

# Chapter1

## Introduction

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Mankind needs energy for living. Besides the energy in our food necessary to sustain our body and its function (100W), 30 times more energy is used on average to make our life more comfortable. Electrical energy is one of the most useful forms of energy, since it can be used for almost everything. As the world is becoming advanced in technology and economy, more energy is being consumed to keep up the development and the demand on energy boomed over the past years. World energy consumption is projected to expand by 50 percent from 2005 to 2030 [1]. In 2007, the world primary energy consumption was increased by 2.4% – down from 2.7% in 2006, but still the fifth consecutive year of above-average growth [2]. The energy economy is still highly dependent on three forms: fossil fuel-oil, natural gases and coal with percentages of 37%, 20% and 27%, respectively [1]. With a daily consumption of 82.5 million barrels, oil might run out in around 40 years at current reserves-to-production (R/P) ratio. Meanwhile, the increasing awareness that the unpleasant environmental pollution arising from the combustion of these feedstocks necessitates urgent promotion of alternatives in renewable energy sources to cover the substantial deficit left by fossil fuels. The photovoltaic effect discovered by the French scientist Edmond Bequerel in 1839 [3] after observing electric potential between two electrodes attached to a solid or liquid system upon light irradiation has

been the base for a variety of concept to convert solar radiation into electricity. This concept has opened a new road for alternative energy generation and is actually a hot topic in current research. One simple reason is that the Earth receives  $1.2 \times 10^{17}$  W insolation or  $3 \times 10^{24}$  Joule energy per year from the Sun and this means covering only 0.13% of the Earth's surface with solar cells with an efficiency of 10% would satisfy our present needs [4]. Apart from the abundance of potentially exploitable solar energy, photovoltaic cells also have other competitive advantages such as little need for maintenance, off-grid operation and silence, which are ideal for usage in remote sites or mobile applications.

Today the photovoltaic market is dominated by silicon in its multicrystalline and monocrystalline form. Further silicon research is concentrated on thin-film crystalline silicon (about 5–30  $\mu\text{m}$  active layer thickness), which avoids the costly crystal growing and sawing processes. The problems arising for this material are: assuring adequate light absorption, assuring good crystal quality and purity of the films, and finding a substrate that fulfils all requirements. Genuine thin-film materials are characterised by a direct band structure, which gives them very high light absorption. Therefore, these materials have a thickness of only 1  $\mu\text{m}$  or less. Other inorganic materials used for photovoltaic devices belong to the group of chalcogenides such as copper indium diselenide (CIS) and cadmium telluride. The interest has expanded from  $\text{CuInSe}_2$  to  $\text{CuGaSe}_2$ ,  $\text{CuInS}_2$  and their multinary alloys  $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ . All belong to the so called second

generation solar cells. The two deposition techniques are either separate deposition of the components followed by annealing or co-evaporation. Laboratory efficiencies for small area devices are approaching 19 % and large area modules have reached 12 %. Cadmium telluride solar cells, which show only slightly lower efficiency, also offer great promise.

From a solid-state physics point of view silicon is not an ideal material for photovoltaic conversion for two reasons: There is a small spectral mismatch between absorption of the semiconductor and the sunlight spectrum, approximated by a black body of 5900 K. A much more serious point is that silicon is an indirect semiconductor, meaning that valence band maximum and conduction band minimum are not opposite to each other in k space. Light absorption is much weaker in an indirect gap semiconductor than in a direct semiconductor. This has serious consequences from a materials point of view: for a 90 % light absorption it takes only 1  $\mu\text{m}$  of GaAs (a direct semiconductor) versus 100  $\mu\text{m}$  of Si. The photogenerated carriers have to reach the p-n junction, which is near the front surface. The diffusion length of minority carriers has to be 200  $\mu\text{m}$  or at least twice the silicon thickness. Thus, the material has to be of very high purity and of high crystalline perfection. In view of these physical limitations a lot of effort has been invested into the search for new materials. Consequently requirements for the ideal solar cell material are a band gap between 1.1 and 1.7 eV and a direct band structure. Furthermore the material should be readily available, nontoxic, reproducible deposition techniques, which are suitable for large

area production. Alternatively to the search of new inorganic semiconductor materials other device geometries have been developed for the purpose of light to electron conversion, such as various concentrating systems including III/V-tandem cells.

In the last years, new concepts of solar cells were conceived and realized. These technologies mainly include dye-sensitized solar cells (DSSCs), polymer solar cells, and nanocrystalline solar cells, all of which are now known as third generation photovoltaics since they are very different from the previous semiconductor devices as they do not rely on a traditional p-n heterojunction to separate photogenerated charge carriers. Instead, they form a 'bulky' junction where charge separation takes place. Because of the low-cost materials and easy fabrication, these technologies are expected to take a significant share in the fast growing photovoltaic areas. Although organic solar cells can still not compete with conventional photovoltaic cells in terms of commercial application, the prospective to develop a long-term technology based on environmentally safer materials with almost unlimited availability justifies the intensive research in this domain.

## 1.1 Photovoltaic: From the beginning to real application

The life on the ground has been always governed by solar power. As early as in the 7<sup>th</sup> century B.C., magnifying glass was already used to concentrate sun's rays to make fire. Later on, the Roman people built the

famous bathhouses (in the first to fourth centuries A.D) with large south facing windows to employ the sun's warmth. They named these sunspaces heliocamini (sun furnaces) [5]. However, it was until the 19<sup>th</sup> century that the photovoltaic effect was discovered. In 1839, Edmund Becquerel, a French experimental physicist of nineteen years old, noticed the generation of an electric current while experimenting with a silver coated platinum electrode placed in the electrolyte [3]. Since this discovery many effort have been made in this field. In 1883, an American inventor [6] developed the first large area solar cells from selenium wafers. However, since the selenium cells converted far less than 1% of all incident sunlight into electric power and deteriorated very rapidly when exposed to strong light, these pioneers in photoelectricity failed to build the solar devices that they had hoped to. These preliminary results opened the road in this technology, which is nowadays amongst hot research topics.

The spectral distribution of the solar spectrum was described by Max Planck in 1901 through his Planck's law [7]. Four years later, Albert Einstein published a simple description of "light quanta" (later called "photons" as suggested by Gilbert Lewis in 1926) and showed how they could be used to explain the photoelectric effect [8], which won him the Nobel Prize in 1921. This is the theoretical basis for all photovoltaic devices and in common semiconductors, photons excite electrons out of the valence band and into the higher-energy conduction band, where they are collected and transported to the outer circuit. In 1904, Wilhelm Hallwachs made a

semiconductor-junction solar cell from copper and copper oxide, a prototype of thin-film Schottky barrier devices. This barrier layer at the semiconductor-metal interface was confirmed by Goldmann and Brodsky in 1914 [9] and later studied in more details by Walter Schottky, Neville Mott and others in the 1930s [10, 11].

In 1932, Audubert and Stora discovered the photovoltaic effect in cadmium sulfide (CdS), opening up a way to II-VI solar cells [12]. In the 1950s with the development of silicon electronic, Fuller[13], intuitively made near-surface p-n junctions by boron trichloride treatment of n type silicon wafer which greatly favoured charge separation of the device, and with these substrates, Chapin got near 6% conversion efficiency - 50 times more efficient than the selenium cells in the 1930s [14]. After this findings, many kinds of p-n junction with CdS, GaAs, InP and CdTe were developed, however the cost of the photoelectricity was so high (several hundred \$ per watt) and was exclusively used in space application. In the 1970s after the work of Dr. Berman's, the cost of single crystal module is cut down to 10-20 \$ per Watt [15]. In the mid 1970s after the political crisis in the Middle East, the embargo and the realization of the limitations in fossil fuel resources, a great interest in the solar cell as an alternative energy source for terrestrial application, awoke. It was during this period that second generation solar cells were developed, such as polycrystalline and amorphous silicon, thin-film deposits of silicon, CdTe, CuInSe<sub>2</sub>, (CIS) and Cu(In,Ga)Se<sub>2</sub> (CIGS), as well as multijunction cell technology. This generation of device turned out to

be advantageous in production cost with respect to silicon device. In the 1990s new concepts were introduced and developed. The type called third generation includes dye-sensitized solar cells, polymers solar cells, and nanocrystalline solar cells. These are different to classical p-n heterojunction since they consist of bulk junctions where charge separation takes place. This approach offers a new alternative for low-cost solar cells.

## 1.2. Photoelectrochemistry, photography and Sensitisation

Becquerel's pioneered photoelectric experiment in 1839. The choice of silver halide as the electrode material in his experiments reflects the rapid growth in knowledge of photochemical effect at that time. Biot [16] was aware of the use of paper sensitized by silver chloride, being contemporary with the introduction of photography by Daguerre and Fox Talbot. Although the art of formulating photography emulsions only became a science a century later with the theoretical analysis of the process by Gurney and Mott in 1938 [17], there was constant empirical progress extending the overall sensitivity of photography emulsion, which had been particularly deficient for mid-spectral visible light and towards the red. The early "orthochromic" materials had limited capability to register scenes observed in colour realistically on a grey scale due to the semiconductor nature of the silver halides with their band gap between 2.7 and 3.2 eV and for which the photoresponse is negligible for wavelengths longer than 460 nm. It was noted, for example, that the origin of the gelatin used as the support

medium for the alkali halide grains significantly modified the film sensitivity. Only in the twentieth century it was demonstrated that the origin of an organosulfur compound present in calf-skin gelatine was responsible [18], and which is now known to have its effect by inducing a superficial nanostructure of silver sulphide on each grain. This can now be recognised as the first sensitisation at a semiconductor heterojunction, silver sulphide to halide. Even more significant was the work of Vogel, Professor of “photochemistry, spectroscopy and photography” in Berlin. In 1873 [19] he established empirically that the silver halide emulsions could be sensitized to red and even infrared light by suitably chosen dyes, thereby making possible the modern “panchromatic” broad – spectrum black and white film, and the more recently colour photography with the use of spectrally-selected dyes.

### 1.3 Dye-Sensitized Solar Cells [DSSC]

Sensitisation of wide band gap semiconductors using dyes has a long history, dating back to early days of photography of the 19th century: Moser observed that the photoelectric effect on silver plates was enhanced in the presence of erythrosine dye [20] and confirmed by Rigollot in 1893 [21]. Systematic mechanistic studies started only in the late 1960's with the work of dye-sensitisation process on ZnO [22-24] and SnO<sub>2</sub> [25-27] electrodes carried out by Gerischer and Memming. Most of these early studies were fundamental in nature, aimed to understand electron–transfer processes

involving valence and conduction bands of a semiconductor immersed in a redox electrolyte. Gerischer combined the stability of large band gap semiconductors with the photosensitivity to light in the visible region by dye adsorption onto semiconductor surface. Though, these works were still on their preliminary stage, the dye sensitized cells obtained were characterised with poor dye anchorage (mostly physisorbed) on the semiconductor surface and low conversion efficiencies restricted by the limited, weak light absorption (in the order of 1 to 2%) of the dye monolayer on the planar surface. Incremental improvements were then achieved both in the chemisorption of sensitizers [28-30], electrolyte redox chemistry and the judicious selection of photoelectrode materials [30-37].

Most semiconductors such as CdS, CdSe, GaP and Si underwent serious photocorrosion or even normal corrosion in the dark, thus a stable, wide band-gap semiconductor, TiO<sub>2</sub>, became the material of choice. The breakthrough of dye-sensitized devices as solar cell was then achieved with the used of TiO<sub>2</sub> having a mesoporous structures with high surface area, which allowed a drastic enhancement of the amount of adsorbed dye.

Furthermore the development of metal organic sensitizers N3 and the later panchromatic “black dye” bearing attachment groups which allow the chemical bonding of the sensitizer to the surface of the TiO<sub>2</sub> lead to a drastic improvement in charge injection efficiency. Based on these innovations overall efficiencies of over 10 % were obtained for dye-

sensitized mesoporous TiO<sub>2</sub> electrodes in contact with an electrolyte containing an iodide based redox system for dye regeneration [38-42]. A variety of dyes are used in the third generation photovoltaic technology, especially metal free dyes exhibiting high extinction coefficients. Since metal organic sensitizer performed well with a thick TiO<sub>2</sub> film, which increases the cell resistance and reduces the photovoltage, metal-free dye with high extinction coefficient could overcome that problem.

### 1.3.1 Basic principle of DSSCs

The process describing the conversion of light into electrons in dye-sensitized solar cells is shown in Figure 1.1. Consisting of an electron-conducting phase (n-type semiconductor) and a hole conducting phase considered as “mediator” (redox species or hole conductors) forming a “bulky” heterojunction, DSSCs are majority carrier devices where electrons and holes are separated in two chemical phases. In these cells, light is absorbed by the surface anchored dye, leading to a photoexcited state. This mode of carrier generation is also observed in organic bulk junction solar cells where a light-absorbing organic polymer works as the sensitizer and a fullerene derivative as the electron acceptor. According to Gregg classification, these devices belong to “excitonic solar cells”. The term refers to the creation (by light absorption) of a molecular excited-state or Frenkel exciton (An exciton in an organic semiconductor (usually a Frenkel exciton) is sometimes considered to be a bound electronhole pair.

However, because of its electroneutrality and the strong binding between the electron and the hole, it is often better characterized as a mobile excited state [43]) as the first step in the series of events that lead to charge separation and collection in the devices [43, 44].

In the bulk heterojunction cell, the exciton must first diffuse several nm to the polymer/fullerene interface for example, where it can dissociate to form an electron-hole pair, with the hole in the polymer phase and the electron in the fullerene network. In the DSSC by contrast, the exciton is created by excitation of the dye at the interface so that it can dissociate readily to create an electron-hole pair, with the electron injected in the conduction band of the semiconductor and the hole located, initially at least, on the dye molecule [44]. The dye is then regenerated by the mediator, which ensures the transfer of the hole to the counter electrode either in a diffusion or hopping mechanism depending on the mediator nature.

Charge separation in a conventional photovoltaic built on p-n junction is fundamentally different from the one in the DSSCs. Figure 1.2a shows energy band diagram of a conventional p-n junction after thermal equilibration of positive and negative charge carriers. Due to the concentration difference between the p and the n type semiconductor, holes move to the n region and electrons to p region.

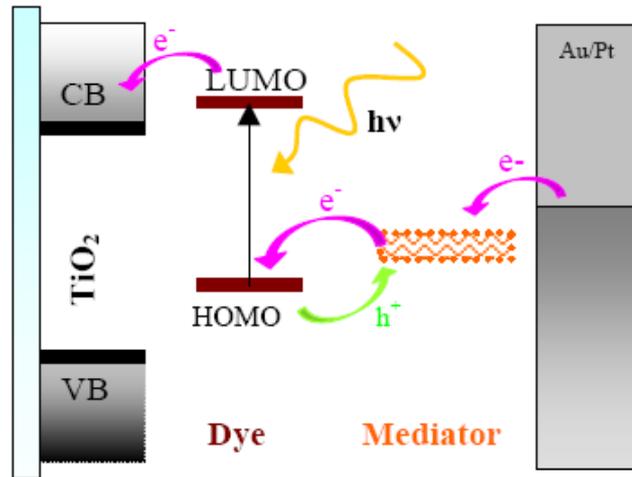


Figure 1.1 Working principle in a illuminated dye-sensitized solar cells under open circuit conditions. VB and CB stand for valence band and conduction band.

The uncompensated charges induced by this diffusion generate a built-in electric field at the junction and impair further percolation of charge carriers since the orientation of the electric field is contrary to the direction of the carrier diffusion. At equilibrium, no net charge diffusion occurs and a depletion region is formed, which is also referred to as a space charge layer. Upon illumination as shown in Figure 1.2b, absorption of photons with energy higher than a threshold, the band gap, results in generation of excitons which interact via columbic forces. Considering that excitons will recombine after a certain time with emission of photons or phonons (heat), therefore only those created in or close to the space charge layer can be separated by the built-in electric field and contribute to the photocurrent. Since both electrons and holes coexist in the same chemical phase, these

cells are called minority carriers devices and their efficiencies are highly dependent on the ability of photogenerated minority carriers (for example, electrons in a p-type material) to be collected out of devices before recombining with the majority carriers (holes, in this case) [45].

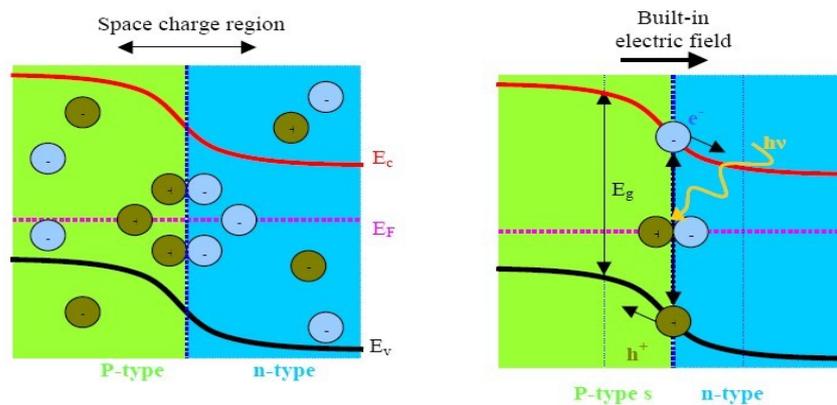


Figure 1.2 a) Energy band diagram of conventional p-n junction under short circuit conditions; b) Charge separation under illumination.

Following the above description, the difference between the conventional solar cells and dyesensitized solar cells can be summarized as follows:

- Upon illumination, light absorption and charge carrier transport are separated in dyesensitized solar cell, whereas both processes are established in the semiconductor in the conventional solar cell.
- In the DSSCs, the nanoparticles of oxide semiconductor are simply too small to sustain a built-in electric field and thereby the charge transport occurs via diffusion. In a conventional p-n junction the

presence of an electric field is necessary for an efficient charge separation.

- DSSCs are majority charges carrier devices in which the electron transport occurs in the  $\text{TiO}_2$  and the hole by the mediator. Thereby, the recombination processes can be only confined at the interface. Inside a p-n junction minority and majority charge carriers coexist in the same bulk volume. Hence these cells are very sensitive to the presence of the trace impurities or defects, which can act as recombination centers.

### 1.3.2 Photoelectrode

The photoelectrode consists of a wide band gap, porous semiconductor of high surface area, which is sensitized for the visible spectrum by a dye adsorbed on its surface. Titanium dioxide ( $\text{TiO}_2$ ) offers some unique properties making it the preferred semiconductor for dye sensitized solar cells. Its conduction band edge lies slightly below the excited state energy level of many dyes, which is one condition for efficient electron injection. The high dielectric constant of  $\text{TiO}_2$  ( $\epsilon = 80$  for anatase) provides good electrostatic shielding of the injected electrons from the oxidized dye molecule attached to the  $\text{TiO}_2$  surface, thus preventing their recombination before reduction of the dye by the redox electrolyte. Due to the presence of band gap, semiconductors only absorb light below a threshold wavelength

$\lambda_g$ , the fundamental absorption edge, which is related to the band gap energy,  $E_g$ , by Eq. 1.8

$$\lambda_g (nm) = 1240 \frac{1}{E_g (eV)} \quad (1.8)$$

TiO<sub>2</sub> occurs in three crystal modifications, namely rutile, anatase and brookite. While rutile is the thermodynamically stable phase, anatase is preferred for dye sensitized solar cells, due to its larger band gap ( $E_g = 3.2$  eV for anatase compared to  $E_g = 3.0$  eV for rutile, corresponding to an absorption edge of  $\lambda_g \sim 390$  nm and  $\lambda_g \sim 410$  nm, respectively). The capability of anatase phase to absorb only ultraviolet light, leaving the rest of the visible until the near infrared of the solar spectrum to the surface anchored dyes, depending on the property of the sensitizers. The hereto related high refractive index of TiO<sub>2</sub> ( $n = 2.5$  for anatase) results in efficient diffuse scattering of the light inside the porous photoelectrode, which significantly enhances the light absorption. So with a rigorous control of the TiO<sub>2</sub> surface one can enhance light absorption and therefore light harvesting efficiency of the photoanode. The light harvesting efficiency (LHE) is given by Eq. 1.9

$$LHE(\lambda) = 1 - 10^{-A} = 1 - 10^{-\Gamma \sigma} \quad (1.9)$$

where  $\Gamma$  is dye coverage [ $\text{mol cm}^{-2}$ ] and  $\sigma$  is the absorption cross section [ $\text{cm}^2 \text{mol}^{-1}$ ] (neglecting the scattering by the film). The cross section  $\sigma$  is related to the molar extinction coefficient  $\epsilon$  by Eq. 1.10

$$\sigma = \frac{\epsilon \cdot 1000}{N_A} \quad (1.10)$$

Typical  $\epsilon$  values for dyes lie between  $10^4$  and  $5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  yielding light-capture cross section values between  $0.0016$  and  $0.08 \text{ nm}^2$  [41,46,47]. However, the area of the sensitizer molecule occupying the surface of  $\text{TiO}_2$  is much larger, about  $1\text{-}2 \text{ nm}^2$  for Ru-complexes [41]. If we suppose a simple planar electrode  $\text{TiO}_2$  surface covered with a monolayer of sensitizer, according to Eq. 1.9 and 1.10 just a few percent of incident light can be absorbed, which is detrimental for device performance. To solve this problem, a porous film consisting of  $10 - 20 \text{ nm}$   $\text{TiO}_2$  particles was turned out to increase the surface area and light capture by the photoelectrode [48]. Depending on the film thickness, the real surface area can be enhanced 1000-fold than the apparent one. With this strategy LHE can be considerably enhanced despite the fact that  $\text{TiO}_2$  surface is recovered by a monolayer of dye.

Since  $\text{TiO}_2$  has high refractive index, the incoming photon can penetrate deeper and deeper within the mesoporous structure and crosses hundreds of adsorbed dye monolayers. In fact this process mimics the light absorption by green leaves. As the chlorophyll-containing thylakoids are

stacked, visible light is absorbed completely by traversing many superimposed vesicles containing the dye. TiO<sub>2</sub> is known to be a stable photoelectrode in photoelectrochemical cells, even under extreme conditions. Last not least TiO<sub>2</sub> is a cheap, easily available and non toxic compound that is already widely employed as white pigment in paints and tooth pastes.

### 1.3.3 Electron Transfer Dynamics

DSSCs are photoelectrochemical devices where several electron transfer processes are in parallel and in competition. The presence of a local electrostatic field is not required to achieve good collection efficiencies as it is the case for conventional p-n junction cells. Figure 1.3 summarises the electron transfer processes occurring at the dye-sensitized heterojunction. Recent studies of the electron injection dynamics from the electronically excited state of [perylene dye] and [Ru(II)polypyridyl complexes] into the conduction band of the TiO<sub>2</sub> demonstrated that the electron injection rate constant ( $k_{inj}$ ) are relatively similar.  $k_{inj}$  was reported to be  $5 \times 10^{13} \text{ s}^{-1}$  for perylene derivatives [49] and  $k_{inj} > 4 \times 10^{14} \text{ s}^{-1}$  for Ru-complexes [50]. Assuming, that the injection kinetics do not significantly change upon replacement of the electrolyte mediator by the solid-state charge transport material [51], the injection of electrons by the sensitizer in both the electrolyte cell and solid-state solar cell is expected to show similar characteristics.



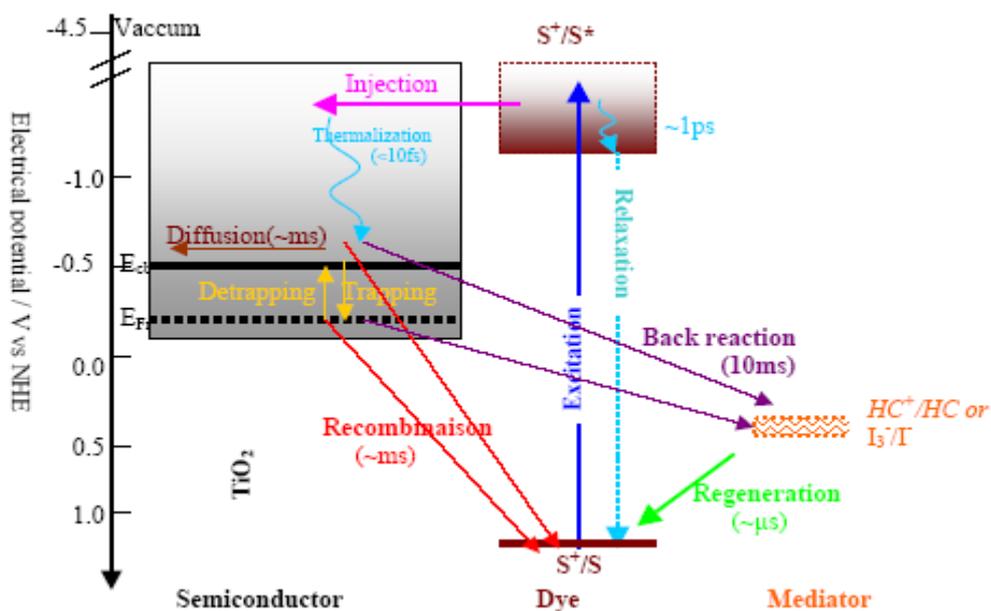


Figure 1.3 Schematic diagram of electron-transfer processes at the dye-sensitized heterojunction.

(a) Electron injection process

The rate of electron injection has been shown to depend on a variety of parameters, such as the length of the spacer between electron donor and acceptor [52], the density of acceptor states [53], and the electronic coupling between the dye and the semiconductor [54]. According to Marcus and Gerischer's theory [55-57], the total ET rate,  $k_{ET}$ , depends on the energetic overlap of donor ( $S^*$ ) and acceptor (semiconductor) states which are related to the density of states (DOS) at energy  $E$  relative to the conduction band edge,  $\rho(E)$ , reorganization energy,  $\lambda$ , and temperature,  $T$ .

At a given temperature, the overlap increases with a higher  $\rho(E)$  and a smaller  $\lambda$  and reaches a maximum when the entire donor distribution function lies above the conduction band edge,  $E_{cb}$ . Significant overlap is associated with a fast  $k_{ET}$ . In the DSSC, the sensitizer is strongly adsorbed on the semiconductor surface with carboxyl groups as the anchor, resulting in a very large electronic coupling between the  $\pi^*$  orbital of the excited state of the sensitizer and the conduction band of  $TiO_2$ , which consists of the unoccupied 3d orbital of  $Ti^{4+}$ . In addition, the conduction band of the semiconductor has a continuous and relatively large density-of-states.

Thus, electron injection from the photosensitizer to the semiconductor occurs at a higher rate [58] than does the relaxation from the excited state to the ground state (i.e. relaxation via emission) [59]. It has been observed that electron injection from N3 dye into  $TiO_2$  occurs on the order of femtoseconds as measured by the time-resolved laser spectroscopy [50, 60]. This ultra-fast rate of electron injection contributes to the high energy-conversion efficiencies of the DSSC. Ultra-fast electron injection  $\sim 13$ fs from perylene to  $TiO_2$  CB was reported.

The ultrafast electron injection is followed by the diffusion of injected electrons in  $TiO_2$  particles. The electron movement in the nanocrystalline  $TiO_2$  to the back contact (percolation) is significantly slower than in the  $TiO_2$  single crystal using Ru-complex as sensitizer.

This has been demonstrated by photocurrent transient measurements after UV illumination of TiO<sub>2</sub> particles, which showed decay times of milliseconds to seconds for film of ~10µm thickness [58, 61-65]. Although electron transport is widely agreed to proceed by diffusion, the observed dynamics are not representative of simple diffusional processes, but contain evidence for charge trapping and trap filling [66, 67].

#### (b) Electron recombination and back reaction

Charge recombination between dye cations and photoinjected electrons occurs nonexponentially over picosecond–millisecond time scales. The wide range of time scales is usually attributed to the trapping of electrons by localized states on the semiconductor surface [65-76]. Nanocrystalline materials, possessing a high surface area, have a high density of such intra-band-gap trap states [58]. The distribution of trap energies results in the distribution of electron de-trapping times leading to dispersive transport. Some experiments results reveal strong sensitivity of the recombination rate to the occupancy of trap levels, which can be controlled by different parameters. By increasing the intensity of the light source it was found that the quasi Fermi level moves toward the conduction band leading to the fill of deep traps so that they no longer retard electron transport [77]. The surrounding electrolyte composition [77] and the applying of an external bias [68, 70, 78] were reported to influence the recombination process. It is known that the nature of dye plays a critical role in the recombination

process. Clifford et al. [79, 80] shown that by modifying the dye structure one can switch between electron transport-limited dispersive recombination dynamics and interfacial electron transfer-limited exponential recombination dynamics. This means that, large physical separation of the dye cation state from the film surface contributes to reducing the recombination process [79-81].

### (c) Dye regeneration

In DSSC dye regeneration is the determining step for the performance of the device. The life time of dye cation can be as long as milliseconds in the presence of pure solvent. In the presence of the most widely used  $I^-/I_3^-$  redox system, dye cation quenching of down to microseconds [82, 83] characterising dye regeneration. Dye regeneration is faster with increasing  $I^-$  concentrations and the lifetime of excited dye ( $S^+$ ) follows the Stern-Volmer law [84]. However, in the solid state version where organic compounds namely spiro- MeOTAD are used as hole conductor [85], the regeneration of the oxidised dye by the hole conductor have been found to proceed with a broad range of time constants from 3 ps to 1 ns [86].

Contrary to the case of the oxidation of  $I^-$  to  $I_3^-$ , which requires the transfer of two electrons, the dye regeneration process in this case is a single electron process and is characterised by a much faster kinetic [85,87]. Multiple phases of injection process were assigned to the heterogeneous

nature of the heterojunction, incomplete pore filling and thereby resulting lateral hole migration between neighbouring dye molecules [88] not in contact with the regeneration material. This phenomenon can be suppressed if the dye architecture is defined in such a way that the wettability of mesoporous TiO<sub>2</sub>/dye hybrid system by organic hole conductor is improved although this aspect could be really difficult to clarify.

#### 1.3.4 Electrolyte and Organic hole conductor material

In a DSSC the hole conductors regenerate the dye after electron injection into the conduction band of oxide semiconductor. However, for an efficient reduction of oxidised dye the redox potential of the mediator must be more negative than that of the oxidised dye:

$$\Phi(D^+ \parallel D) < \Phi^0(S^+ \parallel S) \quad (1.7)$$

With a good choice of mediator one can have a gain in the open circuit voltage since the maximum voltage obtainable is related to the position of the mediator redox potential,  $\Phi(D^+/D)$  should be as positive as possible. However, the difference in the potential should be high enough to provide a driving force for the dye reduction and therefore an optimal regeneration rate. Up to now  $I^-/I_3^-$  system is still the best electrolyte for DSSCs. Efficiency of more than 11% with acetonitrile-based electrolyte and 8% long-term stability at 80 °C with low volatile electrolyte have been achieved

[89-92]. Some new low volatile electrolyte types namely, room temperature ionic liquids have attracted considerable interests as a potential candidate for replacing the volatile organic solvents due to their negligible vapor pressure and high ionic conductivity [93-96]. Stable DSSCs devices were obtained by using binary mixtures of the viscous, pure imidazolium  $I^-/I_3^-$  ionic liquid with a low viscosity, highly stable ionic liquid [97]. Following similar logics, quasi-solid electrolytes have been designed by gelating the electrolytes with aliphatic gels [98, 99], polymers [82,100,101] or even nanoparticles [102].

Other strategies for solidifying the electrolyte include introducing polymer cations [103,104] or plastic crystal [105]. Beside these,  $Br_2/Br^-$  redox system was also reported as mediator [106]. Hole conductors are also a focus of current research since the majority of them are solids or nonvolatile liquids. Inorganic hole conductors of CuSCN [107-109], CuI [110-112], organic hole conductors such as triarylmines [113] and polymer hole conductors such as poly(3-alkyl thiophene) [114], polyaniline [115] have already been tested in DSCs. Among all the candidates, spiro-OMeTAD remains the best to date [77, 85,116]. The electron life time can be increased by reducing the doping level in the OMeTAD, but this also decreases its conductivity. Meanwhile, pore filling is still the most serious problem for increasing the efficiency and stability of the OMeTAD system. However, the structure of dye can help to overcome this problem.

### 1.3.5 Counter Electrode

The counter electrode is an important component in DSSC where the mediator is reduced. It consists of fluorine-doped tin oxide (FTO) glass coated with platinum to afford more reversible electron transfer. Material like graphite [117-119], carbon black [117-119], activated carbon on FTO-glass and organic-ion doped conducting polymere of poly(3,4-ethylenedioxythiophene)(PEDOT) on both indium tin oxide (ITO) and FTO-glass [120,121] have been used as counter electrode in DSSCs.

In the typical case of solid-state dye-sensitized solar cells, noble metal with high work function, such as gold and platinum as well as carbon and conducting polythiophene polymers were found to form ohmic contact with spiro-MeOTAD [122]. Gold and platinum are typically applied by thermal evaporation in UHV or by sputtering in the case of platinum which is a very controllable technique and reproducible [123].

Metal counter electrode have the advantage of reflecting the light transmitted by the photoanode which cause a second transversal of the dye-sensitized film, thus enhancing light absorption for a given amount of dye. Inert metals, which do not chemically react with organic semiconductor, are, however, known for their diffusion on the surface and into the interior of the organic even at room temperature [124-126]. This

effect depends strongly on the evaporation parameters such as evaporation rate and temperature [127].

Carbon and organic polymers have low conductivity and are generally applied in form of a paste by screen-printing or tape casting. In such case the definition of the small active area is difficult although these methods are easy to realize. Carbon can be also applied in form of pressed graphite [108].

#### 1.4. Objective of this work

- Selection of  $\text{SiCl}_2$ ,  $\text{SiO}_2$ ,  $\text{ZnCl}_2$ , Cu, Ni, Co metal substituted Phthalocyanine (Pc) dye sensitizers for solar cell applications.
- To select the appropriate method of optimization for metal substituted Phthalocyanine dye sensitizers.
- Determination of the molecular geometry of the molecule like bond length, bond angle and dihedral angle via quantum chemical calculations using GAUSSIAN 03W software package.
- To study the Ultraviolet-Visible (UV-Vis) spectrum was investigated by using a hybrid method which combines the single-excitation configuration interactions (CIS) with DFT, i.e. CIS-DFT (B3LYP).

- To determine the HOMO-LUMO energy gap of the metal substituted Phthalocyanine dye sensitizers using GAUSSIAN 03W software package.
- From the electronic structure and HOMO-LUMO energy gap study, the chosen dye sensitizers are checked for solar cell applications.

All the above said topological properties will give vital information about the molecule to predict the absorption nature molecules to design good conversion nanocrystalline semiconductor based solar cell.

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