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Recent progress in artificial photosynthesis: CO_2 photoreduction to valuable chemicals in a heterogeneous system

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Introduction

Despite mixed response from the public and scientific communities on climate change, recent reports [1,2] reiterated the grim links among persistent anthropogenic CO_2 emission, rise in global temperature and the increased occurrence of extreme seasonal weather. Together with concerns about energy supply and energy efficiency, artificial photosynthesis process has been emerging as one of the most promising solutions. Artificial photosynthesis is capable of not just generating alternative source of energy but also reducing and/or recycling waste products such as CO_2. Furthermore, with 120 000 TW worth of practically free solar radiation received by the earth each year, development of artificial photosynthesis systems (APS) using CO_2 as feedstock makes an excellent economical affordable and environmentally friendly source of renewable energy.

Photosynthetic reactions, natural or artificial, can be broken down to three primary processes: light-harvesting, charge generation and separation, and catalytic reactions [3] (Figure 1). The net efficiency of the system can be determined by the sum and synergy of these processes, in term of both thermodynamics and kinetics. Because of the limited details of natural photosynthesis steps were known in the early days, artificial photosynthesis studies focused only to explore single material capable of performing all three processes (Figure 1a), which has been proved to be extremely difficult. Very recently, however, a great deal of the natural and artificial photosynthesis studies stimulated the research interest in multiple excitations including physical contact cascade (Figure 1b) or artificial Z-scheme (Figure 1c).

Table 1 contains a short list of possible reduction and oxidation reactions in CO_2 photoconversion in aqueous solution at neutral condition (pH 7, 1 atm, 25 °C). In addition to the listed thermodynamic consideration, there are also considerable kinetic challenges to the conversion of CO_2 to the complex products. Typically, synergistic multiple proton–electron transfer steps (with individual activation energies) must be met. This is where the challenge lies. It has been shown that the water oxidation process is extremely slow in a heterogeneous system when compared to proton reduction [4,5••]. One can imagine that both the multi-electron reduction and four-hole oxidation processes during CO_2 photoconversion are kinetically very challenging caused by fast intrinsic charge recombination [4,5••].

Caused by the limited available space, this short review will only address CO_2 photoreduction in a heterogeneous system. It should be noted that there are substantial studies on homogeneous CO_2 photoreduction system such as [7]. Interested audience are referred to [7,8,9] for a more in-depth and comprehensive review.

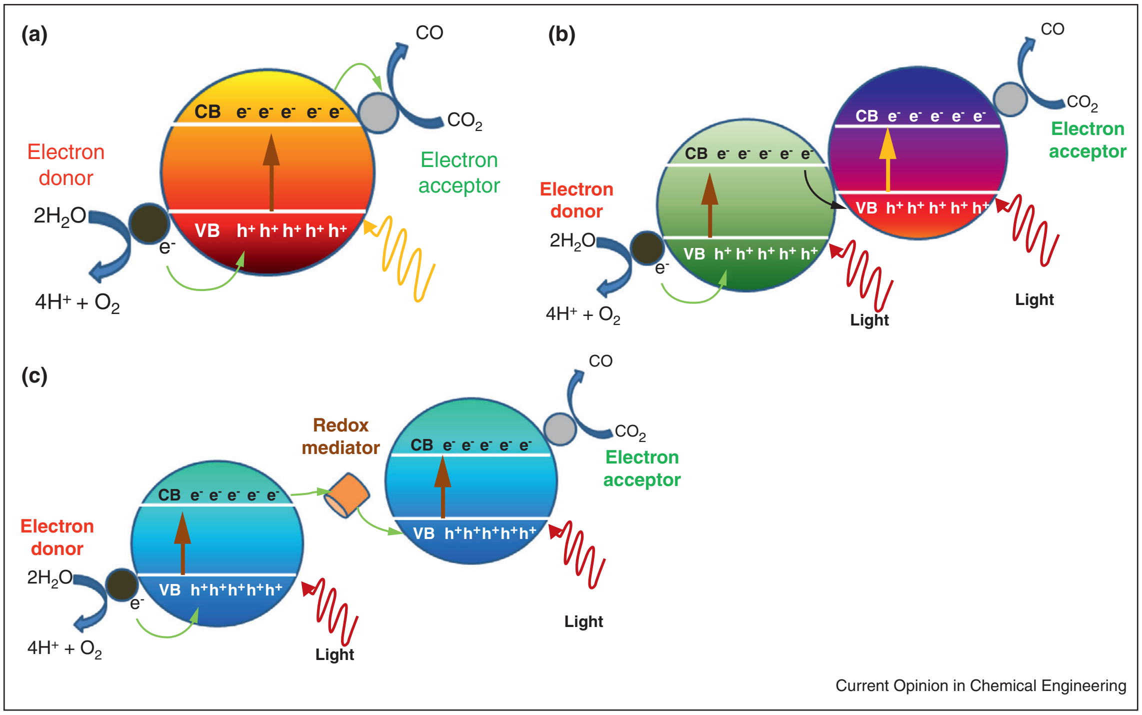
Single inorganic photocatalyst

Oxides

TiO_2, one of the most investigated photocatalysts in artificial photosynthesis, has been known from the ancient times as white pigments. It is inexpensive, safe and fairly stable. Since the early 1920s TiO_2 (rutile) has also been widely known in electronic industry as a capacitor because of its robustness and ease of mass preparation [10]. When organic decomposition by the use of photocatalysis was reported in late 1930s, TiO_2 was one of the most active photocatalyst [11]. In 1970s, Fujishima *et al.* [12,13] reported both photoelectrochemical water splitting and CO_2 photoreduction by TiO_2. Since then, the research on artificial photosynthesis boomed, with typical focus on TiO_2.

Stimulated by the recent breakthroughs in photocatalytic water splitting, research on CO_2 photoreduction is developing fairly quickly. Like photocatalytic water splitting, heterogeneous photocatalytic conversion of CO_2 was first demonstrated using large band gap semiconductor materials (TiO_2, $SrTiO_3$, ZnO, or SiC) under strong UV light [13]. Even today, UV-sensitive materials like TiO_2 [14] and niobate perovskites [15] are popular starting points. To date we note only two materials were reported capable of conducting complete CO_2 photoreduction coupled with water oxidation: ZrO_2

Figure 1



Various strategy of artificial photosynthesis systems: **(a)** single excitation system comprising of a wide bandgap photocatalyst, **(b)** multiple excitation system comprising narrow bandgap photocatalyst pair connected with physical contact (junctions) and **(c)** multiple excitation system connected through electron (redox) mediator, imitating the ''Z-scheme'' in natural photosynthesis system.

(H_2: 19.5 μmol h^{-1}, O_2: 10.8 μmol h^{-1}, CO: 2.5 μmol h^{-1}) [16] and $BaLa_4Ti_4O_{15}$ (H_2: 10 μmol h^{-1}, O_2 7 μmol h^{-1}, CO 4.3 μmol h^{-1}, HCOOH 0.3 μmol h^{-1})[17•], both with massive bandgap between 4 and 5 eV.

Wide-bandgap photocatalysts are not ideal and enhancement has to be made to utilise the wider solar spectrum. One of the popular routes towards visible-responsive materials is by top-down bandgap engineering approach, for example by introducing various dopants to the starting wide bandgap material. A popular example is the nitridation of $ZnGe_2O_4$ (4.4 eV) [18] to $ZnGe_2O_{4-x}N_x$ (≈2.7 eV) [19]. Other methods were also reported, such as the formation of layered perovskite $BaLa_4Ti_4O_{15}$ (3.9 eV) from the basic titanates [17•], introducing hydrogen surface disorder on TiO_2 surface [20] and stabilisation of meta-stable cubic phase of TiO_2 [21]. Although the bandgap values were lower than unmodified materials, UV excitation (ca. 250 nm) is still typically required. Most of these strategies however, are still heavily focused on water splitting and very little on CO_2 photoreduction.

Table 1

List of electronic and redox potential requirement of selected reactions related to artificial photosynthesis. Potentials are converted to SHE reference, pH 7 [6].

Reactions	E°
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	+0.81 V
$2H^+ + 2e^- \rightarrow H_2$	−0.42 V
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.61 V
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.53 V
$CO_2 \rightarrow 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.48 V
$CO_2 \rightarrow 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.38 V
$CO_2 \rightarrow 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.24 V
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	−1.90 V

Inherently lower bandgap materials are advantageous because they are excitable using visible light. The major drawback however, they are usually not stable in operating (aqueous) condition. Cuprous oxide for example, is a good CO_2 photoreduction catalyst but suffers greatly from photocorrosion. Recent publications [22,23] suggest that it may be possible to devise corrosion protection strategy by depositing metal oxide overlayers to protect the main photocatalyst from degradation. Although not perfect, reasonably high photocurrent can be retained for over 30 times longer than bare electrode, increasing the feasibility of using such low bandgap material in real conditions.

Nonetheless, it should be noted that the above-mentioned publication (except the extremely wide bandgap $BaLa_4Ti_4O_{15}$ and ZrO_2) only reported photocatalytic CO_2 reduction products without information on the water photooxidation products. Very recently, we have found a relatively narrow bandgap photocatalyst, $KTaO_3$ ($E_g \approx 3.5$ eV), which can simultaneously reduce CO_2 to CO and oxidise water to O_2, which is clearly desirable. [Simultaneous photocatalytic reduction of CO_2 and water oxidation on potassium tantalate, in revision [24].]

Other photocatalysts

Carbon based nanoparticles, for example graphene, graphene oxide and graphitic-carbon nitride have stolen the limelight from metal-oxide photocatalysts during recent years [25]. Functionalised carbon nanoparticles have been shown active for H_2 generation and CO_2 photoreduction under visible light, yielding primarily formic acid with a quantum yield of ca. 0.3% [26]. Graphitic-C_3N_4 is another promising material because it shows unexpected catalytic activity (not photocatalytic) for a variety of reactions, such as for the activation of benzene, trimerization reactions, and also the activation of carbon dioxide [27]. Further visible light sensitisation are available via oxygen doping [28]. It has also been reported active for hydrogen and oxygen production (note: two separate half-reactions) under visible light [29], although no report so far on CO_2 reduction.

A peculiarly conductive material, graphene is reported useful to mediate charge separation on many semiconducting light absorbers, like TiO_2 nanotubes [30], carbon nitride [31], cuprous oxide [32]. Unlike graphene, partially reduced graphene oxide has semiconducting properties, and thus is plausible to be used as visible light responsive photocatalyst. Hsu *et al.* recently reported CO_2 photoreduction to methanol over graphene oxide with yield of approx. 0.17 μmol g^{-1} h^{-1}[33]. A sufficiently active, visible-light responsive non-metal photocatalyst could potentially lead to an economically viable solution for solar fuels generation.

More recent reports on the use of graphene or graphene oxide to promote charge separation were also reported in a junction and Z-scheme configuration, which is addressed below.

Electron donors

In order to simplify the study on CO_2 photoconversion, electron donor is widely employed to facilitate charge separation. These sacrificial donors are typically organic substances that can be oxidised quickly enough by the photogenerated holes in the photocatalyst, such that it reduces the propensity of charge recombination, that is more photogenerated electrons can be present long enough to react with CO_2. The use of such sacrificial electron donors however is not an ideal solution, because evidently the most popular ones like methanol or triethanolamine are valuable chemicals with high energy density. Recently, researchers from Cardiff University have put forward a very interesting proposal of using a tertiary amine as an electron donor that could itself be recycled by hydrogenation [34••]. Because hydrogen is usually present as a major by-product during photocatalytic CO_2 reduction reaction in aqueous conditions, the use of recyclable tertiary amine electron donor avoid unnecessary consumption of precious hydrocarbons. It should be noted that no quantitative measurement of CO_2 photoreduction were conducted.

Researchers from Argonne National Lab found that *glyoxal* – a recombination product of two formyl radicals – holds significant role in mimicking the multistep, photosynthetic fixation of atmospheric carbon in nature (Figure 2) [35]. The proposed "*glyoxal cycle*" is a more plausible and facile multiple proton reduction route from CO_2 to CH_4 (or other intermediates) compared to the commonly accepted two-electron scheme (Eq. (1)):

$$CO_2 \xrightarrow[+2H^+]{+2e^-} HCO_2H \xrightarrow[+2H^+-H_2O]{+2e^-} H_2CCO \xrightarrow[+2H^+]{+2e^-} CH_3OH \xrightarrow[+2H^+-H_2O]{+2e^-} CH_4 \tag{1}$$

Junctions and Z-scheme

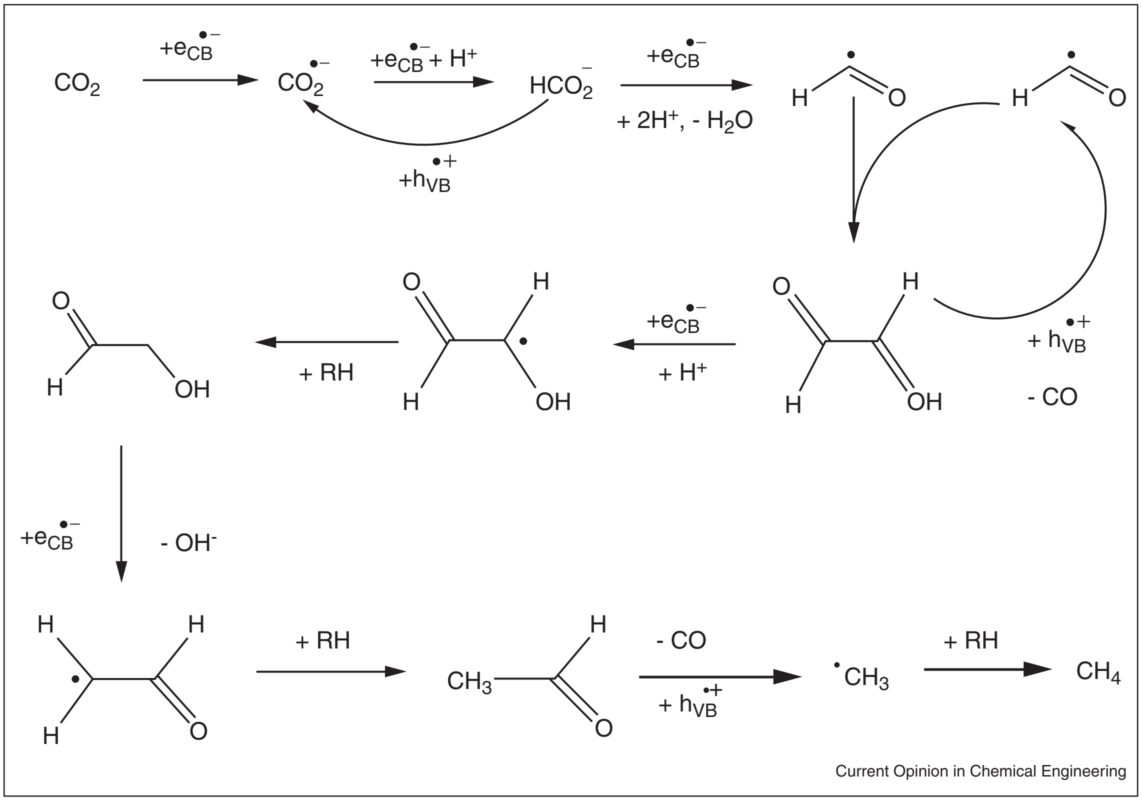
The discovery of Photosystem-II crystal structure in 2004 [36] is probably the pinnacle of dedicated research on natural photosynthesis. It elucidates that the high turnover of natural photosynthesis is caused by the multiple-stage (cascade) excitation with electrons shuttled through electron transport chain mechanism [37]. This finding gives rise to the parallel material design strategy in artificial photosynthesis, including tandem cells (where two-photon excitation is applied), multi-junctions involving combination of two or more materials (Figure 1b), and artificial Z-scheme (Figure 1c).

These multiple-excitation schemes have also been adopted for use in artificial photosynthesis system to harness visible light by pairing two or more photocatalysts with lower bandgap. Most notably, the pairing of N-doped Ta_2O_5 with [Ru-dcbpy] molecular catalyst yields a noble 1.9% quantum yield of formic acid at 405 nm [38•] and enzyme modified TiO_2 [39].

A group from Chiba University had an interesting idea of constructing a *reverse* fuel cell based on polymeric (Nafion) electrodes, supplying CO_2 gas on Zn/Cu/Ga reduction catalyst and either H_2 or water on Pt/C oxidation catalyst [40]. Around 5 μmol g^{-1} h^{-1} of methanol and trace amounts of CO were detected when CO_2 and H_2O feedstock was used. Another interesting idea of using iridium catalyst to reversibly convert CO_2 and H_2 to formate or formic acid by adjusting the solution pH [41].

Aqueous $FeCl_2$–$FeCl_3$ electron mediator system has been demonstrated for various combination of water

Figure 2



Glyoxal cycle. RH represents generic molecular or radical donor of H atoms.
Adapted from with permission from [35] J Phys Chem C. 2012;116:9450–60. Copyright (2012) American Chemical Society.

reduction and oxidation photocatalysts [42]. However, solid-state Z-scheme concept is more interesting, because it eliminates (i) the need for inefficient charge transfer between solid photocatalysts and electron mediator ions in the aforementioned Z-Scheme and (ii) other problems like possible degradation of electron mediators like the $[Fe(CN)_6]^{3-/4-}$. This idea has been first proven by a group in Osaka using CdS–Au–TiO_2 three-component nanojunction system that successfully reduce methyl viologen and oxidise ethanol [43].

Graphene oxide has also been reported very recently to perform as solid state electron mediator between $BiVO_4$ and TiO_2 for water splitting without sacrificial reagents [44,45•]. It is also reported that manipulation of particulate physical contact in solution by controlling the solution pH could also result in similar Z-scheme structure without the use of electron mediator [46]. These concepts were again only proved in water splitting. Our preliminary results over a novel visible driven junction Cu_2O–RuO_x shed some light on the idea, which shows CO_2 can be much more efficiently converted to CO by the junction structure compared with single photocatalyst. [Enhanced CO_2 photoreduction to fuel by a visible-light driven inorganic heterojunction, in revision [47•].] Nevertheless there is very limited study on CO_2 photoreduction using a solid junction structure.

Improvement to photocatalytic performance

Co-catalyst

The most common way to boost photocatalytic performance is by depositing co-catalysts. More often than not, bare photocatalysts could not display high catalytic activity on its own because their surfaces are not suitable for the specific catalytic reactions expected. Noble metals are more commonly used as co-catalyst. For H_2 production for example, most commonly used co-catalyst during water electrolysis is Pt because very slight or almost no overpotential is required to reduce protons to H_2. Researchers from Missouri [48,49] found that reducing the size and high dispersion of nanoparticles, achieved by spraying Pt via aerosol chemical vapour deposition (ACVD) on TiO_2 nanorods, significantly improves TiO_2 performance for CO_2 photoreduction in aqueous solution, with H_2 and methane as the main product. This not only relates to the increased Pt surface area, but also the quantised energy level in nano Pt pushes the work function upwards.

Copper is also one of the popular choices of co-catalyst for CO_2 reduction [50]. However most of the products are CO at lower potentials (more positive than -1.2 V vs. NHE)[51]. An important work by Danish researchers highlighted this is probably because CO binds only weakly to copper surfaces, preventing the stabilisation and protonation of adsorbed CO to form adsorbed CHO, a key step for hydrocarbon formation [52].

Another interesting approach is by exploiting surface plasmon resonance phenomenon which was heavily reported in visible driven organic decomposition, however the detailed mechanism is not clear [53]. Because noble metals like Pt or Au are required for co-catalyst anyway, by simply tuning the size and selecting appropriate photocatalyst-metal pairing could boost the catalyst performance in visible light [53,54]. Another new one is the use of metal–organic hybrid iridium dehydrate pincer complex for (electro-)catalytic reduction of CO_2 to formate [55].

To date, noble metal co-catalysts are always required to achieve decent photocatalytic activity. Search for a new, non-noble metal cocatalyst is economically sensible. Since cobalt phosphate (CoPi) was first reported in 2008 as a water oxidation co-catalyst [56], its popularity has been rising in the recent years. CoPi is easily formed from earth-abundant metal ions (cobalt and phosphates) in aqueous solution. It is proven active as water oxidation catalyst in neutral pH and significantly lower the overpotential normally required for water oxidation reaction. Recent works using transient absorption spectroscopy highlights that CoPi-induced performance improvement may be related to its role to increase photogenerated hole lifetime by at least 3 orders of magnitude [57].

Molybdenum and tungsten sulphides [58,59] have also been reported recently as potential non-noble metal co-catalyst for water reduction to H_2. By itself it could not work as a photocatalyst, but when paired with CdS, the pair clearly shows characteristics of a water reduction catalyst. Considering the price factor, sulphides co-catalyst provides more performance per unit cost compared to Pt-based co-catalyst. The improved performance has been linked to intimate structural similarity to CdS, facilitating quick electron transfer. Other sulphides like MoS also found active when paired with $NaTaO_3$ [60]. On the other hand, there are some concerns about the stability and safety issue about the sulphide co-catalysts.

Geometrical consideration

One of the ways of improving photocatalyst performance is by applying nanostructured morphology. This provides both increased available surface for catalytic reaction and improved light absorption by acting as a non-reflective surface or light traps. There are two things that we can learn from the already established solar cell technology, improved surface area from nanotube arrays [61] and light sensitisation by means of dye absorption [62]. Nanotubes with large porosity can benefit the photoconversion efficiency from two aspects. First, the large surface areas ensure the stronger light absorption and simultaneously a much shorter path towards wall surface than the hole diffusion length. Second, a larger inner space of nanotube is important to accelerate the ion migration in the tube and overcome the kinetic bottleneck [63]. Significant improvements in photoelectrochemical performance have also been reported when highly porous branched TiO_2 was used [64]. These branches not only increase the effective surface area, but also improve light absorption. The other example is ZnO rods. Recent findings show significant photocurrent improvement by ZnO grown on grooved substrate compared to planar nanotube arrays, linked to improved light trapping performance. The novel grooved Si design doubles light absorption as back-reflecting mirror, improving the photoelectrochemical efficiency by a factor of 5 [65•].

Concluding remarks

Despite significant progress in the recent years, photocatalytic solar fuel generation from CO_2 is still far behind its counterpart water splitting. Furthermore one commonly reported problem is the diversity of reaction products, ranging from CO, CH_4, methanol, formate/formic acid which are multi-electron process thus kinetically very challenging. It is also increasingly difficult to switch the reaction preference to favour carbonaceous product rather than highly competitive H_2 generation. The crux of the problem is lack of appropriate co-catalyst, like the widely used Pt for H_2 evolution catalyst.

Achieving the stoichiometric chemistry is another challenge. Stoichiometric water splitting is feasible proved in which protons and water can be reduced and oxidised spontaneously. However, the ideal coupling of CO_2 reduction and water oxidation seems difficult, as H_2 evolution is more favourable than CO_2 reduction when O_2 molecules are evolved. The exact mechanisms of CO_2 photoreduction are not known and still hotly debated, which further limit the development of the CO_2 photoreduction. Therefore, significant efforts should be made to understand the underlying mechanism in the future apart from the efficient photocatalyst development and cocatalyst exploration.

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This paper is interesting because it describes a simple engineering/design approach to improve photoelectrochemical water splitting efficiency by growing on grooved rather than flat surface. The photocurrent was increased by a factor of 5.