Review article

Chemical kinetics in solar to chemical energy conversion: The photoelectrochemical oxygen transfer reaction

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A B S T R A C T

After introducing the basic aspects of the photoelectrochemical processes for the oxygen transfer reaction, we present the simplest kinetics models that have been built to represent the dynamics of light-induced redox reactions. Additionally, we discuss the basic chemical kinetics formalism used in photocatalysis and photoelectrochemistry, where interplay between the oxidation process and non-equilibrium adsorbed states is considered. We also comment about the experimental developments related to the treatment of wastewater with electricity or H_2 generation. Finally, we discuss the need to measure reaction rates to determine and compare the physicochemical parameters describing the chemical interactions during photoelectrochemical processes, in order to understand these reactive systems and apply them to new challenges related to the environment and energy.

Contents

1. Introduction

During the last five decades, numerous investigations have focused on the development of heterogeneous photocatalysts activated by sunlight and their applications to the *environmental purification of wastewater* (Rizzo et al., 2019; Garcia-Segura and Brillas, 2017; Raptis et al., 2017; Etacheri et al., 2015; Spasiano et al., 2015; Fuentes et al., 2017; Tantis et al., 2016; Vargas and Núñez, 2010; D'Oliveira et al., 1993; Hoffmann et al., 1995), *conversion of solar energy into electricity in solar cells and related devices* (Hossain, 2019; Bousiakou et al., 2018; Charfi et al., 2018;

Vinod Kumar and Singh, 2018; Enciso et al., 2017; Bai et al., 2014; Antoniadou and Lianos, 2010; Peter, 2007; O'Regan and Grätzel, 1991) and *production of H_2* as a consequence of a photosynthetic reaction (Hisatomi and Domen, 2019, 2017; Bousiakou et al., 2018; Chen et al., 2017; Giménez and Bisquert, 2016; Ismail and Bahnemann, 2014; Bockris, 2013; Khan et al., 1988; Fujishima and Honda, 1972). According to the Bahnemann group (Mohamed and Bahnemann, 2012; Zhang et al., 2012), there is still a lack of understanding of the interrelationship of the variety of phenomena involved in the applications of photoelectrochemical process, so efforts to carry out fundamental studies on potential application systems are valuable. In this sense, it is convenient to review the chemical kinetic models for the use of solar energy to perform

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chemical reactions related to the treatment of wastewater with the possibility of generating electricity or hydrogen as solar fuel.

The first photoelectrochemistry reports start with the work of Bequerel (1839). Diverse studies of the effect of light on electrodes were carried out in the following 100 years and were summarized by Copeland and coworkers (Copeland et al., 1942). According to the reports, most of the electrodes examined may have been carried out in the presence of undetected oxide films, also numerous studies related to photography based on photoactivity of silver halides colloidal dispersions have been reported (Lianos, 2017; Fujishima et al., 1982). The first interpretations were very incipient, due the lack of conceptualization related to the valence and conduction bands at the solid state. The foundations of semiconductor electrochemistry were laid by the works of Brattain and Garrett (1955) and Garrett and Brattain (1955), who introduced the use of Nernst-type potential expression involving the activity of electrons and holes. Additionally, the pioneering contributions of Gerischer (1969a,b, 1966) allowed linking the anodic or cathodic current at semiconductor electrodes with the availability of excess of holes in the valence band or excess of electrons in the conduction band, respectively. Gerischer introduced the concepts of minority charge carriers and density of states with the concomitant development of an extensive theory related to the physical and chemical processes that concur at the semiconductor–electrolyte interface (Gerischer, 1990, 1991, 1993, 1995; Memming, 2015; Sato, 1998; Morrison, 1980).

The theoretical treatment reported by Bockris and Uosaki (1978, 1977), indicated that the energy state of the surface is the determining factor in the efficiency of the water splitting, as well as energy conversion. During the last years, the contribution of Bisquert bringing the concepts of solid state physics to the nanostructure semiconductor electrode–electrolyte interface (Bisquert, 2017) has built the conceptual framework to explain the role of nanomaterials of diverse nature in the performance of many applications such as solar cells, artificial photosynthesis, self-cleaning coatings, light emitting diodes (LEDs), diverse types of photochemical based sensors, solar fuels production, photocatalytic wastewater treatment and related fuel cells (Photo Fuel Cells). All the works cited up to now, imply a brief summary of the fundamental aspects that are known about the redox reactions induced by light on semiconductor materials, being noted that the kinetics of the physical chemistry phenomena that occur on the electrode–electrolyte interface, defines the experimental behavior and the scope of applications.

In this paper we summarized the scope and mechanisms for the photoelectrochemical oxygen transfer reactions on semiconductor materials, providing examples of the performance of several kinds of organic compounds and wastewaters on various semiconducting materials. To optimize reaction rates in photocatalysis it is fundamental to understand the dynamics of the redox process. For this reason, we focused on the principal aspects of the photocatalytic processes for oxygen transfer reactions and present the basic chemical kinetics theory to represent their characteristics. Additionally, we illustrate the fundamental aspects of the kinetic models that are appropriate to represent the two typical operation conditions: powder photocatalysis and photoelectrochemistry on semiconductor electrodes. The report considers the simplest kinetic models used in powder photocatalysis, as well as a brief discussion on the basic formalism to describe photoelectrochemistry for organic matter oxidation, where interplay between the oxidation process and non-equilibrium adsorbed states are considered. Finally, prospects for further developments related to the potential application of the discussed principles as advanced oxidation processes to current environmental problems, with impact on the solar energy conversion into electricity or the concomitant hydrogen production, have been envisaged.

2. Light induced redox reactions during heterogeneous photocatalysis

In semiconductor (S) solar light photocatalysis (Garcia-Segura and Brillas, 2017; Etacheri et al., 2015; Schneider et al., 2014; Teoh et al., 2012; Vargas and Núñez, 2010; Malato et al., 2009; Fujishima et al., 2008; Hoffmann et al., 1995) an electron from the valence band is promoted to the conduction band:

$$S[] + h\nu \rightarrow S[e^- + h^+] \tag{1}$$

generating a hole h^+ in the valence band (VB) and an electron e^- in the conduction band (CB). The holes can react with organic compounds to generate free radicals,

$$h^+ + -R \rightarrow -R^{\cdot +} + e^- \tag{2}$$

They can also be trapped by water to form hydroxyl radicals on the surface of the photocatalyst:

$$h^+ + H_2O \rightarrow -HO^{\cdot} + H^+ + e^- \tag{3}$$

Reaction of electrons in the CB with acceptor species dissolved in the aqueous solution preserves the charge balance. The reduction potential of this chemical species must be equal or more positive than the potential corresponding to the edge of the CB of the semiconductor; another necessary condition for reactivity is that the electron density of the redox couple in the electrolyte must overlap with the density of states of the photocatalyst (Memming, 2015; Sato, 1998; Hagfeldt and Grätzel, 1995). Typically, in air/water photocatalysis, the charge balance is completed by the oxygen reduction reaction under solar light irradiation, as shown in Fig. 1A,

$$e^- + O_2 \rightarrow -O_2^{\cdot -} \tag{4}$$

or by reduction of an oxidized species O in solution capable of being reduced by an electron from the conduction band,

$$e^- + O \rightarrow R \tag{5}$$

Additionally, reduction can be electrochemically assisted; this implies separating the oxidation and reduction reactions using an appropriate secondary electrode, and after polarization, the electron at the CB can be extracted to the external circuit, enhancing charge separation, as shown in Fig. 1B. Consequently, electron–hole recombination diminishes and general improvement of the light-induced redox reactions obtain.

Radicals forming on the semiconductor surface are highly reactive and generally promote organic substrate oxidation via the well-known organic reactions of hydrogen abstraction, addition to double bonds or to aromatic rings (Friedmann et al., 2016; Hoffmann et al., 1995). The process typically results in mineralization of the organic compound to form CO_2, H_2O and mineral acids in solution (Spasiano et al., 2015; Malato et al., 2009; Hoffmann et al., 1995). Oxidation of methanol, glucose, formic acid, biomass and bio-related compounds (Kaneko et al., 2006) have been reported as proof of the possibility of converting solar light to electrical energy using a TiO_2-based Photo Fuel Cell, and the wastewater photo(electro)chemical treatment of model organic compound molecules such as aliphatics, aromatics, chloroaromatic, phenols, surfactants, herbicides, dyes and polyaromatic heterocyclic compounds, have been also reported with satisfactory results (Papagiannis et al., 2018; Garcia-Segura and Brillas, 2017; Lianos, 2017; Raptis et al., 2017; Sfaelou and Lianos, 2016; Tantis et al., 2016; Michal et al., 2014; Kaneko and Ueno, 2013; Kaneko et al., 2006).

It has been shown that if a good electrocatalyst for the hydrogen evolution reaction (HER) is chosen to electrochemically assist the photocatalytic process, it is then possible to generate H_2
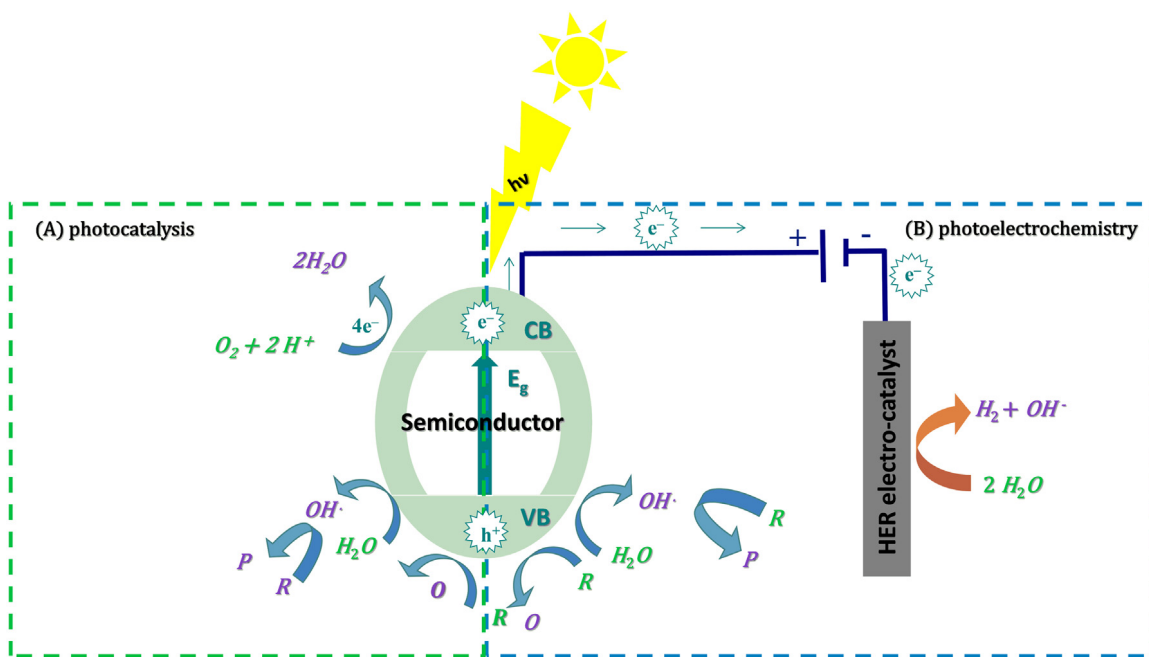
Fig. 1. Scheme of (A) photocatalysis and (B) photoelectrochemistry processes.

as byproduct of the chemical process (Takata and Domen, 2019; Hisatomi and Domen, 2019, 2017; Doukas et al., 2018; Chen et al., 2017; Lianos, 2017; Ismail and Bahnemann, 2014):

$$2e^- + 2H^+ \rightarrow H_2 \tag{6}$$

offering interesting and convenient extension for applications of this technology.

In the discussion above, we have considered that the chemical species participating in photo-induced reactions are adsorbed on the surface of the semiconductor (e.g. S[HO•] or –HO•). For reactions involving hole or electron transfer it is probable that the reaction of transference occurs with the adsorbed species (Sato, 1998). For example, Blesa and coworkers discuss the surface complexation approach in order to account the photo-oxidation rates according to the substrate surface excess, usually expressed in terms of surface concentration of the formed adduct. In fact, the expected consequences of substrate chemisorption as a pre-requisite for heterogeneous photo-oxidation have been considered (Blesa et al., 2004).

On other hand, the kinetic models discussed here consider that an absorbed photon originates an electron–hole pair, and then a recombination and redox reaction occurs. In the case of suspensions, the semiconductor powder is used in a proportion that guarantees the minimum loss by scattering. Therefore, linear dependence with the photonic flux is expected. Additionally, it is necessary also to differentiate processes based on energy balance. If the oxidation of organic compounds leads to the evolution of H_2, then this process can be described as a photosynthetic reaction due to the positive change of Gibbs free energy in the dark. If O_2 completes the charge balance by the reduction reaction, then this is the typical photocatalytic reaction. Nonetheless, photoelectrochemical processes are the simplest and most accurate way to describe these phenomena.

3. Photoelectrochemical oxygen transfer reaction

3.1. Kinetic models I: photocatalysis in water suspensions

The Fujishima group (Liu et al., 2014) has recently commented on the practical kinetic models used to understand the photocatalytic process. To a first approximation, the kinetics of the

photocatalytic phenomenon can be interpreted in terms of the Langmuir–Hinshelwood (LH) mechanism, Table 1, which assumes equilibrium adsorption of reactants, the organic compound and dissolved O_2, followed by surface reaction as the slow rate-determining step (Liu et al., 2014; Hoffmann et al., 1995; Minero, 1995), with reaction rate r given by

$$r = \frac{k_1^{LH} K_1^{LH} C_1}{1 + \sum K_i^{LH} C_i} \tag{7}$$

where C_i are the concentrations of the chemical compounds, $k_1^{LH} = k K_{O2} C_{O2}/(1 + K_{O2} C_{O2})$ is the apparent reaction rate at saturation coverage, k is the reaction constant for the surface reaction and K_i represent the adsorption equilibrium constants of reactants on the catalyst.

This model (Eq. (7)) fits very well most of the experimental results reported in the literature (Ollis, 2018; Liu et al., 2014), even though its assumptions do not account for all known microscopic steps occurring during the photocatalytic process. It is common to find various experimental results such as the decrease in apparent affinity on the surface, zeroth-order dependence on the substrate concentration, surface poisoning due to reaction by-products, and a maximum in the reaction rate depending on the substrate concentration. These effects can be modeled considering Langmuirian equations according to the surface complexation approach (Blesa et al., 2004). In fact, extensions of the LH function have been used to explain satisfactorily the effect of pH and chemical equilibria on the photocatalyst surface (Vargas and Núñez, 2009), as well as the kinetics of degradation when more than one reactive oxygen species is generated (Vargas et al., 2014). More detailed analyses revealed the complexities of the physicochemical processes involved with interplay between the physical and photochemical phenomena defining the scope of interpretations (Emeline et al., 2016; Montoya et al., 2014a,b; Minero, 1995).

Turchi and Ollis (1990) and Ollis (2005) considered a kinetic model based on a steady state hypothesis for reaction intermediates. According to this, during photocatalyzed reactions, adsorption/desorption equilibrium is not established as the high reactivity of the photo-generated radicals displaces continuously the concentration of adsorbed reactants from equilibrium. This

Table 1
Reactions involved in photocatalysis according to LH interpretation.

Description	Reaction
Fast adsorption–desorption equilibrium of O_2 on photocatalyst surface	[1]: $S[] + O_2 \rightleftarrows S[O_2]$
Fast adsorption–desorption equilibrium of R on photocatalyst surface	[2]: $S[] + R \rightleftarrows S[R]$
Slow surface reaction between adsorbed states	[3]: $S[O_2] + S[R] \xrightarrow{H_2O,h\nu} 2S[] + P$

model considers the generation of charge carriers, their recombination, and generation of hydroxyl radicals by oxidation of water. The mechanistic postulates can be summarized according to the reactions shown in Table 2.

The outcome of the suppositions made, together with the experimental validation of the model for the oxidation of many organic compounds of diverse chemical nature, show accurate correlations between experimental data and the resulting equations (Ollis, 2005; Mills et al., 2006a,b) to be described below. This approach is consistent with the reported dependence of the apparent adsorption and desorption rate constants on the intensity of irradiated light, as well as with the catalytic rate constant (Liu et al., 2014). The final expression of the rate law,

$$r = \frac{k_{obs}k_{r1}C_1}{1 + \sum k_{ri}C_i} \tag{8}$$

is similar in mathematical form to that of the LH kinetics, Eq. (7), however, the actual meaning of the kinetic constants is intimately related to physical variables affecting the chemistry of the system, namely the intensity of the radiation and the characteristics of the catalyst,

$$k_{obs} = \alpha a_c k_1 I \qquad \text{(at low light intensity)} \tag{9}$$

$$k_{obs} = \alpha a_s k_{OH} \frac{k_1 a_c I}{K_1 v_p} \qquad \text{(at high light intensity)} \tag{10}$$

$$k_{ri} = \frac{k_{R-OH}K_i[site]a_s}{k_d} \qquad \text{(reaction with adsorbed } {}^{\bullet}\text{OH}$$

$$\text{and organic molecule)} \tag{11}$$

where k_{obs} is the observed rate constant, predicted to be function only of the properties of the catalyst and reaction conditions, k_{ri} is the rate constant of reaction [4] in Table 2, C_1 is the concentration of the organic, α is a constant ($1 < \alpha < 2$) that accounts for the possible formation of a radical via the reduction of O_2 by conduction band electrons (related to stoichiometry and electroneutrality during radical formation), a_c is the particle surface area, k_1 is the reaction rate constant related to the formation of the electron–hole pairs, I is the light intensity, k_{OH} is the reaction rate constant for –HO$\bullet$ formation (related to hole trapping), K_1 is the adsorption constant of the compound on the semiconductor surface, v_p is the volume of the particle, k_{R-OH} is the reaction rate constant of organic species with –HO$\bullet$, k_d is the reaction rate constant for detrapping of holes from –OH to the VB of the semiconductor, [site] is the surface concentration of adsorption sites on the photocatalyst and $\sum K_{ri}C_i$ represents the contributions of the i components of the system.

As already mentioned, according to the Turchi and Ollis model, k_{obs} depends only on the catalyst properties and the reaction conditions, and its value should be independent of the nature of the organic reactant. k_{ri} is affected by the chemical interaction of the organic compounds with the catalyst, but does not correspond to the adsorption–desorption equilibrium constant.

As a matter of fact the two discussed models are capable of representing the experimental evidences in terms of kinetic data fitting by least squares minimization. Only apparent kinetic parameters can be obtained from them, containing the intrinsic constants of the redox processes involved. A common kinetic model of the type $r = kKC/(1 + KC)$ thus arises from multiple reaction schemes; hence the actual mechanisms cannot be elucidated from the kinetic models alone. Moreover, the dependence of the Langmuir–Hinshelwood parameters upon the intensity of irradiated light indicates continuous displacement of the equilibrium to a *pseudo*-steady state, as Turchi and Ollis considered in their more fundamental approach than the presumed equilibrium adsorption assumed by the LH model. For a detailed critical review of this model and its comparison with other kinetic models proposed for powder photocatalysis in aqueous suspensions, the work of Mills and collaborators (Mills et al., 2015) is particularly useful.

3.2. Kinetic models II: photoelectrochemistry for organic matter oxidation

The kinetic models discussed above do not consider a variety of well known photoelectrochemical phenomena. However, on the basis of chemical kinetics, Mandelbaum and co-workers (Mandelbaum et al., 1999b) incorporated into the photocatalytic description other fundamental phenomena, namely surface recombination of hydroxyl radicals with electrons in the conduction band and primary oxidation of organic compounds to form their organic radicals, followed by electron injection to the conduction band leading to current doubling. The simplest mechanism to represent the phenomena is thus represented by the reactions given in Table 3.

The formalism involves representing the rate laws of each elementary step to build the system of differential equations (12)–(15) after considering the effect of the electrochemical potential on the rate constants according to the Butler-Volmer type relation (16):

$$\frac{d\left(h_{VB}^+\right)}{dt} = r_1 - r_2 - r_5 \tag{12}$$

$$\frac{d\left(e_{CB}^-\right)}{dt} = -\frac{I_{ph}}{FA} + r_1 - r_3 + r_6 - r_7 \tag{13}$$

$$\frac{d\left(R^{\bullet}\right)}{dt} = r_4 + r_5 - r_6 - r_7 \tag{14}$$

$$\frac{d\left(OH^{\bullet}\right)}{dt} = r_2 - r_3 - r_4 \tag{15}$$

$$k_i = k^0 \exp\left[\frac{-nF(1-\beta)\eta}{RT}\right] \tag{16}$$

where r_i are the rates of reactions [1] through [7] represented in Table 3, k_i the corresponding reaction rate constants, $k_i{}^0$ the rate constants at their equilibrium potentials, A the surface area, I_{ph} the photocurrent, t the time, n the number of electrons transferred, F the Faraday constant, R the universal gas constant, T the temperature, β the electron transfer coefficient and η the overpotential. The photocurrent was obtained after considering the current flows generated by the charge transfer reactions,

$$\frac{I_{ph}}{FA} = r_2 - r_3 + r_5 + r_6 - r_7 \tag{17}$$

Mandelbaum and collaborators (Mandelbaum et al., 1999a) refer to the concept of oxidation length, defined as the number of oxidation steps that are triggered by a single hole transfer event,

Table 2
Reactions involved in photocatalysis according to Turchi and Ollis (1990) and Ollis (2005) interpretation.

Description	Reaction
Generation of charge carriers	[1]: $TiO_2[] + h\nu \rightarrow TiO_2[e^- + h^+]$
Recombination of charge carriers	[2]: $e^- + h^+ \rightarrow heat$
Radical formation by hole trapping	[3]: $h^+ + TiO_2\left[H_2O/OH^-\right] \rightarrow TiO_2\left[HO^{\cdot}\right]$
Interfacial oxygen transfer reaction	[4]: $TiO_2\left[HO^{\cdot}\right] + TiO_2\left[R\right] \rightarrow TiO_2\left[P\right]$
Radical deactivation	[5]: $TiO_2\left[HO^{\cdot}\right] \rightarrow h^+ + TiO_2\left[H_2O/OH^-\right]$
Non equilibrium adsorption–desorption of R on photocatalyst surface	[6]: $TiO_2[] + R \rightleftarrows TiO_2[R]$

Table 3
Reactions involved in photoelectrochemistry according to Mandelbaum and co-workers (Mandelbaum et al., 1999b) interpretation.

Description	Reaction
Generation of charge carriers	[1]: $TiO_2[] + h\nu \rightarrow TiO_2[e^- + h^+]$
Radical formation by hole trapping	[2]: $-OH^- + h^+ \rightarrow -HO^{\cdot}$
Radical deactivation	[3]: $-OH^{\cdot} + e^- \rightarrow -HO$
Interfacial oxidation of R by hydroxyl radical	[4]: $-OH^{\cdot} + R \rightarrow -HO + R^{\cdot}$
Interfacial oxidation of R by hole	[5]: $R + h^+ \rightarrow R^{\cdot}$
Electron injection at conduction band by organic radical (current doubling)	[6]: $R^{\cdot} \rightarrow R^+ + e^-$
Interfacial reduction of organic radical	[7]: $R^{\cdot} + e^- \rightarrow R$

which can be linked to the photocurrent and reaction rate relationship. This concept is important to distinguish between cases in which many electrons or holes are needed for partial degradation of the substrate molecule. The kinetics of the chemical steps involved in the oxidation of methanol, 2-propanol, tert-butyl alcohol and salicylate on TiO_2 obtained from this model is strongly supported by the photocurrent *vs.* time results obtained using the potential step perturbation method (Mandelbaum et al., 1999a,b). However, the differential equations were solved numerically, although having an analytical solution, even for limiting conditions, would allow relating chemical variables to physical phenomena. In a second work by the same group, Calvo and collaborators (Calvo et al., 2001) studied the photo-oxidation of organic mixtures on biased TiO_2 electrode and concluded that schemes of competitive kinetics describe only cases in which one of the components is weakly adsorbed or not adsorbed on the electrode surface, whereas for two solutes with high affinity for the surface, cooperative effects occur. The latter depend on the pre-adsorption conditions and the surface states, determined by the interaction of the organic compounds with TiO_2. Therefore, including in the kinetic description the complex surface dynamics of the semiconductor is important for the understanding of the phenomenon and to predict its chemical behavior. The application of these chemical kinetic concepts represents a milestone to continue the developments and to include new aspects related with the phenomenology of the surface chemistry involved.

Following these ideas, Carvajal and collaborators (Carvajal et al., 2016) used such formalism (Calvo et al., 2001; Mandelbaum et al., 1999b) to portray the electrochemically assisted photocatalysis for representative organic compound–photoelectrode interactions. The mechanistic implications of a simple kinetic model with the steady state approach proposed by Ollis (2005) and the interplay between the electrochemical steps with the adsorbed states, both in non-equilibrium, have been thus considered to obtain the reaction rate under photostationary conditions, with the photoelectrochemical pathway given in Table 4.

In the scheme described in Table 4, reaction [1] represents the formation of charge carriers; reaction [2] the adsorption/desorption of water on the surface of the semiconductor; reactions [3]–[6] are the realistic mechanism of oxygen evolution by water oxidation on TiO_2 (Fujishima et al., 2008; Praet et al., 1983; Dutoit et al., 1978); reaction [7] is the process of adsorption/desorption of the organic compound at the photoanode taking into account dynamic displacement of water molecules by the organic compound; and reaction [8] represents the oxidation

of the organic compound R to an oxidized compound P after transferring *n* electrons.

After solving the differential equations using the steady-state approximation, an expression for the hydroxyl radical coverage and for the rate law has been obtained,

$$\theta_{OH\bullet} = \frac{\left[(k_8\theta_R)^2 + 16k_1k_4\right]^{\frac{1}{2}} - k_8\theta_R}{8k_4} \tag{18}$$

$$\frac{I_{ph}}{FA} = 2k_1 + \frac{nk_8\theta_R}{8k_4}\left\{\left[(k_8\theta_R)^2 + 16k_1k_4\right]^{\frac{1}{2}} - k_8\theta_R\right\} \tag{19}$$

The last equation links the photocurrent with the coverage of adsorbed organic compound on the semiconductor surface. For instance, at limitingly low coverages of the organic compound, the photocurrent tends to $2k_1FA$, corresponding to the current generated by the oxygen evolution from water splitting reaction. In such condition, the photocurrent is proportional to the charge carriers generated. Therefore, this model also offers the link between the generated photocurrent and the illumination intensity with which the system is stimulated.

On the other hand, Eq. (19) indicates that as the coverage of the organic compound varies from 0 to 1, the photocurrent is affected by the values of the rate constants: k_1, k_4 and k_8. Therefore, their relative dynamics allows explaining the increase and/or decrease observed in the photocurrent according to the solute coverage. These effects depend on the type of organic compound studied. Simple inspection of the rate law (19) thus highlights the behavior of an organic compound with representative adsorption. Finally, being explicit with regard to the coverage of the organic compound on the semiconductor surface, the model opens up the possibility of evaluating and/or predicting effects related to the surface phenomena determining the coverage of the organic compound on the surface of the electrode.

4. Wastewater treatment with concomitant electricity or H$_2$ production and the role of chemical kinetics

4.1. Photocatalytic fuel cells

As discussed above, photocatalysis allows the light-induced combustion reaction of organic matter, and if carried out in a separate compartment, then the final process yields the corresponding electron flux as an added value. To achieve this, the oxygen reduction reaction must be coupled in a cell using an appropriate electrocatalytic material. The determining factors are

Table 4

Reactions involved in photoelectrochemistry according to Carvajal and co-workers (Carvajal et al., 2016) interpretation.

Description	Reaction
Generation of charge carriers	[1]: $TiO_2[] + h\nu \rightarrow TiO_2[e^- + h^+]$
Fast water equilibrium at the surface	[2]: $TiO_2[] + H_2O \rightarrow TiO_2[H_2O]$
Radical formation by hole trapping (OER[a] step 1)	[3]: $TiO_2[H_2O] + h^+ \rightarrow TiO_2[OH^\cdot] + H^+ + e^-$
Peroxide formation (OER[a] step 2)	[4]: $2TiO_2[OH^\cdot] \rightarrow TiO_2[H_2O_2]$
Hydroperoxide radical formation (OER[a] step 3)	[5]: $TiO_2[OH^\cdot] + TiO_2[H_2O_2] \rightarrow TiO_2[OOH^\cdot] + TiO_2[H_2O]$
Oxygen evolution (OER[a] step 4)	[6]: $TiO_2[OH^\cdot] + TiO_2[OOH^\cdot] \rightarrow O_2 + TiO_2[H_2O]$
Dynamic displacement of water molecules by organic compound adsorption	[7]: $TiO_2[mH_2O] + R \rightarrow TiO_2[R] + mH_2O$
Interfacial oxygen transfer reaction	[8]: $TiO_2[OH^\cdot] + TiO_2[R] \rightarrow TiO_2[P] + ne^- + nH^+$

[a]OER: oxygen evolution reaction.

the control of electric loses during operation of the cell as well as selection of appropriate electrodes (Lianos, 2017).

From the pioneering work of Kaneko and collaborators (Kaneko et al., 2006), the idea of using biomass products and water-soluble waste for the photoelectrochemical purification of wastes with electricity production was highlighted. Performance and efficiency during the treatment of water effluents rich in glucose, urea, methanol, aromatic compounds, dyes, etc, have been reported (Papagiannis et al., 2018; Garcia-Segura and Brillas, 2017; Lianos, 2017; Raptis et al., 2017; Sfaelou and Lianos, 2016; Tantis et al., 2016; Michal et al., 2014; Kaneko and Ueno, 2013; Kaneko et al., 2006). Lianos group (Papagiannis et al., 2018; Lianos, 2017; Michal et al., 2014; Antoniadou and Lianos, 2010) reviewed the recent trends in photoelectrochemical conversion of solar energy to electricity and hydrogen. They focused on Photo Fuel Cells and water splitting systems and present both the operational principles and the design of functional devices. Special attention on the construction of photoanodes, photocathodes and tandem cells were commented. Other works comments on the electrolyte composition, current doubling effect and operation modes (Garcia-Segura and Brillas, 2017; Lianos, 2017; Sfaelou and Lianos, 2016; Kalamaras and Lianos, 2015).

Liu and collaborators (Liu et al., 2011), reported a visible light photocatalytic fuel cell system based on TiO_2 nanotubes. Cu_2O and CdS were combined with the photoanode. The generation of electrical currents from the photocatalytic oxidation of various wastewaters with oxygen reduction reaction at the secondary electrode, was evaluated. The effluent composition considered the presence of aromatic compounds, pharmaceutical and personal care products, azo dyes and endocrine disrupting compounds. Antoniadou and coworkers (Antoniadou et al., 2011), determined that small band gap quantum dot sensitizers like CdSe and PbS were not functional in Photo Fuel Cells, owing to the limited oxidative power of their valence-band holes. However, in alkaline electrolyte and using ethanol as fuel, only medium energy gap semiconducting quantum dots proved functional, such as CdS, mixtures of CdS with ZnS, and ZnSe. The best photoanode was $ZnS/CdSe/CdS/TiO_2$ deposited on fluorine tin oxide (FTO) combining panchromatic sensitization with representative efficiency in light harvesting and charge separation. Previous studies by the Gerischer and Morrison groups showed that photocorrosion of (II–VI) semiconductors (e.g. CdS, CdSe) is an unavoidable problem of these systems (Frese et al., 1980; Gerischer, 1977) limiting the scope of their application (Nandjou and Haussener, 2019; Cardon et al., 1980). On other hand, recent research studies on the development of photoelectrodes capable of operating in microbial fuel cells have been carried out, involving the emergence of new biophotoelectrochemical systems for the generation of energy (Antolini, 2019).

4.2. H₂ production

It has been shown that if a good electrocatalyst for the hydrogen evolution reaction is chosen as a cathode, then it is possible to generate H_2 as byproduct of the photoelectrochemical process. Thermodynamically, H_2 production is possible when the photoanode has a more negative conduction band potential than the redox potential required to form H_2 from water. In general, the reaction rates of photocatalytic processes on numerous semiconducting materials are limited by the kinetics of the charge transfer process to a suitable redox species. Therefore, modifications of the electrodes with co-catalysts, such as Pt, Rh, Ru, Re and its alloys, have been used to promote H_2 evolution (Chen et al., 2017; Serpone et al., 2016; Conway and Jerkiewicz, 2002).

Today, several efforts are being made to obtain new materials based on abundant earth for the efficient generation of hydrogen (Yu et al., 2019). These materials could be considered as functional co-catalysts for heterogeneous photocatalysis with concomitant H_2 production. In fact, they perform as more efficient and low cost materials for the reduction of protons (Yu et al., 2019; Callejas et al., 2016). Spanu and co-workers (Spanu et al., 2018), introduced an approach to fabricate an efficient noble metal-free photocatalytic platform for H_2 evolution based on TiO_2 nanotube arrays. By dewetting NiCu bilayers into alloyed NiCu co-catalytic nanoparticles on the nanostructure titania surface, they found improvements in H_2 production when the metals were in equimolar proportion. The new photoanode allowed reaching H_2 generation rates comparable to those delivered by conventional modification of TiO_2 with noble-metals such as Pt. Antoniadou and coworkers (Antoniadou et al., 2011), performed photoelectrochemical water splitting using a Pt-free device. The photoanode was made of nanocrystalline titania on FTO sensitized by quantum dots. Combined ZnS/CdSe/CdS quantum dots were by far more effective for hydrogen production than single-component CdS sensitizer. As noted above, photoactive materials based on (II–VI) semiconductors undergo photodecomposition (Frese et al., 1980; Gerischer, 1977). In fact, their dissolution potential is lower than that required for the oxygen evolution reaction. Therefore, these systems experience photocorrosion. A more recent study reported by Fermín and coworkers (Fermín et al., 1997) reveals that the kinetics of photodissolution of CdS respond to optical and electrical perturbations in the photocurrent onset region. It was confirmed that the mechanism can be described in terms of the capturing a first hole by an active site, generating an intermediate that can capture a second hole to complete the dissolution or recombine with an electron from the conduction band. It was shown that the modification of the surface as a result of the photocorrosion has clear effects on the kinetics of solar energy conversion. In addition, an experimental methodology based on intensity modulated photocurrent spectroscopy and photoelectrochemical impedance spectroscopy was reported to evaluate the photocorrosion behavior of photoelectrodes, with a theoretical development rigorously supporting the kinetic studies carried out. These approaches are therefore highly recommended to standardize the evaluation of new functional materials.

An interesting strategy for splitting water is to employ a two-step mechanism, similar to that in natural photosynthesis by

green plants. Bard (1979, 1982) introduced the idea of using two different photocatalysts, one responsible for H_2 evolution and the other for O_2 evolution, in a strategy known as the Z-scheme (Sun et al., 2018; Chen et al., 2017; Bard, 1979; Tan et al., 2017). A suitable redox couple, typically known as electron mediator, is required to complete the charge balance between the two photocatalysts. The use of an appropriate membrane prevents undesirable backward reactions, due to the reversible redox couple, on the photocatalysts. Recently, a solid-state electron mediator, such as graphene, has been used to promote direct electron transfer between photocatalyst particles (Minella et al., 2018; Tan et al., 2017; Ismail and Bahnemann, 2014). In relation to the use of this latter strategy, it is worthwhile noting that the challenge remains in the synthesis of new functional composite materials (Wang et al., 2019; Hisatomi and Domen, 2019, 2017; Wang et al., 2019; Chen et al., 2017).

According to recent research, solid solutions of GaN and ZnO: $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ (Chen et al., 2017; Kubota and Domen, 2013), $LaTaON_2$ and $LaMg_{2/3}Ta_{1/3}O_3$: $(LaMg_xTa_{1-x}O_{1+3x}N_{2-3x})$ (Chen et al., 2017) and $La_5Ti_2AgS_5O_7$-based powder suspensions (Song et al., 2019), are functional materials for visible light-driven photocatalysts with potential application in the overall water splitting reaction. Currently, integrated monolithic tandem devices based on (III–V)-semiconductors are the only systems reaching solar-to-hydrogen efficiencies above 14%. May and collaborators (May et al., 2015) argue that devices based on (III–V)-semiconductors have adjustable optoelectronic properties allowing high control of doping levels with the formation of tunnel junctions. In addition, they explored an inexpensive and scalable in situ surface functionalization routine developed for a (III–V) photovoltaic tandem absorber, which promotes the direct solar water splitting, yielding a solar energy efficiency of 14%. The photocurrents measured approached the predicted theoretical limit, this according to the optical properties of the tandem absorber material. Finally, Young and coworkers (Young et al., 2017) used inverted metamorphic multi-junction device architecture, yielding over 16% for the solar-to-hydrogen efficiency using GaInP/GaInAs tandem absorbers. The latter represents an improvement of 60% over the classical high-efficiency tandem (III–V) devices.

4.3. The role of chemical kinetics

Chemical kinetic studies need to be applied to the photo-electrochemical detoxification in applied and reliable settings. Operating strategies to incorporate electrocatalytic materials for advanced oxidation of organics into nanostructures and microporous monolithic supports should be established, so as to increase the operative efficiency of the electrochemical reaction and overcome the usually low electroactive surface area, in comparison with the volume of the wastewater needing treatment. However, the reaction rates estimation, or prediction, with the elucidation of the role of the physicochemical parameters describing the chemical interactions during the photocatalytic treatment of organic compounds is essential to meet this challenge.

Fakourian (2019) and Zhang and collaborators (Zhang et al., 2014b), implemented numerical simulations to investigate the detailed potential loss in Photo Fuel Cells. This model is an adaptation of fundamental fuel cell theory (Bockris and Khan, 1993). The effect of the Schottky barrier was accounted for by an estimation of the transfer loss from TiO_2 to FTO, according to the thermionic-emission theory (Ni et al., 2006). The model also uses the Butler–Volmer kinetic theory to consider the activation overpotential of the redox reactions. The authors find that the Ohmic loss contributes to 24% due to the electrical resistance of the semiconductor. It was found that the Schottky barrier height

plays an important role on the performance of the device, with a Schottky barrier of 0.6 eV during typical operation. Using the kinetic models described in the previous section, these emerge as key ideas to develop applied research, since the effects of the microscopic phenomena that govern chemical reactions can be illustrated in relation to the operation of Photo Fuel Cells. Specifically, if Langmuir–Hinshelwood, Turchi–Ollis or other appropriate rate laws are used to describe the photocatalytic reaction at the photoanode instead of the Butler–Volmer model, then the effect of surface phenomena on current density *vs.* voltage and power density *vs.* voltage curves can be explored.

Other issues that need consideration are related to classical semiconductor electrochemistry:

(A) The flux of minority carriers to the surface is not explicitly considered in the kinetic analyses described. The Gärtner theory (Gärtner, 1959) implies fundamental concepts that link the flux of minority carriers to the electrode potential, doping density, penetration depth of the light and carrier diffusion length in the space charge layer of the semiconductor. The main ideas are: (*i*) the carrier generation rate depends on the photon flux and the absorption coefficient of the solid material, (*ii*) all the carriers generated within the depletion layer reach the surface and (*iii*) there are no interfacial recombination losses. Then, the Gärtner equation represents the maximum photocurrent at a given electrode potential (Sato, 1998; Reichman, 1980).

(B) For low and moderately doped semiconductors, the differential capacitance is controlled by the charge carriers accumulated at the space charge layer developed into the energy profile of the solid material. Thereafter, band edge level pinning conditions ensue, i.e. changes in the applied potential affect the space charge layer and the potential drop across the Helmholtz and diffuse layers remains constant. Additionally, the Fermi level pinning condition is also possible, especially for surface state densities larger than 1% of the surface atom density. Then, changes in the applied potential develop into the Helmholtz layer. Noteworthy, under band-edge pinning conditions, changes in the electrode potential mainly develop in the space charge layer of the semiconductor, and the position of the conduction and valence band edges at the electrode surface remain independent of the applied potential. Under these circumstances, the Butler–Volmer expression Eq. (16) cannot be applied, as the activation energy for energy transfer is potential independent. The fact that oxidative photocurrent increases with increasing electrode potential does not imply that interfacial charge transfer rate increases. This is typically the result of a decrease in the recombination kinetics (Memming, 2015; Sato, 1998; Peter et al., 1997).

(C) In nanostructured electrodes the picture is certainly more complex, involving changes in population of trap states and recombination kinetics with the electrode potential (Bisquert, 2017). Additionally, transport of majority carriers also requires attention. The Fermín group (Zhang et al., 2014a; Bunzli et al., 2014) investigated this issue in the case of TiO_2 nanotubes and ZnO nanocrystalline rods in which surface recombination was suppressed by a strong hole scavenger. In their works, the population of deep trap states in nanostructured electrodes and the dynamic photocurrent responses under supra band gap illumination were investigated. Dynamic photocurrent experiments showed that the characteristic rise time of the photocurrent increases as the potential is increased above the onset region for charging deep trap states. The occupancy of these trap states under stationary conditions was a fraction

of the density of states estimated from voltammetric responses. In the presence of a strong hole scavenger (SO_3^{2-}), photocurrent *vs.* potential curves displayed a maximum in the range in which the population of trap states depends on the applied potential. At sufficiently positive overpotential fully depleted trap states were reached, then the photocurrent amplitude strongly decreased with increasing frequency of light perturbation. These ideas are particularly relevant when considering the systematic analysis of photocurrent transients observed with nanostructured electrodes.

These arguments must be included to incorporate the kinetic effects rationally under the consideration of the following fundamentals variables: the nature of the solid state material, the illumination characteristics, and surface phenomena such as adsorption, interaction and electron transfer, as well as the effects of photophysical phenomena such as recombination kinetics in nanostructured materials.

Appropriate kinetic models based upon general concepts applicable to the different situations should be developed and tested. The main kinetic models developed were used in model systems, generally based on TiO_2 photocatalyst. It is necessary to explore, in a fundamental way, the kinetic effect of the nature of the photocatalyst (Peter, 2019; Ollis, 2018; Serpone et al., 2016; Liu et al., 2014; Hisatomi et al., 2012). Additional kinetic studies with different photoelectrodes materials are needed in order to develop structure–function relationships for the oxidation of important types of contaminants. Thus future experimental work with environmentally relevant organic compounds should seek mechanistic information that can be complemented by *in situ* stationary and time-resolved spectroelectrochemical techniques (León and Mozo, 2018; Cen et al., 2017), techniques based on the concept of impedance (Bisquert et al., 2016; Peter et al., 1997), electrochemical hydrodynamics (Lee et al., 2018; Méndez et al., 2015; Vargas et al., 2012; Boxall, 1999; Kesselman et al., 1994) and kinetic isotope effect studies (Núñez et al., 2019; Belhadj et al., 2015). One of the main challenges is to decouple the kinetic phenomena and to quantify the rate constants. In addition, the use of quantum calculations to estimate their magnitudes is a challenge that has been addressed by different research groups (Cinar, 2017; Minakata and Crittenden, 2011; Kiliç and Çinar, 2009; Minakata et al., 2009), and such studies will lead to better understanding of the mechanisms responsible for compound transformations, thus allowing for better designs of photoelectrochemical reactors, defining as well the appropriate operating conditions.

5. Final considerations

The kinetics of photo(electro)chemical reactions were first analyzed in terms of models fitting the mathematical form of the Langmuir–Hinshelwood rate law, yielding apparent kinetic parameters containing intrinsic rate constants that remained unresolved. Chemical kinetics in photocatalysis is still an open problem, in which considerations based on systems far away from equilibrium as well as the systematic validation of mechanistic hypotheses are necessary to understand and represent the observed experimental behavior. Elucidation of mechanisms requires comparison of different systems carried out in terms of a common kinetic formalism, and in this sense the models based on the Turchi and Ollis ideas are representative.

In general, the photoelectrochemical processes on diverse electrode materials yield efficient pathways for the treatment of wastewaters, with the possibility also of operating them as photocatalytic fuel cells or using a photosynthetic scheme for H_2 production. Moreover, the importance of measuring reaction rates to determine and compare the physicochemical parameters describing the chemical interactions during photoelectrolysis has been underlined, in order to apply this understanding to the design, operation and control of reactive systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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