

## Review Article

# Inorganic Photochemistry and Solar Energy Harvesting: Current Developments and Challenges to Solar Fuel Production

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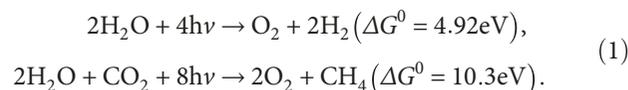
The large and continuous use of fossil fuels as a primary energy source has led to several environmental problems, such as the increase of the greenhouse effect. In order to minimize these problems, attention has been drawn to renewable energy production. Solar energy is an attractive candidate as renewable source due to its abundance and availability. For this, it is necessary to develop devices able to absorb sunlight and convert it into fuels or electricity in a economical, technical and sustainable way. The so-called artificial photosynthesis has called the attention of researchers due to the possibility of using solar photocatalysts in converting water and CO<sub>2</sub> into fuels. This manuscript presents a review of the recent developments of hybrid systems based on molecular photocatalysts immobilized on semiconductor surfaces for solar fuel production through water oxidation and CO<sub>2</sub> reduction and also discusses the current challenges for the potential application of these photocatalyst systems.

## 1. Introduction

The enhancement of renewable sources share in the global energy matrix is a key step towards a sustainable growth of the human society. According to the World Energy Council, in 2013, 76% of the electricity consumed in the world was still originated from fossil fuels [1]. This scenario has raised worries about the intensification of the greenhouse effect due to the increase of CO<sub>2</sub> concentration in the atmosphere. Among the renewable sources, solar energy calls particular attention due to the widespread and enormous amount of energy daily delivered to the Earth. However, direct conversion of radiant energy barely contributes to the current global energy matrix [2]. For example, in 2013, only 0.3% of the electricity was produced by photovoltaics.

The use of solar energy as a primary energy source requires the development of materials and devices able to harvest sunlight and convert it into fuels or electricity in a way that is environmentally and economically feasible [3]. Such a challenge is being faced by different scientists around the world. Specifically, fuel production by solar photocatalysis has been the theme of intensive research due to the

possibility to mimic the natural photosynthesis and convert Earth-abundant substances (water, CO<sub>2</sub>) into fuels (H<sub>2</sub>, CH<sub>4</sub>, etc.) [4–16]. The prime processes in artificial photosynthesis are the water splitting into oxygen and hydrogen, equation (1), and the water reduction of CO<sub>2</sub> to methane (equation (1)) or other hydrocarbons.



In both processes, the key half reaction is the water oxidation to dioxygen (equation (2)) ( $E^{\circ} = -1.23\text{ V}$  at pH=0,  $-0.82\text{ V}$  at pH=7). Finding catalysts to photochemically carry out this apparently simple reaction at high rates for sustained periods and at low overpotentials is one of the greatest scientific challenges that need to be overcome, so solar energy could be used as primary energy source for fuel production.



From a mechanistic point of view, the requirements for a photocatalytic system to be able to split water are

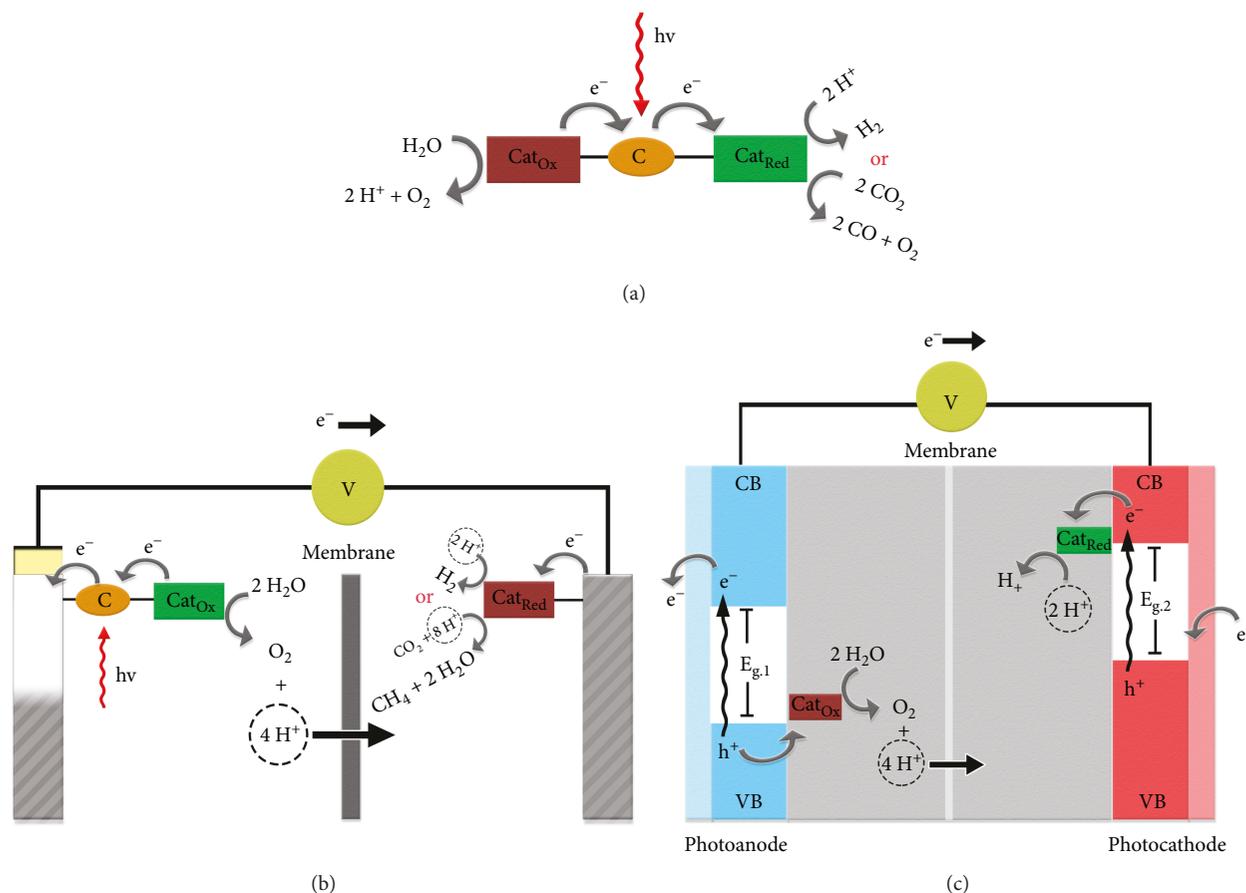


FIGURE 1: Basic components of an artificial photosynthetic system assembled in different ways. (a) Three-component artificial photosynthetic system physically connected. (b) Photoanode-driven photoelectrochemical cell. (c) Tandem photoelectrochemical cell comprised by a photoanode and a photocathode.

problematic. It should be able to efficiently light in the visible range of the spectrum and, though having multiple electron transfer steps accumulate redox equivalents in a single catalyst site that ultimately will promote the formation of the O=O bond. Consecutive one-electron transfers are not desirable, since it would lead to the formation of radicals, such as  $\cdot\text{OH}$ , creating a higher energy barrier for the next oxidation step [17]. In the natural photosynthesis, in the so-called oxygen-evolving complex [18, 19], multiple electron accumulation is reached by a series of proton-coupled electron transfer (PCET) reactions, which also have a key role on the O=O bond formation [20]. Thus, a deep understanding of the fundamental aspects of the PCET reactions can allow for the development of mimetic photosynthetic systems.

Figure 1 illustrates the basic components of an artificial photosynthetic system assembled in different ways. The solar light is absorbed by a chromophore (C), generating the charge carriers. Electrons are transferred from the chromophore to a reduction catalyst ( $\text{Cat}_{\text{red}}$ ), where protons or  $\text{CO}_2$  can be reduced. The oxidation catalyst ( $\text{Cat}_{\text{ox}}$ ) transfers electrons to the photooxidized chromophore enabling the absorption of more photons. Accumulation of redox equivalents in the oxidation catalyst leads to the oxygen evolution from water. As shown in Figure 1, there are basically three different ways to assemble these components. They can

be physically connected as shown in Figure 1(a) through covalent bonds in the case of molecular homogeneous photocatalysts or by forming composites when nanoparticles are employed as heterogeneous photocatalysts. Alternatively, the oxidation and reduction catalysts can be immobilized on the surface of electrodes in a photoelectrochemical cell (PEC). The chromophore can be present in the anode, i.e., a photoanode as shown in Figure 1(b) or two different semiconductors with different bandgaps that can be used in the photoanode and in the photocathode, to maximize the solar light harvesting (Figure 1(c)).

Different materials have been employed in artificial photosynthetic systems including coordination compounds [21–26], metallic nanoparticles [27, 28], and semiconductor metal oxides [29–32]. Seminal works by Fujishima and Honda [33] and others [34–37] on  $\text{TiO}_2$ -based photoanodes or by Meyer [38, 39] on molecular Ru complexes for water oxidation have contributed to the emergence of this very dynamic research field in photochemistry, which experienced a tremendous expansion in the last three decades. Some examples of the recent progress in the field are the Ru(II) complexes ( $[\text{Ru}(\text{bda})(\text{isoq})_2]$ ,  $\text{H}_2\text{bda}=2,2'$ -bipyridine-6,6'-dicarboxylic acid;  $\text{isoq}=\text{isoquinoline}$ ) described by Duan et al. [40], which exhibited a turnover frequency at above  $300 \text{ s}^{-1}$ , comparable with the reaction rate of  $100\text{--}400 \text{ s}^{-1}$  of

the oxygen-evolving complex of photosystem II *in vivo*. The molecular photocatalysts can also be immobilized in the surface of a metal oxide semiconductor in the so-called dye-sensitized photosynthetic cells (DSPECs) [41, 42]. Moreover, Kanan and Nocera have described highly efficient  $\text{Co}^{\text{III}}$  oxide/hydroxide water oxidation catalysts, which have the advantage to use an Earth-abundant metal [43].

In terms of photoelectrochemical devices based on metal oxide semiconductors, different strategies to overcome the main drawbacks of  $\text{TiO}_2$  (low light absorption in the visible region and high recombination rates) [44, 45] have been proposed such as doping [46–48], sensitization [49–51], and formation of nanocomposites [52–54]. Other binary oxides largely investigated are  $\text{Fe}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ , which are also Earth-abundant and have smaller bandgaps than  $\text{TiO}_2$ . However, the charge separation and transport efficiencies on these materials are strongly limited. Promising results have been reported by the use of ternary oxides such as  $\text{BiVO}_4$  [55–57],  $\text{SrTiO}_3$  [58–60], and niobates [61–64]. It seems clear, however, that one single material cannot fulfill all the requirements of large-scale applications, i.e., high efficiency, stability, and cost effectiveness.

In order to develop more efficient systems for water oxidation and solar fuel production, different materials have to be combined in a very organized and well-defined way so one can promote a synergic effect towards the desired photo-reaction. By the so-called molecular/surface engineering, it is possible to produce composites, in which metal oxide semiconductor particles can be combined with different materials such as polymers [65], carbon nanostructures [66, 67], metallic nanoparticles [68–71], molecular cocatalysts [72–75], or other semiconductors [76–78] to improve a desired property. In the case of photocatalytic systems, nanocomposites have been used to improve charge separation, to increase the light harvesting efficiency, and also to create specific reaction sites for a given reaction, like  $\text{H}_2$  and  $\text{O}_2$  evolution. The composites can be produced by different techniques and employed as a powder or as a thin film deposited onto a transparent substrate [79].

Moreover, the advances in the spectroscopic techniques have allowed a deeper understanding on the charge carrier dynamics and reaction mechanisms at the semiconductor/electrolyte interface [80–84]. In particular, *in situ* spectroscopic methods, spectroelectrochemical experiments, and time-resolved techniques, such as transient absorption spectroscopy (TAS) [85–92], have provided new insights on the dynamic of charge transfer in different photocatalytic systems. These fundamental investigations are guiding the material choice and device assembly methods, resulting in significant progress in the last years. However, there are still several questions to be answered on how to exert control on the charge separation and transportation processes and, at the same time, improve the reaction rates for water oxidation or  $\text{CO}_2$  reduction.

In this paper, we focus our attention on hybrid systems based on molecular photocatalysts immobilized on semiconductor surfaces for water oxidation and  $\text{CO}_2$  reduction. Instead of a comprehensively overview of the literature in the field, the main aim of this manuscript is to highlight some

achievements in the last years and the current challenges for large-scale applications.

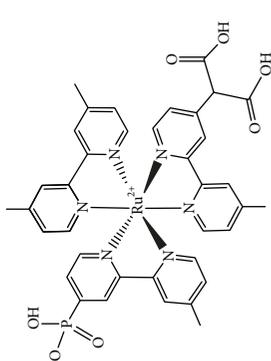
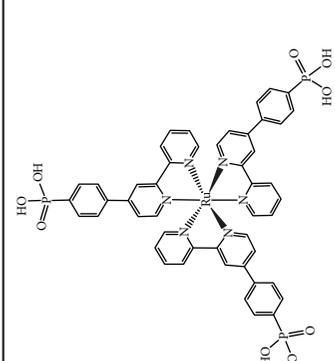
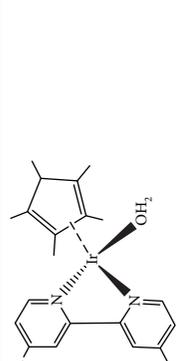
## 2. Dye-Sensitized Metal Oxide Thin Films for Photoelectrochemical Water Oxidation

In a DSPEC, the photosynthetic reactions are divided into two halves, as shown in Figures 1(b) and 1(c). In the photoanode, water is oxidized by a surface-immobilized molecular catalyst, whereas the reduction step occurs in the (photo)cathode. The two electrode compartments are separated by a proton exchange membrane, which allows for proton diffusion and charge balance. In this section, special attention is given to the photoanode architecture, responsible for the oxygen evolution reaction from water. In the photoanode, three basic steps should be efficiently promoted to produce oxygen: solar light must be harvested, leading to the creation of free charge carriers, electrons should be transferred to the external circuit, and, finally, redox equivalents should be accumulated in the catalytic center, where the water oxidation reaction will take place. Based on dye-sensitized solar cells, Meyer's group have proposed a three-component structure composed by an *n*-type wide band gap semiconductor ( $\text{MO}_x$ ) sensitized by a chromophore (C), which is covalently bound to a catalyst ( $\text{Cat}_{\text{ox}}$ ) [93]. Light absorption by C leads to the formation of an excited state  $\text{C}^*$ , which is able to inject electrons into the conduction band of the semiconductor,  $\text{MO}_x - \text{C}^* \rightarrow \text{MO}_x(e^-) - \text{C}^+$ . The injected electrons are transferred to the external circuit. The photooxidized chromophore,  $\text{C}^+$ , is regenerated by the catalyst, typically by a PCET reaction, so oxidative equivalents are transferred to  $\text{Cat}_{\text{ox}}$ , where they are accumulated for the  $4e^-$  oxidation of  $\text{H}_2\text{O}$ . Classic assemblies are based on  $\text{TiO}_2$  mesoporous films, Ru(II) polypyridyl complexes as sensitizers, and Ru- or Ir-based catalysts. Alternatively, the light harvesting function can be also performed by the metal oxide film by using semiconductors with a band gap smaller than 3.0 eV.

The greatest challenge in the photoanode assembly is avoiding recombination losses, i.e., to efficiently keep the photogenerated holes separated from the electrons so the water oxidation reaction can take place. Several strategies have appeared in the literature involving both molecular and band gap engineering, in such a way that the desired interfacial processes can be optimized at the same time as the device stability is enhanced. Some examples of photoanodes employed in DSPECs for water oxidation are shown in Table 1. Their efficiencies are expressed in terms of Faradic efficiency, turnover frequency (TOF), and incident photon-to-electricity (IPCE) maxima, while the stability is given by the turnover number (TON). In the following paragraphs, some key information about each component is discussed.

**2.1. Chromophores.** Different species have been used as sensitizers in DSPECs. These include Ru(II) complexes [110–113], porphyrins [110, 114–116], perylenes [110, 117–122], and other organic dyes. As a prerequisite to be applied in DSPECs, the sensitizers must be adsorbed strongly on the

TABLE 1: Efficiencies of some photoanodes employed in DSPECs for water oxidation.

Dye	Semiconductor	OER catalyst	Steady-state photocurrent ( $\mu\text{A}\cdot\text{cm}^{-2}$ )	Faradaic efficiency of $\text{O}_2$ generation	IPCE (wavelength)	TON $_{\text{O}_2}$ /TOF ( $\text{s}^{-1}$ )	Ref
	$\text{TiO}_2$	$\text{IrO}_2\cdot n\text{H}_2\text{O}$				$10^5/-$	[94]
	$\text{TiO}_2$	$\text{IrO}_x\cdot n\text{H}_2\text{O}$		2.3% (blue light)			[95]
	$\text{IrO}_2/\text{SnO}_2$	$\text{IrO}_2$	1700			$2.1 \times 10^5/6.7$	[96]

L =  $\text{PO}_3\text{H}_2$  ou  $\text{COOH}$

TABLE I: Continued.

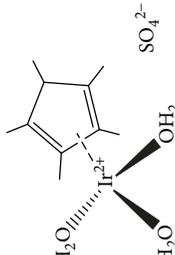
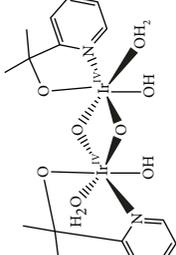
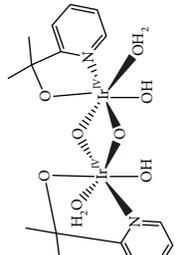
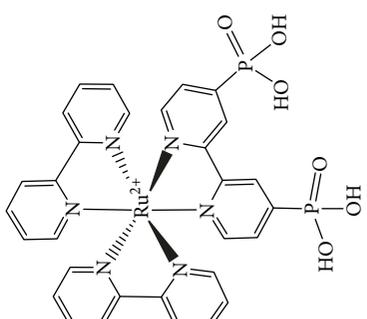
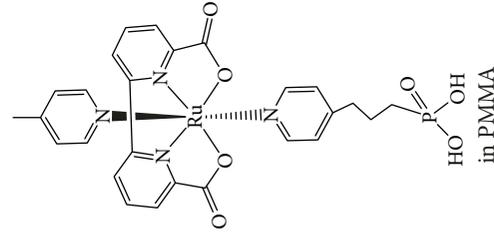
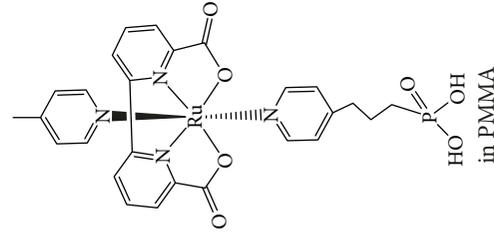
Dye	Semiconductor	OER catalyst	Steady-state photocurrent ( $\mu\text{A}\cdot\text{cm}^{-2}$ )	Faradaic efficiency of $\text{O}_2$ generation	IPCE (wavelength)	$\text{TON}_{\text{O}_2}/\text{TOF}$ ( $\text{s}^{-1}$ )	Ref
	$\text{Fe}_2\text{O}_3/\text{IrO}_x$	$\text{IrO}_x$	200 (0.3 V)				[97]
	$\text{IrO}_x$		0.25 V	99% in 2 h		$10^6/7.9$	[98]
	$\text{TiO}_2/\text{IrO}_2$	$\text{IrO}_2$					[99]
	$\text{TiO}_2$		2200		9.5% (450 nm)		[100]

TABLE I: Continued.

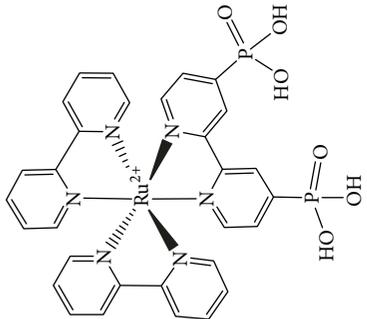
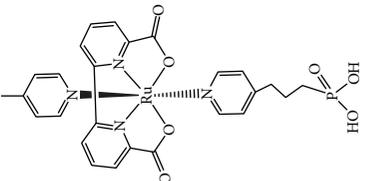
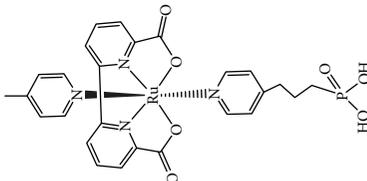
Dye	Semiconductor	OER catalyst	Steady-state photocurrent ( $\mu\text{A}\cdot\text{cm}^{-2}$ )	Faradaic efficiency of $\text{O}_2$ generation	IPCE (wavelength)	$\text{TON}_{\text{O}_2}/\text{TOF}$ ( $\text{s}^{-1}$ )	Ref
	$\text{TiO}_2/\text{SnO}_2$		1750	0.72%	13.8% (450 nm)	-/10	[101, 102]
	$\text{TiO}_2/\text{Si}-\text{Cl}$ ((3-chloropropyl)trimethoxysilane)		1500			-/10	[103]
	$\text{TiO}_2$						[104]

TABLE 1: Continued.

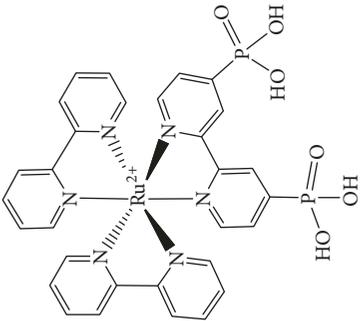
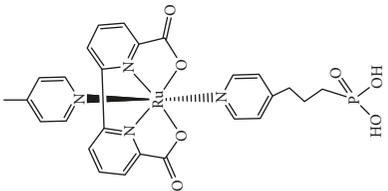
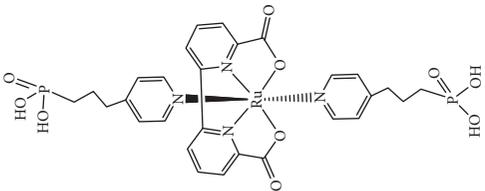
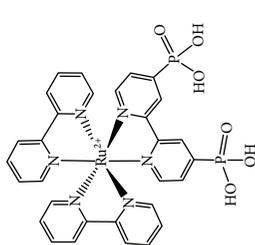
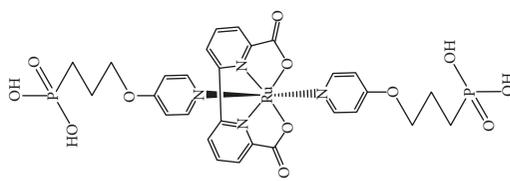
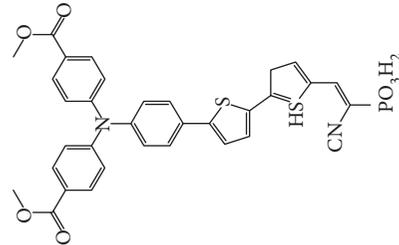
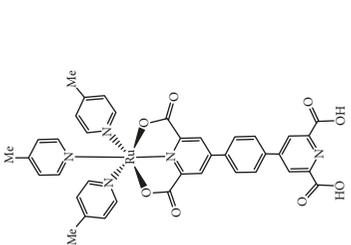
Dye	Semiconductor	OER catalyst	Steady-state photocurrent ( $\mu\text{A}\cdot\text{cm}^{-2}$ )	Faradaic efficiency of $\text{O}_2$ generation	IPCE (wavelength)	$\text{TON}_{\text{O}_2}/\text{TOF}$ ( $\text{s}^{-1}$ )	Ref
	$\text{TiO}_2$		450			0.53 $\mu\text{mol}/-$	[105]
	$\text{TiO}_2$		100			0.15 $\mu\text{mol}/-$	[105]
	$\text{TiO}_2$	$\text{Co}_3\text{O}_4$ modified with 3-aminopropyltriethoxysilane (NP)					[106]

TABLE I: Continued.

Dye	Semiconductor	OER catalyst	Steady-state photocurrent ( $\mu\text{A}\cdot\text{cm}^{-2}$ )	Faradaic efficiency of $\text{O}_2$ generation	IPCE (wavelength)	$\text{TON}_{\text{O}_2}/\text{TOF}$ ( $\text{s}^{-1}$ )	Ref
	$\text{SnO}_2/\text{AgNP}/\text{TiO}_2$		2000	95%	31.8% (450 nm)		[107]
	nanITO (4.5 nm)/ $\text{TiO}_2$ (0.6 nm)		132				[108]
	$\text{TiO}_2$		300		25% (380 nm)		[109]

AgNP: Ag nanoparticles.

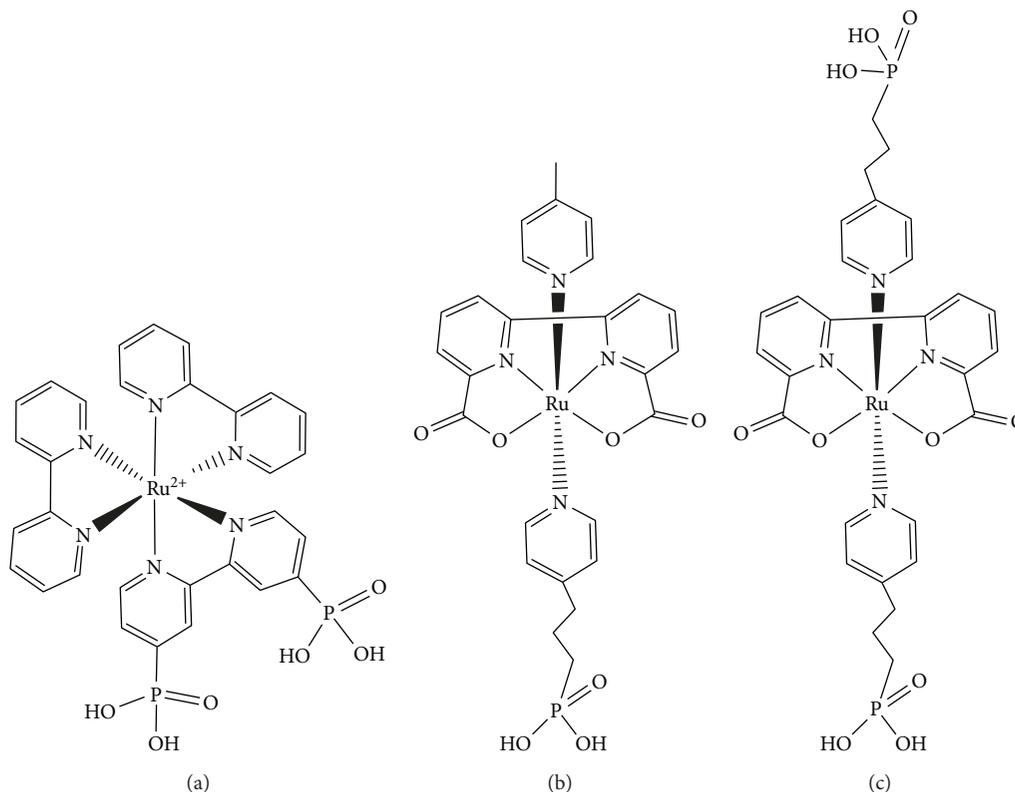


FIGURE 2: Structures of Ru(II)-based photosensitizer (a) and catalysts (b) and (c).

metal oxide surface and remain attached to the surface even at  $\text{pH} > 5$ . This is typically achieved by the use of phosphonic groups as anchors. In Figure 2(a), the structure of the Ru(II) complex  $[\text{Ru}(\text{bpy})_2((4,4'\text{-PO}_3\text{H}_2)_2\text{bpy})]^{2+}$  (Figure 2), a representative example of a metal complex-based light harvester, is shown. Another key aspect of the sensitizer is the ability to efficiently inject electrons on the metal oxide conduction band under excitation. This step initiates the multiple electron transfer processes that can lead to the oxidation of water molecules at the photoanode. The quantum yield and dynamics of the electron injection step for  $[\text{Ru}(\text{bpy})_2((4,4'\text{-PO}_3\text{H}_2)_2\text{bpy})]^{2+}$  were investigated in detail by using laser flash photolysis [123]. The electron injection from  $[\text{Ru}(\text{bpy})_2((4,4'\text{-PO}_3\text{H}_2)_2\text{bpy})]^{2+}$  to  $\text{TiO}_2$  nanoparticle is usually very efficient; c.a. 98% of the adsorbed photons lead to electron injection. However, the back electron transfer process is dependent on changes in pH, surface coverage, incident excitation intensity, and applied bias, which could be significant in limiting long-term storage of multiple redox equivalents [123].

Hence, modifications in the mesoporous metal oxide layer to efficiently transport electrons to the external circuit as well as the selection of ligands or redox shuttles able to quickly promote the electron transfer from the catalytic center to the photooxidized chromophore are necessary to achieve water oxidation. For example, Zhao and coworkers [95] have incorporated a tyrosine-histidine group to the  $\text{IrO}_x$  water oxidation catalyst in order to improve the electron transfer rate to a Ru(II) sensitizer. As the photooxidized chromophore is promptly reduced by the organic redox shuttle, the back

electron transfer is inhibited and quantum yields up to 2.3% are observed for the water oxidation reaction.

**2.2. Metal Oxide Layer.** As for other photoelectrochemical applications, *n*-type  $\text{TiO}_2$  is the most investigated semiconductor in DSPECs [42, 119, 124–129]. Some advantages of  $\text{TiO}_2$  are its chemical stability under aqueous media at different pHs, easiness of synthesis, and nontoxicity. However, the relatively slow electron mobility through the typically 5–15  $\mu\text{m}$  mesoporous  $\text{TiO}_2$  films used in DSPECs limits the device efficiency. Electron migration to the underlying conductive substrate is in competition with back electron transfer to the chromophore or the catalyst. Thus, different research groups have proposed structural or superficial modifications in the mesoporous metal oxide layer in order to avoid recombination losses.

One strategy that has been successfully explored is the use of core/shell oxide layers. In this case, the core is formed by a semiconductor with conduction band potentials more positive than those employed in the shell. In this way, the electron recombination of injected electrons is inhibited by the creation of a Schottky barrier. Alternatively, the core can also be formed by a conducting material, such as *nano*-ITO [130]. Alibabaei et al. [131] have shown that DSPECs with  $\text{SnO}_2/\text{TiO}_2$  core/shell-nanostructured electrodes prepared by atomic layer deposition (ALD) can reach photocurrents up to  $1.97 \text{ mA cm}^{-2}$  depending on the shell thickness. Later, McCool and coworkers [101] have shown that, in  $\text{SnO}_2/\text{TiO}_2$  electrodes sensitized by that in  $[\text{Ru}(\text{bpy})_2((4,4'\text{-PO}_3\text{H}_2)_2\text{bpy})]^{2+}$ , electron injection occurs directly to the

SnO<sub>2</sub> core when the TiO<sub>2</sub> shell has a thickness smaller than 5 Å. For thicker layers, the electron is transferred to TiO<sub>2</sub> and then to the SnO<sub>2</sub> core. In fact, the shell thickness and the overall mesoporous layer depth have profound effects on the electron transport dynamics. Lee and coworkers [94] reported the photoelectrochemical properties of TiO<sub>2</sub>/ZrO<sub>2</sub> and TiO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub> core/shell films sensitized by a Ru(II) polypyridyl complex and having IrO<sub>2</sub>.*n*H<sub>2</sub>O as catalyst. The authors observed that in photoanodes with an overall thickness smaller than 5 nm, the presence of the insulating shell favors the water oxidation process due to a decrease in the electron recombination in the TiO<sub>2</sub>/sensitizer and TiO<sub>2</sub>/catalyst interfaces. However, as the overall thickness is increased, the film conductivity is decreased due to the presence of the ZrO<sub>2</sub> or Nb<sub>2</sub>O<sub>5</sub>, leading to smaller photocurrents. Using a similar strategy, Ding et al. [103] reported the surface modification of TiO<sub>2</sub> films with (3-chloropropyl)trimethoxysilane (Si-Cl) prior the adsorption of the sensitizer (Figure 2(a)) and the catalyst (Figure 2(b)). As a result, after 10 s of the illumination with a 300 W xenon lamp through a 400 nm-long pass filter (light intensity 300 mW·cm<sup>-2</sup>), the efficiency O<sub>2</sub> evolution was improved from 0.43% to 0.72%.

Electron recombination on the surface of the conductive substrate (typically FTO) can also occur and can be successfully controlled by deposition of a compact underlayer [132]. The so-called blocking layers have been deposited by the layer-by-layer technique, a cost-effective technique that provides an unprecedented control of film thickness at molecular and nanometric scales by the sequential deposition of a large variety of materials [79, 133–138]. The use of this technique in photo-induced devices was recently reviewed by us [139]. In the case of DSPECs, the use of TiO<sub>2</sub> LbL compact layers led to an enhancement of 53% in the observed photocurrent [132].

**2.3. Catalyst.** The development of molecular catalysts for water oxidation reactions is a very active field that has been continuously reviewed in the literature [140–150]. Ru-, Ir-, and Mn-based catalysts have been largely investigated, and the mechanisms of O<sub>2</sub> evolution as a function of the molecular structure and the physical-chemical condition have been elucidated [107, 108]. For the Ru-based catalysts, [Ru(bda)(isoq)<sub>2</sub>] (H<sub>2</sub>bda=2,2'-bipyridine-6,6'-dicarboxylic acid; isoq=isoquinoline) described by Duan et al. [40] calls special attention due to its high TOF. More recently, Shaffer et al. have reported the manipulation of the rate-limiting step in the catalytic process by changing the ancillary ligands or by adding -CF<sub>3</sub> groups in the bda ligand [151]. The use of Earth-abundant catalysts such as Co<sub>3</sub>O<sub>4</sub> in conjunction with chromophores has also been explored [152–155]. Ir(III)-based molecular catalysts are also largely investigated, and considerable progress has been achieved in terms of stability and efficiency [143, 156–159]. Some examples are also listed in Table 1.

For DSPECs, the challenge is to immobilize such catalysts in the surface of the photoanode keeping their activity and also to promote their long-term stability. Some strategies include the use of anchor groups in the catalyst (as shown in Figure 3), the covalent linkage of the catalyst to the sensitizer to form molecular assemblies [160–162], polymer

coating [163], and electropolymerization [124, 163, 164]. Physical methods, such as ALD [165, 166] or self-assembly techniques like LbL [163, 167, 168] can also be used to immobilize the chromophore/catalyst assembly onto the electrode surface. Some illustrative examples of photoanode architectures are shown in Figure 3. Not only molecular catalysts have been employed in DSPECs. For example, Wei and coworkers [106] described a DSPEC with a photoanode composed by a TiO<sub>2</sub> film sensitized by that in Figure 2(a) and having Co<sub>3</sub>O<sub>4</sub> as catalyst. Co<sub>3</sub>O<sub>4</sub> was firstly modified by 3-aminopropyltriethoxysilane, and its immobilization was promoted by a Schiff reaction in the oxide surface. The as prepared photoanode exhibited 8 times higher photocurrent in comparison with that without the sensitizer. Moreover, the use of modified IrO<sub>x</sub> nanoparticles as water oxidation catalysts in DSPECs has been successfully reported [169]. A summary of the recent results is shown in Table 1.

While the continuous understanding of the water oxidation mechanism allows for continuous improvements in the photocurrent, the stability issues of the molecular catalysts are still to be overcome in order to have reliable devices. A DSPEC should exceed 10<sup>7</sup> cycles/year while maintaining the initial photocurrents [170]. Despite desorption from the electrode surface, decomposition of the chromophore and catalyst deactivation are critical processes that must be avoided after long-term exposition to solar irradiation. The continuous progress in synthetic chemistry as well as in the in situ spectroscopic methods to better understand the decomposition routes indicates that feasible solutions can appear in the following years. Furthermore, most of the DSPEC studies use a metal surface as cathode (typically Pt wires, where protons are reduced to molecular hydrogen). For an optimal utilization of the solar light, the cathodic reactions need to be promoted in photocathodes that absorb the fraction of the solar spectrum in which the photoanode is transparent.

The research for photocathodes is still less developed than that for photoanodes, and several complications arise in terms of reproducibility and stability. In the photocathode, a *p*-type semiconductor, such as Cu<sub>2</sub>O [171–173] or NiO [117, 174–177] should be employed. In the case of Cu<sub>2</sub>O, direct band gap excitation is used while for that of NiO, the surface of the oxide is derivatized with a chromophore. One example of a so-called tandem DSPEC (Figure 1(c)) having both a photoanode and a photocathode was given by Li et al. [109]. The NiO surface was modified with an organic dye as sensitizer and [Co(dmgbF<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)], dmgbF<sub>2</sub>=difluoroboryldimethylglyoximate, as proton reduction catalyst. The photogenerated hydrogen and oxygen gases evolved with a Faraday efficiency of 68% and 73%, respectively.

### 3. Hybrid Re(I)-Based Systems for Photoinduced CO<sub>2</sub> Reduction

As water is photooxidized, the redox equivalents can be used to produce H<sub>2</sub>, or alternatively, they can also be used to reduce gaseous CO<sub>2</sub> into useful chemicals, such as CO, and fuels, e.g., CH<sub>4</sub>. This could be a sustainable and green route to feed industrial processes based on the Fischer-Tropsch chemistry. As for the oxygen evolution reaction from water,

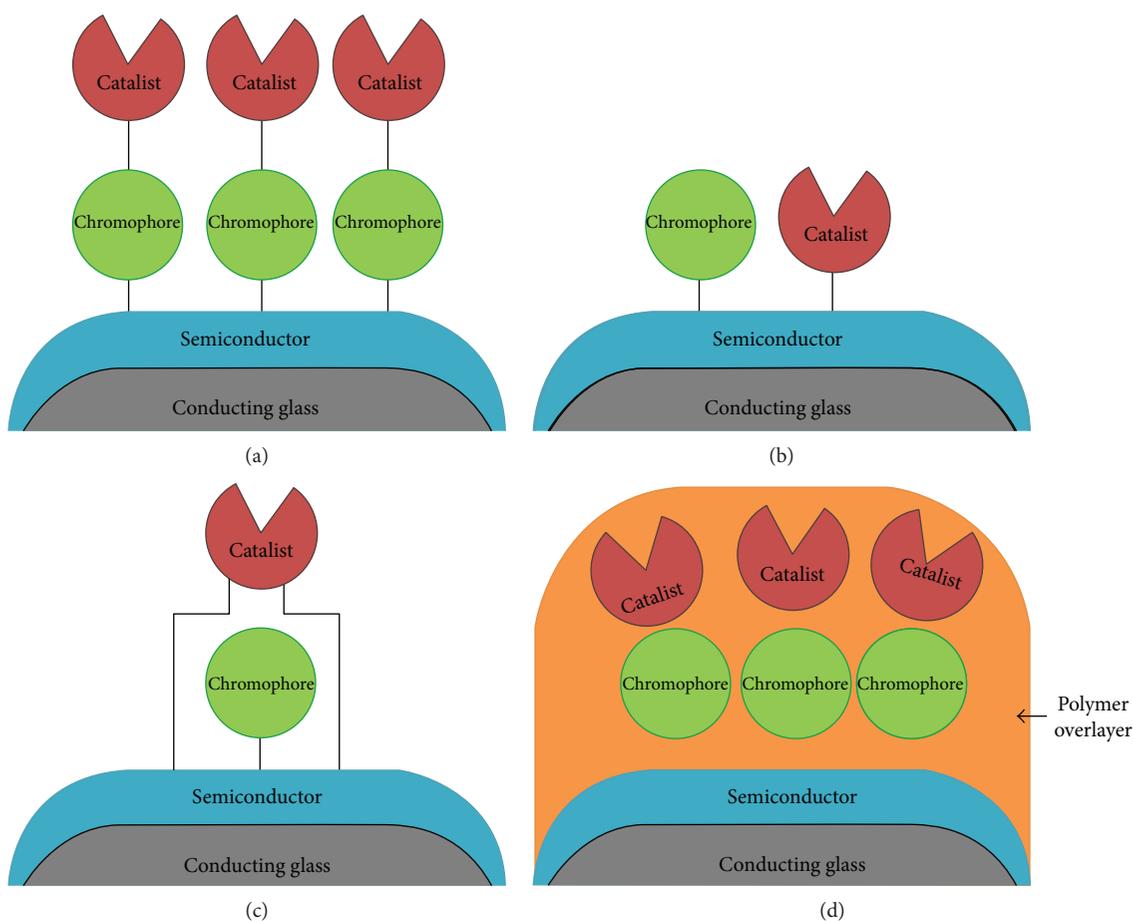
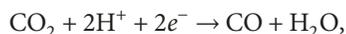
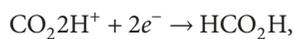


FIGURE 3: Some general schemes of photoanode architectures with (a) molecular assemblies, (b) coloaded strategy, (c) molecular overlayer, and (d) polymer overlayers.

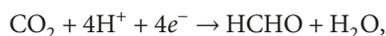
$\text{CO}_2$  reduction requires multiple electron-proton transfers in order to avoid large overpotentials. One-electron reduction of  $\text{CO}_2$  to  $\text{CO}_2^{\bullet-}$  occurs at  $-1.90$  vs NHE (pH 7), while consecutive two-electron reduction products have much smaller potential (equation (3)) [178, 179]. Finding efficient and stable photocatalysts for these reactions is an exciting field for inorganic photochemists.



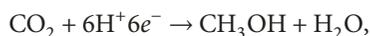
$$E_0 = -0.53\text{V (pH = 7 vs NHE)},$$



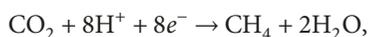
$$E_0 = -0.61\text{V (pH = 7 vs NHE)},$$



$$E_0 = -0.48\text{V (pH = 7 vs NHE)},$$



$$E_0 = -0.38\text{V (pH = 7 vs NHE)},$$



$$E_0 = -0.24\text{V (pH = 7 vs NHE)}.$$

(3)

Different photo- or photoelectrocatalysts for  $\text{CO}_2$  reduction have been reported based on metals and semiconductors [180–182], immobilized enzymes [183, 184], and coordination compounds [185–187] with a large variability in terms of selectivity and stability. While metals and semiconductors exhibit great stability but poor selectivity, enzymes and metal complexes can selectively convert  $\text{CO}_2$  into a specific product but they lack long-term stability. One simple and relatively robust catalyst for  $\text{CO}_2$  reduction into CO is based on Re(I) complexes of the general formula *fac*-[Re(L)(CO)<sub>3</sub>(NN)], NN=polypyridyl ligand, L=leaving group (typically Cl<sup>-</sup> or Br<sup>-</sup>) [188, 189], Figure 4. These species are few examples of mononuclear complexes able to work simultaneously as light harvester and catalyst. As a drawback, they exhibit low stability and poor absorption of solar radiation. For example, the highest reported turnover number ( $\text{TON}_{\text{CO}}$ ) for *fac*-[Re(Cl)(CO)<sub>3</sub>(bpy)] is 30 in a DMF/triethanolamine (TEOA) mixture ( $\lambda > 400$  nm) [190].

In this section, we focus our attention into heterogenized Re(I)-based photocatalysts for  $\text{CO}_2$  reduction. In these systems, the molecular Re(I) catalyst is immobilized in suitable substrates that can act in different steps of the photocatalytic cycle in order to yield higher efficiencies and stability. Moreover, the heterogenized system could be easier recycled and used in different solvents or reaction conditions [72, 191–198].

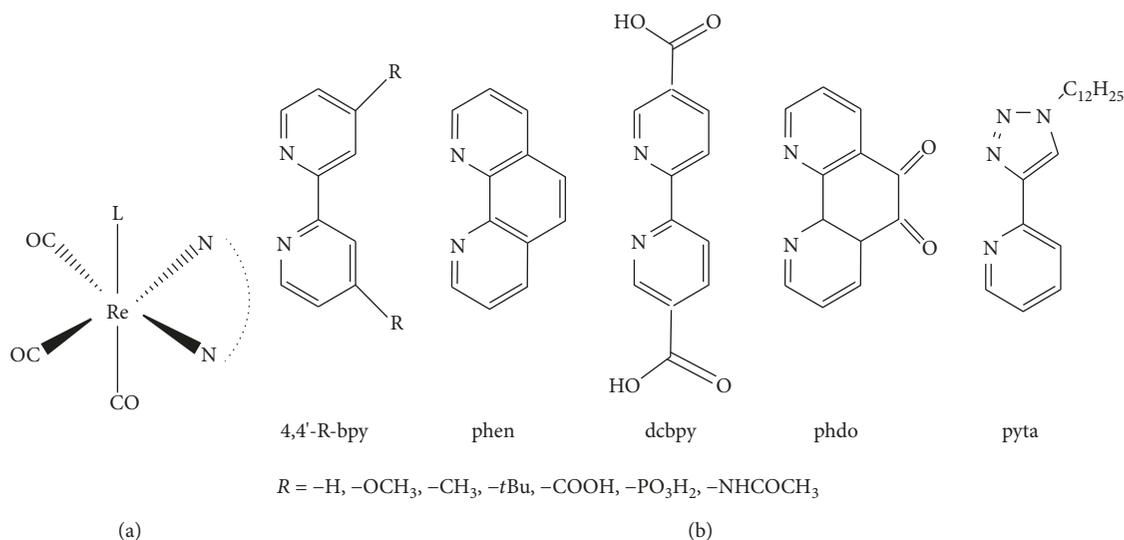


FIGURE 4: (a) General structure of Re(I) complexes. (b) Some typically NN ligands (bpy=2,2'-bipyridine, phen=1,10-phenanthroline, dcbpy=5,5'-dicarboxylic acid-2,2'-bipyridine, phdo=5,6-dione-1,10-phenanthroline, and pyta=2-(1-Dodecyl-1H-1,2,3-triazol-4-yl)-pyridine).

As the development in this topic still involves fundamental studies, typical investigations employ a sacrificial agent, i.e., a species that will work as electron source for the  $CO_2$  reduction, being oxidized at the end of the photocatalytic cycle. Typical examples of sacrificial agents are triethanolamine (TEOA) and trimethylamine (TEA). Some few examples, however, report the  $CO_2$  reduction by Re(I) complexes in photoelectrochemical cells, in which water is the electron donor [199–201]. Different substrates are used in hybrid Re(I)-based systems for  $CO_2$  reduction. The choice depends on the structure of the Re(I) complex and the desired functionality of the substrate. The most common materials employed as substrates are metal oxide semiconductors [202–204], but carbon nanostructures (graphene, nanotubes, etc.) have also been used [197, 205]. The work principle of these hybrid systems is illustrated in Figure 5.

Roughly, the systems can be divided into two classes. In a first strategy (Figure 5(a)), the Re(I) complex works simultaneously as light absorber and catalytic center. They are immobilized on the surface of wide band gap *n*-type semiconductors (such as  $TiO_2$ ) that works as an “electron sink” decreasing recombination losses and side reactions. In some cases, a chromophore can be coadsorbed onto the metal oxide surface to improve the light-harvesting properties in the visible range (Figure 5(b)). The other possibility is the immobilization of the Re(I) catalyst on the surface of a *p*-type semiconductor with a smaller band gap, so they can act as light harvester and electron donor in a photoelectrochemical cell (Figure 5(c)).

The first example of  $CO_2$  reduction by a Re(I) complex immobilized in *n*- $TiO_2$  was described by Cecchet et al. [192]. The authors have deposited the complex *fac*-[Re(Cl)(CO)<sub>3</sub>(v-bpy)] (v-bpy=4-methyl-4'-vinyl-2,2'-bipyridine) on mesoporous  $TiO_2$  films by electrochemical polymerization. The modified films were used as heterogeneous electrocatalyst for  $CO_2$  reduction, and a significant enhancement of the catalytic yield was observed. This

increase was attributed to the nanoporous nature of the substrate that allows a higher number of redox sites per surface area. The effect of surface immobilization and the role of the anchoring group on the photocatalytic activity of Re(I) complexes was further investigated by Liu and coworkers [191]. The authors have used two different amide-derivatized bipyridine ligands. The derivatization with electron-withdrawing amide (–CONH) groups lowered the catalytic activity by a factor of ~6 when the Re(I) compound was directly excited in the absence of additional photosensitizers but facilitated electron transfer between  $Ru(bpy)_3^{3+}$  and the Re(I) catalyst when  $Ru(bpy)_3^{2+}$  was used as a photosensitizer for excited-state electron transfer. The electron-withdrawing amide bond was then applied to graft the Re(I) complex onto the surface of silica nanoparticles. The surface-immobilized Re(I) sites were found to be well separated in a diimine-tricarbonyl coordination environment. The surface-immobilized catalyst showed activity comparable to that of the homogeneous Re(I) compound for photocatalytic  $CO_2$  reduction.

Later, Windle and coworkers have shown that the immobilization of the phosphonated derivative *fac*-[Re(Br)(CO)<sub>3</sub>(P-bpy)], P-bpy=2,2'-bipyridine-4,4'-bisphosphonic acid, on  $TiO_2$  leads to an increase of the photocatalytic activity of this complex.  $TON_{CO}$  was increased from 2 in solution to 52 for the immobilized complex ( $\lambda > 420$  nm) [198]. This enhancement was attributed to an increase in lifetime of the reaction intermediates due to the electron injection into  $TiO_2$ . Later, Abdallah and coworkers performed a detailed investigation of the system based on time-resolved infrared spectroscopy and proposed a reaction mechanism for the  $TiO_2$ -immobilized Re(I) catalyst in DMF/TEOA [206]. The authors concluded that the improved photocatalytic efficiency of the Re(I) catalyst upon immobilization onto  $TiO_2$  is due to the slower charge recombination and the high oxidative power of the  $Re^{II}$  species after electron injection as compared to the metal-to-ligand charge transfer (MLCT) state of the unbound Re(I) species.

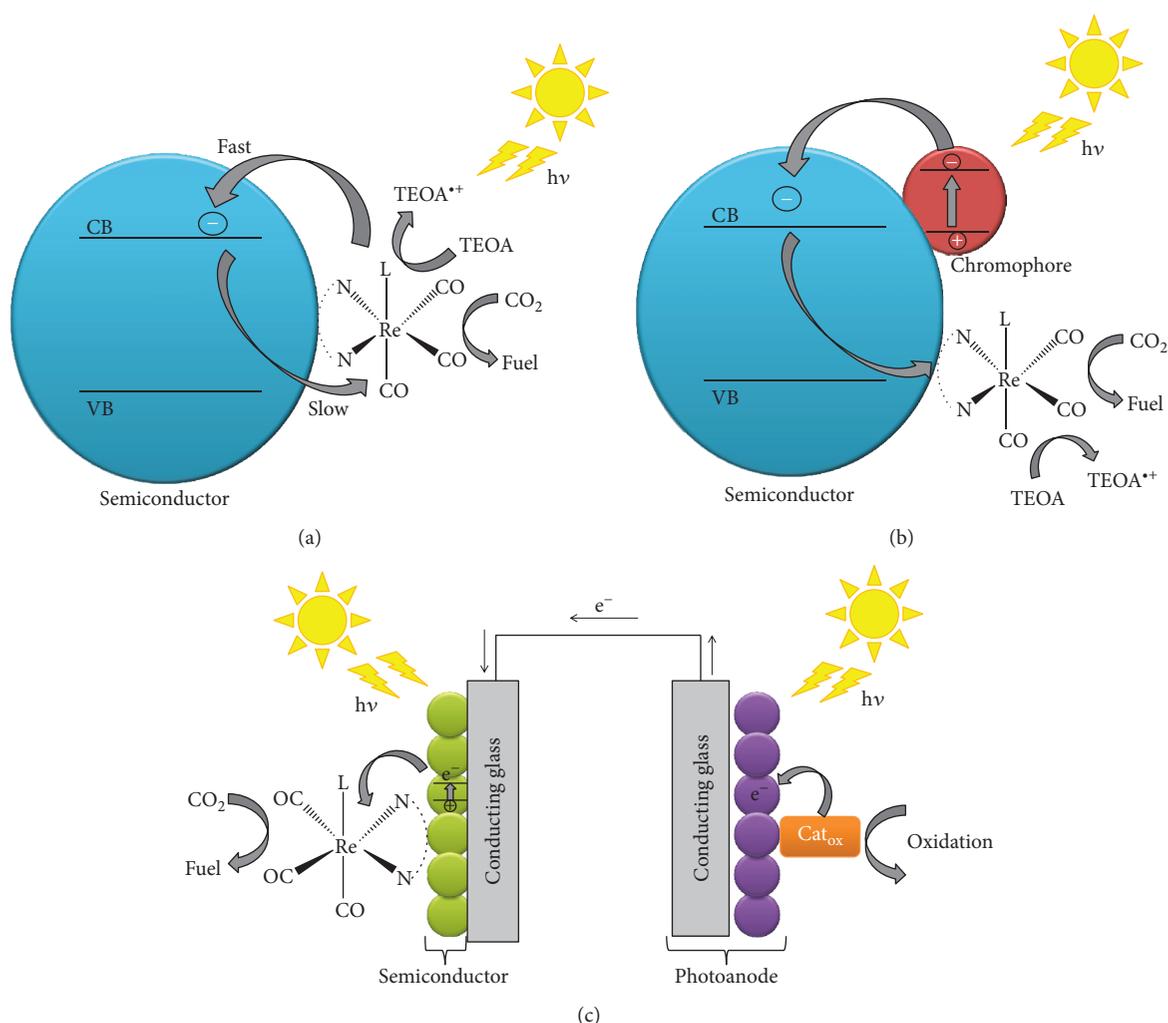


FIGURE 5: Work principle of hybrid Re(I)-based systems for CO<sub>2</sub> reduction. (a) The Re(I) complex works simultaneously as light absorber and catalytic center. (b) Chromophore and a Re(I) complex coadsorbed onto the metal oxide surface. (c) Re(I) catalyst immobilized on the surface of semiconductors with smaller band gaps in a PEC.

The authors proposed that during the catalytic cycle, a fraction of the injected electrons could catalytically reduce the reaction intermediate  $[\text{Re}^{\text{I}}(\text{P-bpy})(\text{CO})_3(\text{CO})]^+$  in order to promote the CO release. Thus, parameters such as electron mobility inside the oxide and reducing ability of the trapped electrons play an important role for the overall photocatalytic efficiency.

Based on these findings, we have proposed the use of hexaniobate ( $\text{K}_x\text{H}_{(4-x)}\text{Nb}_6\text{O}_{17}$ ) nan scrolls as substrates for the immobilization of Re(I) molecular photocatalysts. The hexaniobates exhibit a more negative conduction band energy in relation to  $\text{TiO}_2$ , increasing the reducing ability of the injected electrons. Moreover, its scrolled lamellar morphology can favor the electron mobility. After adsorption, the  $\text{TON}_{\text{CO}}$  in DMF/TEOA of the complex  $\text{fac}[\text{Re}(\text{Cl})(\text{CO})_3(\text{dcbH}_2)]$ ,  $\text{dcbH}_2=4,4'$ -dicarboxylic acid-2,2'-bipyridine was increased from 9 to 58, which is 20% higher than that observed on  $\text{TiO}_2$ , being among the highest reported values for Re(I)-based photocatalysts under visible light irradiation without any sensitizer [207]. A summary of the reported photoactivities of immobilized Re(I) catalysts

is shown in Table 2. As in other substrates, the choice of the anchoring group also profoundly affects the photoactivity of the Re(I) complexes on hexaniobate surfaces. For example, the complex  $\text{fac}[\text{Re}(\text{Cl})(\text{CO})_3(\text{phdo})]$ ,  $\text{phdo}=5,6$ -dione-1,10-phenantrolin has a diketone group which allows a strong interaction with  $\text{Nb}^{5+}$  ions on the hexaniobate surface yielding high surface loadings. However, the electron recombination kinetics after photoinjection is much faster leading to limited photoactivity.

Won and coworkers [208] developed a series of Zn-porphyrin dyes to be anchored onto  $\text{TiO}_2$  surfaces to complete a dye-sensitized photocatalyst system based on Zn-porphyrin- $|\text{TiO}_2|$ - $\text{Re}(\text{Cl})(\text{CO})_3(\text{ByPh})$ . These dyes were tested as low-energy photosensitizers for photocatalytic CO<sub>2</sub> reduction. The immobilization of the porphyrin molecules on Re(I)-modified  $\text{TiO}_2$  particles allows the occurrence of electron transfer processes under visible light with high charge separation yields being reached. Under  $\lambda_{\text{exc}} > 550 \text{ nm}$ , the dye-sensitized system using carboxylic acid ( $\text{ZnP}_{\text{CA}}$ ) as the porphyrin-anchoring group showed more efficient CO<sub>2</sub> to CO reduction activity, reaching a

TABLE 2: Reported photoactivities of immobilized Re(I) catalysts.

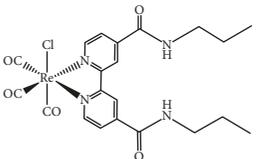
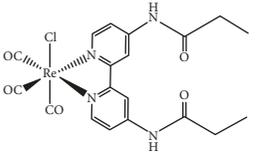
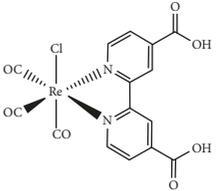
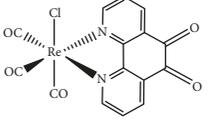
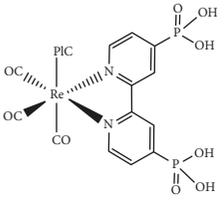
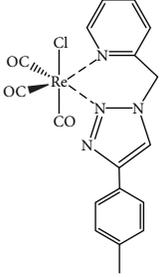
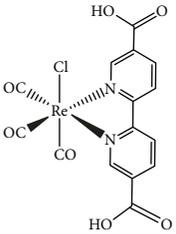
Complex	Substrate	Sacrificial agent	TON <sub>co</sub> /TOF (h <sup>-1</sup> )	Ref
Re-L1 	SiO <sub>2</sub>		6.9/-	
	SiO <sub>2</sub> + Ru(bpy) <sub>3</sub> <sup>2+</sup>	TEOA	11.0/-	[191]
Re-L2 	SiO <sub>2</sub> + Ru(bpy) <sub>3</sub> <sup>2+</sup>	TEOA	0.5/-	[191]
<i>fac</i> -[ReCl(CO) <sub>3</sub> (dcbH <sub>2</sub> )] 	TiO <sub>2</sub>		47/2.4	
	K <sub>x</sub> H <sub>(4-x)</sub> Nb <sub>6</sub> O <sub>17</sub>	TEOA	58/2.9	[207]
<i>fac</i> -[ReCl(CO) <sub>3</sub> (phdo)] 	TiO <sub>2</sub>		40/2.0	
	K <sub>x</sub> H <sub>(4-x)</sub> Nb <sub>6</sub> O <sub>17</sub>	TEOA	35/1.8	[207]
Re(X)(CO) <sub>3</sub> (ByPh) 	TiO <sub>2</sub>		48/8	
	ZrO <sub>2</sub>		8/-	
	SrTiO <sub>3</sub>		20/-	
	CeO <sub>2</sub>		0/-	
	ITO		0/-	
	ZnO		10/-	
	TiO <sub>2</sub> -porphyrin hybrid systems	BIH	~1000/-	[208]
ReCl(CO) <sub>3</sub> (PyBn) 		TEOA	150/12.7	
	TiO <sub>2</sub> -rGO	H <sub>2</sub> O	-/0.0	[197]

TABLE 2: Continued.

Complex	Substrate	Sacrificial agent	TON <sub>CO</sub> /TOF (h <sup>-1</sup> )	Ref
ReCl(CO) <sub>3</sub> (dcbpy)	UiO-67		10.9/–	
	—	TEOA	3.5/–	[209]

ByPh: 2,2'-bipyridine-4,4'-bisphosphonic acid; pic: picoline; PyBn: 1-(2-picolyl)-4-phenyl-1H-1,2,3-triazole; L1: 4,4'-dipropionylamido-2,2'-bipyridyl; dcbH<sub>2</sub>: 4,4'-dicarboxylic acid-2,2'-bipyridine; phdo: 5,6-dione-1,10-phenantroline; dcbpy: (2,2'-bipyridine)-5,5'-dicarboxylic acid; TiO<sub>2</sub>: titanium dioxide; ZrO<sub>2</sub>: zirconium dioxide; SrTiO<sub>3</sub>: strontium titanate; CeO<sub>2</sub>: cerium(IV) oxide; ITO: indium tin oxide; ZnO: zinc oxide; rGO: reduced graphene oxide; SiO<sub>2</sub>: silicon dioxide; K<sub>x</sub>H<sub>(4-x)</sub>Nb<sub>6</sub>O<sub>17</sub>: hexaniobate nanoscrolls; UiO-67: Zr<sub>6</sub>-(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(bpc)<sub>6-x</sub>(dcbpy)<sub>x</sub>; TEOA: triethanolamine; DMF: dimethylformamide; BIH: 1,3-dimethyl-2-phenyl-1,3-dihydrobenzimidazole.

TON<sub>CO</sub> of >1028. However, the photocatalytic activity decreases to almost zero after approximately 40 hours. The high performance of ZnP<sub>CA</sub> at early irradiation times can be attributed to an efficient electron injection, which is facilitated by the anchoring group. The replacement of the carboxylic acid anchoring group by cyanophosphonic acid (ZnP<sub>CNPA</sub>) leads to better performances at long-term irradiation times. In fact, the ZnP<sub>CNPA</sub>-based catalysts showed no decrease in the photocatalytic activity after 90 h of irradiation, reaching TON<sub>CO</sub> of ~800.

In a different strategy to increase the electron mobility in the semiconductor, Cui and coworkers reported TiO<sub>2</sub>/reduced graphene oxide (rGO) composites modified with the molecular Re(I) catalyst *fac*-[Re(Cl)(CO)<sub>3</sub>(PyBn)] (PyBn=1-(2-picolyl)-4-phenyl-1H-1,2,3-triazole) [197]. The PyBn ligand allows the Re(I) complex to be covalently bound to the graphene sheets. The hybrid catalyst exhibited TON<sub>CO</sub> 6 times higher than that observed for the complex in solution. In the mechanism proposed by the authors, the graphene manifold acts as an intermediate, facilitating the electron transfer from the TiO<sub>2</sub> nanoparticles to the Re(I) complex.

The Re(I) molecular catalysts can also be immobilized on the surface of *p*-type semiconductors and be used in a photoelectrochemical cell, in which water is oxidized in the photoanode and CO<sub>2</sub> is reduced in the photocathode (Figure 5(c)). In this case, several criteria need to be fulfilled. Firstly, in order for the electron transfer to occur between the photoelectrodes without external bias, the conduction band potential of the *n*-type semiconductor in the photoanode has to be more negative than the valence band potential of the *p*-type semiconductor in the photocathode. Moreover, both the water oxidation and CO<sub>2</sub> reduction reactions must be thermodynamically favorable and all materials need to be stable at operation conditions [210].

Kou and coworkers reported CO<sub>2</sub> photoreduction by a porphyrin-rhenium dyad metal complex on *p*-type semiconducting NiO. The Zn(II) porphyrin acts as light harvester reducing the Re(I) metal complex and being regenerated by the semiconductor. An electrochemical cell composed of the dyad-adsorbed NiO particle layers on an FTO cathode and platinum as a counter electrode in CO<sub>2</sub>-saturated DMF

solution showed a constant cathodic photocurrent upon visible light irradiation (λ = 420 nm) accompanied by the formation of the two-electron-reduced product (CO) [211]. Further, Schreier et al. reported the covalent immobilization of a Re(I)-based molecular catalyst on Cu<sub>2</sub>O [201] that was protected by a TiO<sub>2</sub> overlayer. High current densities were achieved by using a nanostructured TiO<sub>2</sub> scaffold, processed at low temperature. This led to a 40-fold enhancement of the catalytic photocurrent as compared to planar devices, resulting in the sunlight-driven evolution of CO at large current densities and with high selectivity. In this photoelectrochemical cell, a platinum wire was also used as counter electrode.

First reports on a photoelectrochemical cell employing Re(I)-based CO<sub>2</sub> catalyst able to simultaneously evolve CO and O<sub>2</sub> from CO<sub>2</sub> and H<sub>2</sub>O were performed by Ishitani's group [199, 200, 202, 205, 212]. In a first work, a Ru(II)-Re(I) supramolecular metal complex photocatalyst was immobilized on a NiO electrode, which was then used as photocathode in a photoelectrochemical cell comprising a CoO<sub>x</sub>/TaON photoanode. The device showed activity for visible-light-driven CO<sub>2</sub> reduction using water as a reductant to generate CO and O<sub>2</sub>, with the assistance of an external electrical (0.3 V) and chemical (0.10 V) bias produced by a pH gradient [212]. Further, the same group reported the replacement of NiO by a CuGaO<sub>2</sub>*p*-type semiconductor electrode [199]. The as prepared photocathode displayed photoelectrochemical activity for the conversion of CO<sub>2</sub> to CO in an aqueous electrolyte solution with a positive onset potential of +0.3 V vs Ag/AgCl, which is 0.4 V more positive in comparison to that observed for the NiO-based photocathode. The photoelectrochemical cell comprising the hybrid CuGaO<sub>2</sub> photocathode and a CoO<sub>x</sub>/TaON photoanode enabled the visible-light-driven catalytic reduction of CO<sub>2</sub> using water as a reductant to give CO and O<sub>2</sub> without applying any external bias. This result, as well the other works cited in this brief compilation, demonstrates that as the understanding of the reaction mechanisms in artificial photosynthesis advances, molecular and band gap engineering can be conveniently used to overcome the energetic barriers for the realization of artificial photosynthesis.

## 4. Conclusions

Growing concerns about fuel depletion and global warming caused by rising levels of atmospheric CO<sub>2</sub> have stimulated the development and insertion of new technologies involving renewable sources. In this context, the development of hybrid systems and DSPECs is a promising pathway as it allows to synergically combine advantages of molecular catalyst and metal oxide semiconductors to produce more efficient and stable devices. Moreover, these systems can take advantage of the large variability in terms of chemical structure, morphology, and assembly strategies.

Despite the great progress observed in the last years, some challenges still need to be overcome in aspects regarding the efficiency on the stability of the systems. The critical processes that should be avoided after long-term exposure to solar irradiation are desorption of the electrode surface, decomposition of the chromophore, and deactivation of the catalyst. Continuous interdisciplinary and fundamental research in the field is definitely a key step to reach the main goal of large-scale solar fuel production.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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