

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

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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

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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_2 , 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_2 , 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 ΔH , entropy change ΔS or free energy ΔG) 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_2/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.

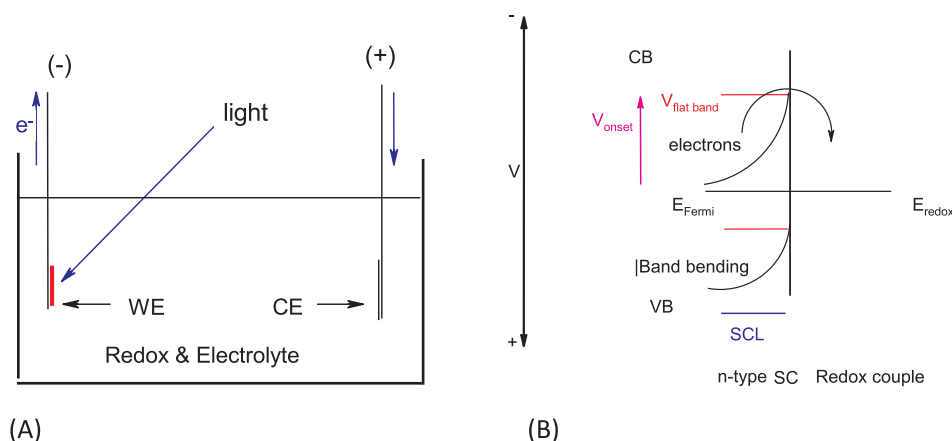


Fig. 1. Schematic PEC systems showing (A) a PEC solar cell involving a monolithic SC working electrode (WE) with another counter electrode (CE) dipped inside a Redox couple solution and (B) Band bending and energetics at SC electrode/Redox couple interface.

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 (η), 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 η 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-

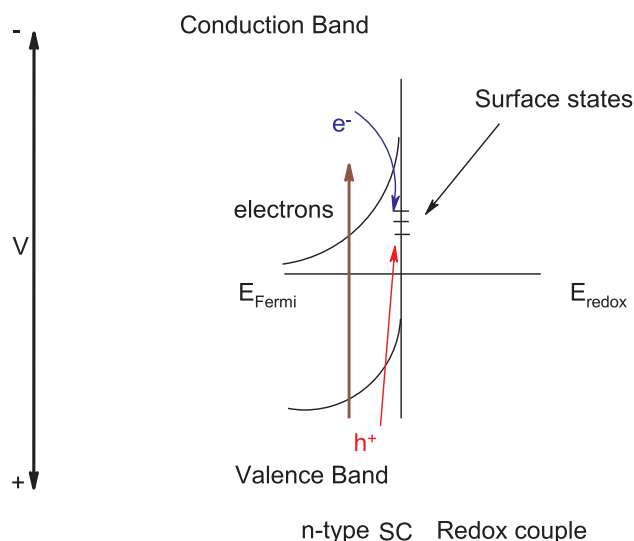


Fig. 2. Surface state formalism and electron-hole recombination in PEC processes.

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_{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 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, 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 H_2 , while the hole oxidizes water to 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

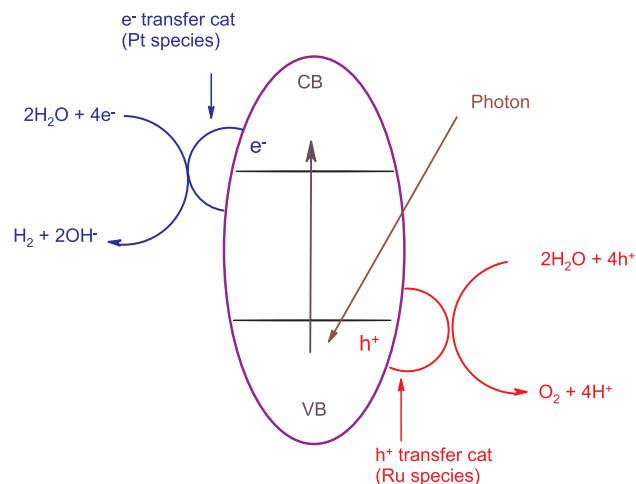


Fig. 3. Schematic for charge transfer catalysis in water splitting by Pt and Ru species.

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 (Ramamy *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/TiO₂ 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/TiO₂ 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/TiO₂ 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 TiO₂ 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

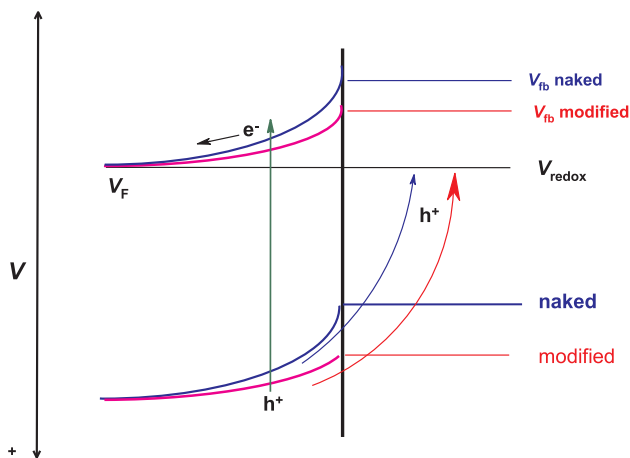


Fig. 4. Lowering of flat band edge positions shifted by attaching positive charges to a SC electrode.

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

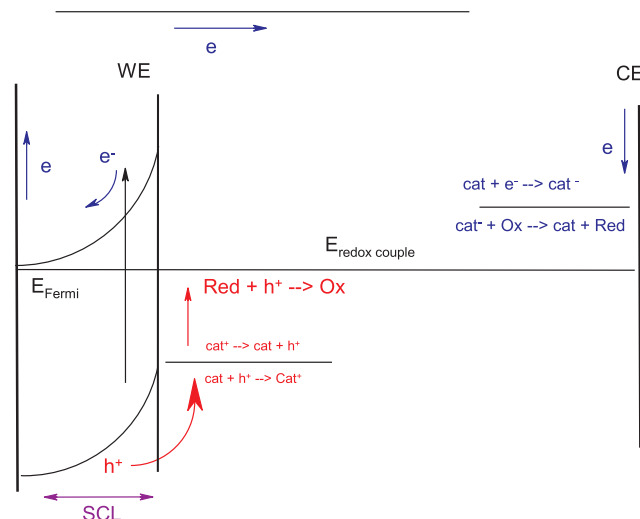
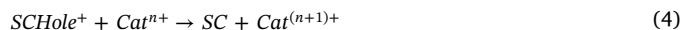


Fig. 5. Effect of charge transfer catalysts at both n-type SC working electrode and counter electrode in a PEC cell.

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.

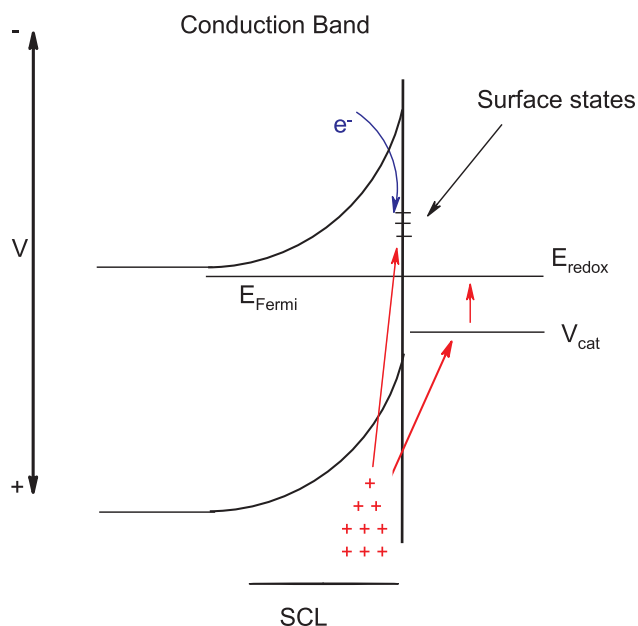


Fig. 6. Competition between SC surface photo-corrosion and charge transfer across SC/Catalyst junction. Surface states encourage SC photo-corrosion. The Schematic shows n-type SC working electrodes.

As described in literature above, one catalyst may be needed for the working electrode and another for the counter electrode. This is explained in Eqs. (4)–(7) where M and M' denote different catalysts. However, this does not rule out the possibility to develop one catalyst that may effectively function at both electrodes. Note that Eqs. (4) through (7) represent a regenerative process with no net chemical change. It is necessary here to know that the charge transfer catalyst does not affect the thermodynamics of the PEC cell. This is a basic principle in catalysis technology as explained in Section 3.1. Even if the catalyst (with a charge) affects the flat band edge position, as explained above, it does not affect the thermodynamics of the process. This is because the energy band levels outside the SCL layer are not affected by the charged species. The mere function for the catalyst is to speed up the charge transfer between the electrode and the Redox couple. Thus, the catalyst undertakes only a kinetic role simply by providing a new path for charge transfer with lower E_{act} .

(4) SC electrode photo-corrosion prevention: As stated above, if holes accumulate in the working electrode SCL, with their enough positive potential, they can oxidize the SC electrode itself. As described in Fig. 6 for an n-type SC working electrode, if the hole direct transfer to Redox couple is slow, hole accumulation occurs. Such accumulation is troublesome and causes photo-corrosion. The holes may also create more surface states at the electrode, which in turn lower photocurrent and induce more electrode photo-corrosion. All such unwanted processes should be avoided to enhance photocurrent and prevent electrode photo-corrosion. Using a suitable charge transfer catalyst at the SC electrode surface may speed up hole transfer, prevent hole accumulation, improve photocurrent and prevent photo-corrosion. Therefore, charge transfer has at least a dual function here.

As stated above, for the charge transfer catalyst to function, its oxidation potential must be above (more negative) than the flat band edge of the electrode VB. Otherwise, if its oxidation potential is lower than the VB level, the catalyst does not function. Therefore, the proper choice for the catalyst should be made carefully. Tailoring the flat band edge position may solve out this difficulty. For instance, if the catalyst oxidation potential is lower than the flat band edge position, then lowering the band edge position makes it possible for holes to reach the catalyst. Fig. 7 summarizes these ideas. This can be achieved by using a charge transfer catalyst with positive charge. In such a case, the

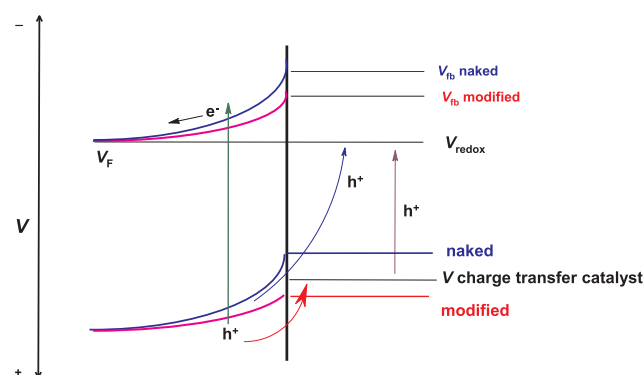


Fig. 7. Ability of charge transfer catalyst (with positive charge) to lower SC electrode band edge position. Hole transfer to the catalyst becomes possible.

presence of the catalyst has a three-fold function, namely lowering band edge position, speeding up charge transfer across the electrode/Redox couple junction and preventing electrode photo-corrosion.

As an example, in tetra(-4-pyridyl)porphyrinatomanganese(III/II), $[Mn(TPPyP)]^{n+}$, the manganese ions exist in both 2+ and 3+ mixed states. (Hilal and Turner, 2006; Hilal et al., 2004; Zyoud et al., 2015; Sabri et al., 2014; Zyoud et al., 2016). The manganese ion may be easily oxidized (from 2+ to 3+) by a hole and reduced (from 3+ to 2+) by a hole loss to the Redox couple. After being oxidized (by holes in SCL) the catalyst may relay the positive charge to solution Redox couple. The complex ion may then be able to behave as charge transfer catalyst that increases photocurrent and prevent photo-corrosion. If additional charges are present at one or more porphyrin rings, by quaternization reactions, the complex ion can lower flat band edge position. All such functions have been reported for $[Mn(Tppy)]^{n+}$ species in cases of monolithic (Hilal and Turner, 2006; Hilal et al., 2002, 2004, 2003) and polycrystalline film electrodes (Hilal et al., 2004; Zyoud et al., 2015; Sabri et al., 2014; Zyoud et al., 2016; Hilal et al., 2017).

In some reports (AbdelHadi, 2016), attaching charged species/polymer composites showed PEC performance lowering. However, the results showed that changing the polymer itself affects PEC performance. This means that more optimizing study is needed to find best parameters for the composite (polymer type, catalyst concentration, catalyst type and film thickness) that yield highest PEC performance for a given metal chalcogenide film electrode. Moreover, the performance decrease could be due to lowering in SC electrode band edge positions which consequently lowers the V_{OC} value as described earlier (Hilal and Turner, 2006). In such a case, a compromise between increased J_{SC} and lowered V_{OC} values should be considered.

Collectively, literature shows that suitable charge transfer catalysts in film electrode PEC processes enhance solar cell performance. Charge transfer catalysts at both working and counter electrodes were reported for DSSC cells. In metal chalcogenide film working electrodes, charge transfer catalysis have been described, to a lesser extent than DSSCs. While charge transfer catalysis at DSSC counter electrodes have been widely described, counter electrode modifications in metal chalcogenide PEC cells have not been reported and need to be addressed in future research. Table 1 shows examples of PEC enhancements by simple modification of cell electrodes.

4. Conclusion

Polycrystalline film electrodes are heavily assessed in regenerative PEC solar energy processes. While such film electrodes are advantageous over conventional p-n junction PV processes, they still suffer two major drawbacks, namely low conversion efficiency and low stability to photo-corrosion. Different strategies are followed to enhance polycrystalline film electrode PEC characteristics, such as using charge transfer catalysts at the working electrode (in DSSCs and metal

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}/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)	
	FTO/Pt & poly(3,4-ethylenedioxythiophene) (PEDOT)				10.3	Tsao et al. (2011)
	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)	
	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 ₂ /PCBM:P3HT**	(9.0)	(0.33)		(2.0)		
CdS quantum dots/P3HT nanowires**				4.1	Ren et al. (2011)	
With chemical graphping and without chemical graphping				(0.6)		
GaN nano-wires with 1,2-ethanedithiol and without				18	Varadhan et al. (2017)	
				(8)		
DSSC, TiO ₂ 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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