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Titanium Dioxide Modifications for Energy Conversion: Learnings from Dye-Sensitized Solar Cells

Hammad Cheema and Khurram S. Joya

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Abstract

During the last two and half decade modifying anatase TiO_2 has appreciably enhanced our understanding and application of this semiconducting, non-toxic material. In the domain of DSCs, the main focus has been to achieve band adjustment to facilitate electron injection from anchored dyes, and high electronic mobility for photo-generated electron collection. In retrospection, there is a dire need to assimilate and summarize the findings of these studies to further catalyze the research, better understanding and comparison of the structure–property relationships in modifying TiO_2 efficiently for crucial photocatalytic, electrochemical and nanostructured applications. This chapter aims at categorizing the typical approaches used to modify TiO_2 in the domain of DSCs such as through TiO_2 paste additives, TiO_2 doping, metal oxides inclusion, dye solution co-adsorbing additives, post staining surface treatment additives and electrolyte additives. A summary of the consequences of these modifications on electron injection, charge extraction, electronic mobility, conduction band shift and surface states has been presented. This chapter is expected to hugely benefit the researchers employing TiO_2 in energy, catalysis and battery applications.

Keywords: modification, co-adsorption, surface treatment, recombination, electron lifetime, electronic mobility, photovoltage

1. Introduction

Global energy demand is expected to increase from 18 TW in 2013 to 50 TW in 2050, along with corresponding increase in CO_2 emissions due to inevitable increase in population and industrialization in the developing world [1, 2]. So far, most of the energy (~80%) have been derived from fossil fuels, which is not sustainable and detrimental to the environment [2]. Thus,

sustainable and fossil-free pathways for producing clean energy and fuels such as conversion of sunlight to electricity and molecules in atmosphere, e.g., water, CO_2 and nitrogen, to H_2, hydrocarbons and ammonia respectively are highly required [3–8]. In this regard, dependence on renewable energy sources such as solar, wind and hydroelectric has been strategically deployed from last few decades with reasonable effect [5, 7]. Among all the renewable energy sources, solar energy is the most potent and exploitable source [9]. However, in order to achieve large scale, cost effective, carbon neutral supply of energy from sun; capture, conversion and storage of energy should be highly efficient and cost effective [6, 9]. In this regard, photovoltaics (PVs) are playing a substantial role in harnessing the sun energy mainly dominated by silicon based solar cells at present. However, manufacturing of silicon PVs require high temperature (>1600°C for silicon melting) and ultra-pure materials, thus adding to the manufacturing complexity and cost [10]. Additionally, the scarcity of silver, a common electrode material greatly limits to meet the future terawatt challenge. This have motivated researchers around the globe to develop strategies for solar energy conversion based on abundant, non-toxic, easy to process, commercially viable and cost effective systems. In this regard solar PVs prepared from mesoscopic metal oxides such as (TiO_2, ZnO, SnO_2, etc.) and organic light absorbing materials could meet the criteria as a suitable alternative, provided high efficiency can be realized. Metal oxide serves as an electron acceptor and facilitates the transport of electrons, along with being a scaffold for the adsorption of light harvesting constituents in many cases [11, 12]. Out of different metal oxides, mesoscopic (10–50 nm size pores) titanium dioxide (TiO_2) by far has been the most widely studied and employed owing to ease process-ability, chemical stability, high surface area, low cost and non-toxic nature. [12–15] Out of the four naturally occurring polymorphs of TiO_2, anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and TiO_2 (monoclinic), anatase is preferred for PV's applications because of higher conduction band energy and slower recombination rate of charge carriers [16–18].

In terms of mesoscopic-TiO_2 based solar cells, dye-sensitized solar cells (DSCs) are the most widely studied with recent surge in research for perovskite solar cells [12, 19, 20]. The discussion in the remaining chapter will be with the reference to DSCs employing TiO_2 as electron accepting and transport layer. The seminal report of 1991 on TiO_2 based DSCs by Grätzel and O' Regan has garnered more than 26,500 citations (November 2017) highlighting the plethora of knowledge generated and wide spread interest of scientific community [11]. It should be noted that nanocrystalline morphology which goes through necking as the result of sintering and lead to mesoscopic film of TiO_2 is essential for the efficient operation of the DSCs, since a monolayer of sensitizer on flat metal oxide surface only absorb small portion of incident light [13]. Realization of this important nanostructure requirement aspect enhanced the adsorption and subsequent light harvesting in DSCs by molecular sensitizers or dyes more than 1000 time [13]. This enabled DSCs only system where charge generation (sensitizer) and transport (semiconductor) is performed by separate components. [14] DSCs are attractive compared to other photovoltaic technologies in terms of economic advantage, tunability of color, can be built on rigid and flexible substrates, made of benign materials such as TiO_2 and metal free organic dyes, offer sustained efficiency for indoor applications, and perform independently of the angle of incidence [11, 12, 21–24]. Current, DSC record power conversion efficiency (PCE) up

to 14.3% has been demonstrated by judicious choice of co-sensitizing organic photosensitizers having strong binding to TiO_2 and broad absorption, post staining surface capping and tailored solution based redox shuttle and electrolyte additives [25]. However, for further improvement in PCE (1) sensitizers with efficient conversion of absorbed photons to electrons (400–900 nm), particularly beyond 650 nm (2) redox shuttles with photovoltage output greater than 1.2 V (3) minimized recombinations and over potential losses and (4) optimized tandem devices are highly required [26–29].

The standard components of a typical DSC embodiment are (1) FTO (fluorine doped tin oxide) deposited on glass substrate (2) mesoscopic TiO_2 film (3) sensitizer, organic or metal complex anchored to TiO_2 (4) mediator, to regenerate the dye (5) counter electrode with platinum (pt) to reduce the mediator (**Figure 1**). Upon illumination the sensitizer gets photo-excited and injects an electron in the conduction band (CB) of TiO_2 thus generating an electric potential difference. This injected electron then diffuses through the mesoporous TiO_2 where it is extracted to outer circuit at photoanode. Meanwhile the oxidized sensitizer is regenerated by the redox mediator, whereas the extracted electron travels through the load to the counter electrode, which then transfers electron to the mediator. At the interface boundary, back electron transfer to the oxidized dye and recombination with the electrolyte has been known the most drastic events which lower the performance along with inefficient light absorption beyond 650 nm [13, 14]. On the same note before printing the mesoporous TiO_2 film a compact TiO_2 layer (mostly from aqueous $TiCl_4$ solution) is deposited on the FTO glass which prevents the short circuiting of the device, improves adhesion of TiO_2 nanoparticles and minimizes the direct contact of electrolyte with FTO [30–32]. In terms of characterization of DSCs, two important measurements are short photocurrent-density (J_{sc}) and open circuit voltage (V_{oc}) curve also known as
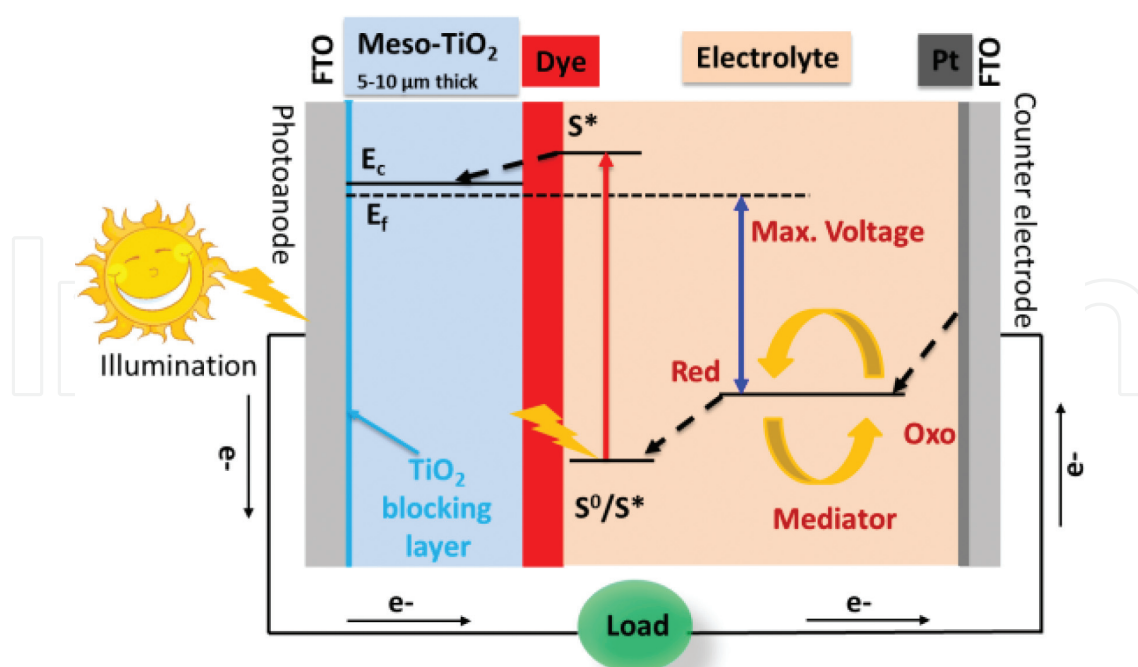

Figure 1. Operational principle of DSCs.

J-V curve and incident photon to current conversion efficiency (IPCE) or EQE (external quantum efficiency). IPCE depicts the photocurrent density response of the device at monochromatic wavelength and depends on the same parameters as J_{sc} [33].

J-V curve is measured by scanning the voltage across the device from 0 to higher voltage (forward bias) or higher to zero voltage (reverse bias) either with a source meter or a potentiostat. Power conversion efficiency (PCE) of the cells, the main performance metric is then calculated according to the equation, PCE = $(J_{sc}V_{oc} FF)/I_0$, where *FF* is the fill factor which is simply the measure of the squareness of the *J-V* curve, and depicts the electrochemical losses in the device with value between 0 and 1 (normally between 0.65 and 0.75 for DSCs) [34]. I_0 is the power input for the incident irradiation which is normally 1 sun (100 mW/cm^2). A high performing DSC should behave an ideal diode with infinite shunt resistance and minimum series resistance which will lead to higher *FF* and PCE ultimately [13]. Briefly, J_{sc} α LHE.φ_{inj}.φ_{reg}.η_{coll}, where LHE is light harvesting efficiency of sensitizer on given thickness of TiO_2, φ_{inj} and φ_{reg} are the quantum yield of electron injection and dye regeneration and η_{coll} is the charge collection efficiency [12].

In **Figure 2**, thermodynamic requirements for electron injection (up to 300 mV) and dye regeneration (100–500 mV) overpotential has been shown. Dotted lines highlight the unwanted recombination reactions with redox shuttle (10^{-2} sec) and oxidized sensitizer (10^{-4} sec) also known as "dark current" [12, 35, 36]. Kinetically, electron injection happens in 100 s of pico seconds and vary with sensitizer, with usual ms to µs range of recombination with electrolyte and oxidized dye, respectively. [24] Tuning of electrochemical properties of sensitizers (Ru (II), organic, and porphyrin) with optimized geometry offering higher light absorption and minimum aggregation and redox shuttles (iodide/triiodide, cobalt and copper) has been widely studied for DSCs with the aim of minimum overpotential loss, broad absorption and higher PCE [37–40]. Interested readers are encouraged to consult the more detailed reviews on design principles of sensitizers and redox shuttles for DSCs [21, 33, 40–43].
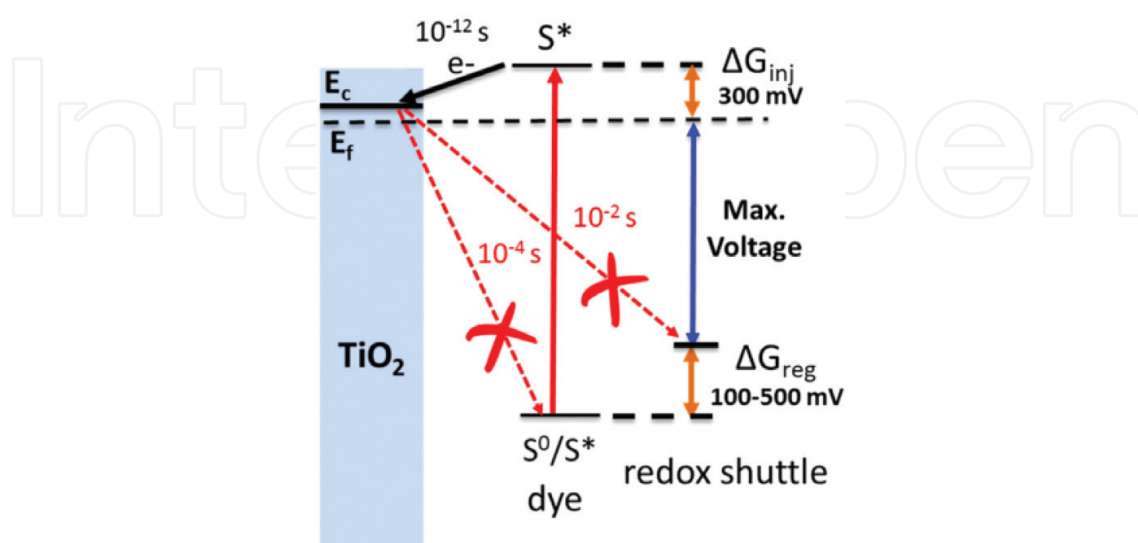

Figure 2. Energy level diagram, overpotential requirements and typical time constants.

J_{sc} can be increased by molecular engineering of the sensitizer, with ideal ground and excited state energetics, high molar absorptivity, and aggregation less anchoring on TiO$_2$ [12]. V_{oc} is the energy difference between the TiO$_2$ fermi level and the redox potential of the mediator and depends on the electron density in TiO$_2$. Higher V_{oc} can be achieved by minimization of the dark current, increase in electron injection, negative (upward) shift in the energy of the conduction band, positive (downward) shift in the energy of the redox shuttle and series connection of devices [35, 44]. Both V_{oc} and FF are hugely related to recombination reactions (dark current) and can be substantially influenced by modification of TiO$_2$ in the presence of additives *vide infra*. Along with *J-V* and IPCE measurements, electrochemical impedance spectroscopy (EIS) and small modulation photovoltage transient measurements have been widely employed to fully characterize the devices. Readers are kindly referred to the previously published reviews to learn about these powerful techniques to characterize interface and charge transfer properties [45–48].

In terms of achieving higher efficiency by modification of TiO$_2$ the main objective is to minimize the recombination losses by blocking the TiO$_2$ surface, increase in electron injection by manipulation of TiO$_2$ CB, aid in better orientation, structure and geometry of the dyes on TiO$_2$ and suppression of dye aggregation and stacking. This enhancement of DSCs devoid of dye and electrolyte designing and arduous manipulations of their molecular structures can be achieved by (1) TiO$_2$ paste additions (2) dye solution co-adsorbing additives (3) post staining surface treatment additives and (4) electrolyte additives (**Figure 3**). This chapter is now further divided into sections as shown in **Figure 3**. to integrate and analyze the most successful strategies, their role in enhancing DSCs performance, similarities among different approaches and discussion of proposed mechanisms.

It is crucial to highlight that just like dyes for DSCs most of the additives will require an anchoring group for immobilization on TiO$_2$, other than plasmonic nanoparticles and composite of TiO$_2$ NPs (Section 1, which become the intrinsic part of TiO$_2$ NPs after sintering also termed as "hard modification"). The most widely used anchoring groups are same as dyes, e.g., carboxylic acid, phosphonic/phosphinic acid, pyridine, and most recently siloxanes. Though multitude of anchoring modes such as covalent attachment, hydrogen bonding, electrostatic interaction, van der Waals interaction and physical entrapment has been proposed [49]. It is important to notice that these anchoring systems should also facilitate the electron transfer. Additionally, due to structural complexity of the interface environment several models are used to elucidate the anchoring. For physical characterization of interface Fourier
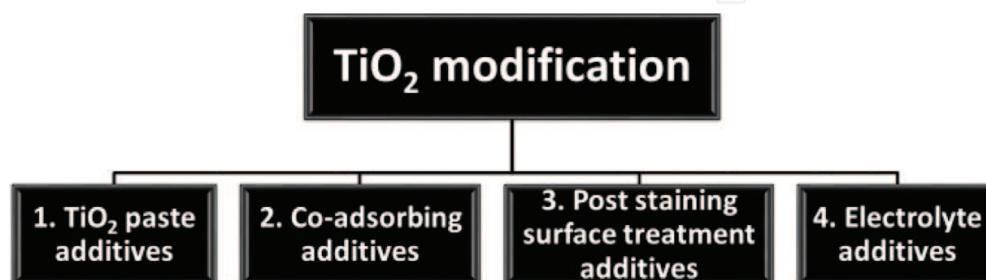

Figure 3. Summary layout for TiO$_2$ modification approaches.

transform infrared spectroscopy (FT-IR) and photoelectron spectroscopy (PES) are mainly employed [50]. However for anchoring on TiO_2 for the well-known carboxylic acid, (similarly anchoring phosphonic/phosphinic acid, siloxane, etc.) (**Figure 4**) covalent interaction can only offer the strongest coupling for stable anchoring with ester type bonds or metal complexation for pyridine additives [51]. For an in depth analysis of anchoring mode and surface adsorption for different anchoring groups, readers are kindly referred to reviews published previously [49, 51].

For efficient light harvesting different kinds of TiO_2 pastes (active layer for dye anchoring with scattering or reflective layer on top of it) are used for achieving specific features such as iodide/triiodide systems mainly employ 18–20 nm size NPs based formulations, whereas for larger size redox shuttles such as cobalt and copper based systems 28–31 nm size NPs are employed [52, 53]. This selectivity comes from the mass-transport related limitations of outer sphere based redox shuttles (cobalt and copper) which is mitigated by the larger pore size of bigger NP size based TiO_2 films [54]. On top of active layer, 4–5 μm thick scattering or reflective layer is printing with NPs size of >100 nm, to back scatter light into the cell.

1.1. Scope

Though synthesis and preparation of TiO_2 paste for film formation has historical importance, however, at this stage more than 95% of the studies employ a commercially available TiO_2 paste which is developed after years of research and employ patented methods [53, 55]. However, design of morphologically new structures, and development of efficient synthesis routes for anatase TiO_2 is an active area to achieve higher loading, better charge transport, and minimum recombinations losses [18]. For this chapter please be referred to commercially available TiO_2 (transparent 18–20 nm from Dyesol or Solaronix, or 30–31 from Dyesol or Dyenamo nm particle size for active layer and > 100 nm size for scattering layer from Dyesol, Solaronix and Dyenamo) for improvement [56–58]. With ready to use TiO_2 paste in hand, its light absorption properties can be enhanced by simple mixing in systematic way with silver
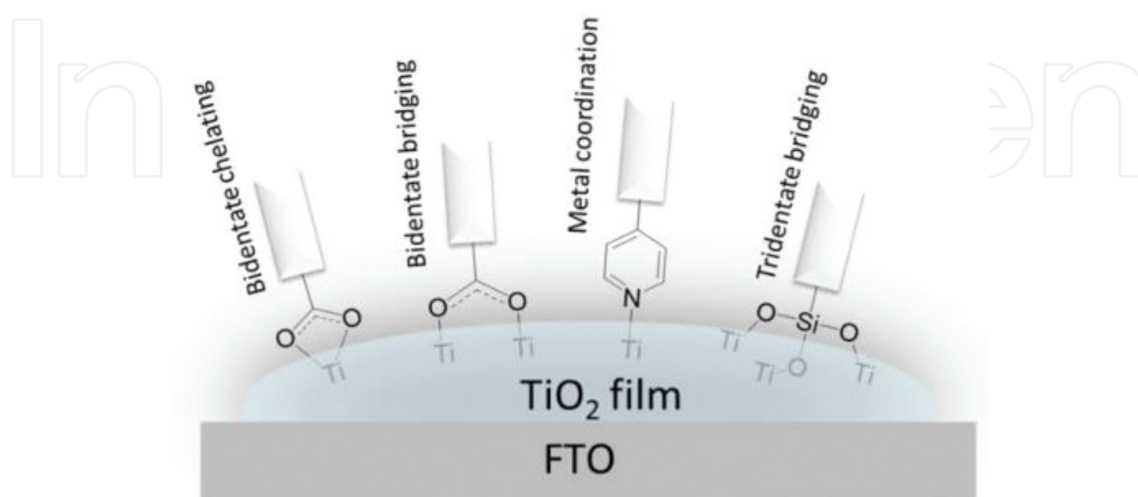
Figure 4. Depiction of anchoring mode of general additives for TiO_2 modifications.

and gold nanoparticles (Section 1). Additionally, different types of TiO_2 geometries such as nanotubes (NTs) and hollow spheres can be mixed with nanoparticles (NPs) to achieve higher loading (Section 1.2 and 1.3). An important class of additives to modify and enhance the interface properties of TiO_2 is the addition of electronically insulating molecules with anchoring groups (Section 2). Quite recently, simple surface treatment by chemical bath method on dye anchored TiO_2 (stained) films has been explored with impressive enhancements, such strategies are discussed in Section 3. Historically, most widely studied approach in regard to enhancement of DSCs and modification of TiO_2 is the introduction of new electrolyte additives including solvent, surface and recombination blocking pyridines and different anchoring groups, which are discussed in Section 4. At the end an overall perspective on the state of DSCs and the role of learnings to other fields is analyzed.

2. TiO_2 paste modifications

Integration of subwavelength plasmonic nanostructures and morphologically varied mesoporous films of TiO2 have been widely explored for enhancing DSCs performance. Hard modification of TiO2, such as sintering step is required at high temperature (500 0C) to activate the functionality are discussed below.
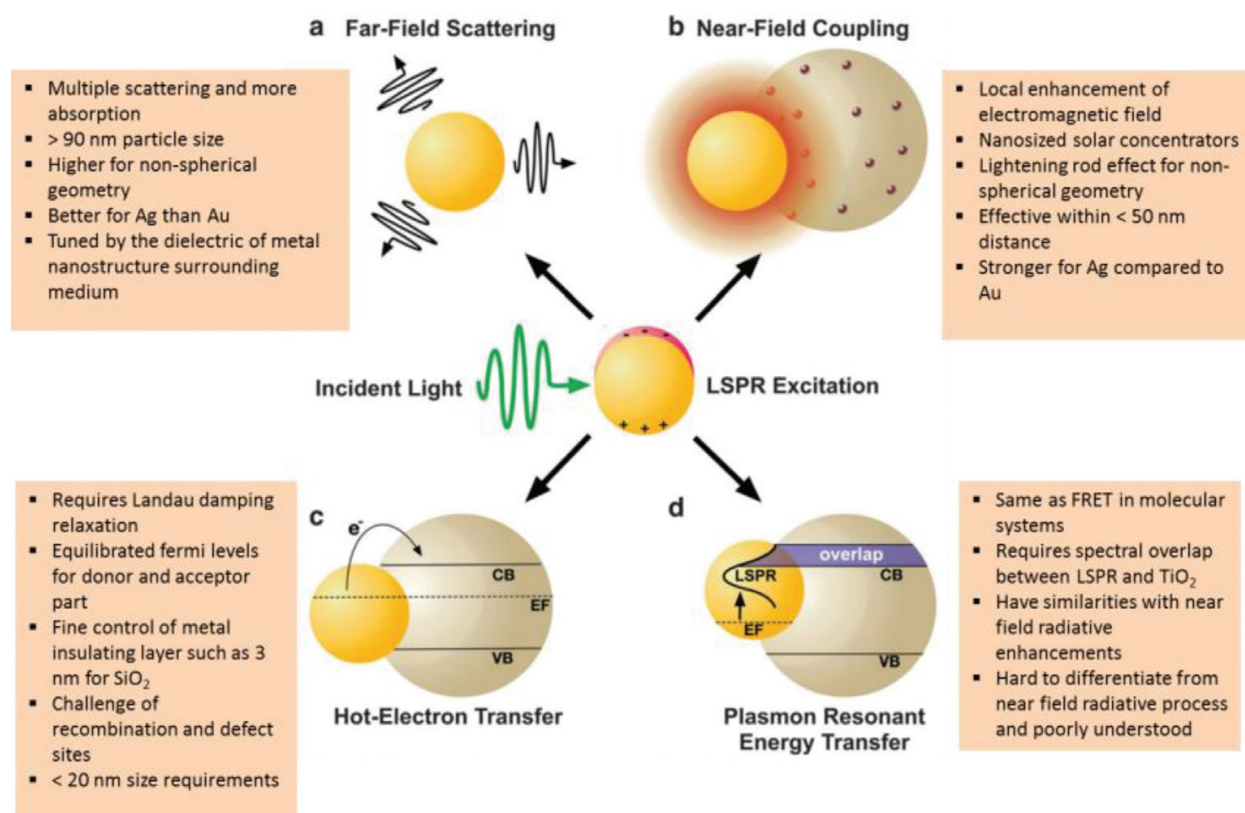
2.1. Plasmonic enhancement of DSCs

Plasmonic enhancement or light entrapment in DSCs by means of the plasmonic resonance of metal nanostructures has been a topic of intense research in the last decade. Since the first report in 2000 of metal nanostructured mediated enhancements in DSCs, many successful studies has been published outlining the role of size, shape and composition of metal nanoparticles on DSCs performance and working mechanisms [59–61]. Metal nanostructures capable of surface plasmon such as Au and Ag has been systematically introduced with TiO_2 NPs. Such as these nanoparticles can be designed and integrated in TiO_2 NPs in a way to offer light entrapment from visible to NIR region [62].

In plasmonic materials the coupling of incident photons to conduction band electrons upon excitation give rise to collective oscillations of electrons defined as *localized surface plasmon resonances* (LSPR) [63, 64]. By the engineering of plasmonic nanostructure's geometry, dimensions and composition LSPR's radiative (hot electron transfer, plasmon resonant energy transfer) and non-radiative (far-field scattering >50 nm size, near field coupling 3–50 nm size) processes can be tailored (**Figure 5**) [55, 56]. Out of four processes summarized in **Figure 5** far-field scattering and near field coupling are easily observed for DSCs such as by improvement in IPCE, whereas role of hot electron transfer and PRET to improve DSCs is thus far poorly explored [62]. Detailed discussion of each process and its implications for DSCs are beyond the scope of this chapter [62, 65].

In radiative effects metal nanostructure acts as a secondary light source and in non-radiative effects absorbed energy is subsequently transferred to neighboring semiconductor NPs (**Figure 5**).

a Far-Field Scattering

- Multiple scattering and more absorption
- > 90 nm particle size
- Higher for non-spherical geometry
- Better for Ag than Au
- Tuned by the dielectric of metal nanostructure surrounding medium

b Near-Field Coupling

- Local enhancement of electromagnetic field
- Nanosized solar concentrators
- Lightening rod effect for non-spherical geometry
- Effective within < 50 nm distance
- Stronger for Ag compared to Au

Incident Light　**LSPR Excitation**

c Hot-Electron Transfer

- Requires Landau damping relaxation
- Equilibrated fermi levels for donor and acceptor part
- Fine control of metal insulating layer such as 3 nm for SiO_2
- Challenge of recombination and defect sites
- < 20 nm size requirements

d Plasmon Resonant Energy Transfer

- Same as FRET in molecular systems
- Requires spectral overlap between LSPR and TiO_2
- Have similarities with near field radiative enhancements
- Hard to differentiate from near field radiative process and poorly understood

Figure 5. Summary of radiative (a) and (b) and non-radiative LSPR-based processes and their features, modified from reference [62], with permission from the Royal Society of Chemistry.

For LSPR based enhancement of DSCs the size of the metal nanoparticles plays huge role. Such as at 5 nm regime of metal nanostructure non-radiative processes are dominant, near field coupling for 45 nm size regime and far field scattering for 120 nm size metal nanostructures [62]. In terms of application, some reports evidence the beneficial effect of topical presence of plasmonic nanoparticles on TiO_2 film, however, homogenous integration of plasmonic nanoparticles throughout active layer have proven more efficient, particularly in enhancing photocurrent response of devices (**Figure 6**) [67, 68].

The highest PCE achieved through plasmonic enhancements so far (2013) is 10.8% which is 30% higher (8.3% PCE) than the control device employing **N719** sensitizer by Belcher et al.. with 0.01–0.32% core shell particles mixed with regular TiO_2 [61]. In this study, oxide-metal-oxide multiple core-shell nanostructured spheres were blended with already available photoactive materials to achieve balanced light harvesting in panchromatic fashion. Kamat et al.. in a pioneering work (2012) identified the plasmonic and charging effect based on the composition of $Au@SiO_2$ and $Au@TiO_2$, leading to achieve a higher photocurrent and photovoltage with overall PCE of 10.2 and 9.7%, respectively [60]. Au nanoparticles of 5 nm size were used in the core with shell as passivation layer of either SiO_2 or TiO_2 and mixed with Solaronix T/SP paste in 0.7 wt%. Wang et al in 2013, in a unique study employed the organic sensitizer **FNE29** and I^-/I_3^-, along with TiO_2 inlaid 2 nm sized Au nanoparticles resulting in 10.1% PCE improved from 5.5% PCE (84% increase) [66]. Au nano colloid in 0–0.8 wt% ratio
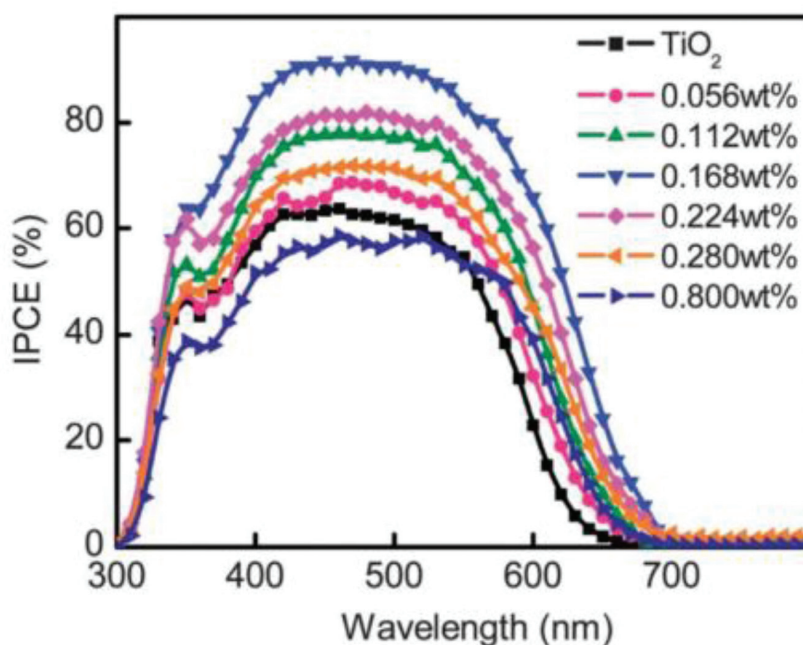
Figure 6. Effect of ~2 nm sized inlaid Au NPs with different wt% in TiO_2 paste on IPCE, adopted from Ref. [66], with permission from the Royal Society of Chemistry.

was blended with TiO_2 paste to constitute the active layer (**Figure 6**). With most prominent current report, DSCs employing organic dye (**FNE29**) compared to Ru (II) dyes for plasmonic enhanced DSCs are rare. With the survey of reports published so far it is clear that though plasmonics has led to increased device efficiencies however, reports lack (1) application of non-precious metal plasmonics for enhanced DSCs such as Al, graphene and semiconducting nanocrystal plasmonics (2) application of metal nanoparticles in conjunction with high photovoltage redox shuttles such as Co (III/II) or Cu (II/I) and organic sensitizers (3) long term stability studies particularly against redox shuttles for corrosion and chemical resistance of plasmonic DSCs [69–74].

2.2. Morphological investigation on TiO_2

NP based mesoporous TiO_2 shows excellent features for DSCs however it suffers from low electrical conductivity and charge recombination losses [75–78]. Additionally, enhanced light scattering and dye adsorption can be achieved by modifying the shape of NPs or mixing nanotubes, nanowires, nanospheres, and hollow TiO_2 [58, 77–81]. On the same note, 2D and 3D structures of TiO_2 such as nanoribbons, nanodisks, nanoleaves, nanoflowers, nanorods, hedgehog nanostructure and dendritic hollow structures have also been explored for DSCs [82–87]. The studies focused on the morphological modification of TiO_2 have demonstrated marginal increase in DSC performance with scattered results, however, due to structural complexity and reproducibility issues such investigations has not resulted in wide spread application for DSCs [76]. For details please refer to the cited work.

2.3. Metals and metal oxides for TiO$_2$ modifications

Doping or intentional addition of impurities while synthesis of TiO$_2$ can have substantial effect on band structure and surface states which dictate charge transport and dye/TiO$_2$ interface in DSCs [88]. The purpose of doping is to achieve higher conductivity and minimized recombinations. In the regime of DSCs, doping has been studied with metals (lithium, magnesium or calcium), metalloids (boron, silicon, germanium, antimony), non-metals (carbon, nitrogen, sulfur, fluorine and iodine), transition metals, post transition metals and lanthanides. For a detailed analysis on choosing the dopant and its effects interested readers are referred to previously published review on the topic [88]. These dopants are generally added during the synthesis stage and require subsequent sintering step to be integrated as the part of crystalline structure of TiO$_2$ (hard modification).

Additionally, to enhance the interface properties of DSCs at TiO$_2$/dye/electrolyte for efficient charge transfer wide bandgap and electronically insulating metal oxides has been widely studied [75, 89]. Wide band gap metal oxides such as ZnO, Nb$_2$O$_5$, and WO$_3$ and electronically insulating oxides such as SrO, Al$_2$O$_3$, ZrO$_2$ and SiO$_2$ are known to form barrier layer at the interface which impedes back electron transfer at the interface boundary thus lowering recombination losses [90]. Most recently, MgO have been studied for TiO$_2$ modification during synthesis, leading to negative shift of up to 200 mV of TiO$_2$ owing to its more basic nature [91, 92]. An alternative approach is to surface treat the TiO$_2$ film with Mg^{+2} precursor such as (Mg (OC$_2$H$_5$) or Mg (NO$_3$)$_2$) followed by high temperature sintering, however, concentration control becomes very critical for final performance [90, 93, 94]. Albeit, these studies report higher V_{oc} for DSCs employing Mg^{+2} and reduced recombination losses. However, negatively shifted conduction band can also lower the electron injection if the sensitizer-excited state potential gets very close to CB energy. Interested readers are referred to relevant reviews for in-depth analysis of such modifications [75, 89].

3. Dye solution co-adsorbing additives

"Soft modification," simple rinse and dry to alter TiO$_2$/dye/electrolyte interface favorably is to add additives along with the dye adsorption solution known as "co-adsorbents" [95–98]. These additives are also known as de-aggregating agents which aid in favorable dye orientation on TiO$_2$ and increased electron injection through minimization of dye–dye intermolecular charge transfer and π-π stacking [99]. These mainly insulating additives are known to occupy the vacant spaces among dye molecules which prevents the diffusion of oxidized redox species (e.g., I$_3^-$) to TiO$_2$ (**Figure 7**) [100, 101]. This approach has been widely explored for DSCs since the first report in 1993, though such modifications of TiO$_2$ surface were already explored by Miayasak et al. in 1978 [95, 96]. These co-adsorbents are amphiphilic in nature and consists of an anchoring group (**Figure 4**) such as carboxylic or phoshonic/phosphinic moiety and a long alkyl chain or three dimensional aromatic and alkyl components acting as a buffer between TiO$_2$ and electrolyte. These co-additives can be divided based on the chemical identity of anchoring group and their influence on the interface can be best studied through EIS and
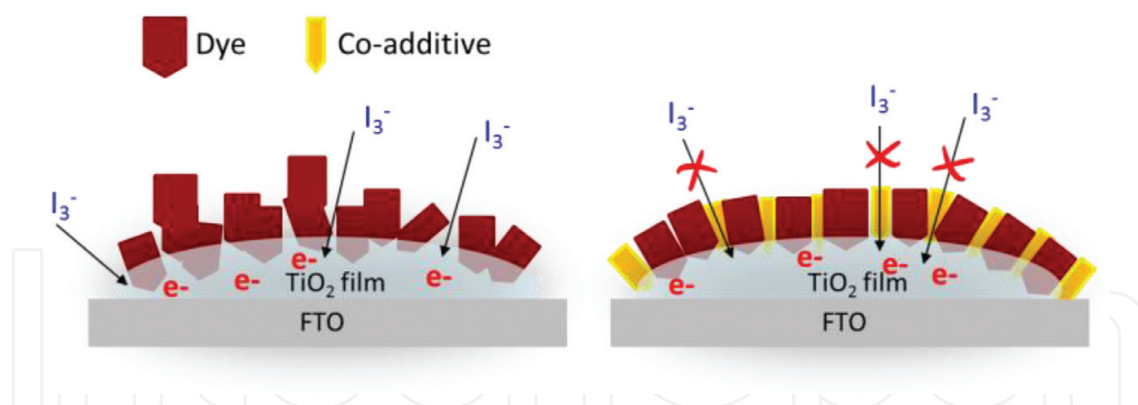
Figure 7. Illustration of dye on TiO$_2$ surface with (right) and without co-additive, I$_3^-$ is the oxidized redox component.
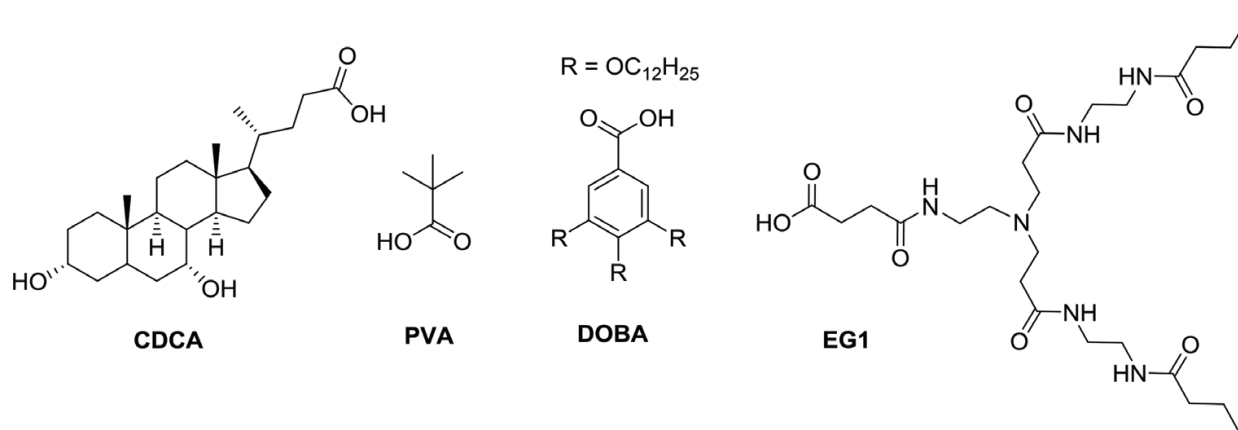
Figure 8. Representative co-additives.

electron lifetime measurements. Since aggregation is a common phenomenon for mostly planar organic sensitizer including phthalocyanine and porphyrin, the effect of co-additives on aggregation can be studied by simple current dynamic measurements at different light intensities [102, 103].

3.1. Carboxylic acid based anchoring co-additives

Since the first report on deoxycholic acid (DCA) and chenodeoxycholic acid (CDCA, **Figure 8**) in 1993 by Grätzel et al. in ethanolic dye solution along with the sensitizers, CDCA has become the most widely used co-additive [96]. CDCA adsorption for pre-stained and post stained TiO$_2$ films was found less effective in terms of enhancing J_{sc} and V_{oc} [104]. Generally, the optimum concentration of CDCA in the dye solution depends on the nature of the dye and study of several concentrations (such as 2, 10, 20, and 40 times, etc., of the dye) is a normal routine [105, 106]. It should be kept in mind that excess of CDCA or any other co-adsorbent can adversely affect the dye loading as well. Under optimum conditions, CDCA is generally known to positively (downward) shift the conduction band of TiO$_2$, increasing electron injection along with lower recombination losses thus enhancing both J_{sc} and V_{oc}. It should be noted that CDCA mainly serves the role of de-aggregating agent for organic, porphyrin and phthalocyanine

sensitizers and a recombination blocking agent for Ru (II) sensitizers since latter dyes do not aggregate on TiO_2 [102]. In a recent study for ladder-like carbazole donor and cyanoacrylic acid (CA) anchor based D-A-π-A type dye, CDCA resulted in up to 9% enhancement in PCE when co-adsorbed with the dye [107]. Concentration of CDCA was 5 mM compared to 0.3 mM of the dye. The effect for the presence of CDCA was analyzed through EIS measurements which confirmed higher recombination resistance leading to 8% increase in J_{sc} and 2% increase in V_{oc} for most efficient dye in the series (C1). In a similar study for an organic phenothiazine based dye (P2), effect of different concentrations of CDCA was studied in detail [106]. CDCA concentration of 10 mM was found to result in optimum improvement in DSCs performance compared to 0.3 mM concentration of the dye.

Figure 8 shows the CDCA alternatives such as pivalic acid (PVA), 3,4,5-Tris(dodecyloxy) benzoic acid (DOBA) and EG1 (an amidoamine dendritic molecule) [108–110]. PVA in a comparative study approach showed enhanced electron lifetime and negative shift in the conduction band of TiO_2. This lead to 53 mV increase in V_{oc} and 8% increase in PCE. Adsorption of PVA before staining was found to be more effective, compared to co-adsorption with the dye. In an example with ss-DSCs (solid state-DSCs), DOBA and Z907 sensitizer resulted in negative shift of the TiO_2 CB, decreased charge recombination, higher hydrophilicity and enhanced PCE as evidenced by EIS, and IMVS (intensity modulated photovoltage decay spectroscopy) measurements. In another example, strategically designed amidoamine-dendron based molecules (EG0–2) were studied as the co-additives and compared with CDCA. This study showed that superior surface blocking, higher electron injection, minimized intermolecular energy transfer and higher PCE can be tailored with increasing size of the dendritic molecules. In spite of co-additives examples (Figure 8), CDCA is mostly widely employed co-additive to modify the interface on TiO_2, however, it should be employed with caution particularly in terms of its co-adsorbing concentration.

3.2. Phosphonic/phosphinic acid anchoring and zwitterion-based co-additives

Co-additives with phosphorous containing anchoring groups are generally believed to anchor strongly compared to carboxylic acid anchors. First example of such an additive was appeared in 2003 by Zakeerudin et al. when 1-decyl phosphonic acid (DPA, Figure 9) was used with a Z-907 (a benchmark hydrophobic dye historically popular for stable devices) [111]. It was claimed as the first example of stable DSCs under heat stress and continuous illumination,
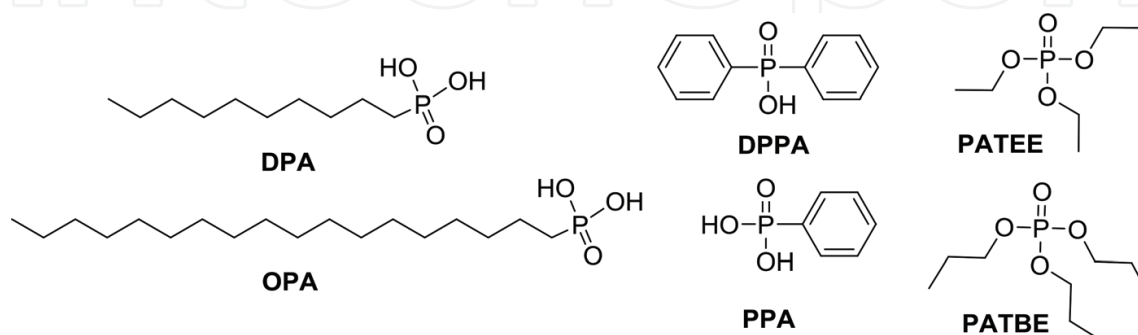
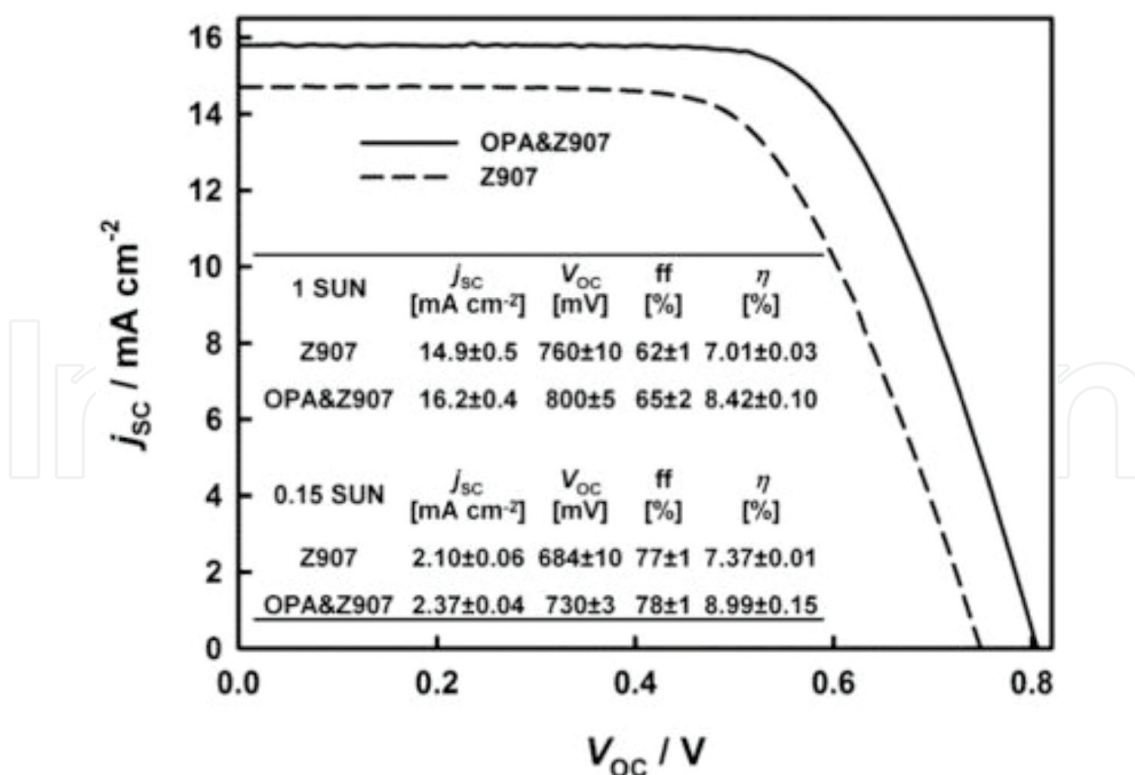**Figure 9.** Representative additives.

with 7% increase in PCE due to DPA (4:1 dye/co-additive concentration was employed). Later on in a unique example octydecyl phosphonic acid (OPA) was also characterized for **Z-907** and cobalt redox shuttle [112].

OPA (18C) was found more effective in blocking recombination compared to DPA (10C) because of longer alkyl chain with overall 20% increase in PCE (8.4% versus 7% no OPA, **Figure 10**) with 18:1 (dye:OPA) concentration ratio. This is one of the highest efficiency reported so far for a Ru (II) dye containing NCS with cobalt redox shuttles, owing to inherently higher recombination losses [113–115].

In this class of co-additives, dineohexyl phosphinic acid (DINHOP, **Figure 11**) is known as an efficient molecular insulator to electronically passivate the oxide junctions such as TiO$_2$, even outperforming CDCA in some comparative studies *vide infra* [105, 116]. DINHOP particularly benefits from the three dimensional orientation leading to better surface coverage [116]. Increase in PCE of 9% was realized for **Z-907** and DINHOP with 1:1 dye concentration (PCE 7.9% versus 7.24%).

In a comparative study for different small molecules (**Figure 9** containing phenylphosphonic acid (PPA), diphenylphosphinic acid (DPPA), phosphoric acid triethyl ester (PATEE), and phosphoric acid tributylester (PATBE) were employed as co-adsorbents [117]. It was found that alkyl chains performed better than the aromatic containing co-additives with ~12% enhancement in device PCE with **N719** sensitizer. The observed effect was established by EIS measurements (Nyquist plot), showing larger semicircle for high performing PATBE, pointing

1 SUN	j_{SC} [mA cm^{-2}]	V_{OC} [mV]	ff [%]	η [%]
Z907	14.9±0.5	760±10	62±1	7.01±0.03
OPA&Z907	16.2±0.4	800±5	65±2	8.42±0.10
0.15 SUN	j_{SC} [mA cm^{-2}]	V_{OC} [mV]	ff [%]	η [%]
Z907	2.10±0.06	684±10	77±1	7.37±0.01
OPA&Z907	2.37±0.04	730±3	78±1	8.99±0.15

Figure 10. Effect of OPA on **Z907** performance, taken from Ref. [66], with permission from The Royal Society of Chemistry.
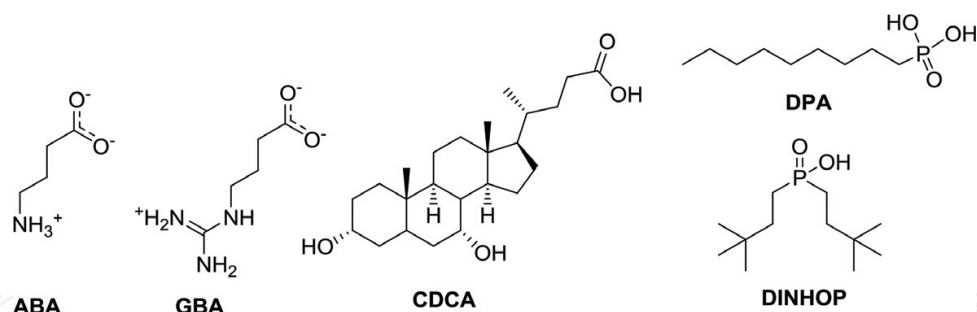
Figure 11. Co-additives employed in the comparative study.

to higher recombination resistance as the result of co-additive pretreatment of TiO_2 film before dipping in dye solution.

4-guanidino butyric acid (GBA, **Figure 8**) was first time employed in 2005 by Grätzel group with a Ru (II) sensitizer **K19** [118]. In that detailed study, cyclic voltammetry was employed to determine the density of states (DOS), EIS to analyze interface charge transfer properties and photovoltage decay measurements for the effect of GAB on electron life time and capacitance of TiO_2. GBA was found to have similar kind of effect as t-butyl pyridine on TiO_2 conduction band with negative shift in the quasi-fermi level of TiO_2. Additionally, increase in V_{oc} did not come as the result of decreased J_{sc}, thus leading to higher overall PCE (~9% increase with 1:1 concentration with the dye). In 2009, same group studied and compared GBA and 4-aminobutyric acid (ABA) for solid state DSCs and additives effect on long term stability (**Figure 11**) [101]. GBA outperformed ABA with about 37% increase in PCE compared to 16% decrease with ABA at 1:1 concentration. This was caused presumably due to more effective barrier formation to recombination and upward shift in the conduction band of TiO_2 by GBA. Enhancement in device performance due to GBA was caused by 15% increase (113 mV) in V_{oc} and 18.5% increase in J_{sc}. GBA was also found to enhance the long term stability.

In a recent study based on **C106** dye, Chandiran et al. studied four different additives (**Figure 11**) for their potential effect on the TiO_2 interface and device performance with different concentrations [105]. For **C106**, 4-guanidino butyric acid (GBA) resulted in 11% PCE, compared to 10.8% with CDCA at 0.5:1 (dye:CDCA) ratio compared to 6:1 for GBA (dye: GBA). In the same study, dineohexyl phosphinic acid (DINHOP) also showed slightly better results compared to CDCA (11% versus 10.8%), whereas dodecyl phosphonic acid (DPA) at 6:1 ratio marginally improved to 9.7% PCE. The device PCE without additives was reported to be 10.6%.

3.3. Dual function dyes as co-additives

An interesting approach to achieve multiple functionality such as light absorption and aggregation/recombination blocking at TiO_2 surface is to employ small molecule organic light absorbing dyes along with main dye [119–122]. Few successful example of such yellow to orange dyes which can be termed as co-sensitizers and co-additives are shown in **Figure 12**. In a detailed study in 2011, it was shown that Y-shaped molecules such as **HC-A**, can
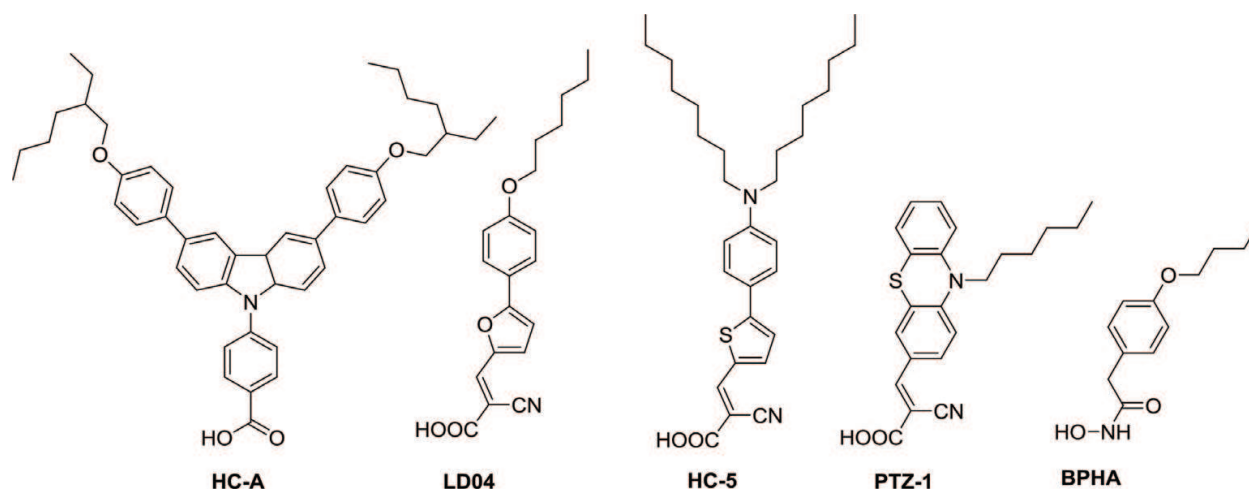
Figure 12. Small molecule co-sensitizing dyes as co-additives to modify TiO_2.

potentially play multiple roles when co-adsorbed along with another organic dye (**NKX2677**) [119, 120]. IPCE confirmed the increased photocurrent response, EIS was used to rationalize the higher V_{oc} due to increased electron lifetime, and transient absorption studies showed the carbazole cation formation favorable for hole conduction. In a detailed study on similar lines with different molecules (**HC3–5**, **Figure 12**), black dye (**BD**) was optimized from 10.3% PCE to 11.3% for **BD + HC-5**, with 1:1 dye solution concentration [121]. As the result of co-sensitization, **BD + HC-5** mainly realized enhancement in J_{sc} (8.5%). It should be noted that CDA (chenodeoxycholic acid) as a co-adsorbent was also added in 100 times excess in this study. In a recent study, similar effects were claimed with **LD03** and **LD04** when co-sensitized along with **N719**. **N719 + LD04** showed highest enhancement of PCE from 7.896% to 8.955% (13.4% increase) due to better light harvesting, decrease in aggregation and higher electron recombination resistance [122]. **BPHA** (2-(4-butoxyphenyl)-N-hydroxyacetamide), **Figure 12**), was recently applied for chemical modification of TiO_2 before dye adsorption [123]. Though **BPHA**, was found to lower the adsorbed dye concentration, however, faster regeneration was reasoned for improved device performance (10–20%). Co-sensitizing approach of adsorbing multiple dyes on TiO_2 for enhanced light harvestings works on the same principles, in addition to order of staining, and dyes ratio, etc., interested readers are referred to the cited work [124–126].

4. Post-staining surface treatment additives

To minimize the non-productive electron recombination pathways at the interface, chemical bath surface treatment of stained or dyed TiO_2 is a very effective approach (soft modification). Such that the highest reported efficiency DSCs (12–14.3%), applied the most extensive surface treatments known (**Figure 13**) [25, 53, 127, 128]. It should be noted that post staining surface treatment additive need to be inert towards the sensitizer, i.e., it should not impede light harvesting and detach it from the surface of TiO_2. Surface treatment is less complex than co-additive approach and offer better control on treatment parameters such as concentration,
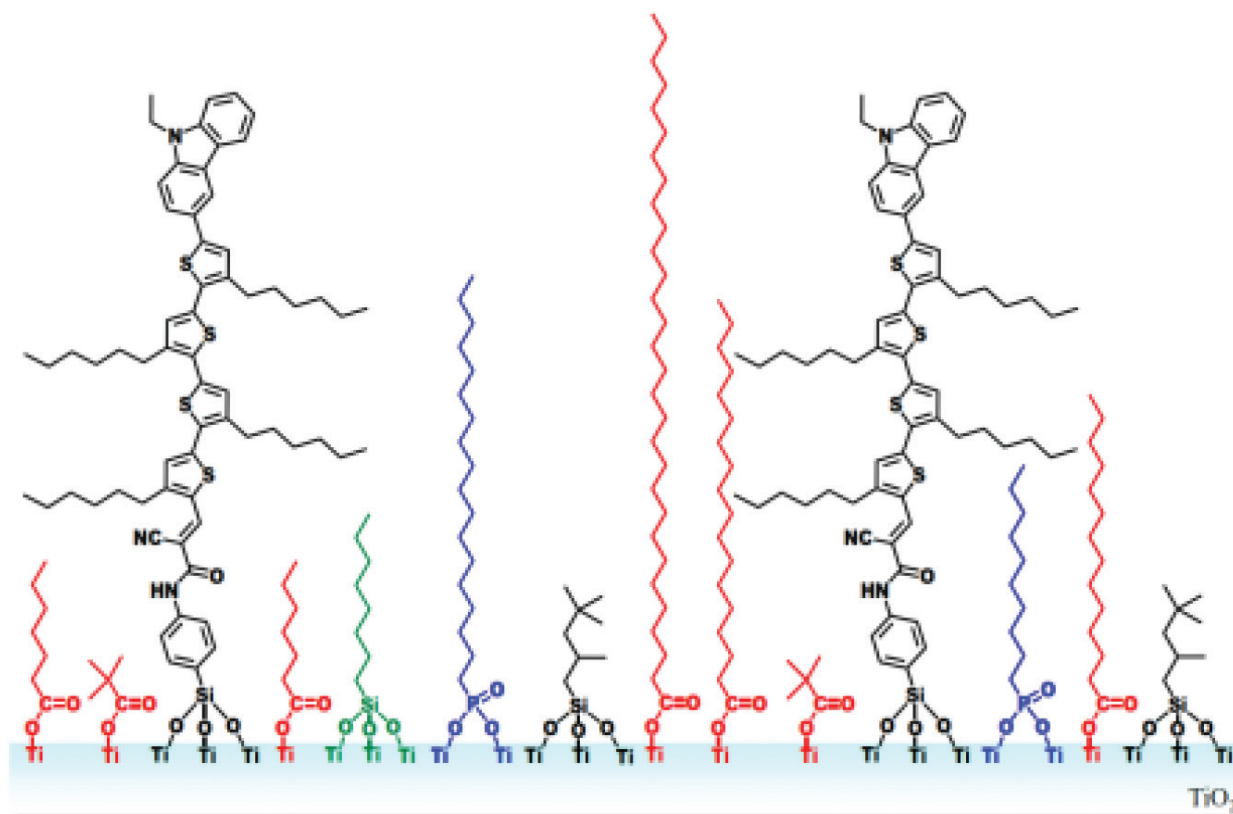
Figure 13. Post staining surface treatment example "alkyl-thicket" layer formation, adopted from Ref. [127], with permission from The Royal Society of Chemistry.

dipping time, etc. Below section highlights the most successful strategies categorized on the basis of anchoring groups.

4.1. Carboxylic/phosphonic acid anchoring additives

Similar to dyes and co-adsorbing additives carboxylic/phosphonic acid anchoring groups are widely applied for surface treatment additives as well (**Figure 14**). Effect of long alkyl chain on enhancing electron lifetime in TiO_2 was already known in conjunction with DSC sensitizers [129–131]. However, Hanaya et al. popularized the concept of "alkyl thicket" as an insulating barrier layer to block unwanted electron recombinations at TiO_2. As the result, overall device PCE increased impressively ~20% (9.44–11.3%), with increase in J_{sc} from 15.1 to 15.8 mA/cm^2 and increase in V_{oc} from 0.826 to 0.958 V (16% increase). It is interesting to note, the presence of long alkyl chains was not found to impede the charge transfer and diffusion with potentially favorable effect on long term stability as well [47]. These additives are usually applied in a hierarchical (stepwise) way with dipping in 0.1 M conc. (empirical) solution with the longest chain additives followed by small chain additives which can penetrate well in smaller cavities. In a very interesting study, a multifunctional methoxy-terminated oligomeric poly(ethylene glycol) (PEG) chain containing a carboxylic acid at one chain end (Mw - 2000) (*m*-PEG-succinic acid, **Figure 14**) is employed for post staining surface treatment [132]. The presence of electron rich oxygen atoms in *m*-PEG was claimed to favorably co-ordinate with vacant sites on TiO_2
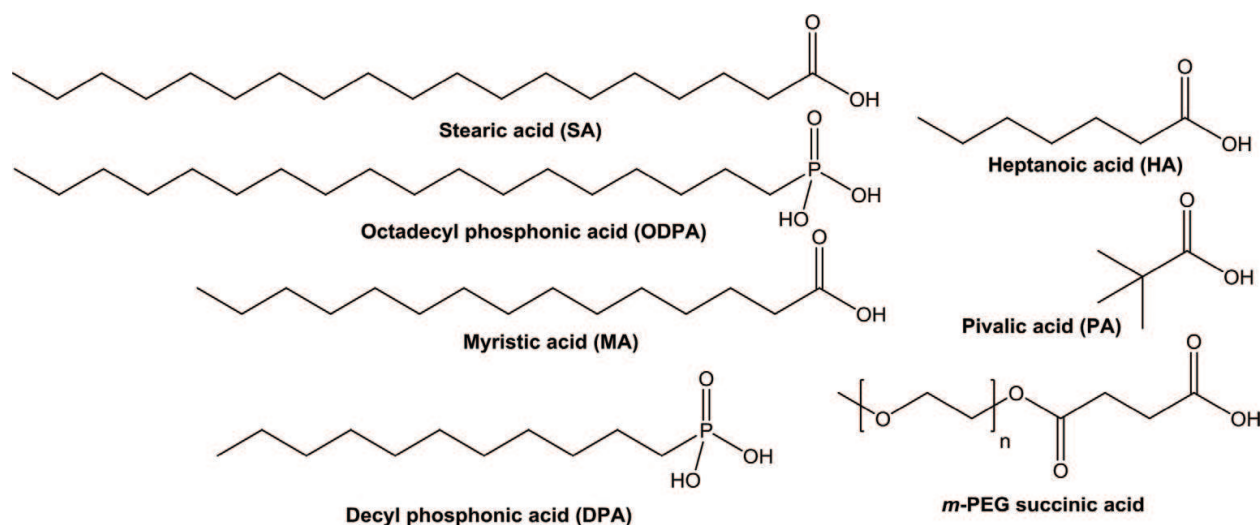
Figure 14. Additives used to modify TiO$_2$ in post-staining fashion.

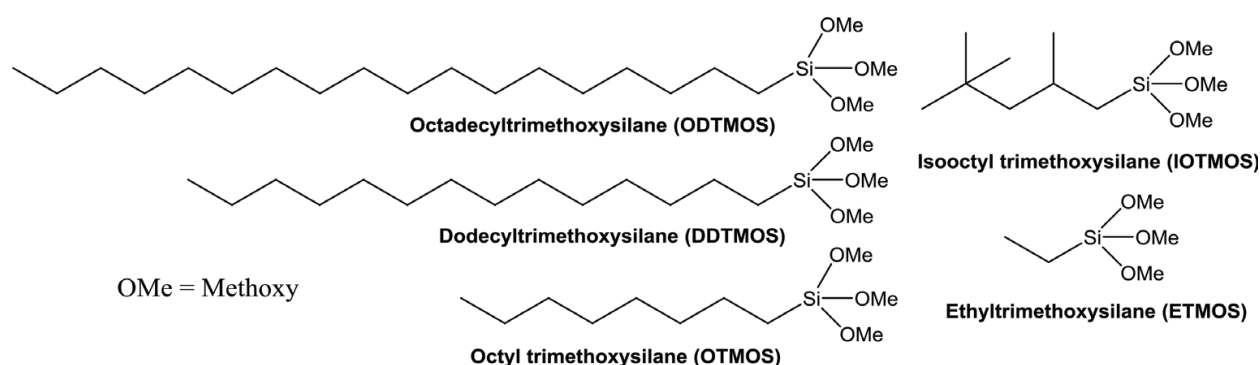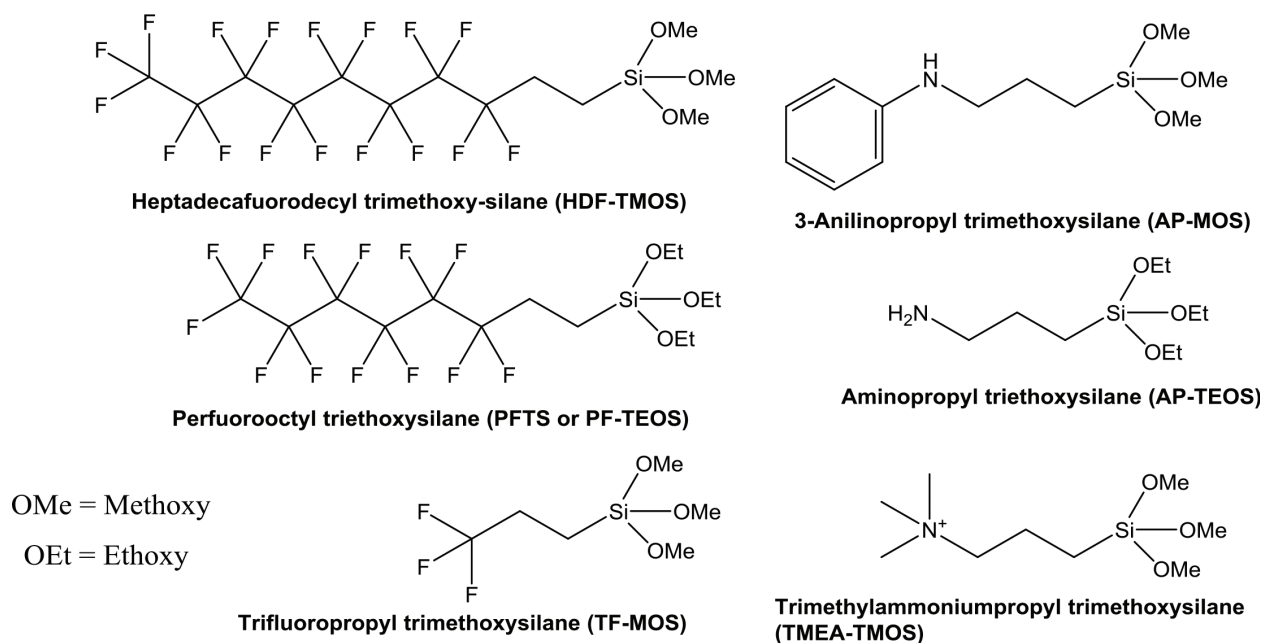**Figure 15.** Alkoxysilyl-based alkyl chain additives to modify TiO$_2$.

and worked collegially with common electrolyte additives such as Li$^+$, and tBP (4-ter butylpyridine). Increase in electron lifetime, decrease in dark current, and entrapment of Li$^+$ resulted in both J_{sc} and V_{oc} enhancements.

4.2. Alkoxysilyl-based anchoring additives

In addition to "alkyl thicket" barrier layer for modifying TiO$_2$ surface, Hanaya et al. also introduced and studied the silanol-based sensitizer and additives for TiO$_2$ anchoring (**Figures 13 and 15**). It was found that titano-siloxane bonds are stronger and are more resistant to detachment from TiO$_2$ compared to carboxylic acid anchors [127, 133]. However, it should be noted, other groups reported on the synthetic challenges related to the inclusion of siloxanes for DSC sensitizers [134].

An interesting and effective evolution is the replacement of hydrocarbon chain by fluorocarbon chain while keeping alkoxysilyl anchoring groups the same (**Figure 16**) [135–138]. In the regime of organic PV's (OPVs) fluorinated alkyl chains has been effectively employed to result in surface segregated monolayer to achieve better charge transfer, polymer alignment and
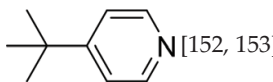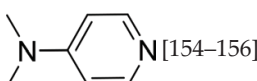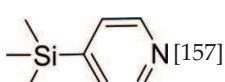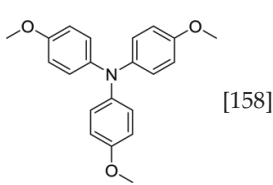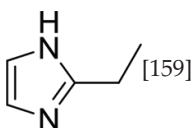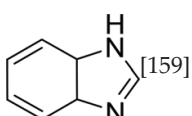
Figure 16. Alkoxysilyl and fluorocarbon based additives to modify TiO_2.

direction of dipole moment at the interface [139–141]. For TiO_2 modification, detailed studies focused on unrevealing the impressive effect of fluorinated alkyl chains evidenced, enhanced electron lifetime in TiO_2, de-aggregating behavior for organic dyes, negative (upward) conduction band shift of TiO_2 with metal complex dye, hydrophobicity and overall PCE enhancements presumably due to fluorinated self-assembled monolayer formation (FSAM) [53, 94, 142–145]. Interestingly, in one study, cationically charged TMEA-TMOS (**Figure 15**) outperformed C16 based alkyl chain analog when used with Ru (II) dye and cobalt redox shuttle. Detailed studies on unrevealing the structure–property relationship of such fluorocarbon chains for modifying TiO_2 are rare in literature at this stage.

5. Electrolyte additives

Electrolyte is an integral component of DSCs, and its composition has huge effect on performance, and long term stability. It consist of redox active species such as iodide/triiodide, Co (III)/Co(II), Fc (I)/Fc (0), and Cu (II)/Cu(I), etc., and certain additives which are known to adsorb on TiO_2 surface such as lithium cation (Li^+), 4-ter butylpyridine (4-tBP) and guanidium thiocyanate (GuNCS) and others as shown in **Table 1** [160–162]. Source of Li^+ is mostly LiI for iodide/triiodide mediator and LiTFI or $LiClO_4$ for cobalt and copper based redox shuttles. Two widely studied redox systems for DSCs are iodide/triiodide and Co(III)/Co(II) with most recent as Cu(II)/Cu(I) [160–162]. Iodide/triiodide redox shuttle has been the favorable choice historically, but it results in lower photovoltage due to higher (less positive) redox potential, higher dye regeneration overpotenial due to complex two step chemistry and corrosion of the DSCs components [160]. On the other hand, one electron redox shuttles such as cobalt and copper offer higher photovoltage, tunability, and less dye regeneration overpotential making them

No.	Additive	Conc. (M)	Electrolyte/dye	CB effect	Electron lifetime	J_{sc}	V_{oc}	PCE
1.	Li^+ [146]	0.05–0.5	I/Co	Down	Inc.	Inc.	Dec.	Inc.
2	CDCA [147]	0.1	Co/Ru (II)	Inc.	Inc.	Inc.	Inc.	Inc.
3	Li_2CO_3 [148]	0.0025	I/Ru (II)	Up	Inc.	Inc.	Inc.	Inc.
4	K_2CO_3 [148]	0.05	I/Ru (II)	Up	Inc.	Inc.	Inc.	Inc.
5	GuNCS [149]	0.1	I	Down	Dec.	Inc.	Dec.	Inc.
6	$GuNO_3$ [150]	0.1	I	Up	Inc.	Inc.	Inc.	Inc.
7	(thiophene structure) [151]	1	I/Ru (II)	Down	Dec.	Inc.	Dec.	Inc.
8	(4-tert-butylpyridine structure) [152, 153]	0.25–0.5	I/Co	Up	Inc.	Dec.	Inc.	Inc.
9	(4-dimethylaminopyridine structure) [154–156]	0.5	I/Ru (II)	Up	Inc.	Dec.	Inc.	Dec.
10	(trimethylsilylpyridine structure) [157]	0.5	Co	Up	Inc.	Dec.	Inc.	Inc.
11	(tris(4-methoxyphenyl)amine structure) [158]	0.1	Co	Up	Inc.	Inc.	Inc.	Inc.
12	(2-ethylimidazole structure) [159]	0.5	I/Ru (II)	Up	Inc.	Dec.	Inc.	Inc.
13	(benzimidazole structure) [159]	0.5	I/Ru (II)	Up	Inc.	Dec.	Inc.	Dec.

Up = upward shift, Down = downward shift, Inc. = increase, and Dec. = decrease.

Table 1. Summarizing the effect of electrolyte additives effect on TiO_2 and DSC parameters.

popular for recent studies [52, 163]. For iodide/triiodide most commonly employed additives are Li^+, GuNCS and 4-tBP, whereas one electron redox shuttles mainly employ Li^+ and 4-tBP only. Generally speaking, cationic additives charge the TiO_2 surface positively thus lowering the conduction band (**Table 1**, entry 1) [56, 146]. Electron rich or nitrogen containing additives on the other hand charge the TiO_2 surface negatively or increase electron density thus raising the conduction band, blocking the recombination and resulting in higher V_{oc}. An important factor is the concentration which is commonly optimized empirically such as for Li_2CO_3, $GuNO_3$, etc., additives [148, 150]. Electrolyte additives and their known effect in terms of TiO_2 modification and subsequent DSC device parameters are shown in **Table 1**.

Since NCS containing Ru (II) sensitizers are incompatible with cobalt, inclusion of CDCA (**Table 1**, entry 2) substantially lowered the recombination losses and increased the PCE from 1.9 to 5.7% [147]. An interesting study, was the inclusion of Li_2CO_3 and K_2CO_3 (**Table 1**, entries 3 and 4) as a source of Li^+, where former outperformed latter [148]. Li_2CO_3 enhanced the device performance (6.5–7.6%) without lowering V_{oc}, presumably due to formation of carbonate layer on TiO_2, as evidenced by FT-IR. In a comparative study, $GuNO_3$ showed overall better performance compared to well-known $GuNCS$, without negative effect on V_{oc} [150]. It was supported by the favorable effect of NO_3^- on TiO_2 CB (upward shift), which was not observed for NCS^- without affecting diffusion negatively. Thiophene (**Table 1**, entry 7) when added in 1 M concentration had Li^+ like effect to enhance the J_{sc} [151]. 4-tBP (**Table 1**, entries 8–10) and its derivatives such as methyl pyridine, pyrimidine, pyrazole, triazole, thiazole and quinolone has been extensively explored by Arakawa et al. [154, 164–167]. Out of these, 4-trimethylsilylpyridine (**Table 1**, entry 10), have particularly shown better overall performance due to its bulkiness to block recombination reaction at interface, and better electron donating ability without negatively effecting the electron injection [157]. In a recent study, tris(4-methoxyphenyl)amine (TPAA, **Table 1** entry 11) as an electron donor was explored by Boschloo et al. [158].

The inclusion of TPAA in cobalt electrolyte particularly blocked the recombination with oxidized sensitizer which lead to 26% increase in the DSC performance. 2-ethylimidazole and benzimidazole (**Table 1**, entries 12 and 13) due to labile proton and lone pairs on electron were expected to be good coordinating candidates to modify TiO_2 as studied by Wei et al. [159]. Benzimidazole and 2-ehtylimidazole were found to perform best when employed in the molar ratio of 9.5/0.5 respectively (7.93% PCE compared to 6.8%). These additives showed pyridine type effect in modifying TiO_2. To this point, only few reports are available on the long term stability effect of these additives on TiO_2 properties and DSC device performance [168, 169].

In this chapter, DSC electrolyte additives are discussed with respect to liquid based systems, whereas liquid in these electrolytes eventually has to be replaced for long term stability either by solid or semi-solid (gel type) systems. Reader are kindly referred to the published literature for semisolid gel type electrolyte which generally apply similar additives and offer better long term stability [162, 170–172].

6. Summary

In summary, this chapter aimed at recognizing and highlighting various approaches to modify TiO_2 material based on the studies focusing on dye-sensitized solar cells. The emphasis was to identify the most successful examples and to rationalize their effect in enhancing electronic mobility, charge carrier generation and diffusion, conduction band shift, surface passivation, light harvesting, long term stability and ease of application. In general, TiO_2 modification can be categorized into hard modification and soft modification. Hard modification involves the addition of moieties such as plasmonic nanostructures, metal oxides, and morphological variations during synthesis such as a high temperature sintering (400–500°C) step is required

to achieve required functionality. On the other hand, soft modification (simple rinse and dry) post sintering surface treatment with additives, co-adsorbents, and electrolyte additives is rather simple to apply. With the discussion and literature provided in the chapter we hope the state of knowledge learned from dye-sensitized solar cells will benefit the scientific community to expand on the functionality of TiO_2 as it is being applied and explored in the fields of energy storage (batteries, super capacitors), photocatalysis, PVs, and sensors.

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