.1            | 77             | 359                      | 1.0             | 10⁻³ M EDTA·4Na + 20⁻³ M Na₂CO₃ aq. (pH 6.4) | [128]           |
| 17    | Rutile        | 0.15            | 3.0                       | 0.2            | 67             | 18                       | 15              | 10⁻³ M EDTA·4Na + 20⁻³ M Na₂CO₃ aq. (pH 6.4) | [128]           |
| 18[^a] | Ta₃N₅        | 0.0             | 3.0                       | 0.07           | 94             | 6                        | 15              | MeCN/TEOA (4:1 v/v) | [129]           |
| 19[^a] | Ta₃N₅        | 0.15            | 3.0                       | 0.48           | 99             | 40                       | 15              | MeCN/TEOA (4:1 v/v) | [129]           |
| 20    | Ta₃N₅        | 0.15            | 3.0                       | 0.72           | 99             | 60                       | 15              | MeCN/TEOA (4:1 v/v) | [129]           |
| 21    | Li₂LaTa₂O₅N   | 0.0             | 3.0                       | 0.66           | 97             | 55                       | 15              | MeCN/TEOA (4:1 v/v) | [140]           |
| 22    | Li₂LaTa₂O₅N   | 0.15            | 3.0                       | 1.44           | 99             | 120                      | 15              | MeCN/TEOA (4:1 v/v) | [140]           |
| 23    | Pb₂Ta₂O₇F₁₂   | 0.0             | 2.7                       | 0.6            | >99            | 26                       | 15              | MeCN/TEOA (4:1 v/v) | [143]           |
clear Ru(II) complex (RuRu') and a non-oxide type semiconductor, as listed in Table 3.

3.1. Proof of Concept

As noted in the Introduction, binuclear Ru(II) and Ru(II–Re(I)) complexes are efficient homogeneous photocatalysts for CO2 reduction with the aid of a strong electron donor such as BIH.[27] The low activity of these supramolecular photocatalysts during oxidation reactions can, in principle, be addressed if they are combined with a suitable semiconductor photocatalyst capable of promoting photo-oxidation. This is similar to the concept of the one-step photoexcitation system (see Figure 3A).

The first successful demonstration of a CO2-reduction Z-scheme system using this concept and constructed with a metal complex and a semiconductor was reported in 2013, based on TaON and RuRu' (abbreviated as RuRu'/TaON), as shown in Figure 11A.[122] RuRu' is composed of a [Ru(bpy)3]2+ type photosensitizer unit and a [Ru(bpy)(CO)2Cl2]-type catalytic unit, covalently connected via an ethylene chain. RuRu' can efficiently reduce CO2 to formate in a homogeneous system, but will not function when using a weak electron donor such as methanol. While TaON is a representative photocatalyst capable of oxidizing water (and thus, of course, methanol) under visible light in the presence of a suitable electron acceptor,[123] it does not work as a photocatalyst for CO2 reduction, most likely due to a lack of active sites. However, combining these two “inactive” compounds resulted in the production of formate with an associated TON of 3.1. In this case, a very small amount of CO was evolved as a second CO2-reduction product, with appreciable H2 evolution due to competitive proton reduction. It was also found that modification of the TaON with Ag nanoparticles, followed by the immobilization of RuRu' on this material, improved both formate production and selectivity. During a subsequent photocatalytic reaction, an oxidation product of HCHO was detected in the liquid phase. Importantly, the total amount of HCHO obtained was close to the overall quantity of reduction products (i.e., formate, CO and H2), which indicated a good electron/hole balance (see Figure 11B). Tracer experiments using 13CO2 and 13CH3OH showed that the formate came from CO2, and that only H13CHO was detected in the reactant solution. These data not only show that the formate was derived from CO2, but also that the electron source was likely the methanol. Thus, the visible-light CO2-reduction reaction can be expressed according to Equation (16)

$$\text{CO}_2 + \text{CH}_3\text{OH} \rightarrow \text{HCOOH} + \text{HCHO} \quad \Delta G^\circ = +83.0 \text{kJ mol}^{-1}$$ (16)

Therefore, light energy was stored as chemical energy in the form of formate and HCHO through the use of the RuRu'/Ag/TaON hybrid photocatalyst.

Control experiments showed that no CO2-reduction products were obtained when either light or CO2 was absent. Modification of the Ag/TaON with model RuRu' mononuclear complexes ([Ru(II)(dmb)2{bpy(CH2PO3H2)}] = Ru(PS) and RuCP) did not yield catalytic formate production. In addition, Ag/TaON did not produce formate. As discussed above, Ag nanoparticles loaded on a semiconductor photocatalyst can serve as cocatalysts for CO2 reduction. However, it appears that, in the case of this RuRu'/Ag/TaON hybrid, Ag did not provide CO2-reduction sites, although it would be expected to serve as a sink for free or shallowly trapped electrons in a semiconductor (as discussed earlier in the text). The other roles of Ag on a semiconductor in Z-scheme CO2 reduction are discussed in a later section.

It was also found that the RuRu'/Ag/TaON photocatalyst exhibited activity for CO2 reduction even in an aqueous solution containing dissolved disodium dihydrogen ethylenediaminetetraacetate (EDTA-2Na) that worked as an electron donor.[124] After optimization of the reaction conditions, such as pH and salt additive, a TON of 750, an AQY of 0.48% at 400 nm, and a maximum CO2-reduction selectivity of 80% were recorded. The RuRu'/Ag/TaON photocatalyst was also...
able to convert visible-light energy to reduce CO₂ to formate in conjunction with the oxidation of methanol, even in aqueous solution. Although examples of CO₂ reduction in aqueous environments using a supramolecular metal-complex photocatalyst are rare,[31,125] the results of this study indicated that supramolecular photocatalysts such as RuRu⁺ can function as a key component for CO₂ reduction in water. The major obstacle to the further development of this type of photocatalyst is the desorption of RuRu⁺ from the Ag/TaON surface during the reaction, which hinders electron transfer from the TaON to RuRu⁺, thereby lowering activity.

3.2. Semiconductor Photocatalysts Applicable to Z-Scheme Systems with a Supramolecular Metal-Complex Photocatalyst

Following the discovery of TaON-based hybrid photocatalysts, several (oxy)nitride-type semiconductors were found to exhibit the same functionality, GaN:ZnO,[98] yttrium–tantalum oxyinitride (YTON),[126] C₃N₄,[84,127] GaN:ZnO solid solutions,[128] and Ta₃N₅,[129] all of which have sufficient potential to oxidize water under visible light.[130–133] They were successfully applied to Z-scheme systems with RuRu⁺. In particular, the RuRu⁺/Ag/mpg-C₃N₄ hybrid photocatalyst gave a very high TON(formate) (~33 000) in a DMA/TEOA mixed solution under visible-light irradiation, with a high CO₂-reduction selectivity (~90%).[84] These values are the highest yet reported for hybrid systems. Very recently, it has been shown that NS-C₃N₄ undergoes robust binding with RuRu⁺ even in basic aqueous solutions, enabling durable, selective CO₂ reduction to formate under visible light in aqueous environments, with a maximum TONₜ(HCOOH) of 2090 under the optimized conditions.[127] It should be noted that this system outperformed the highly active RuRu⁺/Ag/mpg-C₃N₄ hybrid photocatalyst in aqueous environments.

A notable feature of hybrid Z-scheme systems is that certain semiconductors that are supposedly inactive in one-step photoexcitation systems, such as TaON and YTON, can be used as active components in a Z-scheme process. This phenomenon can be, at least in part, attributed to the difference in the driving force for electron transfer from the semiconductor to the metal complex. As an example, electron transfer from the CBM potentials of TaON and YTON to a mononuclear Ru(II) complex catalyst such as RuP and RuCP is thermodynamically uphill, while transfer to the excited state of RuRu⁺ is downhill (see Figure 11A). This allows various semiconductors to be applied to Z-scheme CO₂ reduction even when they possess relatively positive CBM values. The difference in the driving force for electron transfer between these two systems could account for the significantly improved photocatalytic performance of C₃N₄-based hybrids. This can be seen by considering the photocatalytic activity of RuRu⁺/Ag/mpg-C₃N₄ for CO₂ to formate conversion, which is higher than that of RuP/Ag/mpg-C₃N₄.[84]

The rate of formate generation by the RuRu⁺/semiconductor hybrid photocatalyst was found to increase with increasing amount of RuRu⁺ loaded, reaching a plateau at a certain value regardless of the semiconductor employed or the reaction conditions.[84,126] This enhanced activity is ascribed to improved light harvesting by the RuRu⁺ sensitizing unit. Unlike the lower adsorption region, however, the density of the excited state of the sensitizer unit should be sufficiently high, limiting electron transfer from the semiconductor to the excited state of the sensitizer unit. In addition, increasing the RuRu⁺ loading inevitably lowers the TON value on a per RuRu⁺ basis.

Nevertheless, back electron transfer from the excited state of RuRu⁺ to the conduction band of the semiconductor should be carefully considered, because this process can reduce the Z-scheme CO₂-reduction performance obtained with a supramolecular photocatalyst. The impact of back electron transfer on the activity of a hybrid CO₂-reduction system incorporating RuRu⁺ in aqueous EDTA solutions was investigated using three semiconductors with different CBM potentials: GaN:ZnO, TaON, and rutile TiO₂ codoped with Ta and N (represented as TiO₂-Ta,N).[128] Each of these materials has been shown to function as a good photocatalyst for visible-light-driven water oxidation.[59,123,132] In addition, the CBM potentials of these semiconductors are all more negative than the reduction potential of the photoexcited Ru(II) photosensitizer unit (E°ₗ= 0.54 V vs Ag/AgCl), indicating that electron transfer from the conduction band to the excited photosensitizer unit is thermodynamically favorable. Furthermore the valence-band holes in these semiconductors can supply a driving force of at least 250 mV, which is sufficient for the oxidation of EDTA (Eₗ= 1.26 V vs Ag/AgCl).[134] Therefore, all of these semiconductors are potentially useful components in Z-scheme CO₂-reduction systems employing RuRu⁺ in the presence of Na₂EDTA as an electron donor under visible light. Interestingly, each of these materials exhibited a different catalytic activity (see Table 3), with the highest activity shown by the GaN:ZnO solid solution (which has the most negative CBM). Conversely, the TiO₂-Ta,N (with the most positive CBM) was found to have the lowest activity, which was just 5% that of the GaN:ZnO-based system.

RuRu⁺ (more precisely, the associated photosensitizing unit) exhibits emission from the triplet MLCT (′MLCT) excited state that is quenched when the unit undergoes reduction or oxidation.[135,136] Thus, by measuring the degree of emission quenching in a RuRu⁺/semiconductor hybrid, one can obtain useful information concerning the interfacial electron transfer between the two components. Figure 12 presents emission decay curves obtained from RuRu⁺ adsorbed on GaN:ZnO, GaN, and Al₂O₃ with 444 nm photoexcitation. It is important to note that, under these measurement conditions, GaN and Al₂O₃ did not undergo photodegradation due to their large bandgaps, while pure GaN:ZnO did not produce any photoemission. The emission decay of the RuRu⁺/Al₂O₃ shows the absence of any electron transfer events because Al₂O₃ is an insulator that serves as neither an electron acceptor nor an electron donor. More pronounced emission quenching was observed in the case of the RuRu⁺/GaN relative to the RuRu⁺/Al₂O₃, suggesting electron transfer from the excited state of RuRu⁺ to the conduction band of GaN. GaN has a CBM potential similar to that of GaN:ZnO (Eₗ= −1.1 V vs Ag/AgCl), but was unable to absorb the 444 nm excitation light. Since the GaN could not generate electrons in its conduction band in response to 444 nm irradiation, it presumably acted only to accept electrons from the excited state of RuRu⁺. Thus, the more pronounced emission quenching exhibited by the RuRu⁺/GaN as compared to the RuRu⁺/Al₂O₃ can be attributed to electron injection from
the excited photosensitizer unit \(E_{ox} = -1.1\) V vs Ag/AgCl) into the GaN \(E_{CBM} = -1.1\) V). It should be noted that more efficient emission quenching was observed using \(RuRu' / GaN:ZnO\), suggesting the existence of an additional electron-transfer pathway from the conduction band of GaN:ZnO to the excited state of \(RuRu'\), likely via photoexcitation of the GaN:ZnO. Similar results were obtained from hybrids constructed with TaON, \(Ta_2O_5\), and \(Al_2O_3\).

In contrast, the Ti-based hybrids generated different emission-decay curves. \(TiO_2:Ta\) was employed as a model for \(TiO_2:Ta,N\) because it does not undergo photoexcitation at 444 nm but possesses a CBM potential identical to that of \(TiO_2:Ta,N\).\[^{[59]}\] \(RuRu' / TiO_2:Ta\) showed much faster emission decay than an analogue constructed with GaN and \(Ta_2O_5\), indicating that backward electron transfer was more efficient in \(RuRu' / TiO_2:Ta\) than in the other systems. More importantly, the emission-decay curve of \(RuRu' / TiO_2:Ta,N\) was almost the same as that of \(RuRu' / TiO_2:Ta\). This result demonstrated that the forward electron transfer (i.e., from \(TiO_2:Ta,N\) to \(RuRu'\)) was very slow. Therefore, the efficient back electron transfer in \(RuRu' / TiO_2:Ta,N\) hindered forward electron transfer, and this effect was the primary cause of the low photocatalytic activity of the hybrid with \(TiO_2:Ta,N\).

On the basis of the above data, it was concluded that suppressing the backward electron transfer from the excited state of \(RuRu'\) to the conduction band of the semiconductor and accelerating the forward electron transfer from the conduction band to the excited state of \(RuRu'\) are both important for enhancing the \(CO_2\)-reduction activity of these hybrid Z-scheme systems. Suppression of the backward electron transfer could be achieved by elevating the CBM potential of the semiconductor unit. In fact, semiconductor materials that are effective components of Z-scheme \(CO_2\)-reduction systems tend to possess relatively negative CBM potentials (typically with \(E_{CBM} \) values < -1.3 V, as summarized in Tables 1 and 3).

Figure 12. A) Schematic illustration of interfacial electron transfer between the excited state of the Ru photosensitizer unit and various semiconductors under visible light (444 nm), and B) emission time profiles of \(RuRu'\) adsorbed on Ga- and Ti-based semiconductors or on \(Al_2O_3\) in an aqueous \(Na_2CO_3\) solution \((20 \times 10^{-3}\) m) containing \(Na_4EDTA\) \((10 \times 10^{-3}\) m) under a \(CO_2\) atmosphere. The excitation and monitoring wavelengths were 444 and 630 nm, respectively. A,B) Reproduced with permission.\[^{[128]}\] Copyright 2018, American Chemical Society.
3.3. New Mixed-Anion Semiconductors

The aforementioned (oxy)nitrides are known to act as photocatalysts, and they were originally developed for visible-light water splitting. However, recent advances in synthetic inorganic chemistry have led to the synthesis of interesting new materials. In particular, mixed-anion compounds consisting of more than two anionic species in a single phase are emerging materials that exhibit unique properties (including photocatalysis) that may be unattainable with single-anion compounds such as oxides.\[137\]

2D layered metal oxides that contain Ti\(^{4+}\), Nb\(^{5+}\), and Ta\(^{5+}\) as the principal cation are known to be highly active photocatalysts for water splitting and CO\(_2\) reduction. Despite this, as discussed above, these oxides do not function efficiently under visible light due to their large bandgaps (>3 eV). Therefore, 2D-type mixed-anion photocatalysts could be especially beneficial. While nitrogen doping of metal oxides is a simple and conventional means of inducing a visible-light response,\[61,138\] recent spectroscopic studies have shown that the charge imbalance between oxide and nitride anions (O\(^{2-}\) vs N\(^{3-}\)) inevitably introduces defect states. These states, in turn, act as recombination centers for photoexcited carriers and thus lower the photocatalytic activity, as has been demonstrated in work with nitrogen-doped TiO\(_2\).\[59,139\] In addition, the limited amount of nitrogen that is typically added by doping leads to an insufficient degree of visible-light absorption.

In the search for new materials, the undoped, phase-pure oxyxynitride Li\(_2\)LaTa\(_2\)O\(_6\)N was developed.\[140\] This material has a 2D layered perovskite structure that consists of double-layer \([\text{LaTa}_2\text{O}_6\text{N}]^2\) slabs interleaved with two Li\(^+\) cations.\[141\] Scanning transmission electron microscopy (STEM) observations have indicated that synthesized Li\(_2\)LaTa\(_2\)O\(_6\)N specimens are highly crystalline. As expected, Li\(_2\)LaTa\(_2\)O\(_6\)N absorbs visible light up to 500 nm as a result of electron transitions from the valence band formed by N 2p/O 2p hybridized orbitals to the conduction band consisting of empty Ta 5d orbitals, as demonstrated by density functional theory (DFT) calculations. The bandgap of Li\(_2\)LaTa\(_2\)O\(_6\)N was estimated to be 2.5 eV based on the onset wavelength of its diffuse reflectance spectrum. These characteristics suggest that this material is a promising visible-light-driven photocatalyst.

The hybrid system, RuRu'/Li\(_2\)LaTa\(_2\)O\(_6\)N, catalyzed the production of formate from CO\(_2\) as the main product with high selectivity (97%) in a MeCN/TEOA mixture under visible-light irradiation (\(\lambda > 400\) nm). This reaction system was based on the Z-scheme principle. Importantly, the hybrid photocatalyst exhibited much higher photocatalytic performance than other systems incorporating the well-known 3D oxyxynitride perovskites CaTa\(_2\)O\(_6\)N and LiTaO\(_3\). Transient absorption spectroscopy indicated that Li\(_2\)LaTa\(_2\)O\(_6\)N possesses a lower density of the mid-gap states that work as recombination centers for photogenerated electron/hole pairs, but a higher density of reactive electrons, as compared to CaTa\(_2\)O\(_6\)N and LaTaO\(_3\). These differences are thought to be responsible for the higher photocatalytic performance of this layered oxyxynitride.

As discussed above, oxyxynitrides are potential visible-light-driven photocatalysts, because their N 2p orbitals can form valence bands with more highly negative potentials than those obtained from O 2p orbitals. On this basis, oxyfluorides (oxide-fluorides) would appear to be unsuitable because of the higher electronegativity of fluorine. However, very recently, the oxyfluoride Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\), which has an anion-ordered A\(_2\)B\(_x\)X\(_y\)\(_{0.5}\)-type pyrochlore structure (Figure 13A),\[143\] was found to possess an unexpectedly small bandgap (>2.4 eV) and to absorb visible light up to 510 nm (Figure 13B).\[143\] Electrochemical impedance spectroscopy and UV–vis diffuse reflectance spectroscopy indicated that this material has band edge potentials suitable for water reduction/oxidation and CO\(_2\) reduction, as illustrated in Figure 13C. Consequently, Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\) was found to work as a stable photocatalyst for visible-light-driven H\(_2\) evolution and CO\(_2\) reduction when modified with a suitable promoter such as Pt nanoparticles (for H\(_2\) evolution) or RuRu’ (for CO\(_2\) reduction), in the presence of TEOA as an electron donor. In addition, water oxidation to form O\(_2\) was also possible using this catalyst in conjunction with AgNO\(_3\) as an electron acceptor and a RuO\(_2\) cocatalyst.

DFT calculations were performed to investigate the origin of the visible-light response of Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\). Figure 13D shows the total and partial density of state (DOS) results for this material. These data demonstrate that the CBM consists primarily of Ti 3d orbitals with some hybridization of Pb 6p orbitals (especially at the higher energy side), whereas the VBM is formed by O 2p orbitals with a contribution by Pb 6s orbitals. At the lower energy side of the valence band (from ~8 to ~5 eV), Pb 6s orbitals are hybridized with O 2p orbitals. Integral calculations for each partial DOS also determined that the O 2p contribution to the Pb 6s band (per atom) was largest at the X1 site (specifically, five times the contributions at the X1 and X2 sites).

The valence band characteristics of such materials can be interpreted in terms of the revised lone-pair (RLP) model proposed by Walsh et al.\[144\] In this model (schematically shown in Figure 13E), the antibonding orbitals resulting from Pb 6s and O 2p orbitals are stabilized through an interaction with the empty Pb 6p orbitals, which accounts for the increased energy levels of the O 2p orbitals in Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\). Certain Pb(II)-based oxides, such as PbO and PbTiO\(_3\), are known to exhibit this phenomenon.\[144\] However, the bandgaps of these Pb(II)- containing oxides are wider than that of Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\), suggesting that the extent of Pb 6s/O 2p hybridization in the latter material is much greater. This is at least in part due to the unique coordination environment around the A-sites in the pyrochlore structure. Ideally, an A\(_2\)B\(_x\)O\(_y\) structure has two short and six long A–O bonds, and the shortest Pb–O bond in Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\) (is 2.248 Å)\[142\] is much shorter than that in the perovskite PbTiO\(_3\) (2.510 Å). This difference in the local coordination environment could qualitatively explain the narrower bandgap of Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\) (<2.4 eV) as compared to that of PbTiO\(_3\) (~2.8 eV). Thus, the unprecedented visible-light response of Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\) is attributed to strong interactions between Pb 6s and O 2p orbitals resulting from the short Pb–O bond in the pyrochlore lattice. This short bond is, in turn, due to the fluorine substitution in this compound. This hypothesis was supported by a follow-up comparative study of another oxyfluoride: Pb\(_2\)Ti\(_3\)O\(_5\)F\(_{1.2}\).\[145\] The low coordination number of the A sites in the pyrochlore (or defect-pyrochlore) structure tends to strengthen the electronic interaction between M 6s (M = Pb and Bi) and O 2p orbitals, thereby enhancing visible-light absorption.
3.4. Effects of the Structural Properties of Semiconductors on Activity

Work involving semiconductor materials developed for Z-scheme CO₂ reduction shows that these compounds should have a CBM more negative than −1.3 V (vs Ag/AgNO₃), which is equivalent to the excited-state oxidation potential of the photosensitizer unit in RuRu’. This result indicates that suppression of back electron transfer from RuRu’ to the semiconductor is essential.

Nevertheless, other characteristics of the semiconductor component are also important in determining the overall performance of the Z-scheme hybrid. As discussed in the previous section, the physicochemical properties of C₃N₄ (such as specific surface area and crystallinity) greatly affect its activity during visible-light CO₂ reduction with the aid of a mononuclear Ru complex. [65,69] This is also the case for Z-scheme CO₂-reduction systems incorporating RuRu’. [84] A GaN:ZnO solid solution is a useful starting point for studying the effects of physicochemical properties, because the characteristics of this material (e.g., the band-edge potential and bandgap) can be controlled by changing the GaN/ZnO molar ratio in the material via modifying synthetic conditions. [132,146,147]

Four different GaN:ZnO samples possessing different physicochemical properties were tested as the semiconductor component in a hybrid photocatalyst. [128] The results obtained from CO₂-reduction reactions indicated that GaN:ZnO specimens having higher ZnO concentrations (i.e., smaller bandgaps) exhibited superior photocatalytic activities, along with more pronounced emission decay. These results can likely be ascribed to the more efficient photo-oxidation of the electron donor (Na₄EDTA) on these materials (as confirmed by photoelectrochemical data), which promotes the accumulation of electrons in the conduction band, as well as forward electron transfer. Photoelectrochemical measurements also showed that the CBMs of each of the GaN:ZnO samples were almost identical regardless of their composition. In contrast, the VBM was found to shift in the positive direction as the ZnO concentration was decreased (i.e., the bandgaps increased). While a positive shift in the VBM should increase the driving force for the photo-oxidation reactions, the experimental results suggested that a GaN:ZnO sample having superior visible-light-absorption properties was advantageous. This is because such materials generate larger numbers of photoexcited electrons in response to visible light as opposed to increasing the driving force for the oxidation reaction. These electrons, once accumulated in the conduction band, will migrate to the RuRu’ molecular photocatalyst unit, resulting in efficient CO₂ reduction. The AQY for formate generation over the optimized GaN:ZnO formulation was found to be 1.0% at 400 nm, which is higher than that obtained from the RuRu’/Ag/NS-C₃N₄ photocatalyst (0.2%). [127]
3.5. Significant Promotional Effect of Silver Nanoparticles

Another important observation related to Z-scheme CO₂ reduction to formate is that the rate of formate production is often significantly improved by loading Ag, while the presence of Ag without a metal complex does not give appreciable CO₂ conversion. Studies have shown that the formate production rate increases as the Ag loading is increased up to a maximum at a specific Ag concentration, above which the rate decreases. This trend is consistent over a wide range of semiconductors and reaction conditions. Transmission electron microscopy analyses have shown that the Ag nanoparticles on these semiconductors are typically less than 30 nm in size, although the optimal size will vary with the semiconductor to some extent. Excess loading leads to aggregation of the Ag, which negatively affects activity, presumably due to a light-filtering effect and/or coverage of active sites. These effects likely explain the loss of activity at higher loadings.

The primary role of Ag nanoparticles on a semiconductor is believed to be the promotion of charge separation, as demonstrated by studies of the Ag/mpg-C₃N₄ system (see the previous Section 2.4.3). Further investigation on the promotional effect of Ag in Z-scheme systems was made by means of time-resolved emission spectroscopy using a semiconductor and Ru(PS), as a model RuRu’ complex. As discussed earlier, Ru(II) tris-diimine complexes such as Ru(PS) exhibit emission centered at ≈640 nm, due to transitions from the lowest 3MLCT excited state. Emission decays were measured using several semiconductors known to effectively promote Z-scheme CO₂ reduction in conjunction with Ru(PS), so as to observe deactivation of the 3MLCT exited state of Ru(PS). Figure 14 shows typical emission-decay data obtained using CaTaO₂N and Al₂O₃. The emission from Ru(PS) on Al₂O₃ (an insulator) evidently decayed over time (Figure 14A), and this behavior remained unchanged even in the presence of TEOA, indicating that reductive quenching of the excited state of Ru(PS) by TEOA was negligible.

In contrast, the emission decay of Ru(PS) on CaTaO₂N was accelerated upon the addition of TEOA (Figure 14B). In this case, photoexcitation would be expected to occur in both Ru(PS) and CaTaO₂N, and the holes generated in the valence band of the CaTaO₂N should be consumed by TEOA. Therefore, the
observed accelerated decay is attributable to the promotion of reductive quenching by electron transfer from the CaTaO2N to the excited state of the Ru(PS). Importantly, this emission decay was accelerated upon increasing the Ag loading (Figure 14C). A control experiment showed that Ag deposits alone (without semiconductor) did not affect the lifetime of the emission from Ru(PS), and a similar result was obtained using YTON.[126] Note that electron injection from the excited state of Ru(PS) (E'ox = −1.30 V) to the CBM of CaTaO2N (E'CBM = −2.15 V) is thermodynamically uphill. Besides, ultrafast electron injection from the MLCT exited state of a Ru sensitizer to a semiconductor has been found to be inefficient when a methylene spacer is placed between the two.[148,149] Thus, electron transfer from the Ru(PS) to the semiconductor (i.e., oxidative quenching) should be suppressed in RuRu'/Ag/CaTaO2N. This finding suggests that the accelerated decay is attributable to the reductive quenching of Ru(PS) upon accepting an electron from the conduction band of CaTaO2N. In addition, Ag evidently promotes this quenching process, which is essential to achieving efficient Z-scheme CO2 reduction. One of the key factors that contribute to a successful Z-scheme CO2-reduction system should be the suppression of this back electron transfer event, because effective semiconductors have CBMs that are equal to or more negative than the E'ox value of Ru(PS), as discussed above.

Considering the results obtained from transient absorption spectroscopy, emission-decay measurements, and photocatalytic CO2 reduction, it is evident that the Ag particles acted as an electron pool and a mediator for electron transfer from the semiconductor to the excited state of RuRu'. Both of these effects enhanced the photocatalytic activity during CO2 reduction by this Z-scheme system. Other metals in the same XI group as Ag (e.g., Cu and Au) were also assessed in association with mpg-C3N4,[84] but all showed inferior performance. One may consider that the superior functionality of Ag during Z-scheme CO2 reduction is due to a large overpotential for proton reduction that can effectively suppress H2 evolution. Ag also tends not to accept electrons and/or energy from the RuRu' photosensitizer unit in its excited state.

3.6. Switching the Formate/CO Selectivity

Using mpg-C3N4, it was also found possible to control the product selectivity obtained from Z-scheme CO2 reduction by applying a Ru(II)–Re(I) binuclear complex with CH2PO3H2 anchors (RuRe, see Figure 15). As described in the Introduction, this type of Ru(II)–Re(I) binuclear complex is an efficient CO-evolving supramolecular photocatalyst.[27] In this case, the hybrid (RuRe/mpg-C3N4) promoted the photoreduction of CO2 to CO with high selectivity (≈90%) in a mixture of DMA and TEOA at the initial stage of the reaction, recording a TON of 27.[150] No reaction took place in the dark or in the absence of TEOA as an electron donor, while omitting either the RuRe or mpg-C3N4 resulted in negligible CO2 generation. Modification of the mpg-C3N4 with a model RuRe complex (i.e., Ru(PS) or Re,[4,4'-bipy] (CO)2Br) did not give CO either. These results confirmed that the RuRe/mpg-C3N4 hybrid functioned according to the Z-scheme principle, similar to the system based on adsorbed RuRu'. The CO-evolution activity of the RuRe/mpg-C3N4 hybrid increased monotonically with increases in the amount of adsorbed RuRe. Although the RuRe loading was limited to a level of 20–25 μmol g−1 on the mpg-C3N4, silica-modified mpg-C3N4 was capable of immobilizing a greater concentration of RuRe, leading to an increase in the photocatalytic activity by a factor of ≈3. A linear increase in the CO formation rate was also observed as the loading was increased up to 107 μmol g−1, at which point the CO-formation AQY was estimated to be ≈2.5% at 400 nm under optimal conditions. This represented an ≈50% value relative to that for RuRu'/Ag/mpg-C3N4. It is apparent that the added SiO2, which was in the form of highly dispersed nanoparticles, acted as adsorption sites for RuRe. However, when the RuRe loading was held constant, modification with SiO2 did not improve the CO-formation rate, as SiO2 is an insulator that does not modify electronic characteristics such as charge separation. In fact, the addition of an excess of SiO2 led to a decrease in activity, most likely because the efficiency of the electron transfer from the mpg-C3N4 to RuRe was reduced. As expected, RuRe/SiO2 produced negligible CO under the same reaction conditions.

Both improved charge separation and reinforced adsorption of the RuRe would be expected after introducing a semiconductor material having suitable band-edge potentials onto the C3N4 surface. To assess this possibility, rutile TiO2 (which has a CBM ≈−0.9 V more positive than that of g-C3N4 nanosheets) was immobilized on NS-C3N4, followed by the adsorption of RuRe.[151] Photogenerated electrons in the as-prepared RuRe/TiO2/NS-C3N4 hybrid showed a prolonged lifetime based on transient absorption spectroscopy results (Figure 15B). Visible-light-induced CO2 to CO conversion was also achieved using this material, with high selectivity (≈90%), in a DMA/TEOA mixture. The CO evolution rate and TON of this material were four times greater than those obtained from an analogous system without TiO2 (Figure 15C). The rutile TiO2 modifier, introduced in the form of 5–10 nm nanoparticles, was also found to provide suitable sites for the adsorption of RuRe, thus reducing undesirable desorption of the complex and contributing to improved stability. Note that while the same methodology was applied for mpg-C3N4, however, undesirable filling of mesropores with titanium species occurred, resulting in poor photocatalytic performance.

The origin of CO2-reduction selectivity of metal-complex/semmiconductor hybrid photocatalysts is basically related to the reaction mechanism of CO2 reduction on a metal-complex molecule. There are several factors that affect the reaction mechanism of CO2-reducing metal complexes, including the acidity/basicity of the reaction environment, the electron-transfer process from the donor species (i.e., chemical reductant and semiconductor), and so on.[21] For example, the major CO2-reduction product of the RuCP/mpg-C3N4 hybrid in a MeCN/TEOA mixed solution was formate with ≈80% selectivity.[64,68] On the other hand, relatively high selectivity to CO (50–60%) was obtained with the same hybrid in solvent having high donor number (e.g., DMA and DMF) in the presence of TEOA.[68]
4. Photoelectrochemical CO₂-Reduction Systems Using Metal-Complex/Semiconductor Hybrids

4.1. Photocathodes Constructed with a p-Type Semiconductor and a Metal-Complex Catalyst

Construction of a photoelectrochemical cell, in which the oxidation and reduction sites are physically separated (see Figure 3), is an alternative approach to CO₂ photoreduction using water as the electron donor. In this case, the negative effect of backward reactions involving more reducible/oxidizable products should be minimized. In addition, an external electric (or chemical) bias may be applied between the two electrodes to allow the entire reaction to proceed more efficiently, leading to an improved light-energy conversion efficiency. A p-type semiconductor that does not have sufficient VBM potential for water oxidation may be applied as the cathode, even without an external bias if the CBM of the paired n-type semiconductor photoanode is sufficiently negative relative to this VBM. Ideally, the CBM of the p-type semiconductor should be located at a potential more negative than the \( E_{\text{red}} \) of the metal-complex catalyst. In photoelectrochemical reactions, however, band-edge pinning of the p-type semiconductor enables photoreduction of metal-complex catalysts whose \( E_{\text{red}} \) is above the CBM. Of course, a metal-complex catalyst that has a more positive \( E_{\text{red}} \) (in other words, lower overpotential for CO₂ reduction) is highly desirable. This tandem photoelectrochemical cell configuration also enables more efficient utilization of the solar spectrum. That is, the shorter-wavelength region of the incident light is absorbed by a wider-gap semiconductor electrode, whereas a narrower-gap semiconductor utilizes the filtered portion of the light that contains lower-energy photons. This system can therefore be regarded as a type of Z-scheme. Also, CO₂-reduction

Figure 15. A) Band diagram for the RuRe/TiO₂/NS-C₃N₄ hybrid photocatalyst. B) Transient absorption intensity decay curves for NS-C₃N₄ and TiO₂ (27 wt%)//NS-C₃N₄ at 1800 cm⁻¹. C) Time courses of photocatalytic CO₂ reduction under visible light (\( \lambda > 400 \) nm) using RuRe (6.9 µmol g⁻¹)/NS-C₃N₄ with and without TiO₂ modification (27 wt%). A–C) Reproduced with permission. Copyright 2017, American Chemical Society.
and water-oxidation systems can be developed individually in order to maximize the efficiency of the whole system. Over the past two decades, various semiconductor materials have been developed as photoanode components that allow the oxidation of water to O2 under sunlight. [152–155] To realize a bias-free, standalone CO2 fixation system, a p-type semiconductor having a more negative CBM and a metal-complex catalyst with a more positive Ered are necessary. In addition, the entire system should function in an aqueous environment. However, ideal photocathode materials that meet these criteria are very rare. This section describes progress in the development of CO2-photoreduction cathode materials based on metal complexes and p-type semiconductors, starting with systems that incorporate a so-called “dark” anode (as summarized in Table 4) and then moving to tandem systems.

### 4.1.1. CO2-Reduction Photocathodes Combined with a “Dark” Anode

Photocatalytic CO2 reduction using a p-type semiconductor cathode in the presence of a metal-complex catalyst has been studied since the 1980s. [156–161] Various p-type semiconductors, including Si, GaP, GaAs, and InP, have been employed for this purpose, in combination with molecular catalysts such as tetra-azamacrocyclic metal (Ni2+ or Co2+) complexes, [Ni(cyclam)]2+, or a formate dehydrogenase enzyme. A combination of p-type CdTe and a metallophthalocyanine based on first-row transition metals (V, Mn, Fe, Co, Ni, Cu, and Zn) was found to become active for photocatalytic CO2 reduction to CO in a nonaqueous environment, with the highest performance obtained with a cobalt(II) derivative. [161] The selective reduction of CO2 to CO was observed in work using hydrogen-terminated p-type Si as the photocathode in the presence of Re(bipy-Bu′)(CO)3Cl (bipy-Bu′ = 4,4′-di-tert-butyl-2,2′-bipyridine) as a catalyst. [162] The reduction potential required to drive CO2 to CO conversion on p-Si was found to be 600 mV lower than that for the same reaction on a Pt electrode, with nearly 100% Faradic efficiency. Mn(I) tricarbonyl bipyridyl-type complexes worked as good catalysts for the selective conversion of CO2 to CO, in combination with p-type hydrogen-terminated silicon(100) nanowires and >600 nm light. [163] Electropolymerization of a Mn-based complex on p-type silicon was successful without losing the intrinsic electrocatalytic activity of the complex.

Alternative p-type semiconductors based on earth-abundant elements would be preferable to more common materials composed of expensive metals or high-quality Si. In this regard, Cu2O (with a bandgap of 2 eV) is a promising p-type semiconductor that has a negative CBM, although the intrinsic instability of this compound during the reduction reaction restricts its photocatalytic applications. A conformal heterojunction device made of TiO2/ZnO:Al/Cu2O deposited on an FTO substrate using an atomic-layer-deposition method has been employed in a water-splitting photocatalytic cell to allow the stable operation of a Cu2O photocathode. [164] In this system, the Cu2O serves as a light absorber and forms a p/n junction with the n-type ZnO:Al, while the external TiO2 layer acts as a protective layer to avoid photocorrosion of the Cu2O.

This heterojunction TiO2/ZnO:Al/Cu2O unit was found to be capable of reducing CO2 to CO under AM1.5G irradiation with nearly 100% Faradaic efficacy in nonaqueous environments containing a molecular Re(I) catalyst and methanol as a proton source. [165] Because of the nature of a p/n-junction device, [54] the electron transfer in this structure to an acceptor (e.g., a metal-complex catalyst) is governed by the energy difference between the TiO2 CBM and the reduction potential of the acceptor. It should be noted that the flat-band potential of TiO2 in MeCN is more negative than the onset potential of the catalytic wave observed at a glassy carbon electrode. [166,167] The protective TiO2 layer allowed the stable and selective reduction of CO2 over a span of several hours, while the addition of methanol promoted charge transfer from the protected photocathode surface to the Re catalyst. In other trials, the introduction of a mesoporous TiO2 scaffold over top of the TiO2 protector, combined with the use of methyl phosphonic acid anchors to create covalent bonds between the TiO2 layer and the Re(I) catalyst, improved the performance (giving 80–95% selectivity for CO) as compared to that obtained from a planar nonporous device with molecular catalysts homogeneously dissolved in the electrolyte solution. [167] The nanostructured photocathode surface provided greater immobilization of the Re(I) catalyst through the covalent bond linkages, resulting in a greater photocurrent and a TONCO value above 70.

### 4.1.2. Combination with a Water-Oxidation Photoanode toward Bias-Free CO2 Fixation

The majority of the p-type semiconductor/metal-complex combinations discussed above functioned in nonaqueous environments and required relatively negative potentials for efficient operation, together with a substantial amount of metal-complex molecules, which do not participate in the CO2-reduction reaction, in the electrolyte solution. In addition, all were half-cell photoreduction systems that neglect the photodriven water-oxidation process while requiring an additional electrochemical bias. Therefore, these may be unsuitable as photocathodes for Z-scheme photoelectrochemical CO2 reduction combined with water photo-oxidation. This section presents some rare examples of photoelectrochemical CO2 fixation systems that work in water when combined with a suitable water-oxidation photoanode, as summarized in Table 5.

In 2010, a Zn-doped InP (InP:Zn) single crystal modified with a polymerized Ru complex catalyst (Ru1, see Figure 16) was reported to function as a photocathode for the photoelectrochemical production of formate in CO2-saturated water, using a half-cell configuration with a glassy-carbon anode. [168] The polymerized Ru1 was loaded onto the InP:Zn surface through the photo-electropolymerization of the mononuclear Ru1 complex with a cathodic photocurrent from the InP:Zn. Under visible light (λ > 400 nm), the Ru1-polymer/InP:Zn photocathode operated in water with an applied potential lower than that required in conventional electrocatalytic systems, with a selectivity for formate of 62.3% and a TONformate > 12. Other p-type semiconductors, such as Ta2O5:N, GaP, and Cu2ZnSnS4, were also found to function as photocathode components to yield formate in conjunction with a Ru polymer catalyst.
### Table 4. Metal-complex/semiconductor hybrid photocathodes for CO2 reduction incorporating a “dark” anode.

| Entry | Metal complex | p-Type semiconductor | Product distribution (cathodic Faradaic efficiency) | Electrolyte solution | Irradiation conditions | Other remarks | Ref. |
|-------|---------------|----------------------|---------------------------------------------------|-----------------------|-----------------------|--------------|------|
| 1     | Ru1-polymer   | InP:Zn               | 62.3% at −0.6 V vs Ag/AgCl                        | Pure water            | A 300 W xenon lamp (λ > 400 nm) | TON_{formate} = 12 | [168]|
| 2     | Ru2-polymer   | Ta2O5:N              | Formate (48%) at −0.4 V vs Ag/AgCl                | Pure water            | A 300 W xenon lamp (λ > 400 nm, 70 Sun) | | [169]|
| 3     | Ru3-polymer   | GaP                  | Formate (45%) at −0.4 V vs Ag/AgCl                | Pure water            | A 300 W xenon lamp (λ > 400 nm, 70 Sun) | | [169]|
| 4     | Ru4-polymer   | Cu2ZnSnS4            | Formate (79%) at −0.4 V vs Ag/AgCl                | Pure water            | A 300 W xenon lamp (λ > 400 nm, 70 Sun) | | [170]|
| 5     | Ru5-polymer   | InP:Zn               | Formate (81%) at −0.4 V vs Ag/AgCl                | Pure water            | A 300 W xenon lamp (λ > 400 nm, 70 Sun) | | [169]|
| 6     | Cu3O          | CO (100%) at −1.73 V vs Fc/Fc | MeCN containing 0.1 m tetraethylammonium hexafluorophosphate and 1.0 m methanol | A 450 W Xe arc lamp (equivalent to AM1.5G) | | | [165]|
| 7     | Cu2O          | CO (100%) at −1.90 V vs Fc/Fc | 0.1 m tetraethylammonium hexafluorophosphate in MeCN | A 450 W Xe arc lamp (equivalent to AM1.5G) | | | [167]|
| 8     | Fe2O3:Zn:N    | Formate/CO/ | H2 = 52/40/8 (≈100%) at +0.1 V vs RHE | 0.1 m aqueous KHCO3 (pH 6.6) | A solar simulator (100 mW cm⁻²) | TON\[^{CO,formate} \] = 304 | [172]|
Table 4. Continued.

| Entry | Metal complex | p-Type semiconductor | Product distribution (cathodic Faradaic efficiency) | Electrolyte solution | Irradiation conditions | Other remarks | Ref. |
|-------|---------------|----------------------|-----------------------------------------------------|----------------------|-----------------------|--------------|------|
| 19a)  | NiO           | CuGaO₂               | CO (6.2%)                                           | 0.1 μ tetrabutyl ammonium hexafluorophosphate in DMF         | A 500 W xenon lamp (λ = 430 nm, 6 mW) | TONCO = 10. IPCE = 0.91%. | [175] |
| 20    | NiO           | CuGaO₂               | CO/H₂ = 91/9 (64%) at −0.7 V vs Ag/AgCl            | 50 × 10⁻³ μ aqueous NaHCO₃ (pH 6.6) | A 300 W xenon lamp (λ > 460 nm) | TONCO = 32 | [177] |
| 21    | CuGaO₂       | CuGaO₂               | CO/H₂ = 3/2 (81%) at −0.3 V vs Ag/AgCl            | 50 × 10⁻³ μ aqueous NaHCO₃ (pH 6.6) | A 300 W xenon lamp (λ > 460 nm) | TONCO = 125. IPCE = 0.7% at −0.3 V vs Ag/AgCl at 480 nm. | [182] |
| 22    | Polymerized RuRe and a Ru(II) tris-diimine | CuGaO₂ | CO/Formate/H₂ = 65/20/15 (85%) at −0.7 V vs Ag/AgCl | 50 × 10⁻³ μ aqueous NaHCO₃ (pH 6.6) | A 300 W xenon lamp (λ > 460 nm) | IPCE = 0.93% at −0.5 V vs Ag/AgCl at 480 nm. | [181] |

a)No description of the applied electrochemical potential; b)The amounts of other possible reduction products (e.g., CO and H₂) were not reported; c)Structure of the corresponding metal-complex monomer is shown in Figure 16.

Table 5. Metal-complex/semiconductor hybrid photocathodes for CO₂ reduction combined with a water-oxidation photoanode. All systems were in two-electrode configuration (without any reference electrode).

| Entry | Photocathode¹ | Photoanode     | Product distribution (TON) | Cathode Faradaic efficiency [%] | η [%] | Electrolyte solution | Irradiation conditions | Ref. |
|-------|---------------|----------------|----------------------------|---------------------------------|-------|----------------------|------------------------|------|
| 1b, c | (Ru2 + Ru3)−polymer/InP:Zn | P25 TiO₂ | Formate/(CO + H₂) = 70/30 (TONformate > 17) | 100 | 0.03–0.04 | 10 × 10⁻³ μ aqueous NaHCO₃ | Simulated sunlight (0.1 W cm⁻²) irradiated from the anode side. | [169,173] |
| 2b, d | (Ru2 + Ru3)−polymer/InP:Zn | SrTiO₃−d | Formate/(CO + H₂) = 70/30 (TONformate > 18) | 96.6 | 0.14 | 0.1 μ aqueous NaHCO₃ containing phosphoric acid (pH 7.7) | Simulated sunlight (0.1 W cm⁻²) irradiated from each side. For the cathode side, the UV portion was filtered off. | [173] |
| 3     | Ru3−polymer/Fe₂O₃:Zn,N | SrTiO₃−d | Formate/CO/H₂/O = 1.56/0.32/0.12/1 (TONformate = 51) | 101 | 0.15 | 0.1 μ aqueous KHCO₃ (pH 6.6) | Simulated sunlight (0.1 W cm⁻²) irradiated from the anode side | [172] |
| 4d    | RuRe/NiO      | CoO₂/TaON | CO/O₂ = 1/1 (TONCO = 17) | 37 | 1.6 × 10⁻⁵ | 50 × 10⁻³ μ aqueous NaHCO₃ (pH 6.6) | Visible light (λ > 400 nm, >0.22 W cm⁻²) irradiated from the cathode side. | [177] |
| 5d    | RuRe/NiO      | RuO₂/TiO₂:Ta,N | CO/O₂ = 2/1 (TONCO = 15) | 71 | 1.1 × 10⁻⁵ | 50 × 10⁻³ μ aqueous NaHCO₃ (pH 6.6) | Simulated sunlight (0.1 W cm⁻²) for the anode and visible light (λ > 460 nm, >0.04 W cm⁻²) for the cathode. | [180] |
| 6     | RuRe/CuGaO₂   | CoO₂/TaON | CO/H₂/O₂ = 0.9/1.2/1 (TONCO = 125) | 72 | 50 × 10⁻³ μ aqueous NaHCO₃ (pH 6.6) | Two different visible-light sources: λ > 460 nm for the cathode and λ > 400 nm for the anode. | [182] |

¹Structures of metal complexes are shown in Figures 15A and 16; ²It is likely that there was a small chemical bias (<0.1 V) between the two electrodes, although not discussed in detail; ³The generation of O₂ was confirmed by an isotope tracer experiment, but the quantity was not reported; ⁴There was a 0.09 V chemical bias between the two electrodes, which facilitated the forward reactions; ⁵A 0.4 V bias was applied; ⁶A 0.5 V bias was applied.
synthesized via chemical polymerization using pyrrole and FeCl3 as initiators. This polymerization resulted in the formation of polypyrrole chains that were stable under electrochemical conditions. Cyclic voltammetry data indicated that the $E_{\text{red}}$ values of the polymerized Ru complexes were almost equivalent to those of the monomeric analogues. This result can be attributed to negligible electronic interactions between the bpy ligands (representing the LUMO in this system) and the polypyrrole, due to the presence of propyl chains in the Ru complexes.

In such materials, selection of the most suitable Ru-complex catalyst is an essential aspect of maximizing performance, and combinations of Ru2 and Ru3 with InP:Zn showed the highest photoelectrochemical activity. Ru2 appears to bind tightly to the InP:Zn surface and to work effectively as a catalyst because it contains a 4,4′-diphosphate ethyl-2,2′-bipyridine anchor ligand. However, modification with only Ru2 yielded lower performance. In addition, although the use of Ru3 alone resulted in formate selectivity identical to the best combination of Ru2 and Ru3, the rate of formate generation was approximately 45% lower. These results can likely be ascribed to peeling of the polymerized Ru3 from the InP:Zn surface during the photoelectrochemical reaction, as observed by SEM. However, the immobilization of Ru3 along with Ru2 resulted in no detachment of the polymeric catalyst during the reaction. It was reported that the use of both Ru2 and Ru3 gave the polymeric layer a porous texture that provided effective channels for H2 release. The data also suggested that, rather than acting as a catalyst for formate production, the Ru2 promoted electron transfer and thus enhanced CO2 reduction. In contrast, Ru3 did not contribute significantly to CO2 reduction.

Combining the optimized photocathode with a Pt-loaded TiO2 photoanode in a two-electrode configuration resulted in the production of formate and O2 from an aqueous 10 M NaHCO3 solution under simulated sunlight (AM1.5G), even without any external bias. This system showed a formate selectivity greater than 70% together with a TONformate of 17 (24 h) and a solar-energy conversion efficiency of 0.03–0.04%. In a follow-up study, TiO2 was replaced with reduced SrTiO3 (SrTiO3-d), which has a more negative CBM than TiO2. This modification facilitated anode-to-cathode electron transfer, leading to an enhanced solar-energy conversion efficiency of 0.14%. A wireless device containing a SrTiO3 photoanode and a Ru-polymer/InP photocathode in a one-compartment reactor with no proton exchange membrane was found to exhibit both CO2 reduction to formate and water oxidation, with an efficiency of 0.08%.

Fe2O3 codoped with Zn and N (Fe2O3:Zn,N) has also served as an effective photocathode component for CO2 reduction, but with a p-type Cr2O3 underlayer and an n-type TiO2 protecting layer. Both the Cr2O3 and TiO2 layers significantly improved the cathodic photocurrent by tuning the band bending in the Fe2O3:Zn,N and suppressing self-reductive deactivation of this material. It was also found necessary to add a Ru-complex catalyst having a conductive polyppyrorcle network to obtain a stable photocurrent. The optimized hybrid photocathode, when paired with a reduced SrTiO3 photoanode, realized solar-driven CO2 reduction and water oxidation without an external electrical bias under simulated sunlight (AM1.5G). This system produced formate, CO, and H2 as reduction products and O2 as the oxidation product with an electron/hole balance of unity and overall Faradaic efficiencies for both cathode and anode reactions of nearly 100%. The main reduction product was formate, with 79% selectivity and the solar to chemical energy conversion efficiency was 0.15%, which is comparable to the solar-energy conversion efficiency achieved using a Ru complex/single-crystalline InP:Zn photocathode.

Thus, solar-driven photoelectrochemical CO2 reduction combined with water oxidation was demonstrated using either InP:Zn or Fe2O3:Zn,N modified with polymerized Ru complex catalysts. The key to achieving the overall reaction without any applied bias appears to be the use of Ru complex catalysts that exhibit relatively low overpotentials for CO2 reduction and are tightly attached to the surface of the p-type semiconductor through polymerization.

Here, an exceptional example of a semiconductor photocathode, ZnTe, that could give relatively high CO2-reduction selectivity without a metal-complex catalyst is also introduced. ZnTe is a p-type semiconductor that possesses a bandgap of 2.26 eV and a very negative CBM (~1.63 V vs RHE). ZnTe was grown on ZnO nanowires, followed by thermal treatment at ~473 K. Although the as-synthesized ZnTe/ZnO worked as a photocathode to reduce CO2 into CO, H2 evolution that resulted from proton reduction was competed, thereby leading to low CO2-reduction selectivity (<9%). Interestingly, however, modification of the ZnTe/ZnO nanowires with Au nanoparticles resulted in an increase in CO selectivity to 35–66%, which depended on the applied potential (the more negative the applied potential, the higher the CO2-to-CO selectivity). At ~0.7 V_RHE, the Au/ZnTe/ZnO exhibited very high IPCEs of >90% at 350–500 nm region. ZnTe thus appears to be very promising as a component of metal-complex/semiconductor hybrid photosystems.

4.2. Molecular Photocathodes Constructed with a Transparent p-Type Semiconductor and a Supramolecular Metal-Complex Photocatalyst

Supramolecular metal-complex photocatalysts are also attractive as components of CO2-reduction photocathodes, because their drawback (i.e., low photo-oxidation ability) can be mitigated by
supplying electrons from a counter (photo)anode (Figure 3D). There have been several examples of successful photoelectrochemical CO₂ reduction using a supramolecular photocathode and a water-oxidation photoanode, as discussed below (see also Table 5).

The first prototype of a supramolecular-based photocathode material was based on a combination of a Zn(II) porphyrin photosensitizer and a Re(I) complex catalyst for CO₂ reduction, immobilized on a p-type NiO electrode.[175] NiO is, in principle, transparent to visible light due to its large bandgap, and also works as an electron transporter. This hybrid photocathode reduced CO₂ to CO under 436 nm light in DMF, with a TON CO of 10 and Faradaic efficiency of 6.2%.

Much greater Faradaic efficiency (as well as improved selectivity) was obtained with a RuRe-immobilized NiO photocathode.[176] This RuRe/NiO hybrid photocathode was able to generate CO under an external bias of −1.2 V versus Ag/AgNO₃ in a DMF/TEOA mixture under visible light (λ > 460 nm), with high Faradaic efficiency (≈98%) and a TONCO of 32. Neither H₂ nor formate were formed during these trials, and tracer experiments with [¹³C]CO₂ indicated that the origin of the CO generated was CO₂. The VBM of NiO (~0.2 V vs Ag/AgNO₃)[159] is more negative than the redox potential of the excited state of the Ru photosensitizing unit in RuRe (Ru⁰/Ru* = 0.15 V), so electron transfer from the valence band of NiO to RuRe is thermodynamically downhill. As expected, decreased the applied potential associated with anodic polarization led to a lower photosresponse due to the reduced electron flow from the external electric circuit through the NiO electrode. An action spectrum analysis demonstrated that the cathodic photoresponse was induced by ¹MLCT photoexcitation of the photosensitizing Ru unit, and control experiments showed no CO generation in the absence of either light, CO₂, or RuRe. In addition, the modification of a NiO electrode with model RuRe complexes did not yield CO. Therefore, the NiO electrode and RuRe are both required for photoelectrochemical conversion of CO₂ to CO.

The RuRe/NiO hybrid photocathode was found to function even in aqueous environments, although the selectivity for CO (>90%) in a half-cell configuration was slightly lower than that in nonaqueous conditions, due to competitive H₂ evolution.[177] Under visible light (λ > 460 nm), the hybrid photocathode showed an obvious cathodic photoresponse starting at ≈−0.1 V versus Ag/AgCl in a CO₂-purged aqueous solution containing 50 × 10⁻³ M NaHCO₃ (pH = 6.6). The half-cell Faradaic efficiency for CO formation under these conditions was ≈60%. It was suggested that the electrons not contributing to CO formation (that is, the missing ~40%) instead went at least in part to the reduction of Ni⁷⁺ in the NiO during the initial stage of the reaction. The reduction of NiO electrode has been identified in similar photoelectrochemical reactions in both organic and aqueous solutions.[176,178] Formate production below the detection limit would be another possible explanation for the low efficiency.

CO₂/TaON has also been reported to work as a good photocathode for visible-light water oxidation,[179] and was selected as the photoanode material for use with a RuRe/NiO hybrid photocathode to drive visible-light CO₂ reduction using water as the electron source. TaON alone was found to be unstable as a water-oxidation photoanode due to competitive self-oxidation by valence band holes. However, modification of TaON with nanoparticulate CoOₓ, which acts as a water-oxidation site, enabled relatively stable performance. The overall system had a two-electrode configuration, in which the photoanode was separated from the photocathode using a Nafion membrane, and an electrochemical bias of −0.3 V versus CoOₓ/TaON was applied to the RuRe/NiO photocathode to facilitate the overall reaction. In addition, there was a chemical bias of 0.10 V between the two electrodes due to the pH difference, which accelerated the forward reaction. The unit was irradiated from the reverse side of the RuRe/NiO photocathode and some portion of this light penetrated through the RuRe/NiO and the Nafion membrane to be absorbed by the CoOₓ/TaON photocathode. After 60 min of photoelectrolysis in an aqueous 50 × 10⁻³ M NaHCO₃ solution, the two-compartment cell produced CO and O₂ (in a 1:1 molar ratio) with a TONCO of 17 and high CO selectivity (>90%). The Faradaic efficiencies of the cathodic and anodic reactions were 37% and 68%, respectively. The origin of the evolved O₂ was investigated by isotope-tracer experiments with H₂¹⁸O, but quantitative comparisons were very difficult due to exchange reactions of the O₂ in H₂¹⁸O with O₂ in the CoOₓ and NaHCO₃. Nevertheless, the data suggested that the O₂ evolution was at least partially due to water oxidation over the CoOₓ/TaON. Without RuRe, CO₂-reduction products were not generated in the cathode chamber, while a small amount of O₂ was produced in the anode chamber.

The above work demonstrated that a photoelectrochemical cell consisting of a CoOₓ/TaON anode and RuRe/NiO cathode could drive CO₂ reduction to yield CO and O₂ under visible light (Equation (14)) with the aid of external electrical and chemical biases. This was the first successful example of visible-light CO₂ reduction based on a metal-complex photocatalyst combined with a semiconductor photocathode using water as an electron donor, although the product ratio did not exactly match the expected stoichiometric CO/O₂ molar ratio of 2. The use of RuO₂/TiO₂-Ta:N, which is also a stable visible-light water-oxidation photocathode material, enabled the fabrication of a similar photoelectrochemical cell with a RuRe/NiO hybrid photocathode. This device produced CO and O₂ in a stoichiometric ratio with Faradaic efficiencies of ≈70% and a light-energy conversion efficiency similar to that of the previous system.[180] However, there is still room for improvement in these systems. As an example, the light-energy conversion efficiencies were very low (~1 × 10⁻⁹%), primarily because of deficiencies on the photocathode side (e.g., the desorption of RuRe and the intrinsic properties of the NiO support).

There have been several attempts to address the problems associated with RuRe/NiO photocathodes. As discussed in the previous sections,[169,172] compared to the use of anchoring groups, the immobilization of metal complexes through polymerization can increase the absolute amount of the metal complex included in the electrode, while decreasing the negative impact of desorption from the electrode surface. The desorption of RuRe molecules from the NiO surface has also been suppressed to some extent using a new preparation method based on electropolymerization employing RuRe and a Ru(II) tris-diimine photosensitizer having methyl phosphonic acid anchoring groups and vinyl ligand moieties.[181] This technique was reported to increase the amount of metal complex adsorbed on a NiO electrode while also suppressing subsequent
Figure 17. A) Current–potential curves generated by RuRe/CuGaO2 and RuRe/NiO electrodes in an aqueous CO2-saturated 50 × 10−3 M NaHCO3 solution (pH 6.6) under continuous visible-light irradiation (λ > 460 nm) and dark conditions. B) Time courses of the products during visible-light irradiation of a photoelectrochemical cell consisting of a RuRe/CuGaO2 photocathode and a CoOx/TaON photoanode under short-circuit conditions. A,B) Reproduced with permission.[182] Copyright 2017, Royal Society of Chemistry.

As a result, CO formation was enhanced by a factor of 2.5 as compared to the previous electrode using only methyl phosphonic acid anchors, leading to an improved Faradaic efficiency for the reduction reaction (85%) in aqueous 50 × 10−3 M NaHCO3 under visible light at −0.7 V versus Ag/AgCl.

CuGaO2 was applied as an alternative p-type semiconductor support for a supramolecular photocathode, as a replacement for NiO.[182] CuGaO2 with a delafossite crystal structure is a p-type semiconductor that has attracted attention as a transparent conductive oxide[52,183] and a cathode material for solar cells.[184,185] This material exhibits high conductivity and a positive flat-band potential that is ≈0.16 V deeper than that of NiO. These properties are advantageous when constructing a hybrid photocathode with a supramolecular photocatalyst such as RuRe. As a result, a RuRe/CuGaO2 photocathode generated an onset potential of +0.3 V versus Ag/AgCl during CO2 reduction in an aqueous electrolyte solution, which was 0.4 V more positive than that obtained from the NiO analogue (Figure 17A). Controlled potential photoelectrolysis at −0.3 V versus Ag/AgCl for 15 h produced CO and H2 as the reduction products (with a CO selectivity of 61%), together with a TON of 125 and a total reduction reaction Faradaic efficiency of 81%. It was also found possible to fabricate a self-driven photoelectrochemical cell powered solely by visible light and using water as the electron source based on a RuRe/CuGaO2 photocathode and CoOx/TaON photoanode. In this case, CO and H2 were detected as the reduction products in the cathode chamber (TON = 22), while O2 was the oxidation product, with an electron/hole balance of unity (Figure 17B). The total Faradaic efficiency of the reduction reactions (CO and H2) was 72%, while that of the oxidation reaction was 70%.

5. Summary and Outlook

State-of-the-art of metal-complex/semiconductor hybrid materials designed for photocatalytic and photoelectrochemical CO2 reduction under visible light are reviewed here. The literature shows that certain metal complexes can act as suitable electrocatalysts and/or photocatalysts to reduce CO2 with high selectivity and superior TONs, giving desired products such as CO or formate. Metal-complex (photo)catalysts are most useful when immobilized on a semiconductor that has a sufficiently negative conduction-band potential. This immobilization enables the utilization of weaker electron donors that cannot be oxidized by the metal complex. Consequently, these metal-complex/semiconductor hybrid photocatalysts outperform corresponding single component systems that incorporate only a metal complex or a semiconductor under the same reaction conditions. Spectroscopic measurements as well as theoretical studies can, at least in part, elucidate the electron-transfer process that occurs in such hybrid systems, providing a rational approach to further improvements in performance based on optimizing both metal complexes and semiconductors.

The majority of hybrid photocatalysts do not function in water without a sacrificial donor, although applying a Z-scheme system with two different semiconductors and a suitable redox mediator appears to be a promising approach to addressing this issue.[109] Photoelectrochemical cells in which a metal-complex/ p-type semiconductor hybrid is employed as the cathode component are another effective means of accomplishing CO2 reduction using water as the electron source. A solar-to-chemical energy-conversion efficiency of ≈0.15% has been achieved using a photoelectrochemical cell constructed from a reduced SrTiO3 photoanode and a suitable p-type semiconductor (e.g., FeOx, Zn, InP:Zn) further modified with a Ru complex polymer. Incorporating a triple junction based on an amorphous silicon–germanium thin film, a kind of solar-cell device, as the light absorber increased the energy conversion efficiency of 4.6%, when the film was modified with an InOx layer and a porous Ru complex polymer, serving respectively as selective water-oxidation and CO2-reduction sites.[106]

Despite the remarkable advancements detailed here, a significant gap remains between the state-of-the-art photocatalytic/ photoelectrochemical CO2 fixation abilities and the performance required for practical applications. One of the biggest challenges is the requirement for such systems to operate at low CO2 concentrations. In laboratory-scale experiments such as
those employed to assess each of the hybrid systems discussed herein, reactions were conducted in CO₂-saturated solution. In contrast, during practical applications, the CO₂ concentrations will be lower, and the reaction environment may contain other undesirable species such as molecular oxygen in order to reduce costs. Recently, a Ru(II)–Re(I) supramolecular photocatalyst was found to show not only high CO₂-reducing activity but also the ability to capture CO₂. This material retained 60% of its initial CO-formation efficiency (when using pure CO₂) even at a low 0.5% CO₂ concentration.[187] Immobilization of this material on a semiconductor surface could be useful both in photocatalytic and photoelectrochemical hybrid systems. Another serious problem in metal-complex/semiconductor hybrid photosystems is the desorption of metal-complex molecules from the semiconductor surface, which directly contributes to a drop in performance. Herein, several approaches to address this problem have been discussed. However, there still remains a need for further development. This is also related to understanding the electron transfer event(s) that occur at the metal-complex/semiconductor interface, in which advanced spectroscopic techniques and/or theoretical calculations could be the key.

To sum up, it is helpful to stress the most important aspects of metal-complex/semiconductor hybrid materials intended for CO₂ photoreduction. As shown in Figure 18, the development of hybrid photocatalysts and photoelectrodes for CO₂ reduction relies heavily on simultaneous investigations in many diverse areas of the chemical sciences, including photochemistry, photocatalysis, molecular catalysis, coordination chemistry, electrochemistry, inorganic synthetic chemistry, semiconductor physics, materials chemistry, spectroscopy, and biomimetic chemistry. The author believes that the significant progress in metal-complex/semiconductor hybrid photosystems in recent years (as summarized herein) can be attributed to a fusion of interdisciplinary research performed by various communities, even in the absence of pronounced interactions between these communities. Therefore, further developments in this new research field should be possible by further reinforcing interdisciplinary collaborations, with the aim of entrenching metal-complex/semiconductor hybrids as a new class of advanced materials.

Acknowledgements

The author wishes to acknowledge his co-workers, whose names appear in the references cited herein. This work was partly supported by Grant-in-Aids for Young Scientists (A) (JP16H06130) for Scientific Research on the Innovative Area Mixed Anions (JP16H06441) and for Challenging Research (Exploratory) (JP17K19169).

Conflict of Interest

The author declares no conflict of interest.

Keywords

artificial photosynthesis, mixed anion compounds, solar energy conversion, solar fuel, water oxidation

Received: December 20, 2018
Revised: February 20, 2019
Published online: May 8, 2019

[1] K. Maeda, K. Domen, J. Phys. Chem. Lett. 2010, 1, 2655.
[2] J. S. Lee, Catal. Surv. Asia 2005, 9, 217.
[3] K. Maeda, K. Domen, J. Phys. Chem. C 2007, 111, 7851.
[4] A. Kudo, Y. Miseki, Chem. Soc. Rev. 2009, 38, 253.
[5] W. J. Youngblood, S.-H. A. Lee, K. Maeda, T. E. Mallouk, Acc. Chem. Res. 2009, 42, 1966.
[6] R. Abe, Bull. Chem. Soc. Jpn. 2011, 84, 1000.
[7] K. Maeda, J. Photochem. Photobiol., C 2011, 12, 237.
Y. Uchimoto, M. Kakihana, O. Ishitani, H. Kageyama, K. Maeda, Angew. Chem., Int. Ed. 2018, 57, 8154.

[141] M. Kaga, H. Kurachi, T. Asaka, B. Yue, J. Ye, K. Fukuda, Powder Diff. 2011, 26, 4.

[142] K. Oka, H. Hojo, M. Azuma, K. Oh-ishi, Chem. Mater. 2016, 28, 5554.

[143] R. Kuriki, T. Ichibha, K. Hongo, D. Lu, R. Maezono, H. Kageyama, O. Ishitani, K. Oka, K. Maeda, J. Am. Chem. Soc. 2018, 140, 6648.

[144] A. Walsh, D. J. Payne, R. G. Egdell, G. W. Watson, Chem. Soc. Rev. 2011, 40, 4455.

[145] H. Wakayama, K. Utimula, T. Ichibha, R. Kuriki, K. Hongo, R. Maezono, K. Oka, K. Maeda, J. Phys. Chem. C 2018, 122, 26506.

[146] K. Maeda, K. Teramura, T. Takata, M. Hara, N. Saito, K. Toda, Y. Inoue, H. Kobayashi, K. Domen, J. Phys. Chem. B 2005, 109, 20504.

[147] K. Maeda, K. Domen, Chem. Mater. 2010, 22, 612.

[148] J. B. Asbury, E. Hao, Y. Q. Wang, H. N. Ghosh, T. Q. Lian, J. Phys. Chem. B 2001, 105, 4545.

[149] J. B. Asbury, E. Hao, Y. Q. Wang, H. N. Ghosh, T. Q. Lian, J. Phys. Chem. B 2000, 104, 11957.

[150] K. Wada, M. Eguchi, O. Ishitani, K. Maeda, ChemSusChem 2017, 10, 287.

[151] K. Wada, C. S. K. Ranasinghe, R. Kuriki, A. Yamakata, O. Ishitani, K. Maeda, ACS Appl. Mater. Interfaces 2017, 9, 23869.

[152] S. Shen, S. A. Lindley, X. Chena, J. Z. Zhang, Energy Environ. Sci. 2016, 9, 2744.

[153] S. S. M. Bhat, H. W. Jang, ChemSusChem 2017, 10, 3001.

[154] Y. Yang, S. Niu, D. Han, T. Liu, G. Wang, Y. Li, Adv. Energy Mater. 2017, 7, 1700555.

[155] J. Seo, H. Nishiyama, T. Yamada, K. Domen, Angew. Chem., Int. Ed. 2018, 57, 8396.

[156] M. G. Bradley, T. Tysak, J. Electroanal. Chem. Interfacial Electrochem. 1982, 135, 153.

[157] M. G. Bradley, T. Tysak, D. J. Graves, N. A. Viachiopoulos, J. Chem. Soc., Chem. Commun. 1983, 349.

[158] B. A. Parkinson, P. F. Weaver, Nature 1984, 309, 148.

[159] J.-P. Petit, P. Chartier, M. Beley, J.-P. Deville, J. Electroanal. Chem. Interfacial Electrochem. 1989, 269, 267.

[160] C. R. Cabrera, H. D. Abruña, J. Electroanal. Chem. Interfacial Electrochem. 1986, 209, 101.

[161] J. O’M. Bockris, J. C. Wass, Mater. Chem. Phys. 1989, 22, 249.

[162] B. Kumar, J. M. Smieja, C. P. Kubiak, J. Phys. Chem. C 2010, 114, 14220.

[163] E. Torralba-Penalver, Y. Luo, J.-D. Compain, S. Chardon-Noblat, B. Fabre, ACS Catal. 2015, 5, 6138.

[164] A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, E. Thimsen, Nat. Mater. 2011, 10, 456.

[165] M. Schreier, P. Gao, M. T. Mayer, J. Luo, T. Moehl, M. K. Nazeeruddin, S. D. Tilley, M. Grätzel, Energy Environ. Sci. 2015, 8, 855.

[166] G. Redmon, D. Fitzgerald, J. Phys. Chem. 1993, 97, 1426.

[167] M. Schreier, J. Luo, P. Gao, T. Moehl, M. T. Mayer, M. Grätzel, J. Am. Chem. Soc. 2016, 138, 1938.

[168] T. Arai, S. Sato, K. Uemura, T. Morikawa, T. Kajino, T. Motohiro, Chem. Commun. 2010, 46, 6944.

[169] S. Sato, T. Arai, T. Morikawa, K. Uemura, T. M. Suzuki, H. Tanaka, T. Kajino, J. Am. Chem. Soc. 2011, 133, 15240.

[170] T. Arai, S. Tajima, S. Sato, K. Uemura, T. Morikawa, Chem. Commun. 2011, 47, 12664.

[171] L.-Z. Fan, J. Maier, Electrochem. Commun. 2006, 8, 937.

[172] K. Sekizawa, S. Sato, T. Arai, T. Morikawa, ACS Catal. 2018, 8, 1405.

[173] T. Arai, S. Sato, T. Kajino, T. Morikawa, Energy Environ. Sci. 2013, 6, 1274.

[174] Y. J. Jang, J.-W. Jang, J. Lee, J. H. Kim, H. Kumagai, J. Lee, T. Minegishi, J. Kubota, K. Domen, J. S. Lee, Energy Environ. Sci. 2015, 8, 3597.

[175] Y. Kikuta, S. Nakatani, G. Sunagawa, Y. Tachikawa, D. Masui, T. Shimada, S. Takagi, D. A. Tryk, Y. Nabetani, H. Tachibana, H. Inoue, J. Catal. 2014, 310, 57.

[176] G. Sahara, R. Abe, M. Higashi, T. Morikawa, K. Maeda, Y. Ueda, O. Ishitani, Chem. Commun. 2015, 51, 10722.

[177] G. Sahara, H. Kumagai, K. Maeda, N. Kakefune, V. Artero, M. Higashi, R. Abe, O. Ishitani, J. Am. Chem. Soc. 2016, 138, 14152.

[178] K. Kakefune, J. Massin, C. Lebrun, O. Renaut, M. Chavarot-Kerlidou, V. Artero, J. Am. Chem. Soc. 2016, 138, 12308.

[179] M. Higashi, K. Domen, R. Abe, J. Am. Chem. Soc. 2012, 134, 6968.

[180] A. Nakada, T. Uchiyama, N. Nakawaki, S. Nishioka, R. Kamata, H. Kumagai, O. Ishitani, Y. Uchimoto, K. Maeda, ChemPhotoChem 2019, 3, 37.

[181] R. Kamata, H. Kumagai, Y. Yamazaki, G. Sahara, O. Ishitani, ACS Appl. Mater. Interfaces 2019, 11, 5632.

[182] H. Kumagai, G. Sahara, K. Maeda, M. Higashi, R. Abe, O. Ishitani, Chem. Sci. 2017, 8, 4242.

[183] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, Nature 1997, 389, 393.

[184] A. Renaud, B. Chavillon, L. Le Pleux, Y. Pelleguin, E. Blart, M. Boujtita, T. Pauporté, L. Cario, S. Jobic, F. Odobel, J. Mater. Chem. 2012, 22, 14353.

[185] M. Yu, G. Nats, Z. Ji, Y. Wu, J. Phys. Chem. Lett. 2012, 3, 1074.

[186] T. Arai, S. Sato, T. Morikawa, Energy Environ. Sci. 2015, 8, 1998.

[187] T. Nakajima, Y. Yamazaki, T. Morimoto, O. Ishitani, J. Am. Chem. Soc. 2016, 138, 13818.