

CHAPTER 2

LITERATURE REVIEW

2.1 Characteristic of Solid Polymer Electrolyte

The word ‘polymer’ (from the Greek *polys*, “many” and *meros*, “parts”) was coined by Jon Jakob Berzelius in 1827 to denote molecular substances of high molecular mass formed by the polymerization (joining together) of monomers, molecules with low molecular mass [22]. Development of polymer researches has contributed to the electrochemistry area especially as the electrolytes. Polymer electrolyte has become an interesting topic since Wright and coworkers started the investigation in 1970s [23]. This leads to the development of chemical energy devices such as fuel cells, sensors, rechargeable batteries, photoelectrochemical cells, dye-sensitized solar cells and super capacitor [23-25].

Solid polymer electrolyte is said to be excellent compared to liquid electrolyte in terms of stability. Utility of solid polymer electrolytes in power sources is due to its advantages [16,26-28] such as:

- i. wide operating temperature range
- ii. high ionic conductivity
- iii. high energy density
- iv. solvent-free condition
- v. minimize the leakage problem
- vi. wide electrochemical stability windows
- vii. easy process ability; desirable shape mould ability and flexibility of design

viii. Light weight.

In dye sensitized solar cells, an electrolyte assures internal electrical contact between the two electrodes and mainly provides the potential barrier necessary for photovoltaic conversion [29]. The role of polymer electrolyte as a polymer passivating layer in minimizing the charge recombination at TiO₂/electrolyte interphase is support by results reported in [23]. Polymer electrolytes also used as a kind of adhesive between the working electrode and photoactive electrode.

2.2 Chitosan

Industry is undergoing a reemergence of the use of natural polymers since natural polymers are typically regenerable resources and nature can continue to synthesize as we harvest them. In addition, most of natural polymers are present in large quantities and one of the examples is carbohydrate. Carbohydrates are an important class of naturally occurring substances found in both plant and animal matters. The name carbohydrates (hydrate of carbon) comes from the empirical formulas for most substances in this class, which can be written as C_x(H₂O)_y. *Figure 2.1* summarizes the classification of the carbohydrates to simple and complex carbohydrates. Simple carbohydrates consist only of monosaccharides, which is single sugar such as glucose, C₆H₁₂O₆. By linking together two sugar units, for example, glucose and fructose, C₆H₁₂O₆, disaccharide sucrose, C₁₂H₂₂O₁₁, is obtained. Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages.

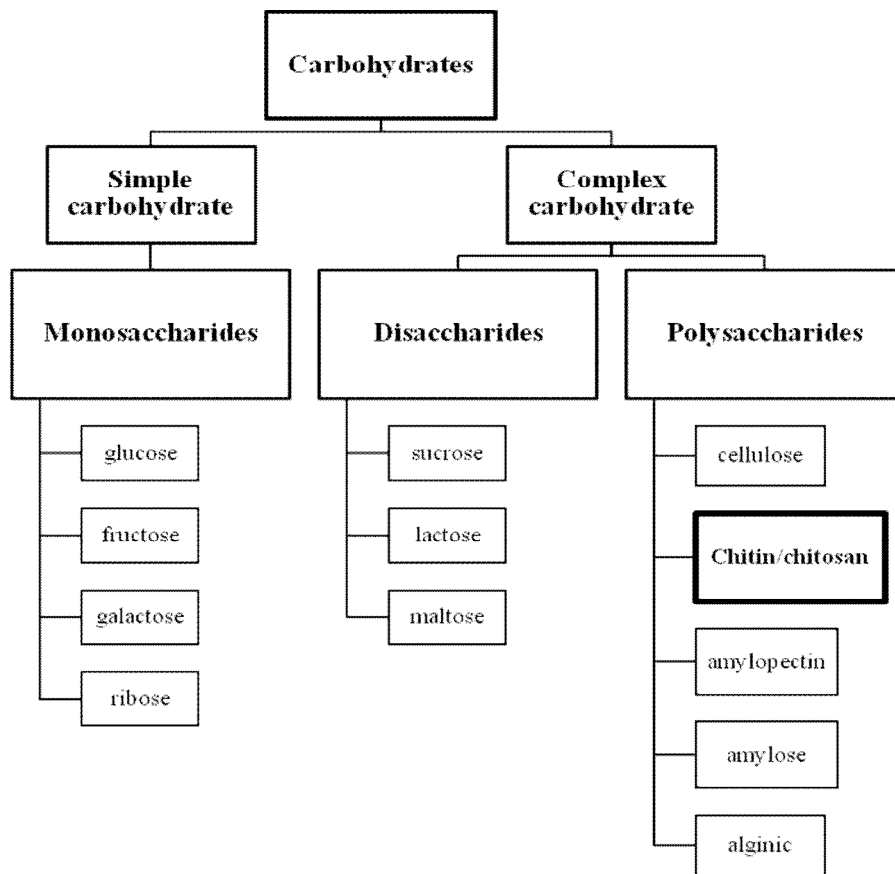


Figure 2.1: Naturally occurring polysaccharides

Among the natural polysaccharides, chitosan, a derivative of N-deacetylation of chitin, has attracted much research interest due to its advantages namely non-toxic, non-immunogenic, biocompatible in animal tissues and enzymatically biodegradable. Chitosan a derivative of N-deacetylation of chitin which is the most second abundant natural polymer is produced by hydrolysis of acetamide groups of chitin through alkaline hydrolysis treatment. It is widespread in the outer shells of insects (scorpions, ants, cochroaches, spider and beetles) and sea animals (annelid, mollusca coelenterate and crustaceans like crab and shrimp). Other source of chitin and chitosan is from microorganisms such as algae, yeast, *mycelia penicillium*, spores and also in the cell wall of certain fungi [30]. *Figure 2.2* shows the extraction of chitin and chitosan from the raw materials.

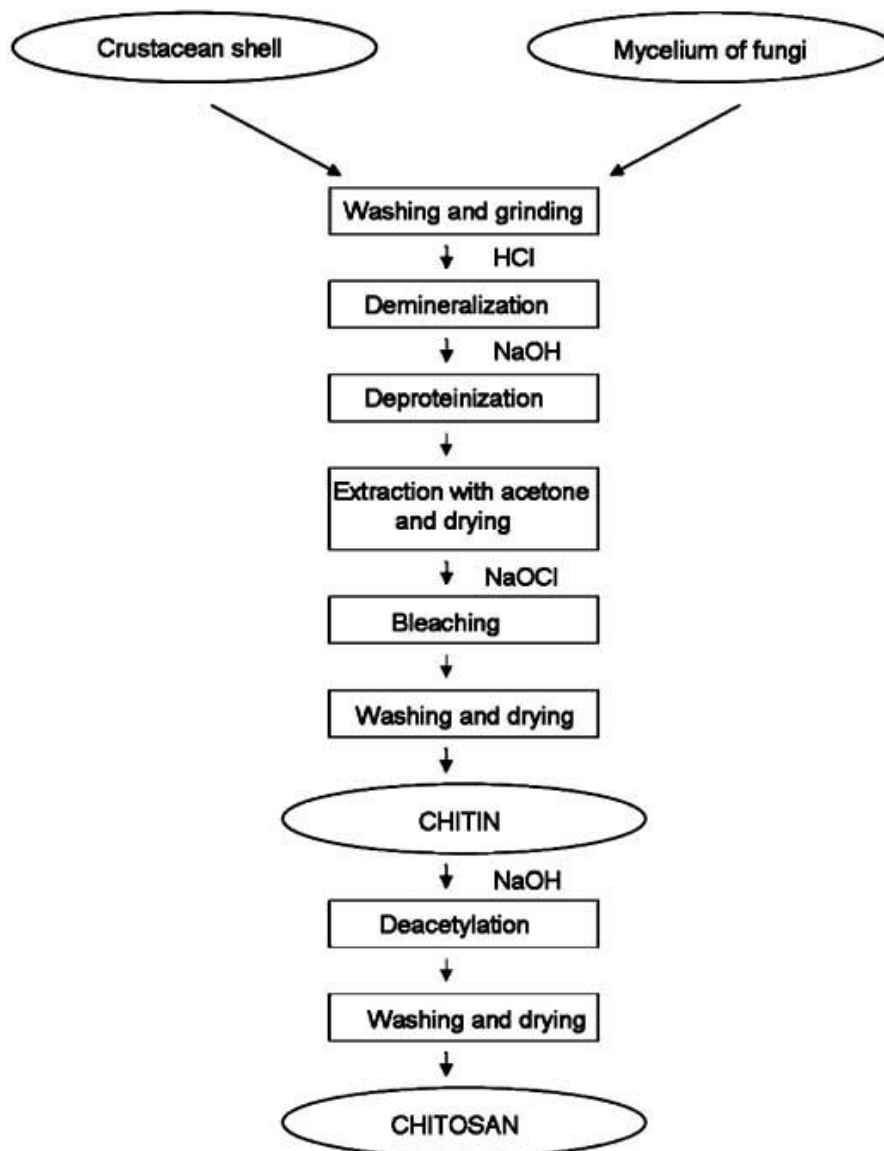


Figure 2.2: Preparation of chitin and chitosan from raw material [31]

Chitosan contains the repeating structure of β -(1-4) linked 2-amino-2-deoxy-D-glucopyranose (*Figure 2.3*). Chitosan backbone has amino groups at second carbon and hydroxyl groups at the third and sixth carbons. The -NH_2 in the C-2 position is the important point of difference between chitosan and cellulose, where three hydroxyl groups of nearly equal reactivity are available.

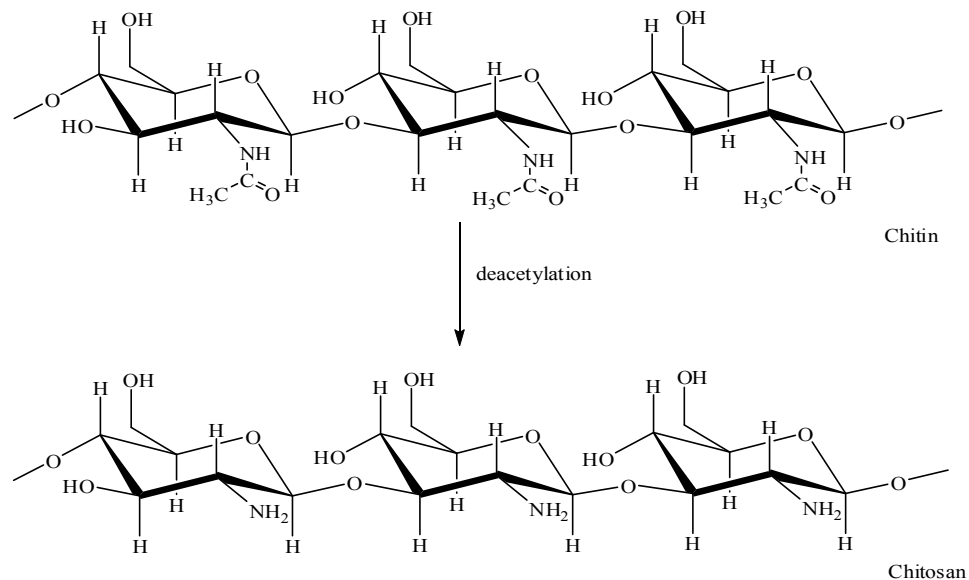


Figure 2.3: Structure of chitin and chitosan

Chitosan has been chosen to be the subject in so many researches as it offers many advantages such as:

- i. **Biocompatible:** Chitosan has the ability of a material to perform with an appropriate host response in a specific application. Chitosan lacks irritant or allergic effects and is biocompatible with both healthy and infected human and animal skins [32]
- ii. **Enzymatically biodegradable:** Chitin and chitosan are absent from mammals but they can be degraded *in vivo* by several proteases (lysozyme, papain, pepsin etc.). Biodegradability of chitosan derivatives as a binder is required for the environmental factor in the case of recycling such as plastics [33].
- iii. **Non-toxic**

It is one of the promising membrane materials that have been studied widely for various applications such as:

- i. **Pharmaceutical:** Chitosan shows very interesting biological, chemical and physical properties which make it possible to use chitosan for various pharmaceutical applications. Chitosan has been considered for pharmaceutical formulation and drug delivery applications in which attention has been focused on its absorption-enhancing controlled release and bioadhesive properties [32]. Issa et. al [34] had reviewed the potential of chitosan to significantly improved the transmucosal delivery of macromolecule drugs.
- ii. **Cosmetic:** Maintain skin moisture, treat acne, improve suppleness of hair, and reduce static electricity in hair, tone skin and oral care such as in toothpaste and chewing gum [35].
- iii. **Biomedical:** Research of chitosan for biomedical and environmental application is undergoing rapid expansion. Chitosan plays a role in tissue engineering and antimicrobial agents in wound healing applications [30].
- iv. **Environmental:** Chitosan also one of the active subjects in environmental researches such as flocculation [36] and water treatment [37]. Divakaran et. al [38] reported of the removal of suspended titanium dioxide particles in water by flocculation using chitosan in presence of humic acids. Chitosan flocculation is also involved in the removal of phytoplankton cells from aquaculture systems to reduce the nitrogenous waste and improves water quality [39]. Chitosan is applied as ion-exchanger in order to achieve simultaneous purification of the waste water and methanation of the concentrated organic content without preliminary separation of the connection to the carrier organic substances [40].

- v. **Agricultural:** Chitosan separated from at different irradiation doses showed a strong effect on the growth of Faba bean plant and can be used in agriculture fields as a growth promoter [41]. Li et. al [42], in his studies had suggested chitosan is a promising handling as a natural fungicide to partially substitute for the synthetic fungicides in fruit and vegetables.
- vi. **Biotechnological:** Research of chitosan has been contributed to the textile industry. The effect of chitosan on the resistance of wool fabric to felting on washing has been studied using nine structurally different samples of chitosan. Chitosan may be used to impart a shrink-resist finish to wool enabling machine-washable garments to be produced [34].
- vii. **Food industries:** Fernandez-Saiz et. al [43] had reported on the development and characterization of the antimicrobial properties of novel fully renewable blends of chitosan with more water-resistant gliadin proteins isolated from wheat gluten for application fields such as food packaging or food coating applications. Besides, chitosan have also been involved in many kind of foods such as papaya [44], Pacific oyster (*Crassostrea gigas*) [45], fish oil [46] and ham steak [47]

2.3 Polyelectrolyte complexes of chitosan

Polyelectrolyte is different from solid or gel electrolyte because in polyelectrolyte charged cationic or anionic groups are chemically bonded to a polymer chain, while their counterions are solvated by a high dielectric constant solvent and are free to move. Chitosan is known to have good complexing ability as the $-NH_2$ groups on the chain are involved in specific interactions with metals [35]. One of the recent attractive topics is its ability to form non-covalent complexes with other polyelectrolytes [48]. Complexation is greatly affected

by the conformation and molecular mass of chitosan macromolecules, degree of polydispersity, degree of deacetylation (DD), dissociation constant (pK_a) of the protonated amino groups of chitosan and the distribution of functional (amino and acetamido) groups along the polymer chain. Since the complexation between oppositely charged polyelectrolytes is a complicated process, it depends on many parameters such as concentration, degree of ionization and molar ratio of polyelectrolytes in a complex, charge density and distribution along polymer chains.

In recent years, researches have focused on chitosan polycomplexes with biopolyelectrolytes, modified natural polyanions and synthetic polyanions. Polyelectrolytes complexes of chitosan can be found in the form of gels, nano- and microparticles, films, membranes, porous structures and liquid-crystalline dispersions. Polyelectrolyte complexes of chitosan with other natural sources such as DNA and proteins have also been reported. Denuziere et. al [49] had studied the chitosan polyelectrolyte complexes with polysaccharides, including those with glycosaminoglycans (GAG). In the field of chitosan PEC with synthetic polyacid anions, the largest numbers of publications were devoted to chitosan polyelectrolyte complexes with polyacrylic acid (PAA) [50-53].

2.4 Chitosan as polymer electrolyte

Chitosan has been used in the development of high conductivity polymeric systems because it demonstrates polyelectrolyte behaviour due to the protonated amino group in the polymeric backbone [54-56]. Moreover, chitosan attracts more attention with its chelating properties with various anions and substances, such as fats, metals, proteins, and others [57]. Interaction of polymer with the doping salt will lead to the complexation. Four factors that

have been identified for the formation of complexes are high concentration of sequential polar solvating groups (-O-, -NH-, -CN-), the donor number and polarizability of the solvating groups, low lattice energy of the salt involved, low lattice energy of the polymer [58]. Amino and hydroxyl groups with electron pair, act as an electron donor that is able to interact with metal salt. The criteria mentioned fulfill the objective of the work in order to develop polymer electrolytes. Some examples of chitosan as polymer electrolytes host are show in *Table 2.1*.

Table 2.1: Examples of Chitosan-based polymer electrolyte

Chitosan	Salt/acid	References
Chitosan in acetic acid	Lithium acetate	Yahya et al. (2002,2004)
Chitosan in acetic acid	Sodium Alginate	Smitha et al. (2005)
chitosan in acetic acid	Sulfuric acid	Smitha et al. (2008)
Chitosan in acetic acid	Ammonium nitrate	Ng et al. (2006)
Chitosan in acetic acid	Phosphoric acid	Majid et al. (2007)
Chitosan in acetic acid	Sodium alginate	Vogt Sther et al. (2008)
Chitosan in acetic acid	Phosphoric acid	Seo et al. (2009)
Chitosan in hydrochloric acid	Hyaluronic acid.	Denuziere et al. (1996)
Chitosan with vinylphosphonic acid		Göktepe et al. (2008)

2.5 Limitation of chitosan

Solubility of chitosan is a very difficult parameter to control: it is related to the degree of acetylation, the ionic concentration, the pH, the nature of the acid used for protonation and the distribution of acetyl groups along the chain, as well as the conditions of isolation and drying of the polysaccharide [35]. The β -1,4'-glycosidic linkages give chitosan its structural rigidity and crystalline structure besides promoting the formation of intra-

molecular hydrogen bonds [59], involving the hydroxyl groups. Chitosan is reported to be insoluble in water and organic solvent but soluble in dilute aqueous acidic solution (pH 6.5) [60-62].

This limits its usage as reaction under heterogeneous conditions and leads to some disadvantages such as poor extent of reaction, structural ambiguity of the products and partial degradation due to harsh reaction conditions [7,63]. Having great potential in many applications and found abundantly in nature, chitosan should be more efficiently modified to fully explore its ability and development. In the presence of two functional groups in its backbone, $-NH_2$ and $-OH$, chitosan shows potential to be modified.

Many researchers have reports on the need to modify chitosan in order to fulfill the requirement in certain area of applications. Sashiwa et. al [33], had reported that chemical modification of chitosan was necessary to improve its adhesion to the plastics as well as its organosolubility so as to be able to put on the surface of the plastics which is hydrophobic.

2.6 Modification of chitosan

Modified polymers that show excellent properties such as high abrasion resistance, elongation, tensile strength, flexibility, chemical stability, easy film-forming and hydrophobicity, serve as attractive materials for use as polymer electrolytes [16]. Many possible ways were discovered through the chemical modifications namely nitration, phosphorylation, sulfonation, xanthation, acylation, hydroxyalkylation, graft copolymerization and alkylation [64]. *Figure 2.4* shows some of the potential method to modify chitin/chitosan.

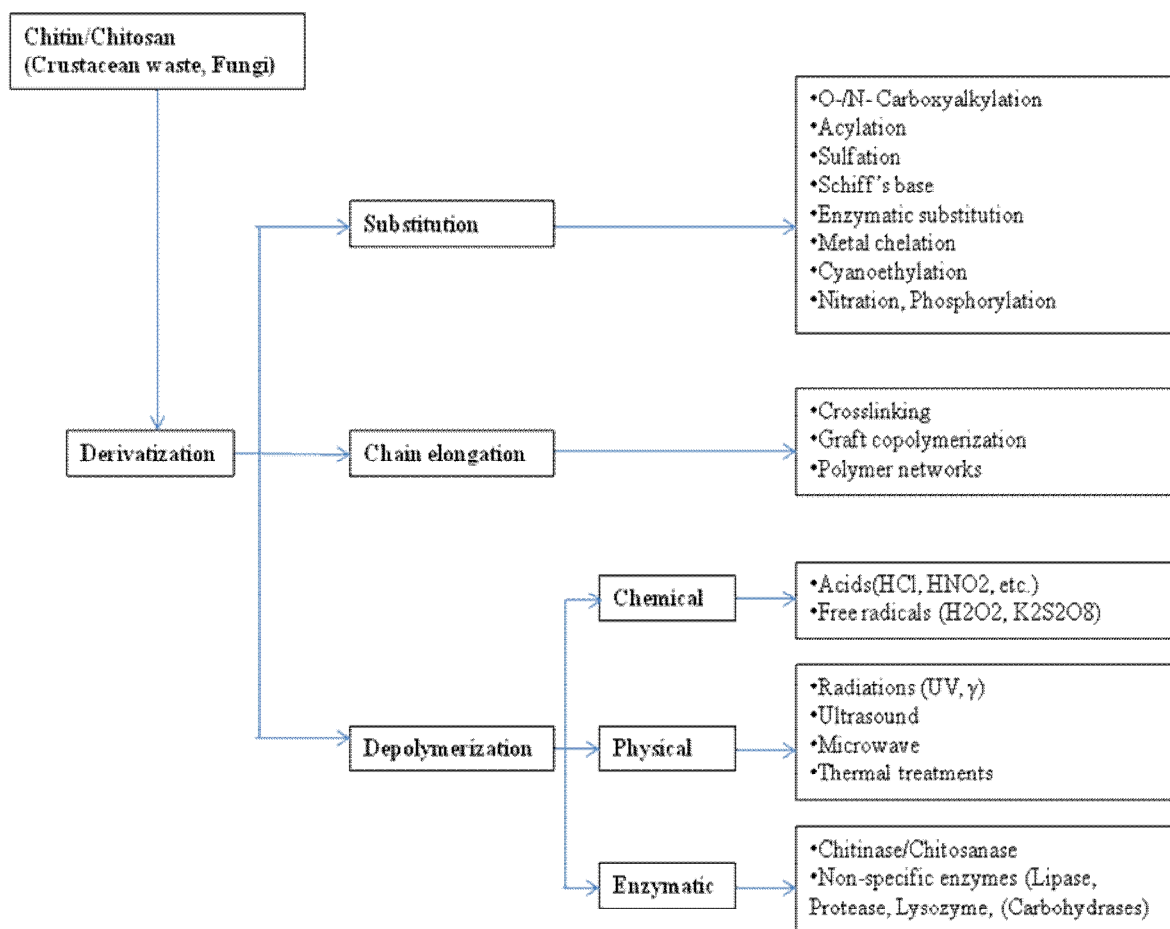


Figure 2.4: Multifaceted derivatization potential of chitin/chitosan
[Prashanth et al. (2007)]

Nguyen et. al obtained a N-carboxyalkylation product by reacting deacetylated chitosan with monochloroacetic acid at 90 °C for applications in agriculture and also pharmaceutical areas [65]. Other popular substitution method onto chitosan is acylation. Acylation using long chain aliphatic carboxylic acid chloride such as hexanoyl, decanoyl, and lauroyl chlorides [66] dibenzoylchloride (DBC) and tribenzoylchloride (TBC) [67] shows excellent solubility in organic solvents. Regioselective modifications of chitosan through C-6 position of glucosamine units by poly(ethylene glycol) has also been studied for the first time by Gorochovceva [68].

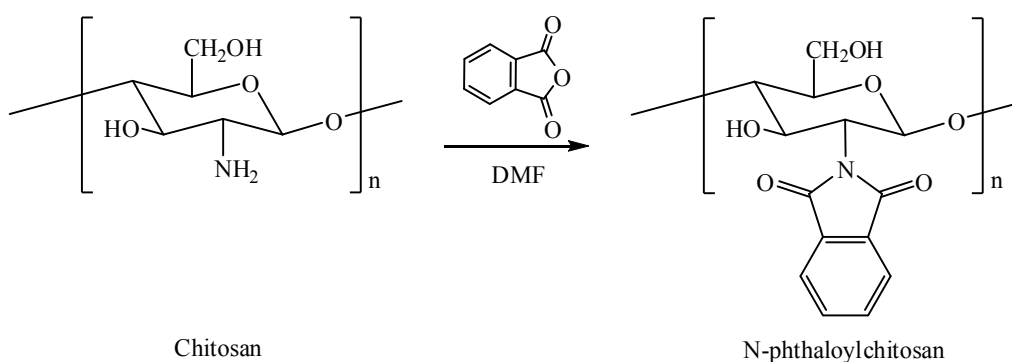
Chemical modification is also the most promising route in the development of chitosan-based anti-felting treatment for wool. Roberts et. al [69], suggested that the effectiveness of the process can be increased by increasing the hydrophobic character of the chitosan by the introduction of long-chain *N*-acyl groups through reaction with hexanoic anhydride or similar long chain acid anhydride.

Recently researchers have shown that after primary derivation followed by graft modification, chitosan can achieved much improved water solubility, antibacterial and antioxidant properties, chelating, complexation properties, bacteriostatic effect and enhancing adsorption properties that are useful for biomedical applications [30]. Graft copolymerization allows the formation of functional derivatives by covalent bonding of a molecule, the graft, onto the chitosan backbone. Although the grafting of chitosan modifies its properties, it is possible to maintain some interesting characteristics such as mucoadhesivity, biocompatibility and biodegradability. A new chitosan-based hydrogels, “Smart chitosan” that can undergo a reversible discontinuous volume phase change in response to various external physicochemical factors such as temperature or pH has been widely studied and applied *in vivo*.

In the environmental area applications, the high sorption capacities of modified chitosan for metal ions can be of great use for the recovery of valuable metals or the treatment of contaminated effluents. A great number of chitosan derivatives have been obtained with the aim of adsorbing metal ions by including new functional groups onto the chitosan backbone. The new functional groups are incorporated into chitosan to increase the density of sorption sites, to change the pH range for metal sorption and to change the sorption sites in order to increase sorption selectivity for the target metal [30].

2.7 N-phthaloylation of chitosan

Phthaloylation of chitosan usually performed in DMF with excess phthalic anhydride at 120 – 130 °C. Phthaloyl is particularly attractive for the amino group of chitosan from all the practical viewpoints of protection, deprotection and solubilization [70]. The structure of N-phthaloylchitosan is shown in *Scheme 2.1*.



Scheme 2.1: Phthaloylation of chitosan

2.7.1. Solubility of N-phthaloylation

In order to improve its solubility in organic solvents, N- phthaloylation is said to be one of the convenient methods. This improvement of solubility in organic solvents is due to presence of the phthaloyl group in chitosan that disrupts the formation of specific hydrogen bond interactions between its amino and hydroxyl groups with the solvents. The hydrophobic group also protects the amino group [7,71-72] that promotes solubility in acidic solutions [24]. Phthaloyl chitosan shows excellent solubility in organic solvents such as DMF, DMSO, DMAc, and pyridine [70-71].

2.7.2. N-phthaloylation

N-Phthaloylation is commonly used in synthesizing process as an intermediate step as it can easily be deprotected to generate free amino group [74-76]. Phthaloylated chitosan is thus a suitable precursor for a variety of site-specific and quantitative modification reactions to construct well-defined molecular environments on chitosan.

Janciauskaite et. al [7] had done grafting of dextran on the C-6 position of the glucosamine residues of chitosan by protecting the amino functionality via phthaloylation. The hydrophilic products exhibited polyelectrolytic effect, indicating that these copolymers retained the cationic properties of chitosan. γ -ray radiation of chitosan flakes and introduction of hydrophobic chain onto hydroxyl groups to form chitosan derivatives are also discussed by Yoksan et. al [75] via N-PhCh intermediate as shown in *Figure 2.5*. Under γ -ray irradiation at 25 kGy, the chains degraded without cross-linking thus reducing the molecular weight to one-fourth.

N-phthaloylation is also involved as one of the steps with tritylation, acetylation, detritylation and trimethylsilylation in preparation of 3-O-Acetyl-2-N-phthaloyl-6-O-trimethylsilylchitosan from fully deacetylated chitosan and the mechanism is shown in *Figure 2.6*. The product acts as an acceptor to synthesize non-natural branched polysaccharides, chitosan derivatives having β -maltoside branches at C-6 [77]. In a similar manner, N-phthaloyl chitosan was also used as a key precursor in the synthesis of chitin and chitosan with α -mannoside branches [78].

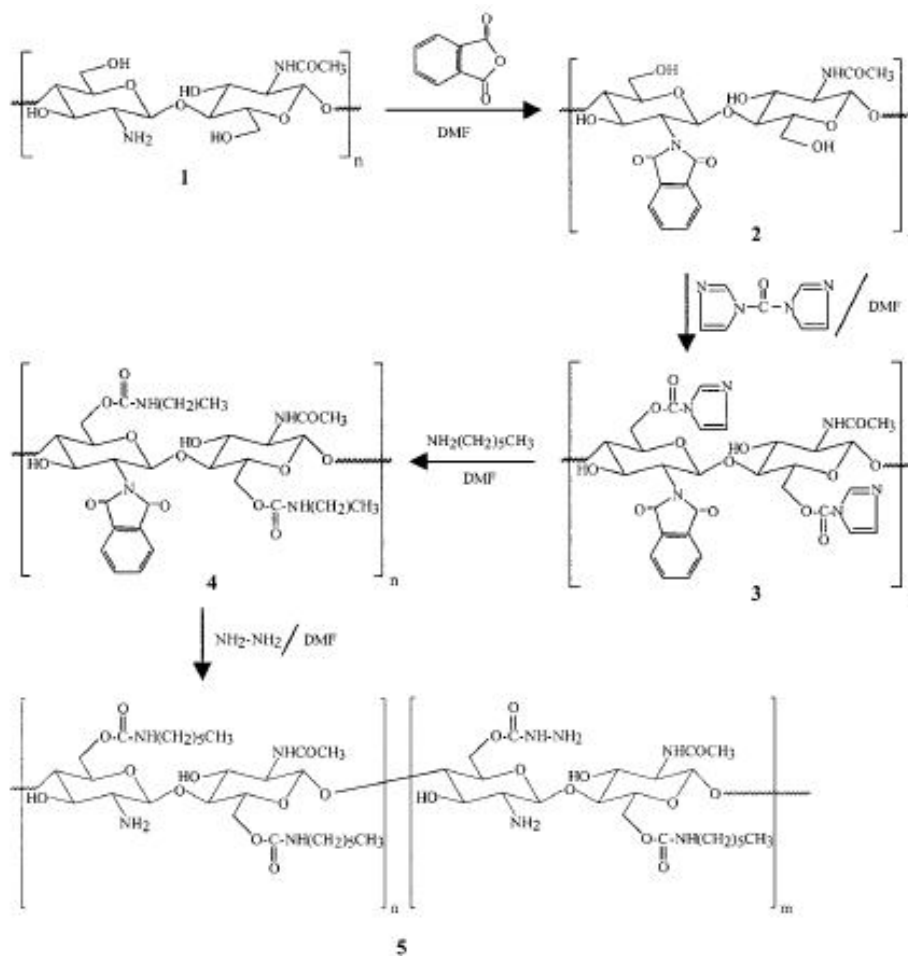


Figure 2.5: Preparation of γ -Ray Irradiated Chitosan Derivatives: N-Phthaloyl γ -Ray Irradiated Chitosan (2), N-Phthaloyl γ -Ray Irradiated Chitosan-CDI (3), N-Phthaloyl γ -Ray Irradiated Chitosan-CDI-(n-hexylamine) (4), and γ -Ray Irradiated Chitosan-CDI-(n-hexylamine) (5)

In order to overcome difficulties in the specific C-6 oxidation by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) of chitosan and chitosan derivatives, Bordenave et. al had used N-phthaloylation method to protect the amino groups. Oxidation with TEMPO was carried out after phthaloylation under milder conditions to avoid unwanted deprotection [57]. In the production of self-assembled polymeric micelles for drug delivery, phthaloylation is also involved as the hydrophobic site [72,79], a condition also needed for polymer electrolytes for devices application.

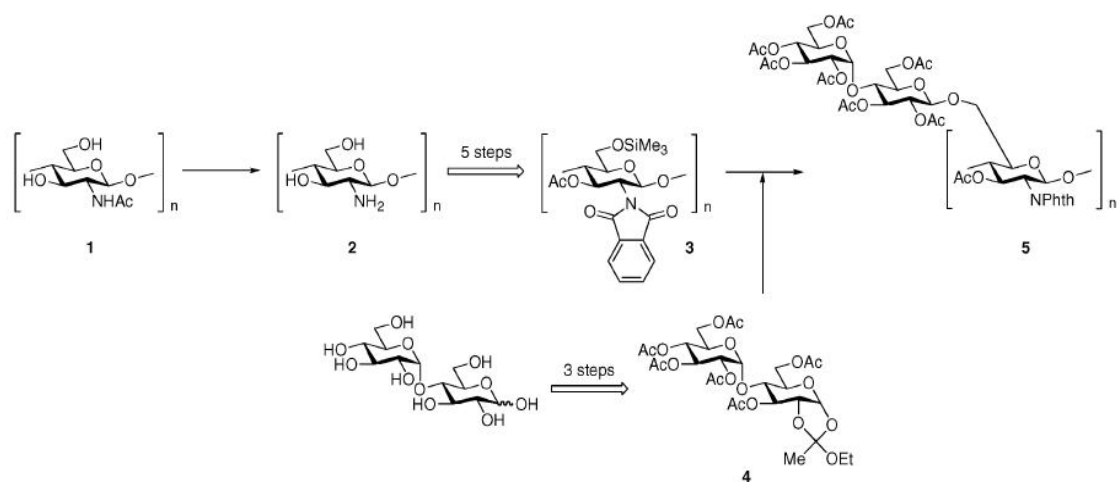


Figure 2.6: Synthesis of Chitin (**1**) and Chitosan (**2**) Having Disaccharide Maltose Branches (**5**) via 3-*O*-acetyl-2-*N*-phthaloyl-chitosan and the derived 6-*O*-trimethylsilyl derivative (**3**) and ortho ester of D-mannose (**4**) [77].

2.7.3. N-phthaloylchitosan as polymer electrolytes

PhCh has potential to be used as polymer electrolytes based. The presence of lone pair electrons, -C=O and -N- and -OH in the structure of PhCh, complexation of polymer-salt can be occurred. In this work, PhCh was used to produce polymer electrolyte membranes by doping the modified chitosan with different concentrations of lithium iodide (LiI).

2.8 Dye-sensitized solar cell (DSSC)

A solar cell is any device that directly converts the energy in light form into electrical energy through the process of photovoltaic. The general understanding of how solar cells work is that sunlight is that composed of photons of various energies. Photons can interact with atoms, and if sufficient energy, it can break the bond between an electron and the atom. In order to make solar cells produce electricity, it has to be able to “collect” the electron once it has been separated from the atom. The resulting flow is called the photocurrent. The

solar cells currently produced are generally divided into several types according to their material composition, such as silicon solar cell and dye solar cell.

Dye-sensitized solar cell has become an attractive device since Gratzel and O' Regan firstly reported the prototype of this type of solar cell in 1991 [80]. The dye-sensitized solar cell provides an attractive alternative to solid-state photovoltaics for the conversion of solar energy to electricity. This device has gained a lot of attentions due to low production cost, simple preparation technique over conventional solar cell and high energy conversion efficiency [1,5]. Chang et. al also stated that the production cost of the silicone-crystal based solar cells are higher than the DSSCs as DSSCs can be assembled in general environment at room temperature with their cost only around a third of the traditional silicone-based solar cells.

A DSSC consists of three parts as illustrated in *Figure 2.7* which are:

- a) Photo-active electrode
- b) Electrolyte
- c) Counter electrode

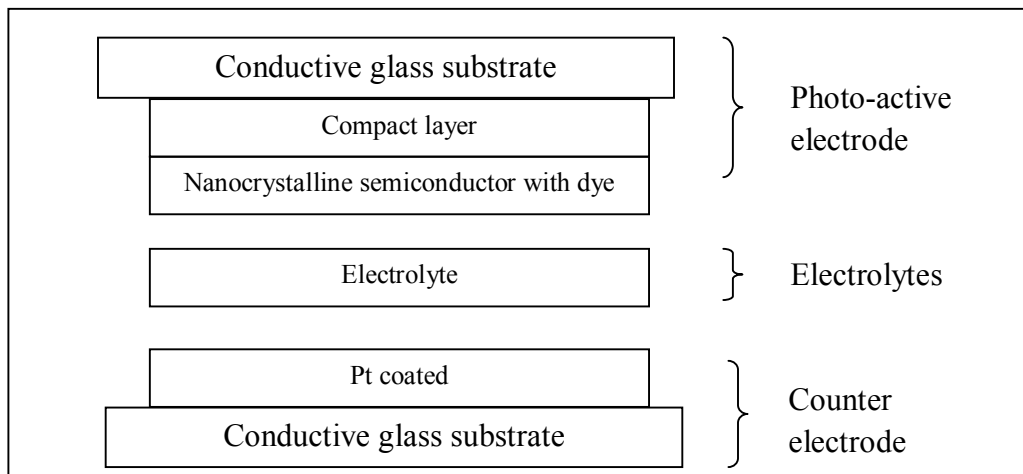


Figure 2.7: Dye-sensitized solar cell configuration

2.8.1 Photo-Active Electrode of DSSC

Photo-active electrode consists of two layers coated onto the conducting glass substrate. Compact layer is coated first onto the glass followed by nanocrystalline semiconductor with dye on the top of it.

2.8.1.1 Conducting glass Substrate.

Conducting glass substrate provides a transparent electrode that is normally used in DSSCs. It gives an advantage since it holds the dye-sensitized semiconductor film and reflects and absorbs the incident light. It also relays electric current to the external circuit [3]. Some of the examples of conducting glass substrate are:

- i. Fluorine doped tin oxide (FTO) [6,8,12,81]
- ii. Indium doped tin oxide (ITO) [11]
- iii. TEC8 conductive glass substrate by Hartford Glass CO, USA [13]

2.8.1.2 Compact layer

The compact layer acts as a blocking layer from the charge recombination process that takes place mainly at the TiO_2 /sensitizer and conductive glass substrate/ TiO_2 interfaces that limit the performance of DSSCs. In addition, the compact layer improves the adhesion of the TiO_2 to the conducting glass substrate and provides a larger TiO_2 /conducting glass substrate contact area [82]. Semiconductors such as TiO_2 [83], Nb_2O_5 [5], ZnO and some insulating materials such as CaCO_3 and BaCO_3 have been used as a blocking compact layer for fabrication DSSCs.

The compact TiO₂ layer is amongst the most suitable candidate as the blocking layer and has been most frequently investigated [84]. It has been deposited by different methods such as spray pyrolysis, dip-coating, spin-coating and chemical vapor deposition [83]. It has been shown that the TiO₂/polystyrene sodium sulfonated (PSS) layer is an effective blocking layer whereby the compact film has reduced porosity that is capable to prevent the physical contact of the I₃⁻ anions to the conductive glass substrate [83].

2.8.1.3 Nanocrystalline semiconductor with dye

The thin film of mesoporous nanocrystalline semiconductor, where dye molecule is absorbed is one of the important parts in DSSCs. The photovoltaic performances depend significantly on kind of inorganic material, morphology of the nanoparticle and the film porosity of the semiconductor [81].

TiO₂ is frequently used as a nanocrystalline semiconductor since it has demonstrated best performance compared to other oxide materials [81]. TiO₂ modified by chemical attachment of a dye monolayer, usually a ruthenium complex strongly absorbs light within wide range of the visible spectrum [13]

2.8.1.4 Dye Sensitizer

Natural dyes were numerously used as the sensitizer in DSSCs as shown in *Table 2.2*. Most of natural dyes contain anthocyanins. Anthocyanins (of the Greek *anthos* = flower and *kianos* = blue) are the most important pigments of the vascular plants as they are harmless and easy to incorporate in aqueous media. Anthocyanins is a class of highly conjugated compounds that is responsible for the red, purple, and blue colors of many

flowers (poppies, peonies, cornflowers), fruits (cranberries, rhubarb, strawberries, blueberries) and vegetables (beets, radishes, red cabbage) [69,85]. The anthocyanidins shown in *Figure 2.8* are the basic structures of anthocyanins. They are a huge variety of anthocyanins spread in nature and the main differences between them are the number of hydroxylated groups, the nature and the number of bonded sugars in their structure, the aliphatic or aromatic carboxylates bonded to the sugar in the molecule and the position of these bonds [85-86].

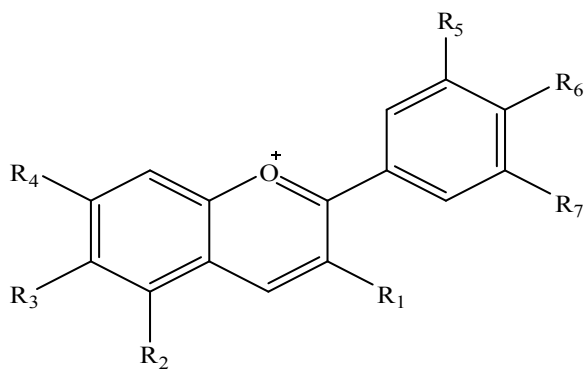


Figure 2.8: General structure of anthocyanidins

Isolated anthocyanins are highly instable and very susceptible to degradation [85,87]. Their stability is affected by several factors such as pH, storage temperature, chemical structure, concentration, light, oxygen, solvents, presence of enzymes, flavanoids, proteins and metallic ions [85,88]. The basic molecular structure of anthocyanin and the binding between anthocyanin molecule and TiO₂ particle is shown in *Figure 2.9* as the adsorption occurs with hydroxyl groups attached to phenyl group.

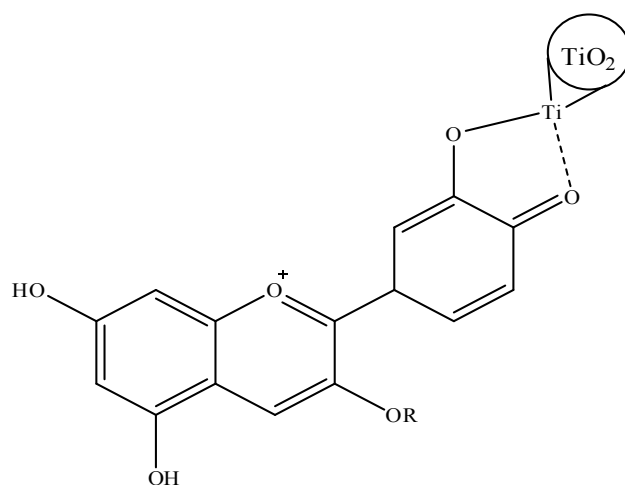


Figure 2.9: The basic molecular structure of anthocyanin and the binding between anthocyanin molecule and TiO₂ particle [80].

Table 2.2: Examples of natural dyes applied in DSSCs

No.	Natural dye	J _{sc} /mA cm ⁻²	V _{oc} /mV	FF	% η	Ref.
1	Pomegranate *	2.05	0.56	0.52	0.597	[9]
2	Mulberry	1.89	0.55	0.52	0.548	
3	Rosella	1.63	404	0.57	0.37	[8]
4	Blue pea flowers	0.37	372	0.33	0.05	
5	Red silician orange	3.84	340	0.50	0.66	[89]
6	Purple eggplant	3.40	350	0.40	0.48	
7	Spinach *	0.467	550	0.51	0.131	[90]
8	Ipomoea leaf *	0.914	540	0.56	0.278	
9	Canna indica L.	0.82	540	0.59	0.59	[10]
10	Salvia splendens	0.7	558	0.61	0.26	
11	Cowberry	0.4	556	0.54	0.13	
12	Solanum n. L	1.01	540	0.51	0.31	

* Chlorophyll

i. Black Rice

According to study by Hao et. al [80], natural dyes extracted from black rice performed the best photosensitized effect compared to the dye extracted from capsicum, erythrina variegata flower, rosa xantina and kelp. It is reported that from the I-V characteristic curve the value of I_{SC} , V_{OC} and FF are 0.551 V, 1.14 mA and 0.52, respectively. This is due to the better interaction between carbonyl and hydroxyl groups of anthocyanin molecule in the black rice extract that can be bound with the surface of TiO_2 porous film which is favored for the photoelectric conversion effect.

ii. Red Cabbage

Extract from red cabbage is rich with anthocyanins. Gluska et. al [91] revealed that the role of anthocyanins in the protection of meristematic cells of *A. cepa L.* roots against ions of Cd, Cr and Pb in mitodepressive and turbogenic effects. The antioxidative and chelating properties of the anthocyanins-rich extract were responsible for that positive action. Photosensitized parameter obtained by Furukawa et. al [92] by using dye of red cabbage were 0.68 mA/cm^2 , 0.52 V and 0.70 for J_{SC} , V_{OC} and FF, respectively.

2.8.2 Electrolytes

Solar cell is configured into three main parts and each under different conditions as shown in *Figure 2.10 (a)*. This includes an electrolyte which acts as kind of adhesive between photo-active electrode and counter electrode. Fabrication of compatible, non-liquid electrolyte system with good ionic conductivity for TiO_2 solar cells will facilitate large scale fabrication of highly efficient DSSCs [93]. Thus, a variety of factors that influence the cell

reaction has to be taken into consideration. It is impossible to predict the reaction rate and efficiency in the actual solar cell simply from the device design.

It would be expected that if the ionic conductivity is a rate determining step among the many transport processes, the electrolytes with maximum conductivity would match with the best cell efficiency in the solid state DSSCs. However, the results obtained by Cha et. al [5] showed that the maximum ionic conductivity did not match with the DSSC performance. Thus, it was suggested that the electron recombination also plays an important role in determination of cell performance. Meanwhile, a different situation was obtained by Ilperuma et. al [6], whereby the highest I_{sc} and V_{oc} values were observed for sample with high conductivity.

It should be noted that in DSSCs, iodine were added to polymer electrolyte to give the I/I_3^- redox couple.

2.8.3 Counter Electrode

The counter electrode normally is platinum or carbon-based coated on the conducting glass substrate. A thin reflecting platinum film is deposited onto the conducting glass to catalyze the iodide regeneration. Catalyst coating such as Pt on the counter electrode is important as absence of catalyst will lead to a slower rate reduction of I_3^- to I^- .

2.8.4 DSSC operation

In DSSCs, there are three important steps for photocurrent generation [11,81] as shown in *Figure 2.10*.

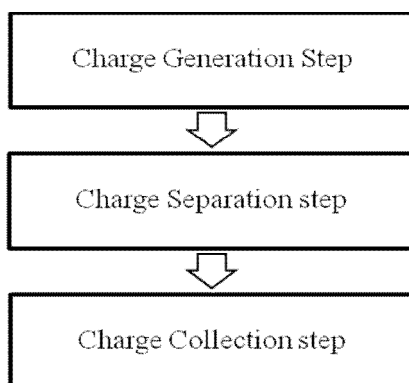


Figure 2.10: Steps for photocurrent generation in DSSCs

Salts in the electrolytes dissociated to form cation and anion (which is free iodide). The free iodide, Γ will forms triiodide with the iodine according to the equation reaction:



Charge generation step occurred when chemisorbed dye in DSSC absorbs visible light and the electrons on the ground state (Highest Occupied Molecular Orbital, HOMO) of dye are excited to the excited state (Lowest Unoccupied Molecular Orbital, LUMO) of dye.

At charge separation step, photo-excited electrons are injected from the excited sensitizer into the semiconductor's conduction band within pico- to femto-seconds. Then, the photo-injected electrons are transported through the porous TiO_2 network with rate of about micro to milli-seconds and eventually collected on conducting glass substrate. This step is referred to the charge collection step. Those three steps are essential for photocurrent generation.

Charge collection efficiency is not always 100% since photo-injected electron may recombine with oxidized dye via surface state of TiO_2 . At the interface, the triiodide is reduced by the electrons to Γ as in the following reaction:



The oxidized dyes are regenerated by oxidation of iodide within nano-second time scale as shown in this equation:



The dye is regenerated by an electron donor in the electrolyte solution. DSSC is fully regenerative, and the electron donor is again obtained by electron transfer to the electron acceptor at the counter electrode. These processes are illustrated in *Figure 2.11*.

In DSSC, it is essential to match up the energy level of each component as shown in *Figure 2.11 (b) below*. The conduction band of wide band gap material, such as TiO₂ lies on the position lower than the excited state of dye. In addition, the energy level of redox potential should be equal to or higher than the ground state of dye. Usually, the redox potential of the solution is hardly affected by the current and it is the same in both the dark and the light. Regarding electron transport, photo-inject electrons are transported by diffusion process because of lack of the built-in electric field in the entire TiO₂ film. Under the circumstance of constant generation of photocharge and removal at the conductive glass substrate contact, the Fermi energy level decrease in the direction of the conductive glass substrate contact at short-circuit condition.

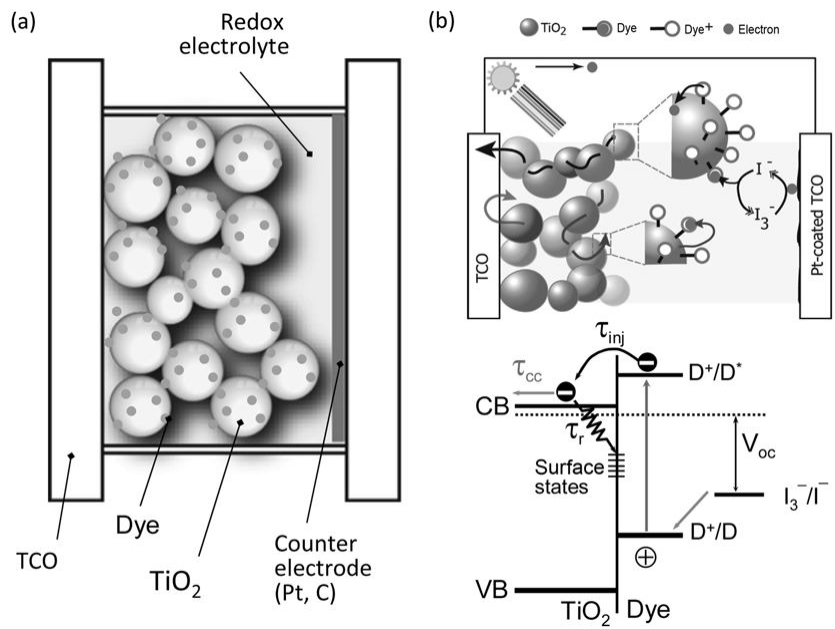


Figure 2.11: (a) Structure and constituting materials and (b) working principle of dye sensitized solar cell. In (b), the upper figure shows electron transport pathway and the lower figure represents energy position of each component in DSSC showing electron injection time constant (τ_{inj}), charge collection time constant (τ_{cc}) and time constant for recombination (τ_r) [81].