

# Charge transfer catalysis at solid/liquid interface in photoelectrochemical processes: Enhancement of polycrystalline film electrode stability and performance

Hikmat S. Hilal<sup>a,\*</sup>, Ahed Zyoud<sup>a</sup>, Mohammad H.S. Hilal<sup>a</sup>, Heba Bsharat<sup>a</sup>, Heba Nassar<sup>a</sup>, Ali Cheknan<sup>b</sup>

<sup>a</sup> SSERL, Department of Chemistry, College of Sciences, An-Najah National University, Nablus, Palestine

<sup>b</sup> Laboratoire des semiconducteurs et matériaux fonctionnels, Université Amar Telidji de Laghouat, Bd des Martyrs BP37G, Laghouat 03000, Algeria

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## ABSTRACT

Photovoltaics (PVs) show high conversion efficiency in renewable energy. However, PV systems demand advanced preparations and relatively large amounts of starting materials. Photoelectrochemical (PEC) systems, with monolithic semiconductor (SC) electrode/Redox couple interface, emerged, but still demand special preparation conditions and relatively large amounts of starting materials. Polycrystalline film electrodes, are studied as replacement for monolithic SC electrodes, both theoretically and experimentally. Examples are dye-sensitized solar cells (DSSCs) and metal chalcogenides. With narrow-to-medium band gaps, metal chalcogenides are suitable for the abundant visible solar light. However, polycrystalline film electrodes suffer major shortcomings. Pristine films show low conversion efficiency. Being polycrystalline, they have low carrier mobility. They are also unstable to photo-corrosion, due to charge build-up in the space charge layer (SCL). Enhancement of polycrystalline film electrode PEC performance and stability was reported using different methods. Among those, *charge transfer catalysis at the film electrode surface*, is focused here. The modification involves attaching electroactive species to the electrode surface. Ability of electroactive species to behave as charge transfer catalysts at the solid/liquid interface is discussed. By such behavior, the catalysts speed up charge transfer and consequently increase photocurrent. Moreover, charge build-up in the SCL is prevented by quick charge transfer, which protects the electrode surface from photo-corrosion. Ability of charged electroactive species to shift flat band edge position, with its consequences, is also described. Recommended features of an effective catalyst species for PEC systems are described together with recommendations for more future research in the field.

## 1. Introduction

Based on human increased demand for future sustainable energy sources, solar energy is becoming a must choice. Solar energy is renewable in nature with friendly effects on environment. Among the widely spread solar energy processes are the p-n junction photovoltaic (PV) systems which have now reached high conversion efficiency values of more than 31% (Bhattacharya and John, 2019). However, PV systems, still have shortcomings in terms of advanced preparation methods, need for ultra-high vacuum and relatively high amounts of starting materials.

Photoelectrochemical (PEC) processes, where a monolithic semiconductor (SC) electrode is brought into contact with a redox couple, normally in liquid phase, emerged. In addition to electricity production

(Sato, 1998; Finklea, 1988), different areas were targeted by PEC processes including water splitting and water purification (Murphy et al., 2006). Due to different reasons, PEC processes suffer low conversion efficiency and electrode low stability to photo-corrosion. Such shortcomings which were reported in earlier literature (Skompska, 2010) still exist even in recent reports (Zhang et al., 2017). Finding methods to enhance efficiency and stability of PEC processes is imperative (Yang et al., 2019). Recently Park et al (Park et al., 2019) reported that still relatively low PEC efficiency (less than 10%) is exhibited by PEC systems except those using electrodes prepared by advanced methods. Attempts to enhance monolithic electrode stability and conversion efficiency were made for soundly long time. Electrochemical etching for Si monolithic electrodes was reported for monolithic electrodes (Mao et al., 1995). Coating monolithic electrode surfaces with conducting

\* Corresponding author.

E-mail address: [hshilal@najah.edu](mailto:hshilal@najah.edu) (H.S. Hilal).

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polymer films has also been examined (Glenis and Frank, 1989; Frank and Glenis, 1991; Frank et al., 1989; Kumar et al., 1993). Monolithic electrode modification with other electroactive species was studied (Hilal and Turner, 2006; Hilal et al., 2002, 2004, 2003). The reports showed that conversion efficiency, stability or both, can be enhanced by careful modification. However, monolithic SC electrodes have the other shortcoming of being relatively thick (~0.5 mm) which demands relatively high starting material amounts. Advanced preparation methods are also needed for the monolithic SC electrodes (Park et al., 2019).

Polycrystalline film electrodes have emerged as possible future alternatives. Such films can be prepared by simple chemical or electrochemical methods with no need for advanced techniques. Such films involve nano-size crystallites (Sendy, 2016). The crystallites may occur inside larger agglomerates in the range 50–200 nm in diameter. Typically, the film electrode thickness is in the range 100–1000 nm. This means that the film demands far fewer starting materials than monolithic electrodes. In principle, the film can be employed as replacement for monolithic SC working electrode in PEC processes (Sendy, 2016).

Film electrodes prepared from different materials were widely studied. Wide-band gap materials, such as TiO<sub>2</sub>, ZnO, SnO and others are known (Nazeeruddin et al., 1997; Studenikin et al., 1998; Guo et al., 2010). Such materials need UV light to function. In order to activate such materials in the visible solar light, which is a major component in the reaching in solar radiations, sensitizers are often described such as Ru based dyes (Wang et al., 2005); CdS quantum dots (Samadpour et al., 2012) and natural dyes (Hao et al., 2006). Dye sensitized solar cells (DSSCs) are widely studied for light conversion into electricity, but not without shortcomings (Husain et al., 2018). One main concern is their stability under working conditions (Carella et al., 2018; George et al., 2016; Iftikhar et al., 2019; Listorti et al., 2011). In a recent review Sharma et al. reported a maximum conversion efficiency of 12% for DSSCs (Sharma et al., 2018).

Narrow-to-medium band gap semiconducting materials, most notably metal chalcogenides of the type (MX: M = Cu, Cd, Pb or Zn; X = S, Se or Te), are also heavily studied in PEC processes (Pawar et al., 2011; Ho, 2016; Li and Wu, 2015). This is due to the suitability of the band gap values of such materials which demand the abundant visible solar light, without the need for sensitizers. However, metal chalcogenide film electrodes are not trouble free. Due to their polycrystalline nature, they suffer low charge carrier mobility, which adds to the circuit internal resistance and consequently lowers the photocurrent (Emin et al., 2011; Kim et al., 2015). Moreover, the metal chalcogenide film electrodes are not stable to photo-corrosion under PEC conditions (Kim et al., 2015). Charge transfer at the electrode/redox couple is another difficulty in metal chalcogenide film electrodes. Low conversion efficiency values are known for different types of metal chalcogenide film electrodes (Hilal et al., 2019). Attempts to enhance PEC stability and PEC performance of metal chalcogenide film electrodes were made. Doping the electrode material with different dopants was described to enhance PEC efficiency and stability (Yang et al., 2012; Grecu et al., 2000). Careful annealing of the metal film at suitable temperature was reported (Hilal et al., 2009; Zyoud et al., 2015, 2013). Effect of cooling rate of the annealed film PEC characteristics was also studied (Zyoud et al., 2013). Physical protection of the electrode surface by coating with polymers is known (Frank, 1984). Using multilayers of metal chalcogenides, such as CdSe/CdTe (Quang et al., 2019; Cheng et al., 2012) and others (Li et al., 2019). Coating with salt layers, such as CdTe/CdCl<sub>2</sub>, has been described (Deyneko et al., 2019). The described modification methods have effect on the treated film electrode in one or more ways, leading to PEC and stability enhancement.

Theories and models that explain SC electrode/Redox couple interface phenomena have been in depth reported and reviewed. Catalysis in electrochemical processes, where chemical change occurs at the electrode, has been studied (Rajeshwar, 2007; Bard et al., 1993). Attachment of a catalyst at a SC electrode to facilitate charge transfer was reported.

A catalyst is commonly defined as a substance that increases the reaction rate to reach equilibrium without being consumed in the reaction. As such the catalyst does not affect the thermodynamics (equilibrium constant K, enthalpy change  $\Delta H$ , entropy change  $\Delta S$  or free energy  $\Delta G$ ) of the reaction, but provides new routes with lower activation energy ( $E_{act}$ ) values. In this review, where the focus is on film electrode/liquid junctions in PEC systems, *charge transfer catalyst is a substance that speeds up the charge transfer process between the electrode and the solution Redox couple*. In case of n-type SC film working electrodes, the charge is meant to be the minority carrier (hole). On the counter electrode, the charge is the electron.

Literature described different types of conventional chemical catalysts, which speed up various chemical reactions, such as hydrogenation (Widegren et al., 2017), oxygenation (Lewera et al., 2019; Chen and Wu, 2019); oligomerization (Pires et al., 2019), cracking (Tamele, 1950) and others. Homogeneous and heterogeneous catalysts are well reported. In electrochemical processes, where chemical changes involve electric power generation or consumption, catalysts speed up charge transfer between the electrodes (conventionally solid phase) and liquid phase reactants. Examples of widely studied electrocatalysts are copper nano-particles (Yu et al., 2019). In all non-regenerative processes net electrochemical changes occur (Jia et al., 2014).

In PEC water splitting, the semiconductor electrode is modified with charge transfer catalysts to facilitate electrochemical oxidation and reduction processes (Bertoluzzi et al., 2016). Photocatalysts have been widely described in transfer of charges to produce hydrogen and oxygen from water (Kudo and Miseki, 2009; Zou et al., nature, 2001). Pt and Ru have been described as charge transfer catalysts for water splitting processes (Liu et al., 2004; Yamasita et al., 2004; Miseki et al., 2017; Oh et al., 2019). While these photocatalysts, and charge transfer catalysts, are heavily encountered in different types of PEC processes, this critical review is more concerned with the roles of charge transfer catalysts in regenerative PEC processes. Both DSSC and metal chalcogenide PEC processes are included here. In DSSCs, literature describes using charge transfer catalysis at both the working electrode (TiO<sub>2</sub>/Dye) and the counter electrode, *vide infra*. In metal chalcogenide film electrodes, research is still mainly focused on the working electrode itself (metal chalcogenide film electrode). In this article, catalytic processes at either working electrode and counter electrode are considered.

This review will answer a number of questions: Can a suitable charge transfer catalyst (at either or both working electrode and counter electrode) affect a PEC cell performance and stability? How? Does the catalyst enhance photo-current and short-circuit current density ( $J_{sc}$ )? What is the mode of action of the charge transfer catalyst? How can the catalyst protect the electrode surface from photo-corrosion? Does the catalyst possibly affect SC film electrode band edge positions? How can the catalyst affect electrode surface states and recombination? All such questions will be answered in this review. A qualitative model, based on energetics at the electrode/Redox couple interface is described for both the working electrode and counter electrode, is presented here, from earlier literature, for the first time. To achieve goals of this review, this Introductory Section 1 is presented. Section 1 describes general developments in the areas of PEC, and how film electrodes have emerged, together with their short comings and attempts (specifically charge transfer catalysis) to solve them out. Defining charge transfer catalysis is also shown in Section 1. Section 2 describes basic models known to explain photocurrent production in conventional photovoltaic and PEC systems. Emergence of thin film electrodes, including metal chalcogenide materials, is described. Section 2 cites literature findings that describe how charge transfer catalysts may enhance PEC performance and stability of different types of electrodes, including metal chalcogenide systems. Models and discussions are presented in Section 3. Section 4 summarizes conclusions and recommendations on what needs to be done in the subject area of this review.

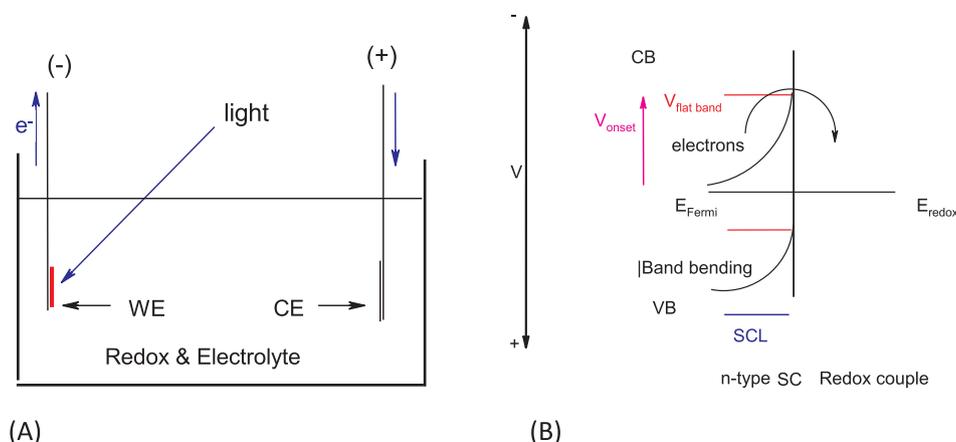


Fig. 1. Schematic PEC systems showing (A) a PEC solar cell involving a monolithic SC working electrode (WE) with another counter electrode (CE) dipped inside a Redox couple solution and (B) Band bending and energetics at SC electrode/Redox couple interface.

## 2. Basics of PEC processes

Light-to-electricity conversion processes, in both PV and PEC systems, are understood in terms of band theory formalism. Both systems essentially follow same logic in the sense of having p-n junction. In PVs, a p-n junction occurs when an n-type semiconductor is brought in contact with a p-type semiconductor. A homojunction occurs if both sides are made of same material, while a heterojunction occurs if two different materials are used. Once formed, band bending occurs, where a space charge layer (SCL) is formed and a potential drop is created.

Once excited with a photon of energy higher than the band gap ( $h\nu \geq E_{bg}$ ), an electron moves to conduction band (CB) leaving a hole in the valence band (VB) (Green, 2002). Charge separation and photocurrent occur.

In PEC systems (Babu et al., 1994), if n-type semiconductor electrode is brought into contact with a solution Redox couple (considered as p-type system), band bending occurs just as in PV systems. This is summarized in Fig. 1. In case of n-type SC electrode, CB electrons move to the Redox couple. Less number of electrons should thus occupy the CB. Fermi level ( $E_F$ ) is therefore lowered, as it is related to electron density occupancy in the CB (Atanacio et al., 2018). The  $E_F$  is lowered to reach equilibrium with the solution  $E_{Redox}$ . If p-type semiconductor electrode is used, similar behavior occurs where the Redox couple behaves as n-type (Kohl and Bard, 1979).  $E_F$  change with occupancy in the CB (n-type) and VB (p-type) SC electrodes is described in Eqs. (1) and (2) (Atanacio et al., 2018):

$$E_F = Constant + kT \ln\left(\frac{n}{N_n}\right) \quad (1)$$

$$E_F = Constant - kT \ln\left(\frac{p}{N_p}\right) \quad (2)$$

where  $k$  is Boltzmann's constant,  $T$  is Kelvin temperature,  $n$  is effective electronic concentration in the CB,  $N_n$  is n-type dopant atom concentration, and  $p$  is effective hole concentration in the VB and  $N_p$  is p-type dopant atom concentration.

Band bending is necessary for photocurrent to occur. Even in the absence of any applied potential, once a photon with enough energy strikes the SC electrode, photocurrent may occur, similar to PV systems. A PEC system with n-type SC electrode is described in Fig. 1, while p-type SC systems can also be found in literature (Finklea, 1988). The incident photon excites an electron from the valence band (VB) to the conduction band (CB), leaving a positive hole inside the VB. The electron then moves toward the positive potential and goes through the metal wire to reach the counter electrode to react with solution Oxidized species. On the other hand, the hole moves to the electrode/Redox interface and oxidizes the solution Reduced species (Alpuche-

Aviles and Wu, 2009). As such, there is no net chemical change in the PEC system, and the photon energy is converted into electricity. Such a cell is so-called Regenerative PEC cell.

Just like PV systems, plots of photocurrent density ( $J$ ) vs. applied potential ( $V$ ) can be measured. PEC characteristics, namely open circuit potential ( $V_{OC}$ ), short circuit photo current density ( $J_{SC}$ ), Fill factor ( $FF$ ) and conversion efficiency ( $\eta$ ), can easily be extracted from the measured  $J$ - $V$  plots. PEC performance can be determined from values of PEC characteristics (Butler and Ginley, 1980). The higher the PEC values, the higher performance will the cell have. Therefore, increasing values of  $V_{OC}$ ,  $FF$  and  $J_{SC}$  should increase the  $\eta$  value, as described by the relation in Equation (3):

$$\eta = \frac{J_{SC} \times V_{OC} \times FF}{incident\ power} \times 100\% \quad (3)$$

In PEC research, either for monolithic or polycrystalline film SC electrodes, these characteristics are main parameters to enhance. The  $V_{OC}$  value is a characteristic for the semiconductor electrode and the Redox types (Hamann and Ondersma, 2011). The film electrode type, surface morphology, crystallite interconnectivity, potential difference in SCL, and other parameters, all affect the  $V_{OC}$  value. Similarly, the  $FF$  value can be increased by enhancing electrode parameters. Value of  $J_{SC}$  can be enhanced by lowering circuit resistance. This can be achieved by a number of methods. Enhancing carrier mobility can be achieved by interconnecting particles through sintering, as described earlier for polycrystalline film electrodes (Albu et al., 2010; Mazzolini et al., 2015). Lowering resistance at semiconductor/metal back contact, in the Ohmic contact, increases photocurrent values, as reported earlier for both monolithic and polycrystalline electrodes (Burgelman et al., 2000; Rhoderick, 1982).

In PEC processes, charge (hole) transfer rate between the electrode and the Redox couple, at the electrode/liquid interface, also affects value of photocurrent density. As electrons are excited by photons, to the CB, holes remain inside the VB. Due to the SCL nature, the holes move upward and accumulate in the VB within the SCL. If the holes move forward towards the Redox couple, with no hindrance, assuming perfect conduction elsewhere as mentioned above, then high photocurrent density will be observed (Alpuche-Aviles and Wu, 2009; Finklea, 1983). On the other hand, if holes accumulate in the SCL layer, and do not move forward to the Redox couple, photocurrent density will then be lowered (Hiramoto et al., 1994). Therefore, high resistance at the solid/liquid junction lowers PEC cell performance in two ways. Firstly, by lowering photocurrent density and consequently the conversion efficiency. Secondly, the accumulated holes may oxidize the semiconductor electrode surface, in a process so-called photo-corrosion. Photo-corrosion may involve the electrode material itself (Wu and Lee, 2018) or the sensitizing dye itself (Zyoud et al., 2011). In fact photo-

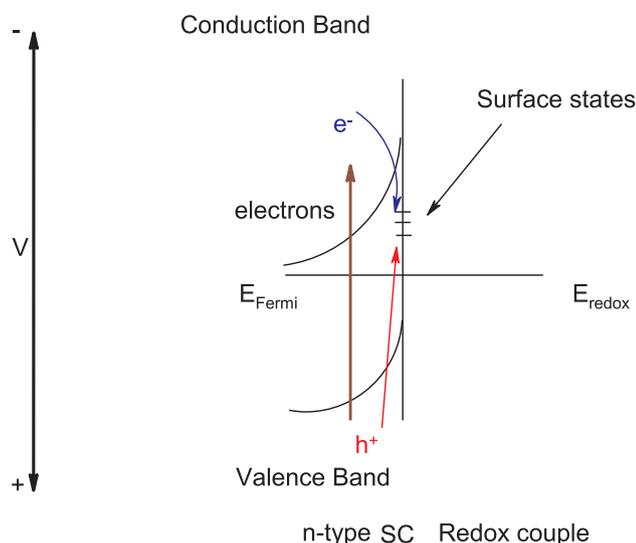


Fig. 2. Surface state formalism and electron-hole recombination in PEC processes.

corrosion is considered as a process that competes with charge transfer between electrode and Redox couple (Bockris et al., 1982). Such a process is completely unwanted and should be avoided in PEC research and in technological applications. Photo-corrosion, and photocurrent density lowering, are also assisted by the so-called *surface states*. Surface states may exist at the electrode surface within the forbidden energy band gap, between VB and CB, as described in Fig. 2. These states enable electron-hole recombination at the expense of photocurrent density. While surface states may occur by photo-corrosion itself, they may also encourage the photo-corrosion by facilitating bond breaking at the surface (Bockris et al., 1982).

Speeding up the hole transfer between the electrode surface and the Redox couple is therefore expected to avoid hole accumulation in the SCL. This consequently increases PEC photocurrent density and lowers photo-corrosion simultaneously. Different methods were examined to achieve this specific goal. Redox couple type is detrimental in increasing photocurrent density and photo-corrosion prevention (Morandeira et al., 2008; Frese, 1983; Zhang et al., 2019b; Mingyuan et al., 2008). For a given SC electrode, with its band gap edge positions, the Redox couple must have a suitable potential ( $E_{\text{Redox}}$ ) as clarified in Fig. 1. The rate of charge transfer between the SC working electrode and the Redox couple affects photocurrent. Moreover, speedy electron transfer between the counter electrode and the Redox couple also increases photocurrent. Surface passivation is known to prevent electrode photo-corrosion (Huang et al., 2018; Kois et al., 2019). When a SC surface is passivated, the coordinatively unsaturated atoms are inactivated and the dangling bonds are suppressed. The solvent type also affects photo-induced charge transfer (Lee et al., 2012). Photocurrent and conversion efficiency can be increased when using the proper solvent type, as water may not be recommended in many PEC solar cells (Grancini et al., 2017; Sauvage et al., 2011). In some cases ionic liquids are examined due to their special feature as high boiling point solvents (Lei et al., 2017; Shen et al., 2010).

As discussed in Section 1 above, SC polycrystalline film electrodes are emerging as replacement for monolithic SC electrodes due to many reasons. In addition to  $\text{TiO}_2$  based DSSCs, most widely studied film electrodes are those based on metal chalcogenide materials which are easy to manufacture, have suitable band gap values and non-costly, *vide supra*. In case of metal chalcogenide film electrodes, the interconnectivity between different particles may be low, which adds to the shortcomings of such materials in PEC processes. Carrier mobility is therefore compromised which leads to increased circuit resistance and

lower PEC performance. Such difficulties are normally overcome by annealing the film electrode in order to sinter different particles together (Bucherl et al., 2013). With annealing, charges can move more freely between different particles (Liu et al., 2018; Kwon et al., 2013).

All such methods may enhance stability and PEC performance of different semiconductor film electrodes. Another method to achieve these goals is using charge transfer catalysts. Charge transfer catalysts at the solid/liquid interface in film electrode PEC processes is the focal subject of this review and is discussed in detail below. While monolithic SC electrodes can be enhanced by adding charge transfer catalysis, polycrystalline film electrodes, the focal issue here, can also be enhanced by these species.

### 3. Results and discussion

#### 3.1. General

PEC processes are commonly divided into regenerative and non-regenerative processes. As charge transfer catalysis is involved in both processes, they are both discussed below, with more focus on the regenerative process.

#### 3.2. Types of PEC processes involving charge transfer

##### 3.2.1. Charge transfer catalysis in non-regenerative PEC processes:

Non-regenerative processes involve net chemical changes. Moreover, in non-regenerative PEC processes, where light is used to induce net chemical changes, different types of catalysts are studied. For instance, in radiation induced water splitting,  $\text{TiO}_2$ , ZnO, CdS or other nano-particles are widely described as photocatalysts. In such systems, the SC particle absorbs a photon after which an electron is excited from VB to CB. The electron itself reduces water into  $\text{H}_2$ , while the hole oxidizes water to  $\text{O}_2$  (Shi et al., 2018; Zhu et al., 2018). The electron and hole transfer may not occur quickly enough which leads to their recombination and lowers the reaction yield. To speed up the charge transfer at the solid/liquid junction, additional suitable charge transfer catalysts are used, Fig. 3. For electron transfer, platinum (Zhang et al., 2011; Fang et al., 2018), gold (Priebe et al., 2015), palladium (Ye et al., 2012) and other catalysts (Chen et al., 2015) are described to speed up the hydrogen production. To speed up oxygen production (hole transfer) ruthenium-based catalysts are commonly used (Tseng et al., 2013; Forgie et al., 2010; Dou et al., 2018). Zhang et al. (2011), Wang et al. (2009) described how CuSe clusters, deposited onto ZnS working electrode, behave as charge transfer mediators between ZnS working electrode and water molecules, in light-induced splitting of water. In

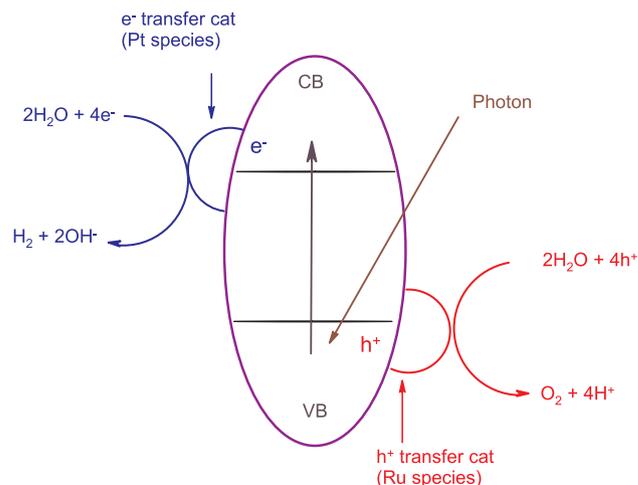


Fig. 3. Schematic for charge transfer catalysis in water splitting by Pt and Ru species.

Zhang's report the ZnS (with band gap 2.94 eV) absorbs at longer than 400 nm, which is in the visible range. The CuSe cluster should thus behave both as a sensitizer (for longer wavelength region) and as a charge transfer catalyst.

In addition to the vast experimental study in the area, simulation and modeling studies are also available. Simulation studies on PEC processes have been made on non-regenerative processes. Dohn *et al.* simulated the dynamics of charge transfer in regenerative molecular photocatalysis, and highlighted the effect of solvent in speeding up the charge transfer process (Dohn *et al.*, 2016). Modeling of charge transfer in single molecules and molecular clusters was theoretically studied, with focus on conductance in the molecules themselves (Li *et al.*, 2019). Simulation study of basic concepts and models at the solid surfaces of heterogeneous and supported catalysts is useful in optimizing their efficiencies and stabilities in thermally driven chemical processes (Gao and Goodman, 2012). The simulation study reveals the importance of charge transfer speed in different processes including enzyme catalyzed reactions (Kulik, 2018) and other biological reactions (Kubař and Elstner, 2013). Non-regenerative PEC processes are naturally a priority area to study by simulation (Akimov *et al.*, 2013). In these processes light-driven water splitting is a notably major subject (Sapp *et al.*, 2016). However, while charge transfer has been studied by simulation, the term charge transfer catalysis in non-regenerative processes has not been specifically described in simulation studies. More work is therefore needed in this specific, vide Section 3.2.2.

All processes described above in this Section are non-regenerative in nature where a net chemical change occurs. Charge transfer catalysts speed up the process be it just a thermal chemical change, an electrochemical change or a light-driven PEC change.

### 3.2.2. Charge transfer in regenerative PEC processes

In regenerative processes, charge transfer catalysts were described. Catalysts, with suitable features, were reported to speed up charge transfer at both the SC working electrode and the counter electrode. Compared to Pt, CoS was proposed as a superior charge transfer catalyst between the film electrode and the  $I^-/I_3^-$  Redox couple in regenerative processes (Wang *et al.*, 2009). Developing charge transfer catalysts at solid/liquid interface is an active research area, especially in DSSCs. Yen *et al.* showed that combined Pt/graphene counter electrodes yield higher photocurrent and lower internal resistance, than separate Pt or graphene in DSSCs (Yen *et al.*, 2011). Polyaniline/carbon nano-fibers showed sound efficiency as counter electrodes in DSSC systems using the  $I^-/I_3^-$  Redox couple, by behaving as effective electrocatalysts (Chen *et al.*, 2011). Replacement of platinum electrocatalyst in DSSCs, with lower cost nitrogen-doped graphene, has been reported. The doped graphene charge transfer catalytic activity, in reducing the  $I_3^-$  species, was attributed to its electroactive sites (Yen *et al.*, 2012). Nanofiber counter electrodes based on Carbon-wrapped  $VO_2(M)$  exhibited high power conversion efficiency of 6.53% under standard testing conditions (Gnanasekar *et al.*, 2019). Other materials have been examined as charge transfer catalysts at the solid/liquid junctions (Yue *et al.*, 2012; Lee *et al.*, 2012; Halme *et al.*, 2006; Yue *et al.*, 2013). All these reports describe the role of charge transfer catalysts at solid/liquid junctions in regenerative PEC processes, where the counter electrodes, not the working semiconductor electrodes, are involved. Ability of a catalyst to speed up charge transfer at counter electrode/Redox couple lowers the circuit resistance and consequently enhances PEC performance.

Carbon nano-tubes (CNTs) were deposited onto counter electrodes in regenerative PEC systems in order to speed up reduction of the  $I_3^-$  ions (Ramamany *et al.*, 2008). Cell efficiency was enhanced by the ability of the CNTs to transfer the electrons at the counter electrode/Redox couple interface. Due to their relatively low cost, electrochemical activity and conductivity, CNTs have also been considered as replacement for Pt in DSSC counter electrodes (Nam *et al.*, 2010; Hwang *et al.*, 2015). Both  $J_{SC}$  and  $V_{OC}$  values were enhanced with CNT electrode. The enhancement was attributed to large surface areas of the CNTs, which

facilitated charge transfer at the counter electrode/Redox couple interface. Based on their special features, CNTs and graphenes have been widely studied in counter electrodes for PEC processes (Yu *et al.*, 2019; Monreal-Bernal *et al.*, 2019; Rosli *et al.*, 2019).

Working electrodes, with CNT materials, in solar cells have also been studied (Chan *et al.*, 2013). Chen *et al.* used CNTs in manufacturing working electrodes themselves in DSSCs and reported relatively low conversion efficiency ( $< 0.5\%$ ) due to low dye molecule uptake in the absence of FTO substrates (Chun *et al.*, 2009).

Using CNTs in DSSCs is a subject for simulation studies. In case of CNT based DSSCs, the CNT thickness in the working electrode had major role in determining cell efficiency as observed from simulation studies (Gacemi *et al.*, 2018). Mehmood *et al.* simulated the CNT/TiO<sub>2</sub> composites in DSSC working electrodes and found that the CNT concentration significantly affects the cell performance (Mehmood *et al.*, 2015). On the other hand, Lin showed that increasing CNT concentrations in CNT/TiO<sub>2</sub> composite working electrodes increases the DSSC cell efficiency (Lin *et al.*, 2011). The literature contradicting results show the need for more optimizing study (both experimentally and theoretically) on inclusion of CNTs in DSSC working electrodes.

The type of the CNT may also have significant role on the DSSC efficiency. Jeon showed that single walled CNTs are advantageous over multi walled CNT in DSSCs, due to their special features of light harvesting and charge transport (Jeon *et al.*, 2019). Using CNT in both working electrodes and counter electrodes was examined. Kyawa *et al.* showed that CNT/TiO<sub>2</sub> composites in the working electrode and CNT/black carbon in the counter electrode yielded enhanced PEC performance (Kyaw *et al.*, 2012). The role of CNT in both cases can be attributed its ability to gain the charge and convey it to the Redox couple. Thus, the CNT undertakes a charge transfer catalytic role in the process. In case of thick CNT layers, increased resistivity counteracts their catalytic roles and lowers the cell performance.

Liquid ionics are new promising materials with many features for various applications. Liquid ionics have been described in different catalytic processes (Zhao *et al.*, 2002; Mawdsley, 2006; Welton, 2004). Solid ionics as solvents for catalytic reactions are known (Welton, 1999). Electrode/liquid ionic interface has also been reported and reviewed in different electrochemical processes (Liu *et al.*, 2010; Hapiot and Lagrost, 2008). Using liquid ionics as solvents for Redox couple systems (such as  $I^-/I_3^-$ ) has been reported (Kawano and Watanabe, 2003; Kawano and Watanabe, 2005; MacFarlane *et al.*, 2010). Liquid ionics have also been described as catalysts and co-catalysts in non-regenerative chemical processes, as ligand sources and as solvents for catalysts and electrocatalysts (Welton, 2004). Modification of heterogeneous catalyst surfaces with liquid ionics has been described (Steinrück *et al.*, 2011). Liquid ionics have been examined in DSSCs as electrolytes (Wang *et al.*, 2003; Zakeeruddin and Grätzel, 2009; Ito *et al.*, 2008). Unfortunately, the ability of liquid ionics to catalyze charge transfer at solid/Redox interface in DSSCs has not been specifically described. This is a worth subject to study, because liquid ionics may be able to gain charges and relaying them, and their ability to behave as Redox couple systems (Doherty, 2018).

Catalysis by conducting polymers was reported (Zhou and Shi, 2016). Conducting polymers have been described in DSSCs. The materials were mostly described as coating for the counter electrode to enhance charge transfer at the solid/Redox junction therein (Saranya *et al.*, 2015; Qin *et al.*, 2010; Murakami and Grätzel, 2008). Coating monolithic n-CdS semiconductor electrode with poly-(3-methylthiophene) stabilized the SC electrode to photo-corrosion in PEC processes. The polymer intervened with charge transfer at the SC electrode/Redox but after some time the polymer itself corroded (Frank *et al.*, 1989). Using polymers to prevent photoanode decomposition has been reviewed (Rabek, 1988; Gratzel, 2012). More study on charge transfer catalytic activity of conducting polymers is therefore needed, both experimentally and theoretically. This is due to the ability of the conducting polymers to undergo redox reactions with the solution Reox

couples, as documented earlier (Maksymiuk and Doblhofer, 1994).

Chemically anchoring metalloporphyrin species to monolithic n-GaAs electrode enhanced conversion efficiency. The positively charged metalloporphyrin species caused lowering in flat band edge positions for the n-GaAs electrode. The band edge lowering increased with increased charge density at the electrode surface. The flat band edge lowering made it possible for the metalloporphyrin to act as charge transfer catalyst at the SC/Redox interface (Hilal and Turner, 2006). With time SC electrode photo-corrosion washed the metalloporphyrin molecules/ions away from the surface. Embedding the metalloporphyrin species inside polysiloxane film matrices, and attaching them to monolithic n-GaAs electrodes enhanced PEC performance and stability (Hilal et al., 2002; Hilal et al., 2004; Hilal et al., 2003). In polycrystalline metal chalcogenide film electrodes, which are known to be unstable under PEC conditions as discussed above, attachment of metalloporphyrin species inside polysiloxane showed added value in enhancing both stability and conversion efficiency of the electrode (Sabri et al., 2014).

As in case of monolithic SC electrodes, metal chalcogenide film electrodes were coated with metalloporphyrin/polymer matrices, which enhanced PEC stability and performance of SC film electrodes such as CuS (Zyoud et al., 2016), CuSe (Zyoud et al., 2015) and CdSe (Sabri et al., 2014). However, in some studies, attaching metalloporphyrin/polymer matrices showed no significant enhancement in metal CdTe and CdSe film PEC performance (Zyoud et al., 2019; Zyoud et al., 2016) where untreated pristine films showed higher performance. Again, as in CNT cases, coating with metalloporphyrin/polymer may increase or lower the SC electrode PEC performance, depending on different factors. The type of the polymer itself and its thickness may affect PEC performance and stability (AbdelHadi, 2016). Metalloporphyrin species concentration also affects PEC performance (Sabri et al., 2014). In some reports, conversion efficiency values as high as 14% and 18% for CuS and CuSe films, respectively, were reported (Zyoud et al., 2015; Zyoud et al., 2016). Therefore, more optimization (simulation and experimental) study on metalloporphyrin/polymer coated metal chalcogenide film electrodes is needed. More experimental study needs to address optimal metalloporphyrin/polymer matrices (in terms of polymer type, ion concentration, matrix thickness) for different SC types in the film electrodes. As no simulation studies have been made in these areas, it is strongly recommended to undertake similar studies. Other types of electroactive materials need also to be studied. Types of redox couple and solvent are also important parameters to address. Attaching the Redox couple species themselves to the electrode surface in the solid/liquid junction could be also of special value.

Using CNT composite systems as charge transfer catalysts is also worth to investigate. Using new types of liquid ionics (as solvents and as electrolytes) also needs to be studied.

Simulation study of regenerative PEC processes has been reported. Charge transfer dynamics at solid/liquid interface has been a subject of theoretical study (Akimov et al., 2013; Gacemi et al., 2013). Regenerative PEC processes in DSSCs are a major area in these studies. The charge transfer between the sensitizing dye and the TiO<sub>2</sub> film electrode is affected by the type of the sensitizer as confirmed by experimental and theoretical studies (Ramli et al., 2019). The focal issue is optimizing PEC cell parameters aiming at maximum performance (Shahroosvand and Eskandari, 2018). Both working electrode (Gacemi et al., 2018; Gacemi et al., 2013) and counter electrode (Gong et al., 2017) were simulated. As simulation helps in optimizing DSSCs, more simulation investigations are needed specifically in charge transfer catalytic behaviors.

### 3.2.3. Possible effects of charge transfer catalysis in regenerative processes

As described above, different types of charge transfer catalysts can be effectively used to enhance stability and PEC performance of metal chalcogenide film electrodes. CNTs may enhance electrode PEC by a number of ways, one of which is increased surface area, increased

absorptivity and increased charge transfer at electrode/Redox interfaces (electrons at the counter electrode and holes at the working electrode). By doing so, the CNTs stabilize the electrodes to photo-corrosion as hole build-up is prevented by quick transfer of the holes. Electroactive species can also enhance photocurrent and electrode stability by behaving as charge transfer catalysts.

Depending on its nature, the charge transfer catalyst may affect charge transfer dynamics in more than one way.

(1) Affecting flat band position: If charged species are brought in close proximity to a SC electrode surface, they affect the SC flat band edge positions. This should apply to both monolithic and polycrystalline SC electrodes (Gujarro et al., 2015). If the species is positively charged, such as adsorbed cations (Bansal et al., 1993; Chazalviel et al., 2000; Parkinson et al., 1979), they should lower the flat band edge positions to more positive potentials. On the other hand, negatively charged species should repel and destabilize the flat band edge positions to higher energies and more negative potentials (Turner and Parkinson, 1983; Reincke et al., 2002; Agostinelli et al., 2006). Neutral species may not cause shifting in flat band edge positions.

The issue of flat band edge position shifting is understandable from basic sciences (Huheey et al., 2006) where attraction and repulsion between orbitals and applied potentials is known, see page 364 in (Miessler et al., 2014). The SC band involves a continuum of huge number of energy levels (molecular orbitals). If a positive potential is applied at the SC surface, be it from applied potential or from attached positively charged ions, the orbitals at band edge should be attracted and lowered to more positive potentials (lower energy). When negative potentials (or negative charges) are applied, the molecular orbitals are repelled to more negative potential positions (higher energy). However, as the effect of the applied potential is more pronounced at the SC surface, shifting should be more significant on the band edge position near the surface (SCL). At inner places, farther away from the surface, the effect is less pronounced and exponentially decays. The logic follows the well-known Coulombic attraction and repulsion law, where energy of attraction varies with distance between the charges. The amount of shifting at the SC surface is thus higher than that in the bulk. This is clarified in Fig. 6 formalism, where positive charges lower flat band potential.

Conducting polymers, which can be positively (or negatively) charged affected the Schottky energy barriers at SC/Polymer interfaces (Lonergan, 2002; GiorgioáZambonin and PeraldoáBicelli, 1992). Examples of positively charged species attached to SC surfaces are tetrapyrrolyl porphyrinatomanganese(III) ions which originally carry positive charges.

Chemical anchoring of the pyridine groups with halogen atoms bonded via carbon chains to the SC surface creates more positive charges per each linkage site. Results showed the possibility to lower flat band edge positions by as much as 300 mV (Hilal and Turner, 2006). Such techniques are useful in tailoring positions of flat band edges to meet the desired potentials needed for non-regenerative PEC processes (such as water splitting studies) (Morikawa et al., 2019; Yao et al., 2019). In order to effectively function in light-induced splitting of water, the flat band edges for a given SC electrode must span both oxidation and reduction potentials for water. If the flat band edge position of a given SC electrode is higher or lower than necessary, it can be tailored as required by attaching positive or negative charges to the surface, as described in Fig. 4. Similarly, band edge tailoring can be useful in regenerative PEC processes. If flat band edge position is tailored to suite the other energetics at the electrode/Redox junction, photocurrent enhancement can be achieved, *vide infra*. Surface modification can affect relative positions of the SC electrode flat bands to the Redox couple potential, and can be a means to tune the Schottky barrier (Son et al., 2016) and the open circuit potential values (Xue et al., 2017).

(2) Surface state removal: In PEC processes surface states may form in the forbidden region (band gap) at the SC electrode surface (Boschloo

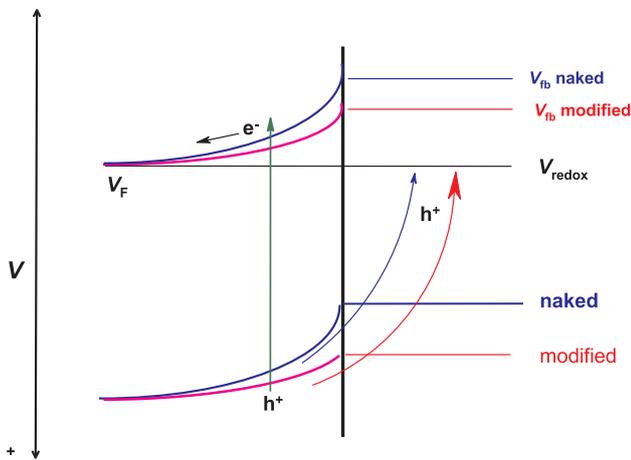


Fig. 4. Lowering of flat band edge positions shifted by attaching positive charges to a SC electrode.

and Fitzmaurice, 1999) as described above. Since the surface states behave as traps for carrier charges and decrease the PEC cell efficiency by inducing charge re-combinations (Sachs et al., 2016), removal of such states should enhance PEC performance. This can be achieved by modification of electrode surfaces (Moser et al., 1991; Li et al., 2010). Modifying a SC electrode surface with a suitable material that removes surface states should always be considered in order to improve the PEC performance. Instead of charge recombination, the charge transfer at the electrode/Redox interface will therefore be encouraged. Passivation of GaN nano-wires, with 1,2-ethanedithiol, enhanced light-to-current conversion efficiency from  $\sim 8\%$  to  $\sim 18\%$ , in addition to stability (Varadhan et al., 2017). Multifunctional modification charge transfer catalytic materials that remove surface states and encourage charge transfer, *vide infra*, should also be considered (Zyoud et al., 2015). Metal chalcogenide film electrodes should be a special beneficent from these strategies.

(3) Charge transfer speed-up: This is a focal function for a charge transfer catalyst at electrode/Redox interface. Consider an n-type SC electrode/Redox couple. As the SC is excited by suitable photons, electrons are excited to the conduction band (CB). As the bands are bent, the electrons should move down to the positive potential inside the CB, till they reach the metallic wiring and move to the counter electrode. If the electrons are allowed speedy transfer to the counter electrode, that will encourage photocurrent occurrence. Depending on type and properties of the counter electrode, such speedy transfer may not be possible. In such a case a charge transfer catalyst is needed at the counter electrode surface, Fig. 5.

On the other hand, the holes that remain in the valence band (VB) should be allowed to transfer to the Redox couple. If such holes are not given speedy transfer, they accumulate inside the SCL at the working electrode. Again, the circuit resistance will then be increased and the photocurrent will be lowered. Other consequences are also expected as discussed below. To speed up the hole transfer at the electrode/Redox couple interface charge transfer mediators (catalysts) are needed.

Polycrystalline n-type Si electrodes showed higher stability to photo-corrosion when coated by polypyrrol, as the polymer speeded up charge transfer at the electrode/Redox couple (Noufi et al., 1981). By speeding up hole transfer to the Redox couple the catalyst enhances photocurrent and lowers circuit resistance (Frank, 1984).

Based on above discussions, charge transfer catalysts are useful at both counter electrodes and working electrodes, in n-type SC film electrode cells as examples. The SC working electrode surface catalyst can be carefully chosen to have the following features:

- (i) Must be able to accept the holes formed in the SC working electrode VB. Therefore, the catalyst should have a tool to acquire the

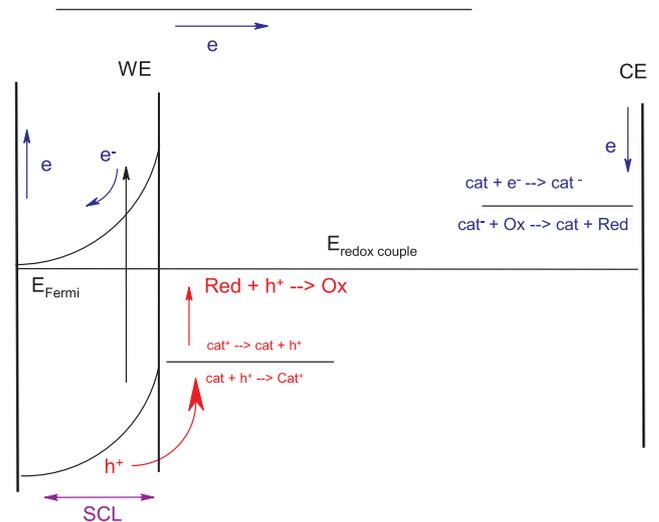


Fig. 5. Effect of charge transfer catalysts at both n-type SC working electrode and counter electrode in a PEC cell.

holes. If catalyst species are bonded or adsorbed to the electrode surface that will be possible, otherwise a co-catalyst is needed. Moreover, the catalyst itself must be easy to oxidize at n-type SC electrodes. Otherwise it does not easily accept the oncoming holes. It should also be easy to reduce by relaying the positive charge to the Redox couple.

- (ii) The oxidation potential for the catalyst must be above (more negative) than the flat band edge for the electrode VB. Otherwise holes would not transfer to the catalyst.
- (iii) The catalyst must be able to relay the positive charges to the solution Redox couple. The oxidation potential level for the catalyst must be therefore be lower than the oxidation potential for the solution Redox couple.
- (iv) The catalyst must be well adhered to the SC film electrode, and must itself be stable photocorrosion.

The catalyzed charge transfer process at the SC electrode/Redox couple can thus be summarized in Eqs. (4)–(5).



where SC hole means positive hole in the SC electrode,  $Cat^{n+}$  is a charge transfer catalyst (ion), Red and Ox are the reduced and oxidized species in the Redox couple, respectively.

For an effective counter electrode catalyst, the following features are necessary:

- (i) The catalyst must be easy to reduce and must be able to accept electrons from the counter electrode. The catalyst needs to have a work function that fits with that for the counter electrode.
- (ii) The catalyst be easy to oxidize by relaying the gained electron to the Redox couple.
- (iii) The catalyst must have good adherence to the counter electrode surface.

On the counter electrode, where reduction occurs by electrons, charge transfer catalytic process is summarized in Eqs. (6)–(7):



where  $Cat'$  is a catalyst species,  $CE^{e-}$  is the counter electrode with coming electrons, and  $Ox^+$  is the oxidized form of the Redox couple, and  $CE^0$  is the counter electrode after loss of electrons.



**Table 1**  
Effects of electrode modification and charge transfer catalysts on PEC cell performance.

Electrode	PEC cell materials with modification (without modification)	$J_{sc}/\text{mA cm}^{-2}$	$V_{oc}/\text{V}$	FF%	$\eta\%$	Ref.	
DSSC Counter Electrodes	CE using carbon black/Stainless steel counter electrode	16.3	0.79	71.4	9.15	Murakami and Grätzel (2008)	
	Pt-coated stainless steel	(15.4)	(0.78)	(73.7)	(8.86)		
	Pt nanoparticles/Graphene				6.35	Yen et al. (2011)	
	FTO/Pt				(5.27)		
	Graphene				(2.89)	Tsao et al. (2011)	
	FTO/Pt & poly(3,4-ethylenedioxythiophene) (PEDOT)				10.3		
	FTO/Pt				(7.9)		
	MWCNT/PEDOT/Polystyrenesulfonate acid)	15.5	0.66		6.5	Fan et al. (2008)	
	MWCNT/Polystyrenesulfonate acid	(9.7)	(0.60)				
	CNT/Graphite black/Graphene mass ratio 6:3:1	13.59	0.67	69%	6.29	Zhang et al. (2019a)	
	with mass ratio 8:4:1	(13.95)	(0.63)	(60%)	(5.29)		
	Working electrode	CuSe*	2.05	−0.53	77	15.01	Zyoud et al. (2015)
			(2.05)	(−0.18)	(43)	(2.83)	
		CuS*	2.05	−0.56	86	17.36	Zyoud et al. (2016)
			(−)	(−)	(−)	(−0)	
CdS*		0.28	−0.46	33	0.28	Sabri et al. (2014)	
		(−)	(−)	(−)	(−0)		
CdSe* prepared by combined ECD & CBD		0.56	−0.44	34	2.0	Abdul-Rahman (2014)	
		(0.29)	(−0.49)	(33)	(1.5)		
CdS/PCBM:P3HT**		11.1	0.50		2.81	Thanihaichelvan et al. (2019)	
TiO <sub>2</sub> /PCBM:P3HT**		(9.0)	(0.33)		(2.0)		
CdS quantum dots/P3HT nanowires**				4.1	Ren et al. (2011)		
With chemical graphiting and without chemical graphiting				(0.6)			
GaN nano-wires with 1,2-ethanedithiol and without				18	Varadhan et al. (2017)		
				(8)			
DSSC, TiO <sub>2</sub> 10 μm film	12.75	0.742	58.7	5.93	Selvaraj et al. (2018)		
3.2 μm film	(7.36)	(0.733)	(46.6)	(2.51)			

\* Coating with porphyrinatomanganese(III) ions inside polymers.

\*\* PCBM is phenyl-C61-butiric acid methyl ester, and P3HT is poly(3-hexylthiophene).

chalcogenide systems) and/or the counter electrode (in DSSCs). The catalysts speed up charge transfer at the solid/Redox junctions, which enhances both PEC conversion efficiency and stability of the metal chalcogenide film electrode. With its charge, the catalyst may also affect the flat band potential position which enables the PEC cell to function in other non-regenerative PEC processes. Therefore, more work is needed to bring new types of charge transfer catalysts, especially in the area of metal chalcogenide film electrodes, with multi-fold functions (tailoring band edge positions, increasing photocurrent density and preventing photo-corrosion).

## Declaration of Competing Interest

The authors declare that this work carries no conflicts of interest.

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## References

- AbdelHadi, D., 2016. Electrochemically deposited CdTe film electrodes with enhanced photoelectrochemical characteristics, MSc Thesis, An-Najah National University, Nablus, Palestine.
- Abdul-Rahman, N., 2014. CdSe Thin Film Photoelectrochemical Electrodes: Combined Electrochemical and Chemical Bath Depositions, in: MSc Thesis. An-Najah National University, Nablus, Palestine.
- Agostinelli, G., Delabie, A., Vitanov, P., Alexieva, Z., Dekkers, H., De Wolf, S., Beaucarne, G., 2006. Very low surface recombination velocities on p-type silicon wafers passivated with a dielectric with fixed negative charge. *Sol. Energy Mater. Sol. Cells* 90, 3438–3443.
- Akimov, A.V., Neukirch, A.J., Prezhdo, O.V., 2013. Theoretical insights into photo-induced charge transfer and catalysis at oxide interfaces. *Chem. Rev.* 113, 4496–4565.
- Albu, S.P., Tsuchiya, H., Fujimoto, S., Schmuki, P., 2010. TiO<sub>2</sub> nanotubes–annealing effects on detailed morphology and structure. *Eur. J. Inorg. Chem.* 2010, 4351–4356.
- Alpuche-Aviles, M.A., Wu, Y., 2009. Photoelectrochemical study of the band structure of Zn<sub>2</sub>SnO<sub>4</sub> prepared by the hydrothermal method. *J. Am. Chem. Soc.* 131, 3216–3224.
- Atanacio, A.J., Bak, T., Rahman, K.A., Nowotny, J., 2018. Defect engineering of photosensitive oxide materials. Example of TiO<sub>2</sub> solid solutions. *Mater. Sustain. Energy* 72.
- Babu, K.C., Srivastava, O., Rao, G.S., 1994. Photoelectrochemical solar cells: present status. *Curr. Sci.* 715–729.
- Bansal, A., Tan, M.X., Tufts, B.J., Lewis, N.S., 1993. Distinguishing between buried semiconductor/metal contacts and hybrid semiconductor/metal/liquid contacts at n-gallium arsenide/potassium hydroxide-selenium (Se-/2-)(aq) junctions. *J. Phys. Chem.* 97, 7309–7315.
- Bard, A.J., Abruna, H.D., Chidsey, C.E., Faulkner, L.R., Feldberg, S.W., Itaya, K., Majda, M., Melroy, O., Murray, R.W., 1993. The electrode/electrolyte interface—a status report. *J. Phys. Chem.* 97, 7147–7173.
- Bertoluzzi, L., Lopez-Varo, P., Tejada, J.A.J., Bisquert, J., 2016. Charge transfer processes at the semiconductor/electrolyte interface for solar fuel production: insight from impedance spectroscopy. *J. Mater. Chem. A* 4, 2873–2879.
- Bhattacharya, S., John, S., 2019. Beyond 30% conversion efficiency in silicon solar cells: a numerical demonstration. *Sci. Rep.* 9, 1–15.
- Bockris, J., Conway, B., White, R.E., 1982. *Modern Aspects of Electrochemistry*, No. 14, in, Springer.
- Boschloo, G., Fitzmaurice, D., 1999. Spectroelectrochemical investigation of surface states in nanostructured TiO<sub>2</sub> electrodes. *J. Phys. Chem. B* 103, 2228–2231.
- Bucherl, C.N., Oleson, K.R., Hillhouse, H.W., 2013. Thin film solar cells from sintered nanocrystals. *Curr. Opin. Chem. Eng.* 2, 168–177.
- Burgelman, M., Nollet, P., Degraeve, S., 2000. Modelling polycrystalline semiconductor solar cells. *Thin Solid Films* 361, 527–532.
- Butler, M., Ginley, D., 1980. Principles of photoelectrochemical, solar energy conversion. *J. Mater. Sci.* 15, 1–19.
- Carella, A., Borbone, F., Centore, R., 2018. Research progress on photosensitizers for DSSC. *Front. Chem.* 6.
- Chan, Y.F., Wang, C.C., Chen, B.H., Chen, C.Y., 2013. Dye-sensitized TiO<sub>2</sub> solar cells based on nanocomposite photoanode containing plasma-modified multi-walled carbon nanotubes. *Prog. Photovolt. Res. Appl.* 21, 47–57.
- Chazalviel, J.-N., Belaidi, A., Safi, M., Maroun, F., Erne, B., Ozanam, F., 2000. In situ semiconductor surface characterisation: a comparative infrared study of Si Ge and GaAs. *Electrochim. Acta* 45, 3205–3211.
- Chen, J., Li, B., Zheng, J., Zhao, J., Jing, H., Zhu, Z., 2011. Polyaniline nanofiber/carbon film as flexible counter electrodes in platinum-free dye-sensitized solar cells. *Electrochim. Acta* 56, 4624–4630.
- Chen, Y., Tran, P.D., Boix, P., Ren, Y., Chiam, S.Y., Li, Z., Fu, K., Wong, L.H., Barber, J.,

2015. Silicon decorated with amorphous cobalt molybdenum sulfide catalyst as an efficient photocathode for solar hydrogen generation. *ACS Nano* 9, 3829–3836.
- Chen, K., Wu, C.-D., 2019. Designed fabrication of biomimetic metal–organic frameworks for catalytic applications. *Coord. Chem. Rev.* 378, 445–465.
- Cheng, S., Fu, W., Yang, H., Zhang, L., Ma, J., Zhao, H., Sun, M., Yang, L., 2012. Photoelectrochemical performance of multiple semiconductors (CdS/CdSe/ZnS) co-sensitized TiO<sub>2</sub> photoelectrodes. *J. Phys. Chem. C* 116, 2615–2621.
- Chun, K., Park, B., Sung, Y., Kwak, D., Hyun, Y., Park, M., 2009. Fabrication of dye-sensitized solar cells using TiO<sub>2</sub>-nanotube arrays on Ti-grid substrates. *Thin Solid Films* 517, 4196–4198.
- Deyneko, N., Kryvulkin, I., Matiushenko, M., Tarasenko, O., Khmyrov, I., Khmyrova, A., Shevchenko, R., 2019. Investigation of photoelectric converters with a base cadmium telluride layer with a decrease in its thickness for tandem and two-sided sensitive instrument structures. *Eureka: Phys. Eng.*, pp. 73–80.
- Doherty, A.P., 2018. Redox-active ionic liquids for energy harvesting and storage applications. *Curr. Opin. Electrochem.* 7, 61–65.
- Dohn, A.O., Kjaer, K.S., Harlang, T.B., Canton, S.E., Nielsen, M.M., Möller, K.B., 2016. Electron transfer and solvent-mediated electronic localization in molecular photocatalysis. *Inorg. Chem.* 55, 10637–10644.
- Dou, S., Tao, L., Wang, R., El Hankari, S., Chen, R., Wang, S., 2018. Plasma-assisted synthesis and surface modification of electrode materials for renewable energy. *Adv. Mater.* 30, 1705850.
- Emin, S., Singh, S.P., Han, L., Satoh, N., Islam, A., 2011. Colloidal quantum dot solar cells. *Sol. Energy* 85, 1264–1282.
- Fan, B., Mei, X., Sun, K., Ouyang, J., 2008. Conducting polymer/carbon nanotube composite as counter electrode of dye-sensitized solar cells. *Appl. Phys. Lett.* 93, 143103.
- Fang, X., Shang, Q., Wang, Y., Jiao, L., Yao, T., Li, Y., Zhang, Q., Luo, Y., Jiang, H.L., 2018. Single Pt atoms confined into a metal–organic framework for efficient photocatalysis. *Adv. Mater.* 30, 1705112.
- Finklea, H.O., 1983. *Photoelectrochemistry: introductory concepts*, in: ACS Publications.
- Finklea, H.O., 1983. *Semiconductor Electrodes*, 1988.
- Forgie, R., Bugosh, G., Neyerlin, K., Liu, Z., Strasser, P., 2010. Bimetallic Ru electrocatalysts for the OER and electrolytic water splitting in acidic media. *Electrochem. Solid-State Lett.* 13, B36–B39.
- Frank, A.J., Glens, S., 1991. Pn heterojunction and Schottky barrier formation between poly (3-methylthiophene) and n-type cadmium sulphide. In: *Photochemistry and Photoelectrochemistry of Organic and Inorganic Molecular Thin Films*, International Society for Optics and Photonics, pp. 50–57.
- Frank, A.J., Glens, S., Nelson, A.J., 1989. Conductive polymer-semiconductor junction: characterization of poly (3-methylthiophene): Cadmium sulfide based photoelectrochemical and photovoltaic cells. *J. Phys. Chem.* 93, 3818–3825.
- Frank, A.J., 1984. Organic conductive films for semiconductor electrodes, in: *Google Patents*.
- Frese, K.W., 1983. Electrochemical studies of photocorrosion of n-CdSe. *J. Electrochem. Soc.* 130, 28–33.
- Gacemi, Y., Cheknane, A., Hilal, H.S., 2013. Simulation and modelling of charge transport in dye-sensitized solar cells based on carbon nano-tube electrodes. *Phys. Scr.* 87, 035703.
- Gacemi, Y., Cheknane, A., Hilal, H.S., 2018. Effect of carbon nano tube working electrode thickness on charge transport kinetics and photo-electrochemical characteristics of dye-sensitized solar cells. *Mater. Res. Exp.* 5, 025513.
- Gao, F., Goodman, D.W., 2012. Model catalysts: simulating the complexities of heterogeneous catalysts. *Annu. Rev. Phys. Chem.* 63, 265–286.
- George, A., Thanseema, A., Sreelatha, K., Sreekal, C., Jinchu, I., 2016. Device stability study of dye sensitized solar cells incorporated with MWCNTs. In: *2016 International Conference on Electrical, Electronics, and Optimization Techniques (ICEEOT), IEEE*, 2016, p. 4631–4635.
- GiorgioZamboni, P., PeraldoBicelli, L., 1992. Development and electroanalytical investigation of a novel rectifying semiconductor/polymer interface. *J. Chem. Soc., Faraday Trans.* 88, 3183–3186.
- Glens, S., Frank, A., 1989. Schottky barrier formation between poly (3-methylthiophene) and n-type cadmium sulfide. *Synth. Met.* 28, 681–686.
- Gnanasekar, S., Kollu, P., Jeong, S.K., Grace, A.N., 2019. Pt-free, low-cost and efficient counter electrode with carbon wrapped VO<sub>2</sub> (M) nanofiber for dye-sensitized solar cells. *Sci. Rep.* 9.
- Gong, J., Sumathy, K., Zhou, Z., Qiao, Q., 2017. Modeling of interfacial and bulk charge transfer in dye-sensitized solar cells. *Cogent Eng.* 4, 1287231.
- Grancini, G., Roldán-Carmona, C., Zimmermann, I., Mosconi, E., Lee, X., Martineau, D., Narbey, S., Oswald, F., De Angelis, F., Graetzel, M., 2017. One-Year stable perovskite solar cells by 2D/3D interface engineering. *Nat. Commun.* 8, 15684.
- Gratzel, M., 2012. *Energy Resources Through Photochemistry and Catalysis*. Elsevier.
- Greco, D., Compaan, A., Young, D., Jayamaha, U., Rose, D., 2000. Photoluminescence of Cu-doped CdTe and related stability issues in CdS/CdTe solar cells. *J. Appl. Phys.* 88, 2490–2496.
- Green, M.A., 2002. Photovoltaic principles. *Physica E* 14, 11–17.
- Guijarro, N., Prévot, M.S., Sivula, K., 2015. Surface modification of semiconductor photoelectrodes. *PCCP* 17, 15655–15674.
- Guo, W., Fu, L., Zhang, Y., Zhang, K., Liang, L., Liu, Z., Cao, H., Pan, X., 2010. Microstructure, optical, and electrical properties of p-type SnO thin films. *Appl. Phys. Lett.* 96, 042113.
- Halme, J., Toivola, M., Tolvanen, A., Lund, P., 2006. Charge transfer resistance of spray deposited and compressed counter electrodes for dye-sensitized nanoparticle solar cells on plastic substrates. *Sol. Energy Mater. Sol. Cells* 90, 872–886.
- Hamann, T.W., Ondersma, J.W., 2011. Dye-sensitized solar cell redox shuttles. *Energy Environ. Sci.* 4, 370–381.
- Hao, S., Wu, J., Huang, Y., Lin, J., 2006. Natural dyes as photosensitizers for dye-sensitized solar cell. *Sol. Energy* 80, 209–214.
- Hapiot, P., Lagrost, C., 2008. Electrochemical reactivity in room-temperature ionic liquids. *Chem. Rev.* 108, 2238–2264.
- Hilal, H.S., Zyoud, A., Al-Kerm, R., 2017. Highly efficient & stable metal chalcogenide thin-film electrodes in solar energy conversions. In: *Proceedings Book of 1st International Conference on Progress in Applied Science*, 2017.
- Hilal, H.S., Turner, J.A., 2006. Controlling charge-transfer processes at semiconductor/liquid junctions. *Electrochim. Acta* 51, 6487–6497.
- Hilal, H.S., Masoud, M., Shakhshir, S., Jisrawi, N., 2002. Metalloporphyrin/polysiloxane modified n-GaAs surfaces: effect on photoelectrochemical efficiency and surface stability. *J. Electroanal. Chem.* 527, 47–55.
- Hilal, H.S., Masoud, M., Shakhshir, S., Jisraw, N., 2003. n-GaAs band-edge repositioning by modification with metalloporphyrin/polysiloxane matrices. *Act. Passive Electron. Compon.* 26, 11–21.
- Hilal, H.S., Ateereh, W.M., Al-Tel, T., Shubeita, R., Saadeddin, I., Campet, G., 2004. Enhancement of n-GaAs characteristics by combined heating, cooling rate and metalloporphyrin modification techniques. *Solid State Sci.* 6, 139–146.
- Hilal, H.S., Ismail, R.M., El-Hamouz, A., Zyoud, A., Saadeddin, I., 2009. Effect of cooling rate of pre-annealed CdS thin film electrodes prepared by chemical bath deposition: enhancement of photoelectrochemical characteristics. *Electrochim. Acta* 54, 3433–3440.
- Hilal, H.S., Zyoud, A., Helal, M.H., Bsharat, H., Helal, H.H., Ali, C., 2019. Effects of annealing temperature and cooling rate on photo-electrochemical performance of pristine polycrystalline metal-chalcogenide film electrodes. *Sol. Energy* 183, 704–715.
- Hiramoto, M., Imahigashi, T., Yokoyama, M., 1994. Photocurrent multiplication in organic pigment films. *Appl. Phys. Lett.* 64, 187–189.
- Ho, S.M., 2016. Metal chalcogenide thin films for photoelectrochemical cell applications: a review. *Middle-East J. Scient. Res.* 24, 1232–1235.
- Huang, D., Wang, K., Yu, L., Nguyen, T.H., Ikeda, S., Jiang, F., 2018. Over 1% efficient unbiased stable solar water splitting based on a sprayed Cu<sub>2</sub>ZnSnS<sub>4</sub> photocathode protected by a HfO<sub>2</sub> photocorrosion-resistant film. *ACS Energy Lett.* 3, 1875–1881.
- Huheey, J.E., Keiter, E.A., Keiter, R.L., Medhi, O.K., 2006. *Inorganic chemistry: principles of structure and reactivity*, Pearson Education India, 2006.
- Husain, A.A., Hasan, W.Z.W., Shafie, S., Hamidon, M.N., Pandey, S.S., 2018. A review of transparent solar photovoltaic technologies. *Renew. Sustain. Energy Rev.* 94, 779–791.
- Hwang, S., Batmunkh, M., Nine, M.J., Chung, H., Jeong, H., 2015. Dye-sensitized solar cell counter electrodes based on carbon nanotubes. *ChemPhysChem* 16, 53–65.
- Iftikhar, H., Sonai, G.G., Hashmi, S.G., Nogueira, A.F., Lund, P.D., 2019. Progress on electrolytes development in dye-sensitized solar cells. *Materials* 12, 1998.
- Ito, S., Zakeeruddin, S.M., Comte, P., Liska, P., Kuang, D., Grätzel, M., 2008. Bifacial dye-sensitized solar cells based on an ionic liquid electrolyte. *Nat. Photon.* 2, 693.
- Jeon, I., Matsuo, Y., Maruyama, S., 2019. Single-walled carbon nanotubes in solar cells. In: *Single-Walled Carbon Nanotubes*, Springer, pp. 271–298.
- Jia, F., Yu, X., Zhang, L., 2014. Enhanced selectivity for the electrochemical reduction of CO<sub>2</sub> to alcohols in aqueous solution with nanostructured Cu–Au alloy as catalyst. *J. Power Sources* 252, 85–89.
- Kawano, R., Watanabe, M., 2003. Equilibrium potentials and charge transport of an I<sup>−</sup>/I<sup>3−</sup> redox couple in an ionic liquid. *Chem. Commun.* 330–331.
- Kawano, R., Watanabe, M., 2005. Anomaly of charge transport of an iodide/tri-iodide redox couple in an ionic liquid and its importance in dye-sensitized solar cells. *Chem. Commun.* 2107–2109.
- Kim, H.-J., Kim, J.-H., Kumar, C.S.P., Punnoose, D., Kim, S.-K., Gopi, C.V., Rao, S.S., 2015. Facile chemical bath deposition of CuS nano peas like structure as a high efficient counter electrode for quantum-dot sensitized solar cells. *J. Electroanal. Chem.* 739, 20–27.
- Kohl, P.A., Bard, A.J., 1979. Semiconductor electrodes XVIII liquid junction photovoltaic cells based on electrodes and acetonitrile solutions. *J. Electrochem. Soc.* 126, 603–608.
- Kois, J., Polivtseva, S., Bereznev, S., 2019. The cost-effective deposition of ultra-thin titanium (IV) oxide passivating layers for improving photoelectrochemical activity of SnS electrodes. *Thin Solid Films* 671, 152–156.
- Kubař, T., Elstner, M., 2013. A hybrid approach to simulation of electron transfer in complex molecular systems. *J. R. Soc. Interface* 10, 20130415.
- Kudo, A., Miseki, Y., 2009. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* 38, 253–278.
- Kulik, H.J., 2018. Large-scale QM/MM free energy simulations of enzyme catalysis reveal the influence of charge transfer. *PCCP* 20, 20650–20660.
- Kumar, A., Wilisch, W.C.A., Lewis, N.S., 1993. The electrical properties of semiconductor/metal, semiconductor/liquid, and semiconductor/conducting polymer contacts. *Crit. Rev. Solid State Mater. Sci.* 18, 327–353.
- Kwon, J.-H., Ahn, J.-S., Yang, H., 2013. Chemical bath deposition of CdS channel layer for fabrication of low temperature-processed thin-film-transistors. *Curr. Appl. Phys.* 13, 84–89.
- Kyaw, A.K.K., Tantang, H., Wu, T., Ke, L., Wei, J., Demir, H.V., Zhang, Q., Sun, X.W., 2012. Dye-sensitized solar cell with a pair of carbon-based electrodes. *J. Phys. D Appl. Phys.* 45, 165103.
- Lee, T.H., Do, K., Lee, Y.W., Jeon, S.S., Kim, C., Ko, J., Im, S.S., 2012. High-performance dye-sensitized solar cells based on PEDOT nanofibers as an efficient catalytic counter electrode. *J. Mater. Chem.* 22, 21624–21629.
- Lee, H.Y., Issa, J.B., Isied, S.S., Castner Jr, E.W., Pan, Y., Hussey, C.L., Lee, K.S., Wishart, J.F., 2012. A comparison of electron-transfer dynamics in ionic liquids and neutral solvents. *J. Phys. Chem. C* 116, 5197–5208.
- Lei, Z., Chen, B., Koo, Y.-M., MacFarlane, D.R., 2017. Introduction: Ionic liquids, in: *ACS Publications*.

- Lewera, A., Jurczakowski, R., Połczyński, P., 2019. Selective catalyst, particularly for electroreduction of oxygen, an electrochemical system containing thereof, an palladium-inert gas alloy and use thereof, and a cell, particularly a photovoltaic cell containing thereof, in, Google Patents.
- Li, M., Liang, W., Yuan, R., Chai, Y., 2019. CdTe QD–CeO<sub>2</sub> complex as a strong photoelectrochemical signal indicator for the ultrasensitive microRNA Assay. *ACS Appl. Mater. Interfaces* 11, 11834–11840.
- Li, R., Liu, J., Cai, N., Zhang, M., Wang, P., 2010. Synchronously reduced surface states, charge recombination, and light absorption length for high-performance organic dye-sensitized solar cells. *J. Phys. Chem. B* 114, 4461–4464.
- Li, Y., Wang, H., Wang, Z., Qiao, Y., Ulstrup, J., Chen, H.-Y., Zhou, G., Tao, N., 2019. Transition from stochastic events to deterministic ensemble average in electron transfer reactions revealed by single-molecule conductance measurement. *Proc. Natl. Acad. Sci.* 116, 3407–3412.
- Li, J., Wu, N., 2015. Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: a review. *Catal. Sci. Technol.* 5, 1360–1384.
- Lin, W.-J., Hsu, C.-T., Tsai, Y.-C., 2011. Dye-sensitized solar cells based on multiwalled carbon nanotube–titania/titania bilayer structure photoelectrode. *J. Colloid Interface Sci.* 358, 562–566.
- Listorti, A., O'Regan, B., Durrant, J.R., 2011. Electron transfer dynamics in dye-sensitized solar cells. *Chem. Mater.* 23, 3381–3399.
- Liu, W., An, R., Wang, C., Zheng, Z., Tian, Y., Xu, R., Wang, Z., 2018. Recent progress in rapid sintering of nanosilver for electronics applications. *Micromachines* 9, 346.
- Liu, H., Liu, Y., Li, J., 2010. Ionic liquids in surface electrochemistry. *PCCP* 12, 1685–1697.
- Liu, M., You, W., Lei, Z., Zhou, G., Yang, J., Wu, G., Ma, G., Luan, G., Takata, T., Hara, M., 2004. Water reduction and oxidation on Pt–Ru/Y 2 Ta 2 O 5 N 2 catalyst under visible light irradiation. *Chem. Commun.* 2192–2193.
- Loneragan, M.C., 2002. Devices having a semiconductor/conducting polymer interface, in, Google Patents.
- MacFarlane, D.R., Pringle, J.M., Howlett, P.C., Forsyth, M., 2010. Ionic liquids and reactions at the electrochemical interface. *PCCP* 12, 1659–1669.
- Maksymiuk, K., Doblhofer, K., 1994. Kinetics and mechanism of charge-transfer reactions between conducting polymers and redox ions in electrolytes. *Electrochim. Acta* 39, 217–227.
- Mao, D., Kim, K., Tsuo, Y., Frank, A.J., 1995. Improved efficiency and stability of silicon photocathodes by electrochemical etching. *J. Phys. Chem.* 99, 3643–3647.
- Mawdsley, P.R., 2006. Catalytic hydrogenations in ionic liquids.
- Mazzolini, P., Gondoni, P., Russo, V., Christina, D., Casari, C.S., Li Bassi, A., 2015. Tuning of electrical and optical properties of highly conducting and transparent Ta-doped TiO<sub>2</sub> polycrystalline films. *J. Phys. Chem. C* 119, 6988–6997.
- Mehmood, U., Hussein, I.A., Harrabi, K., Mekki, M., Ahmed, S., Tabet, N., 2015. Hybrid TiO<sub>2</sub>–multiwalled carbon nanotube (MWCNTs) photoanodes for efficient dye sensitized solar cells (DSSCs). *Sol. Energy Mater. Sol. Cells* 140, 174–179.
- Miessler, G., Fischer, P., Tarr, D., 2014. Inorganic chemistry fifth edition, in, New York: Pearson Education, Inc.
- Mingyuan, Z., Gongquan, S., Huanqiao, L., Lei, C., Qin, X., 2008. Effect of the Sn (II)/Sn (IV) redox couple on the activity of PtSn/C for ethanol electro-oxidation. *Chin. J. Catal.* 29, 765–770.
- Miseki, Y., Fujiyoshi, S., Gunji, T., Sayama, K., 2017. Photocatalytic Z-scheme water splitting for independent H<sub>2</sub>/O<sub>2</sub> production via a stepwise operation employing a vanadate redox mediator under visible light. *J. Phys. Chem. C* 121, 9691–9697.
- Monreal-Bernal, A., Vilatela, J.J., Costa, R.D., 2019. CNT fibres as dual counter-electrode/current-collector in highly efficient and stable dye-sensitized solar cells. *Carbon* 141, 488–496.
- Morandeira, A., Boschloo, G., Hagfeldt, A., Hammarstrom, L., 2008. Coumarin 343 – NiO films as nanostructured photocathodes in dye-sensitized solar cells: ultrafast electron transfer, effect of the I<sup>3</sup>–/I<sup>–</sup> redox couple and mechanism of photocurrent generation. *J. Phys. Chem. C* 112, 9530–9537.
- Morikawa, T., Sato, S., Sekizawa, K., Arai, T., Suzuki, T.M., 2019. Molecular catalysts immobilized on semiconductor photosensitizers for proton reduction toward visible-light-driven overall water splitting. *ChemSusChem* 12, 1807–1824.
- Moser, J., Punchedewa, S., Infelta, P.P., Graetzel, M., 1991. Surface complexation of colloidal semiconductors strongly enhances interfacial electron-transfer rates. *Langmuir* 7, 3012–3018.
- Murakami, T.N., Grätzel, M., 2008. Counter electrodes for DSC: application of functional materials as catalysts. *Inorg. Chim. Acta* 361, 572–580.
- Murphy, A., Barnes, P., Randeniya, L., Plumb, I., Grey, I., Horne, M., Glasscock, J., 2006. Efficiency of solar water splitting using semiconductor electrodes. *Int. J. Hydrogen Energy* 31, 1999–2017.
- Nam, J.G., Park, Y.J., Kim, B.S., Lee, J.S., 2010. Enhancement of the efficiency of dye-sensitized solar cell by utilizing carbon nanotube counter electrode. *Scr. Mater.* 62, 148–150.
- Nazeeruddin, M.K., Pechy, P., Grätzel, M., 1997. Efficient panchromatic sensitization of nanocrystalline TiO<sub>2</sub> films by a black dye based on atrithiocyanato–ruthenium complex. *Chem. Commun.* 1705–1706.
- Noufi, R., Frank, A.J., Nozik, A.J., 1981. Stabilization of n-type silicon photoelectrodes to surface oxidation in aqueous electrolyte solution and mediation of oxidation reaction by surface-attached organic conducting polymer. *J. Am. Chem. Soc.* 103, 1849–1850.
- Oh, A., Kim, H.Y., Baik, H., Kim, B., Chaudhari, N.K., Joo, S.H., Lee, K., 2019. Topotactic transformations in an icosahedral nanocrystal to form efficient water-splitting catalysts. *Adv. Mater.* 31, 1805546.
- Park, K., Kim, Y.J., Yoon, T., David, S., Song, Y.M., 2019. A methodological review on material growth and synthesis of solar-driven water splitting photoelectrochemical cells. *RSC Adv.* 9, 30112–30124.
- Parkinson, B., Heller, A., Miller, B., 1979. Effects of cations on the performance of the photoanode in the n-GaAs | K 2Se-K 2Se2-KOH | C semiconductor liquid junction solar cell. *J. Electrochem. Soc.* 126, 954–960.
- Pawar, S., Pawar, B., Kim, J., Joo, O.-S., Lokhande, C., 2011. Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films. *Curr. Appl. Phys.* 11, 117–161.
- Pires, R.V., Pessoa, L.M.B., Sant'Anna, M.d.A.d., Fainleib, A., Nunes, R.d.C.P., Lucas, E.F., 2019. Synthesis and characterization of isoprene oligomers to compare different production chemical processes. *Polímeros*, vol. 29.
- Priebe J.B., Radnik, J.r., Lennox, A.J., Pohl, M.-M., Karnahl, M., Hollmann, D., Grabow, K., Bentrup, U., Junge, H., Beller, M., 2015. Solar hydrogen production by plasmonic Au–TiO<sub>2</sub> catalysts: impact of synthesis protocol and TiO<sub>2</sub> phase on charge transfer efficiency and H<sub>2</sub> evolution rates. *ACS Catal.*, vol. 5, pp. 2137–2148.
- Qin, Q., Tao, J., Yang, Y., 2010. Preparation and characterization of polyaniline film on stainless steel by electrochemical polymerization as a counter electrode of DSSC. *Synth. Met.* 160, 1167–1172.
- Quang, N.D., Hien, T.T., Chinh, N.D., Kim, D., Kim, C., Kim, D., 2019. Transport of photo-generated electrons and holes in TiO<sub>2</sub>/CdS/CdSe core-shell nanorod structure toward high performance photoelectrochemical cell electrode. *Electrochim. Acta* 295, 710–718.
- Rabek, J.F., 1988. Applications of polymers in solar energy utilization. *Prog. Polym. Sci.* 13, 83–188.
- Rajeshwar, K., 2007. Fundamentals of semiconductor electrochemistry and photoelectrochemistry. *Encyclop. Electrochem.* 6, 1–53.
- Ramasamy, E., Lee, W.J., Lee, D.Y., Song, J.S., 2008. Spray coated multi-wall carbon nanotube counter electrode for tri-iodide (I<sup>3</sup>–) reduction in dye-sensitized solar cells. *Electrochem. Commun.* 10, 1087–1089.
- Ramli, M.A., Saad, S.K.M., Mawarnis, E.R., Umar, M.I.A., Visvanathan, P.S.M.N., Rahman, M.Y.A., Umar, A.A., 2019. Facile charge transfer in fibrous PdPt bimetallic nanocubes counter electrodes. *New J. Chem.*
- Reincke, F., Hickey, S., Kelly, J., Braam, T., Jenneskens, L., Vanmaekelbergh, D., 2002. Electrochemical and topological characterization of gold (111) oligo (cyclohexylidene) gold nanocrystal interfaces. *J. Electroanal. Chem.* 522, 2–10.
- Ren, S., Chang, L.-Y., Lim, S.-K., Zhao, J., Smith, M., Zhao, N., Bulovic, V., Bawendi, M., Gradecak, S., 2011. Inorganic–organic hybrid solar cell: bridging quantum dots to conjugated polymer nanowires. *Nano Lett.* 11, 3998–4002.
- Rhoderick, E.H., 1982. Metal-semiconductor contacts. *IEE Proc. I-Solid-State Electron Dev.* 129, 1.
- Rosli, N.N., Ibrahim, M.A., Ludin, N.A., Teridi, M.A.M., Sopian, K., 2019. A review of graphene based transparent conducting films for use in solar photovoltaic applications. *Renew. Sustain. Energy Rev.* 99, 83–99.
- Sabri, H., Saleh, S., Zyoud, A., Abdel-Rahman, N.N., Saadeddin, I., Campet, G., Park, D., Faroun, M., Hilal, H.S., 2014. Enhancement of CdSe film electrode PEC characteristics by metalloporphyrin/polysiloxane matrices. *Electrochim. Acta* 136, 138–145.
- Sachs, M., Pastor, E., Kafzas, A., Durrant, J.R., 2016. Evaluation of surface state mediated charge recombination in anatase and rutile TiO<sub>2</sub>. *J. Phys. Chem. Lett.* 7, 3742–3746.
- Samadpour, M., Giménez, S., Boix, P.P., Shen, Q., Calvo, M.E., Taghavinia, N., Toyoda, T., Míguez, H., Mora-Seró, I., 2012. Effect of nanostructured electrode architecture and semiconductor deposition strategy on the photovoltaic performance of quantum dot sensitized solar cells. *Electrochim. Acta* 75, 139–147.
- Sapp, W., Koodali, R., Kilin, D., 2016. Charge transfer mechanism in titanium-doped microporous silica for photocatalytic water-splitting applications. *Catalysts* 6, 34.
- Saranya, K., Rameez, M., Subramania, A., 2015. Developments in conducting polymer based counter electrodes for dye-sensitized solar cells—an overview. *Eur. Polym. J.* 66, 207–227.
- Sato, N., 1998. *Electrochemistry At Metal and Semiconductor Electrodes*. Elsevier.
- Sauvage, F., Chhor, S., Marchioro, A., Moser, J.-E., Graetzel, M., 2011. Butyronitrile-based electrolyte for dye-sensitized solar cells. *J. Am. Chem. Soc.* 133, 13103–13109.
- Selvaraj, P., Baig, H., Mallick, T.K., Siviter, J., Montecucco, A., Li, W., Paul, M., Sweet, T., Gao, M., Knox, A.R., 2018. Enhancing the efficiency of transparent dye-sensitized solar cells using concentrated light. *Sol. Energy Mater. Sol. Cells* 175, 29–34.
- Sendy, A., 2016. Pros and Cons of Monocrystalline vs. Polycrystalline Solar Panels, Retrieved December, 16, 2016.
- Shahroosvand, H., Eskandari, M., 2018. Ultrafast interfacial charge transfer from the LUMO + 1 in ruthenium (II) polypyridyl quinoxaline-sensitized solar cells. *Dalton Trans.* 47, 561–576.
- Sharma, K., Sharma, V., Sharma, S., 2018. Dye-sensitized solar cells: fundamentals and current status. *Nanoscale Res. Lett.* 13, 381.
- Shen, X., Sun, B., Yan, F., Zhao, J., Zhang, F., Wang, S., Zhu, X., Lee, S., 2010. High-performance photoelectrochemical cells from ionic liquid electrolyte in methyl-terminated silicon nanowire arrays. *ACS Nano* 4, 5869–5876.
- Shi, R., Ye, H.F., Liang, F., Wang, Z., Li, K., Weng, Y., Lin, Z., Fu, W.F., Che, C.M., Chen, Y., 2018. Interstitial P-Doped CdS with long-lived photogenerated electrons for photocatalytic water splitting without sacrificial agents. *Adv. Mater.* 30, 1705941.
- Skompska, M., 2010. Hybrid conjugated polymer/semiconductor photovoltaic cells. *Synth. Met.* 160, 1–15.
- Son, Y., Li, J., Peterson, R.L., 2016. In situ chemical modification of Schottky barrier in solution-processed zinc tin oxide diode. *ACS Appl. Mater. Interfaces* 8, 23801–23809.
- Steinrück, H.P., Libuda, J., Wasserscheid, P., Cremer, T., Kolbeck, C., Laurin, M., Maier, F., Sobota, M., Schulz, P., Stark, M., 2011. Surface science and model catalysis with ionic liquid-modified materials. *Adv. Mater.* 23, 2571–2587.
- Studenikin, S., Golego, N., Cocivera, M., 1998. Fabrication of green and orange photo-luminescent, undoped ZnO films using spray pyrolysis. *J. Appl. Phys.* 84, 2287–2294.
- Tamele, M., 1950. Chemistry of the surface and the activity of alumina-silica cracking catalyst. *Discuss. Faraday Soc.* 8, 270–279.
- Thanihachelvan, M., Loheeswaran, S., Balashangar, K., Velauthapillai, D., Ravirajan, P., 2019. Polymer/fullerene blend solar cells with cadmium sulfide thin film as an

- alternative hole-blocking layer. *Polymers* 11, 460.
- Tsao, H.N., Burschka, J., Yi, C., Kessler, F., Nazeeruddin, M.K., Grätzel, M., 2011. Influence of the interfacial charge-transfer resistance at the counter electrode in dye-sensitized solar cells employing cobalt redox shuttles. *Energy Environ. Sci.* 4, 4921–4924.
- Tseng, H.-W., Wilker, M.B., Damrauer, N.H., Dukovic, G., 2013. Charge transfer dynamics between photoexcited CdS nanorods and mononuclear Ru water-oxidation catalysts. *J. Am. Chem. Soc.* 135, 3383–3386.
- Turner, J.A., Parkinson, B.A., 1983. The application of chronocoulometry to the study of adsorption at the semiconductor/electrolyte interface. *J. Electroanal. Chem. Interfacial Electrochem.* 150, 611–617.
- Varadhan, P., Fu, H.-C., Priante, D., Retamal, J.R.D., Zhao, C., Ebaïd, M., Ng, T.K., Ajia, I., Mitra, S., Roqan, I.S., 2017. Surface passivation of GaN nanowires for enhanced photoelectrochemical water-splitting. *Nano Lett.* 17, 1520–1528.
- Wang, M., Anghel, A.M., Marsan, B., Cevey Ha, N.-L., Pootrakulchote, N., Zakeeruddin, S.M., Grätzel, M., 2009. CoS supersedes Pt as efficient electrocatalyst for triiodide reduction in dye-sensitized solar cells. *J. Am. Chem. Soc.* 131, 15976–15977.
- Wang, P., Zakeeruddin, S.M., Comte, P., Exnar, I., Grätzel, M., 2003. Gelation of ionic liquid-based electrolytes with silica nanoparticles for quasi-solid-state dye-sensitized solar cells. *J. Am. Chem. Soc.* 125, 1166–1167.
- Wang, P., Klein, C., Humphry-Baker, R., Zakeeruddin, S.M., Graetzel, M., 2005. A high molar extinction coefficient sensitizer for stable dye-sensitized solar cells. *J. Am. Chem. Soc.* 127, 808–809.
- Welton, T., 1999. Room-temperature ionic liquids. *Solvents for synthesis and catalysis. Chem. Rev.* 99, 2071–2084.
- Welton, T., 2004. Ionic liquids in catalysis. *Coord. Chem. Rev.* 248, 2459–2477.
- Widegren, M.B., Harkness, G.J., Slawin, A.M., Cordes, D.B., Clarke, M.L., 2017. A highly active manganese catalyst for enantioselective ketone and ester hydrogenation. *Angew. Chem. Int. Ed.* 56, 5825–5828.
- Wu, J.J., Lee, G.-J., 2018. *Advanced Nanomaterials for Water Splitting and Hydrogen Generation. In: Nanomaterials for Green Energy, Elsevier, pp. 145–167.*
- Xue, Q., Bai, Y., Liu, M., Xia, R., Hu, Z., Chen, Z., Jiang, X.F., Huang, F., Yang, S., Matsuo, Y., 2017. Dual interfacial modifications enable high performance semitransparent perovskite solar cells with large open circuit voltage and fill factor. *Adv. Energy Mater.* 7, 1602333.
- Yamasita, D., Takata, T., Hara, M., Kondo, J.N., Domen, K., 2004. Recent progress of visible-light-driven heterogeneous photocatalysts for overall water splitting. *Solid State Ion.* 172, 591–595.
- Yang, W., Prabhakar, R.R., Tan, J., Tilley, S.D., Moon, J., 2019. Strategies for enhancing the photocurrent, photovoltage, and stability of photoelectrodes for photoelectrochemical water splitting. *Chem. Soc. Rev.* 48, 4979–5015.
- Yang, F., Yan, N.-N., Huang, S., Sun, Q., Zhang, L.-Z., Yu, Y., 2012. Zn-doped CdS nanoarchitectures prepared by hydrothermal synthesis: mechanism for enhanced photocatalytic activity and stability under visible light. *J. Phys. Chem. C* 116, 9078–9084.
- Yao, B., Zhang, J., Fan, X., He, J., Li, Y., 2019. Surface engineering of nanomaterials for photo-electrochemical water splitting. *Small* 15, 1803746.
- Ye, M., Gong, J., Lai, Y., Lin, C., Lin, Z., 2012. High-efficiency photoelectrocatalytic hydrogen generation enabled by palladium quantum dots-sensitized TiO<sub>2</sub> nanotube arrays. *J. Am. Chem. Soc.* 134, 15720–15723.
- Yen, M.-Y., Teng, C.-C., Hsiao, M.-C., Liu, P.-I., Chuang, W.-P., Ma, C.-C.M., Hsieh, C.-K., Tsai, M.-C., Tsai, C.-H., 2011. Platinum nanoparticles/graphene composite catalyst as a novel composite counter electrode for high performance dye-sensitized solar cells. *J. Mater. Chem.* 21, 12880–12888.
- Yen, M.-Y., Hsieh, C.-K., Teng, C.-C., Hsiao, M.-C., Liu, P.-I., Ma, C.-C.M., Tsai, M.-C., Tsai, C.-H., Lin, Y.-R., Chou, T.-Y., 2012. Metal-free, nitrogen-doped graphene used as a novel catalyst for dye-sensitized solar cell counter electrodes. *RSC Adv.* 2, 2725–2728.
- Yu, F., Wei, P., Yang, Y., Chen, Y., Guo, L., Peng, Z., 2019a. Material design at nano and atomic scale for electrocatalytic CO<sub>2</sub> reduction. *Nano Mater. Sci.* 1, 60–69.
- Yu, F., Shi, Y., Yao, W., Han, S., Ma, J., 2019b. A new breakthrough for graphene/carbon nanotubes as counter electrodes of dye-sensitized solar cells with up to a 10.69% power conversion efficiency. *J. Power Sources* 412, 366–373.
- Yue, G., Lin, J.-Y., Tai, S.-Y., Xiao, Y., Wu, J., 2012. A catalytic composite film of MoS<sub>2</sub>/graphene flake as a counter electrode for Pt-free dye-sensitized solar cells. *Electrochim. Acta* 85, 162–168.
- Yue, G., Wu, J., Xiao, Y., Lin, J., Huang, M., Lan, Z., Fan, L., 2013. Functionalized graphene/poly (3, 4-ethylenedioxythiophene): polystyrenesulfonate as counter electrode catalyst for dye-sensitized solar cells. *Energy* 54, 315–321.
- Zakeeruddin, S.M., Grätzel, M., 2009. Solvent-free ionic liquid electrolytes for mesoscopic dye-sensitized solar cells. *Adv. Funct. Mater.* 19, 2187–2202.
- Zhang, S., Jin, J., Li, D., Fu, Z., Gao, S., Cheng, S., Yu, X., Xiong, Y., 2019a. Increased power conversion efficiency of dye-sensitized solar cells with counter electrodes based on carbon materials. *RSC Adv.* 9, 22092–22100.
- Zhang, L., Jin, Z., Ma, X., Zhang, Y., Wang, H., 2019b. Properties of iron vanadate over CdS nanorods for efficient photocatalytic hydrogen production. *New J. Chem.* 43, 3609–3618.
- Zhang, D., Liu, L., Zhang, L., Qi, K., Zhang, H., Cui, X., 2017. An anti-photocorrosive photoanode based on a CdS/NixSy@NF heterostructure for visible-light-driven water splitting. *Appl. Surf. Sci.* 420, 161–166.
- Zhang, J., Yu, J., Zhang, Y., Li, Q., Gong, J.R., 2011. Visible light photocatalytic H<sub>2</sub>-production activity of CuS/ZnS porous nanosheets based on photoinduced interfacial charge transfer. *Nano Lett.* 11, 4774–4779.
- Zhao, D., Wu, M., Kou, Y., Min, E., 2002. Ionic liquids: applications in catalysis. *Catal. Today* 74, 157–189.
- Zhou, Q., Shi, G., 2016. Conducting polymer-based catalysts. *J. Am. Chem. Soc.* 138, 2868–2876.
- Zhu, M., Sun, Z., Fujitsuka, M., Majima, T., 2018. Z-scheme photocatalytic water splitting on a 2D heterostructure of black phosphorus/bismuth vanadate using visible light. *Angew. Chem. Int. Ed.* 57, 2160–2164.
- Zou, Z., Ye, J., Sayama, K., Arakawa, H., 2001. Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature* 414, 625.
- Zyoud, A., Zaatari, N., Saadeddin, I., Helal, M.H., Campet, G., Hakim, M., Park, D., Hilal, H.S., 2011. Alternative natural dyes in water purification: anthocyanin as TiO<sub>2</sub>-sensitizer in methyl orange photo-degradation. *Solid State Sci.* 13, 1268–1275.
- Zyoud, A., Saa'deddin, I., Khudruj, S., Hawash, Z.M., Park, D., Campet, G., Hilal, H.S., 2013. CdS/FTO thin film electrodes deposited by chemical bath deposition and by electrochemical deposition: a comparative assessment of photo-electrochemical characteristics. *Solid State Sci.* 18, 83–90.
- Zyoud, A., Al-Kerm, R.S., Al-Kerm, R.S., Waseem, M., Mohammed, H.H., Park, D., Campet, G., Sabli, N., Hilal, H.S., 2015. High PEC conversion efficiencies from CuSe film electrodes modified with metalloporphyrin/polyethylene matrices. *Electrochim. Acta* 174, 472–479.
- Zyoud, A., Alkerm, R.S., Alkerm, R.S., Park, D., Helal, M.H., Campet, G., Muthaffar, R.W., Kwon, H., Hilal, H.S., 2016. Enhanced PEC characteristics of pre-annealed CuS film electrodes by metalloporphyrin/polymer matrices. *Sol. Energy Mater. Sol. Cells* 144, 429–437.
- Zyoud, A., Abdul-Rahman, N.N., Campet, G., Park, D., Kwon, H., Kim, T.W., Choi, H.-J., Helal, M.H., Hilal, H.S., 2016. Enhanced PEC characteristics for CdSe polycrystalline film electrodes prepared by combined electrochemical/chemical bath depositions. *J. Electroanal. Chem.* 774, 7–13.
- Zyoud, A.H., Doa'hi, A., Helal, M.H., Zyoud, S.H., Bsharat, H., Abu-Alrob, S.M., Sabli, N., Qamhieh, N., Hajamohideen, A.R., Hilal, H.S., 2019. Enhancement of electrochemically deposited pristine CdTe film electrode photoelectrochemical characteristics by annealing temperature and cooling rate. *Optik* 163220.
- Zyoud, A., Saadeddin, I., Khurduj, S., Mari'e, M.m., Hawash, Z.M., Faroun, M.I., Campet, G., Park, D., Hilal, H.S., 2013. Combined electrochemical/chemical bath depositions to prepare CdS film electrodes with enhanced PEC characteristics. *J. Electroanal. Chem.*, vol. 707, pp. 117–121.