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Dyed sensitized solar cells: A technically and economically alternative concept to p-n junction photovoltaic devices

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Nanocrystalline dyed sensitized solar cells (DSSC) are photo-electrochemical cells based on principles similar to the processes in natural photosynthesis. They are based on photo sensitization of nanocrystalline semiconductor electrodes by absorbed dyes. The DSSC provides a technically and economically credible alternative concept to present day p–n junction photovoltaic devices. The DSSC work on a different principle, whereby the processes of light absorption and charge separation are differentiated. This is in contrast to the conventional systems where the semiconductor assumes both the task of light absorption and charge carrier transport. In the DSSC, the bulk of the semiconductor is used solely for charge transport; the photoelectrons are provided from a separate photosensitive dye. Charge separation occurs at the surfaces between the dye, semiconductor and electrolyte. This paper introduces the structure and operating principles of dye sensitized solar cells (DSSC). The key components including the semiconductor oxides, conducting substrates, the dye sensitizers, the electrolytes and the counter electrodes used in dye sensitized solar cell was reviewed in details. The result of various researches done especially to improve the performance and the conversion efficiency of the dye cell was presented. Hence this paper reviews the progress which has been made and the mechanism involved in the operation of dye sensitized solar cell.

Key words: Dye sensitized solar cell, nanocrystalline oxide semiconductor, counter electrodes, electrolytes, dyes.

INTRODUCTION

The sun's energy is the primary source for most forms of energy found on the earth. Solar energy is clean, abundant and renewable, hence holds a tremendous potential to benefit our world by diversifying our energy supply, reducing our dependence on fossil fuels, improving the quality of the air we breathe and stimulating our economy. It is no longer news that in order to reduce our over dependence on fossil fuels, renewable sources of energy must be employed. Sunlight on earth drives the wind, fills hydroelectric reservoirs with rainwater and produces heat, light and biomass.

Hydropower is the major source of electricity consumed in the country contributing about 32% of the total installed commercial capacity (Ismaila, 2006). With the fluctuations and outages in the supply of this electricity, there is need to tap into other renewable sources of energy.

To date, many of the solar energy systems are significantly more expensive than the traditional options available to customers (e.g. engines, gas heaters and grid electricity) in the short term. The cost, performance and convenience of these systems must be improved if solar energy is to compete in energy markets against more traditional alternatives. Large scale solar technologies like the solar photovoltaic system is yet to compete with the conventional energy systems. The biggest problem with the conventional approach is cost;

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photovoltaic cells require a comparatively thick layer of silicon in order to have reasonable photon capture rates, and silicon is an expensive commodity. There have been a number of different approaches to reduce this cost over the last decade, notably the thin-film approaches, but to date they have seen limited application due to a variety of pragmatic troubles. The dye sensitized solar cell (DSSC) has been around for a long time, but obtained only low conversion efficiencies, to a value well below 1% (Haiying, 2004). After the announcement of high efficiencies by Professor Grätzel and his research group in the early 1990s, at the Swiss Federal Institute of Technology, Lausanne, dye sensitized solar cell became a subject of much research. It tends to offer some solution in terms of simplicity of fabrication, low cost of production and availability of materials needed. Though more research is needed and is ongoing for the commercialization of these types of solar cells, the dye solar cells provide leverage for producing low cost electricity from the sun.

Nanocrystalline dyed sensitized solar cells are photo-electrochemical cells based on principles similar to the processes in natural photosynthesis. Both use organic dye to absorb the incoming light and produce excited electrons. A film of interconnected nanometer (nm) sized titanium dioxide (TiO_2) or other nanocrystalline semiconductor particles replaces nicotinamide adenine dinucleotide phosphate ($NADP^+$) and carbon dioxide as the electron acceptor, and iodide and triodide (I^-, I_3^-) replace water and oxygen as the electron donor and oxidation product, respectively (Greg and Grätzel, 1998). Hence DSSC are based on photo sensitization of nanocrystalline TiO_2 semiconductor electrodes by absorbed dyes. Like the coupled processes of photosynthesis and respiration found in the biosphere, the light driven electrochemical process in the nanocrystalline solar cell is regenerative and forms a closed cycle that converts light energy from the sun into useful forms (Greg and Grätzel, 1998). Direct energy conversion relies on the semiconductor material, which can absorb a fraction of the solar spectrum depending on its band gap energy. Unfortunately, many materials with adequate band gaps are susceptible to photo corrosion, due to destructive hole-based reactions. Also, the semiconductors less susceptible to photo corrosion, such as metal oxides like TiO_2 and SnO_2, exhibit a too large band gap to permit significant collection of visible light. An alternative to overcome the limited spectral sensitivity of the wide band-gap semiconductors, which are restricted to UV light, is surface modification with visible-light absorbing dye molecules. The sensitization of semiconductors using dyes is a century old technology, when it was used in the development of photography. Their application in solar energy conversion is more recent and progressed considerably after the seventies, with the advances in the development of dye sensitizers (Longo and De Paoli, 2003). The absorption spectrum of a sensitizer plays an important role in determining the conversion efficiency of a DSSC. Energy conversion efficiencies of up to 11% have been reported by using ruthenium (Ru) complex such as N3, N719 and black dye (Lin et al., 2007; Bessho et al., 2010). The dye molecules are quite small (nanometer sized), so in order to capture a reasonable amount of the incoming light, the layer of dye molecules needs to be made fairly thick, much thicker than the molecules themselves. To address this problem, a nanomaterial is used as a scaffold to hold large numbers of the dye molecules in a 3-D matrix, increasing the number of molecules for any given surface area of cell. In existing designs, this scaffolding is provided by the semiconductor material, which serves dual purposes (Wikipedia, 2009).

GENERAL OPERATING PRINCIPLES

Dye-sensitized solar cell is composed of nanocrystalline semiconductor oxide film electrode, dye sensitizers, electrolytes, counter electrode and transparent conducting substrate. Typically, dye-derived nanocrystalline titania films were used as photo anode and platinized counter electrode, filled with electrolyte solution of I_3^-/I^- in organic solvent, then the sandwiched solar cells are formed (Kong et al., 2007). The TiO_2 film on the glass plate is dipped into a solution of a dye such as an organometalic complex or a green chlorophyll derivative. A single layer of dye molecules adsorbs to each particle of the TiO_2 and acts as the absorber of light. To complete the device, a drop of liquid electrolyte containing iodide is placed on the film to percolate into the pores of the film. A counter electrode of conductive glass, which has been coated with a thin catalytic layer of platinum or carbon, is placed on top and the sandwich is illuminated through the TiO_2 side (Linda et al., 2008). These low-cost solar cells are manufactured by highly productive roll-to-roll printing methods over rigid or flexible substrates affording modules coloured in widely different tones. This attributes render DSSC a photovoltaic technology particularly well suited for BIPV applications and for electrification in developing countries (Pagliaro et al., 2009).

Conventional solar cells convert light into electricity by exploiting the photovoltaic effect that exists at semiconductor junctions. In a solid-state semiconductor, a photovoltaic cell is made from two doped crystals, one treated with n type impurities (n-type semiconductor), which has extra free electrons, and the other treated with p type impurities (p-type semiconductor unit), which is lacking free electrons but has excess hole. When directly in contact, some of the electrons in the n-type portion will flow into the p-type to "fill in" the missing electrons, also known as hole. Eventually enough will flow across the boundary to match the Fermi levels of the two materials. The result is a region at the interface of the p-n junction,

where charge carriers are exhausted and/or accumulated on each side of the interface. In silicon, this transfer of electrons produces a potential barrier of about 0.6 V to 0.7 V (Energy Business Daily, 2009). When placed in the sun, photons in the sunlight can strike the bound electrons in the p-type side of the semiconductor, giving them more energy, a process known technically as photoexcitation. In silicon, sunlight can provide adequate energy to push an electron out of the lower-energy valence band into the higher-energy conduction band. As the name implies, electrons in the conduction band are free to move about the silicon. When a load is connected across the cell, these electrons will flow out of the p-type side into the n-type side, thereby losing energy while moving through the external circuit, and then back into the p-type material where they can once again re-combine with the valence-band hole they left behind. In this way, sunlight creates electrical current.
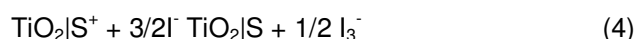
In any semiconductor unit, the band gap means that only photons with that measure of energy, or more, will contribute to producing an electric current. In the case of silicon, the majority of visible light from red to violet has enough energy to make this come about. This also means that the higher energy photons, at the blue and violet end of the spectrum, have more than enough energy to cross the band gap; while some of this extra energy is channelized into the electrons, the vast majority of it is consumed as heat. Another issue is that in order to have a reasonable chance of capturing a photon in the p-type layer, it has to be fairly thick. This also increases the chance that a freshly-ejected electron will meet up with a previously-created hole in the material before reaching the p-n junction. These limit the maximum efficiency of silicon photovoltaic cells, which is currently around 12 to 15% for common examples and about 25% for the best laboratory modules (Energy Business Daily, 2009). The semiconductor in the conventional solar cell performs two processes simultaneously: absorption of light, as well as providing the electric field for the separation of the electric charges ("electrons" and "holes") which are formed as a consequence of that absorption. However, to avoid the premature recombination of electrons and holes, the semiconductors employed must be highly pure and defect-free. The fabrication of this type of cell presents numerous difficulties, preventing the use of such devices for electricity production on an industrial scale.

In contrast, the dyed sensitized solar cells work on a different principle, whereby the processes of light absorption and charge separation are differentiated. In the DSSC, the bulk of the semiconductor is used solely for charge transport and the photoelectrons are provided from a separate photosensitive dye. Charge separation occurs at the surfaces between the dye, semiconductor and electrolyte. The structure and operating mechanism of the DSSC cells is shown in Figures 1 and 2, respectively.

Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of an oxide semiconductor film. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter-electrode by electrons passed through the load. The open circuit voltage of the solar cell corresponds to the difference between the redox potential of the mediator and the Fermi level of the nanocrystalline film that is E_f - E_{redox}. The second dashed (Figure 2) line represents an unwanted pathway by which electrons can be transferred directly from TiO$_2$ to I$_3^-$ short circuiting the cell so that electrons do not pass through the load.

The dye sensitized solar cell is composed of two surfaces of transparent conductor (mostly a conducting oxide on glass), onto one of which a few micrometer thick film of wide band gap semiconductor has been deposited in the form of a self-connected network of nanometer (nm) -sized particles, with a network of similarly or large sized self-connected pores in-between the particles. Under the irradiation of sunlight, the dye molecules became photo-excited and inject an electron into the conduction band of the semiconductor electrode, and then the original state of the dye is subsequently restored by electron donation from the electrolyte, usually the solution of an organic solvent or ionic liquid solvent containing the I$_3^-$/I$^-$ redox system. The initial events of electron injection and dye regeneration leading to photo induced charge separation occur on a femto- to nanosecond or microsecond time scale (Bach et al., 1999) while the redox capture of the electron by the oxidized relay and the electron migration across the nanocrystalline film, take place within milliseconds or even seconds (Grätzel, 2006a). The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. Regeneration of iodide ions, which are oxidized in this reaction to triodide, is achieved at a platinized counter electrode. This is shown in Equations 1 to 6.

$$TiO_2|S + hv \rightarrow TiO_2|S^* \tag{1}$$

$$TiO_2|S^* \rightarrow TiO_2|S^+ + e^- \tag{2}$$

$$TiO_2|S^+ + e^- \rightarrow TiO_2|S \tag{3}$$

$$TiO_2|S^+ + 3/2I^- \rightarrow TiO_2|S + 1/2\ I_3^- \tag{4}$$

$$1/2\ I_3^- + e^- \rightarrow 3/2\ I^- \tag{5}$$

$$I_3^- + 2e^- \rightarrow 3I^- \tag{6}$$

where S: represents the dye sensitizer (Haiying, 2004) and S* represents the excited state.

The circuit is completed through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the semiconductor electrode and the redox potential of the electrolyte. If only the earlier reactions take place, the
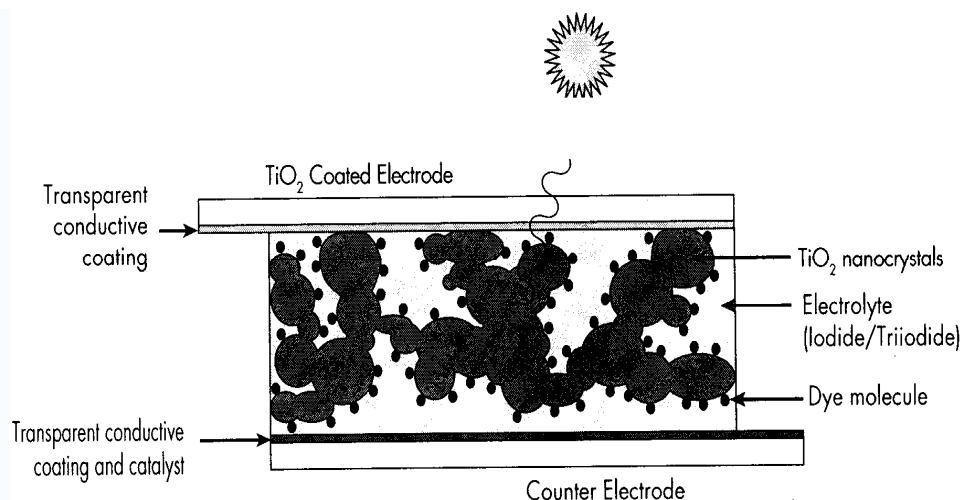
Figure 1. The structure of dye sensitized solar cell.
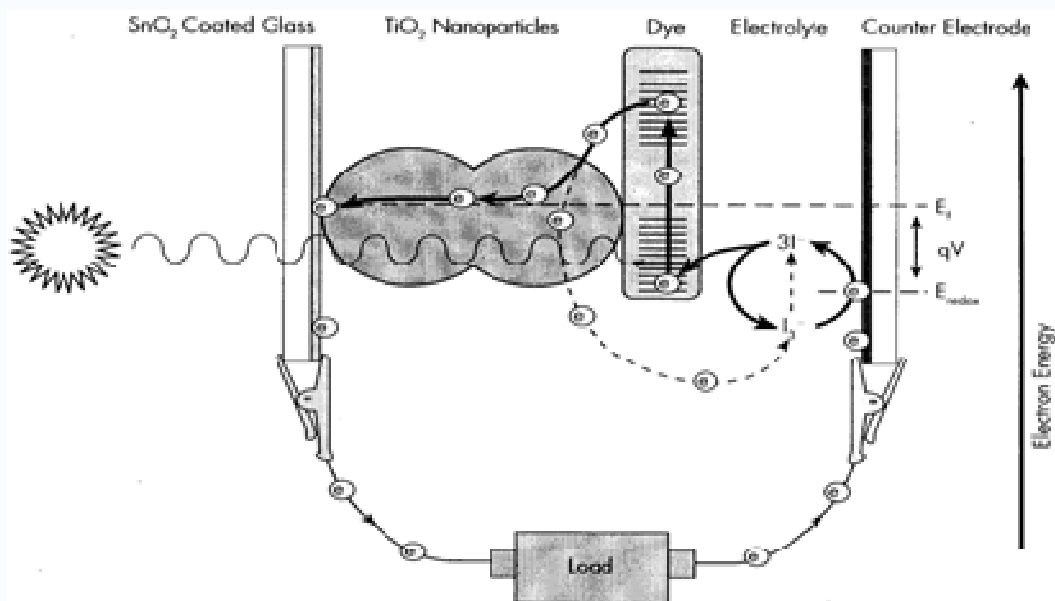
Figure 2. Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell (Adapted from Linda et al., 2008).

solar cell would be stable, delivering photocurrent indefinitely. The photocurrent yield depends on the spectral and redox properties of the dye, its excited state lifetimes, the efficiency of charge injection, the ionic conductivity of the electrolyte and the properties of the semiconductor electrode to collect and channel the electrons through the external circuit. For efficient operation of the cell, the rate of electron injection must be faster than the decay of the dye excited state. Also, the rate of re-reduction of the oxidized sensitizer (or dye cation) by the electron donor in the electrolyte must be higher than the rate of back reaction of the injected electrons with the dye cation, as well as the rate of reaction of injected electrons with the electron acceptor in the electrolyte. The kinetics of the reaction at the counter-electrode must also guarantee the fast regeneration of charge mediator or this reaction could also become rate limiting in the overall cell performance (Longo and De Paoli, 2003).

Overall, electric power is generated without permanent chemical transformation. Along with these processes, electrons in the conduction band of semiconductor may be recombined with the oxidized dye sensitizers or electron acceptor species in the electrolyte solution.

This probably occurs via traps and intermediate reactions. This reaction, also called "dark current", is the main loss mechanism for the DSSC (Longo and De Paoli, 2003).

In the case of solid-state dye-sensitized solar cells, the electrolyte solution is replaced by a wide band gap inorganic semiconductor of p-type polarity, such as copper iodide or copper thiocynate (CuI or CuSCN), or a hole-transmitting solid; for example, an amorphous organic arylamine and its derivatives. The excited dye injects electrons into the n-type oxide, and it is regenerated by hole injection in the p-type material. Then the operating principle of DSSC based on liquid electrolyte is corresponding with that of solid-state DSSC (Kong et al., 2007).

DSSC MATERIALS

As aforementioned, DSSC materials include nanocrystalline semiconductor oxide film electrode, dye sensitizers, electrolytes, counter electrode and transparent conducting substrate. The light-to-energy conversion performance of the cell depends on the relative energy levels of the semiconductor and dye and on the kinetics of the electron-transfer processes at the sensitized semiconductor/electrolyte interface. The rate of these processes depends on the properties of its components. DSSC has been under intense investigation in order to improve: 1. architecture of TiO_2 nanoparticles to have better electron transportation and diffusion, 2. electrolyte for faster redox reaction and stability at high temperature and 3. dye molecules for wider spectral coverage. Each of these will be discussed in details.

Nanocrystalline semiconductor film electrode

Semiconductor oxides used in dye-sensitized solar cells include TiO_2 (Haiying, 2004; Greg and Grätzel, 1998; Longo and De Paoli, 2003; Lin et al., 2007; Kong et al., 2007; Linda et al., 2008; Bach et al., 1999), zinc oxide, ZnO (Law et al., 2005; Charoensirithavorn and Yoshikawa, 2007; Guillen et al., 2008; Doh et al., 2011), tin dioxide (SnO_2), niobium oxide (Nb_2O_5), etc., which serve as the carrier for the monolayers of the sensitizer using their huge surface as the medium of electron transfer to the conducting substrate. Due to low-cost, abundance in the market, non-toxicity and biocompatibility, and as it also exhibits higher performance than other semiconductor oxides, TiO_2 became the best choice for DSSC till now. The TiO_2 is a wide band gap semiconductor Ebg ~ 3.2 eV. TiO_2 films are covered on the conducting substrate such as conducting glass, metal foil and flexible polymer film. Polycrystalline TiO_2 is prepared by either using the sol gel procedure which involves the anodic or thermal oxidative

hydrolysis of titanium precursors followed by autoclaving at temperatures up to 240°C to achieve the desired nanoparticle dimensions and crystallinity (Grätzel and Durrant, 2008; Kavan et al., 1993), pyrolysis of titanium alkoxides on Ti support (Kavan and Grätzel, 1995), radio frequency (RF) sputtering or sintering of TiO_2 powder using the commercially available TiO_2. The conducting substrate used is mostly indium-tin-oxide (ITO) (Ngamsinlapasathian et al., 2006), indium-zinc-oxide (Doh et al., 2011) and fluorine or antimony doped tin oxide (FTO, ATO) (Grätzel and Durrant, 2008; Ngamsinlapasathian et al., 2006). ITO and SnO_2 can be prepared on a glass substrate by chemical vapor deposition, sputtering, spray pyrolysis, electron beam evaporation and oxygen ion beam assisted deposition. General requirements for transparent conducting substrates are low electrical resistivity and high transparency in visible spectral region. The resistivity of glass-ITO electrodes can increase considerably after thermal treatment, which causes an increase in the series resistance in the DSSC, decreasing its performance. According to Longo and De Paoli (2003), this effect is not observed when glass-FTO electrodes are heated to such temperatures; hence transparent electrodes based on FTO are more adequate for application in DSSC than ITO electrodes. Both glass-ITO and glass-FTO electrodes are commercially available. However, transparent electrodes based on tin oxide thin films doped with F or Sb can be easily prepared by the spray pyrolysis technique, which consists in spraying over heated glass a methanol solution of $SnCl_4$ (or other precursor) containing the appropriate dopant (Longo and De Paoli, 2003). If this is not available, a standard soda lime glass can be coated with a layer of conductive antimony doped (Sb-doped) SnO_2 as described in (Greg and Grätzel, 1998). The doping of the SnO_2 is to reduce its resistivity. Fluorine substitutes O^{2-} and therefore acts as an electron donor resulting in a conduction mechanism of the n- type semiconductor.

When using the P25 TiO_2 powder, it is first ground in a mortar with a few drops of very dilute acetic or nitric acid. A small amount of water containing acetylacetone or bases or other TiO_2 chelating agents could also be used (Wikipedia, 2009). After a colloidal suspension is obtained, a few drops of Triton X-100 surfactant or a clear dishwashing detergent is added and mixed with TiO_2. The TiO_2 suspension is then applied on the conducting side of the conducting substrate and spread using doctor blading method (that is sliding a paste of semiconductor with a glass rod on the substrate using adhesive tape to control the thickness of the film), or screen printing techniques that is using a rigid squeege. This is then sintered at 450 to 550°C. This thermal treatment is to improve the electronic contact between the particles and the support and also among the particles of the film. It also eliminates contamination by residues of organic compounds present in the

suspensions used to prepare the film.

Other methods of preparing semiconductor film on flexible substrate have been identified. The nanocrystalline TiO_2 could be pre- and post-treated with $TiCl_4$ (Sommeling et al., 2006; Ito et al., 2008) and an increase in the photocurrent and conversion efficiency was achieved due to a shift in the conduction band edge of the TiO_2. Senadeera and Kobayashi (2005), used a technique they called "simple spraying technique" in which an ethanolic solution of titanium tetra-1-methylethoxide containing a few drops of HNO_3 (pH = 2) was spin-coated on pre-cleaned glass. An increase in the photocurrent and voltage was observed as against the normal method. One important limiting factor in the DSSC cell performance is electron transport. The replacing of the nanoparticle film with an array of oriented single crystalline nanorod offers the potential for improved electron transport leading to higher photo-efficiencies (Charoensirithavorn and Yoshikawa, 2007).

The sintering temperature of forming a robust film which is over 450°C limits the substrate to transparent conducting glass; hence limiting the flexibility, weight and overall thickness of the solar cell for commercial applications. Attempts to lower the costs and broaden the applicability of the DSSC led to the use of flexible polymer and plastic electrodes. Flexible electrodes, like the films of poly (ethylene terephthalate) coated with tin-doped indium oxide (PETITO) which present lower cost and some technological advantages relative to glass-ITO electrodes has been developed (Longo and De Paoli, 2003; Sommeling et al., 1998; Li et al., 2008). Plastic electrodes based on low temperature interconnection process were also developed (Grätzel, 2006b). But these methods are carried out at low temperature hence it precludes total elimination of organic residues from the surfactants. The DSSC prepared with such electrodes (active area of 0.32 cm^2) exhibited efficiencies of 4 to 5%. However, their stability was poor, which was associated with the water permeability of the flexible electrodes (Longo and De Paoli, 2003).

As mentioned previously, the high surface area of the nanocrystalline TiO_2 film plays a crucial role for increasing the performance of the photo electrochemical cell in energy conversion. Smaller grains have bigger surface area per volume, and thus absorb more rays. But bigger clumps, closer to the wavelength of visible light, cause light to ricochet within the thin light-absorbing surface so it has a higher chance of being absorbed. For a planar electrode, light harvesting is poor due to the small absorption cross section of a monolayer of the dye. In highly porous films of a few micrometer thicknesses, the available surface area for dye adsorption can be enormous, leading to near extinction of incident light. In a report (University of Washington, 2008), what was called a popcorn design in which the researchers made only very tiny grains of ZnO of about 15 nm across was shown. They clumped these into larger agglomerations,

about 300 nm across. The larger balls scatter incoming rays and force light to travel a longer distance within the solar cell. The balls' complex internal structure, meanwhile, creates a surface area of about 1,000 square feet for each gram of material. This design more than doubled the efficiency which was achieved when using only small particles. To guarantee the regeneration of the oxidized dye, the structure of the pores was as such that they permitted the penetration of the electrolyte containing the redox couple, and also an effective mass transport of electroactive species by diffusion.

Dye sensitizer

The role of the dye in DSSC consists in acting as a molecular electron pump. It absorbs the visible light, pumps an electron into the semiconductor and accepts an electron from the redox couple in the solution, and then repeats the cycle. The ideal sensitizer for a single-junction photovoltaic cell converting standard global air mass 1.5 (AM1.5) sunlight to electricity should absorb all light below a threshold wavelength of about 920 nm, and should upon excitation inject electrons into the solid with a quantum yield of unity (Grätzel, 2004). In addition, it must also carry attachment groups such as carboxylate or phosphonate to firmly graft it to the semiconductor oxide surface. Sensitizers having the general structure ML2(X)2 where L stands for 2,2′bipyridyl-4,4′-dicarboxylic acid, M is ruthenium (Ru) or osmium (Os) and X represents a halide, cyanide, thiocyanate, acetyl acetonate, thiocarbamate or water substituent, are particularly promising (Grätzel, and Durrant, 2008).

An efficient photo sensitizer should therefore fulfill some requirements such as an intense absorption in the visible region, strong adsorption onto the semiconductor surface and efficient electron injection into the conduction band of the semiconductor. Moreover, it must be rapidly regenerated by the mediator layer in order to avoid electron recombination processes and be fairly stable, both in the ground and excited states (Ismaila, 2006). A solar cell must be capable of producing electricity for at least twenty years, without a significant decrease in efficiency hence the dyes used should be stable for such a long time. Many natural dyes can be utilized, but they must possess a chemical group that can adsorb to the TiO_2 surface and they must have energy levels at the proper positions necessary for the electron injection and sensitization. The dyes used in dye sensitized solar cell are divided into two types; the organic and inorganic dyes according to their structure. Inorganic dyes includes metal complexes such as polypyridly complexes of ruthenium and osmium, metal porphyrin, phthalocyanine and inorganic quantum dots while organic dyes includes natural organic and synthetic organic dyes. Compared with organic dyes, inorganic complex dyes have high thermal and chemical stability. Among these, the most

efficient sensitizers in nanocrystalline TiO_2 DSSC are based on polypyridyl complexes of transition metals, particularly ruthenium (II) and osmium. This is because they show a strong and broad absorption band in the visible range due to metal-to-ligand charge transfer (MLCT) leading to excited states with long lifetimes. Polypyridyl ruthenium dye may be divided into carboxylate polypyridyl, phosphonate and polynuclear bipyridyl ruthenium dyes. The difference between the first two types of sensitizers lies in the adsorption group. The first two types of sensitizers differ from the last type of sensitizer in the number of metal center. The carboxylate polypyridyl ruthenium dye is in level structure, which enables the electron injection into the conduction band of the semiconductor quantitatively.

Among these sensitizers, cis-bis(isothiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II), which is usually referred to as 'N3', or in its partially deprotonated form (a di-tetra-butyl ammonium salt) also known as 'N719' are most commonly used. The absorption spectrum of fully protonated N3 has maxima at 518 and 380 nm, with extinction coefficients of 1.3×10^4 M-1 cm^{-1} and 1.33×10^4 M-1 cm^{-1}, respectively. The complex emits at 750 nm, the excited-state lifetime being 60 ns. The optical transition has MLCT character: excitation of the dye involves transfer of an electron from the metal to the π^* orbital of the surface-anchoring carboxylated bipyridyl ligand, from where it is released in a timescale of femtoseconds to picoseconds into the conduction band of TiO_2, generating electric charges with unit quantum yield. Carboxylate polypyridyl ruthenium sensitizers are easy to be desorbed from the surface in the aqueous solution when the pH value is lower than 5 while the phosphonate polypyridyl ruthenium sensitizers uses phosphonate group to be anchored to the surface of the semiconductor, which is hardly desorbed from the semiconductor surface even at high pH (Longo and De Paoli, 2003; Kong et al., 2007; Grätzel and Durrant, 2008).

Attempting to further improve the efficiency of such systems requires an enhanced spectral response of the sensitizer toward longer wavelengths, that is, in the red and near-IR region. This was accomplished with the dye tris(cyanato)-2,2',2''-terpyridy1-4,4',4''-tricarboxylate) Ru(II), called "black dye". Black dye displayed very efficient panchromatic sensitization of TiO_2 over the whole visible range extending to near-IR region up to 920 nm, which results in a better overlap with the solar spectrum. The photocurrent action spectrum for a cell prepared with nanocrystalline TiO_2 sensitized with black dye exhibited incident photon-to-current efficiency (IPCE) values of 80% over a broad wavelength range extending from 400 to 700 nm. IPCE is calculated as the ratio of collected electrons to incident photons. Under standard AM 1.5 solar emission, the cell exhibited a photocurrent of ~ 20 mA cm^2 and an overall efficiency exceeding 10% (Grätzel and Durrant, 2008; Longo and De Paoli, 2003).

Figure 3 shows the structure of some dyes. The incorporation of carboxylate groups allows ligation to the film surface via the formation of bidendate and ester linkages, whilst the (–NCS) groups enhance the absorption of visible light.

Some authors have proposed and are investigating using two sensitizers; one being the red or black ruthenium complex and the other an organic dye showing strong absorption in the near-infrared region to increase the spectral response though most of the results are yet to be published. NaRu(4-carboxylic acid-40-carboxylate)(4,40-bis[(triethylene-glycolmethylether) heptylether]-2,20-bipyridine)(NCS)2 (coded as K68) was used (Kuang et al., 2008) and power conversion efficiency of 6.6% was obtained using an ionic liquid electrolyte containing 1-propyl-3-methyl-imidazolium iodide (PMII) and 1-ethyl-3-methyl-imidazolium tetracyanoborate (EMIB(CN)4). For a non-volatile organic solvent based electrolyte, a photovoltaic power conversion efficiency of 7.7% was obtained under simulated full sun light and the cell exhibited a good thermal stability during the accelerated test under 80°C in the dark. Amphiphilic ruthenium dyes having long alkyl chains (N621, N918) (Kawano et al., 2007) and Z907 (Lukas and Grätzel, 2006) have been used. N621 and N918 were used with ionic liquid crystal electrolyte while N3 dye was used as a reference. A conversion efficiency of 3.5 and 2.4% were obtained while using N621 and N918, respectively. McCall et al. (2009) synthesized and characterized two series of ruthenium bipyridyl dyes incorporating sulfur-donor bidentate ligands with general formula [Ru(R-bpy)$_2$C2N2S2] and [Ru(R-bpy)$_2$(S2COEt)][NO$_3$] (where R=H, C2N2S2=cyanodithioimidocarbonate, S2COEt=ethyl xanthogenate and bpy =bipyridyl.

Some organic dyes have been synthesized and used. C103 was synthesized and used by Shi et al. (2008), JK 53 and JK 54 (Kawano et al., 2007), JK51 and JK52 (Lukas and Grätzel, 2006) and Xanthene dyes by Guillen et al. (2008). The synthesis and the photovoltaic characterizations of a series of perylene imide sensitizers have been carried out (Fortage et al., 2008). When considering organic dyes for use in DSSCs, porphyrins and phthalocyanines have attracted particular attention, the former because of the analogy with natural photosynthetic processes, while the latter is because of their photochemical and phototherapeutic applications. However, porphyrins cannot compete with the N3 or black dye sensitizer due to their lack of red light and near-IR absorption. Phthalocyanines, on the other hand, show intense absorption bands in this spectral region. However, problems with aggregation and the unsuitable energetic position of the lower unoccupied molecular (LUMO) level, which is too low for electron transfer to the TiO_2 conduction band, have turned out to be intractable for the moment (Grätzel and Durrant, 2008). Table 1 shows the conversion efficiency of some dyes when
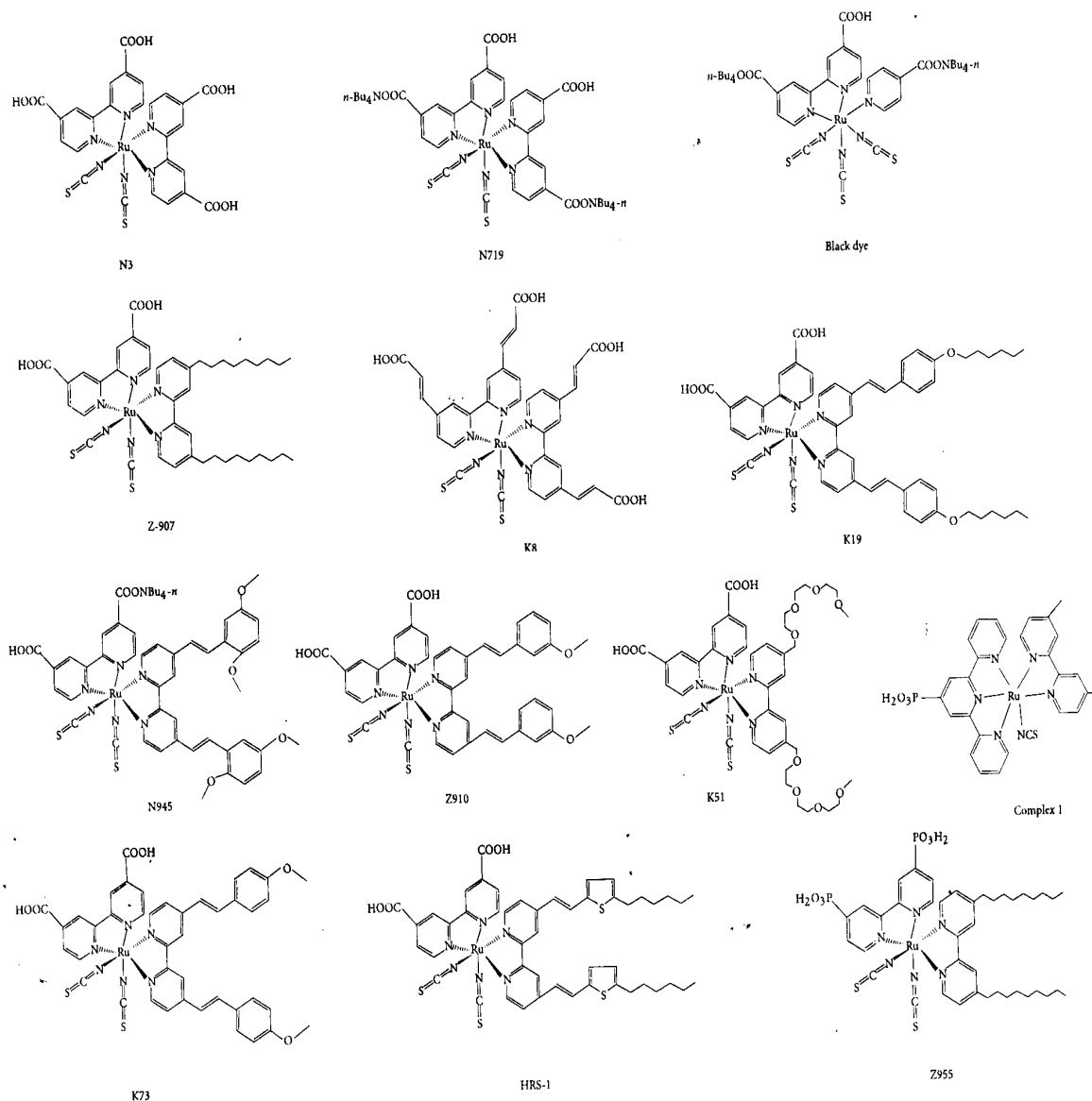
Figure 3. Molecular structure of ruthenium dyes (Adapted from Kong et al., 2007).

used with certain electrolytes.

Semiconductor quantum dots are another attractive option for panchromatic sensitizers. These are nanoscale colloidal semiconductor particles with band gaps tunable by the size of the colloid. The principle is governed by quantum mechanics and the particles small enough to produce quantum confinement effects (Guyot-Sionnest, 2007). The absorption spectrum of such quantum dots can be adjusted by changing the particle size. Such principle has been used by Lin et al. (2007) and the result of the research showed an efficiency of 1.35%. One problem with this approach is the photo-corrosion of the quantum dots that will almost certainly happen if the junction contact is a liquid redox electrolyte. However, quantum dots are expected to display higher stability in solid state heterojunction devices. The advantage of Q-dots over conventional dyes as sensitizers is their very high extinction coefficients, which allows thinner films of the mesoporous oxide to be used. This should reduce the dark current, increasing the open circuit voltage (Voc) and the overall efficiency of the cell (Grätzel and Durrant, 2008).

Electrolyte

The electrolyte is one of the key components for dye-sensitized solar cells and its properties have much effect on the conversion efficiency and stability of the solar cells. Subsequent electron injection depends on the

Table 1. Conversion efficiency of some dyes.

Dye	Electrolyte	J_{sc} (mA.cm^{-3})	V_{oc} (V)	FF	η (%)
N3	Ionic liquid crystal	8.4	0.57	0.54	2.6 (Kawano et al., 2007)
N3	Ionic liquid	7.2	0.62	0.52	2.4
N621	Ionic liquid crystal	9.1	0.66	0.58	3.5
N621	Ionic liquid	6.3	0.64	0.62	2.5
N918	Ionic liquid crystal	7.4	0.62	0.52	2.4
N918	Ionic liquid	5.0	0.63	0.64	2.0
C103	Low volatility electrolyte	9.11	0.76	0.74	10.0 (Shi et al., 2008)
C103	Solvent free ionic liquid electrolyte	8.55	0.688	0.77	8.9
Z907	Ionic liquid	13.9	0.73	0.69	7.0 (Kuang et al., 2008)
K51	Ionic liquid	14.8	0.73	0.72	7.7
K68	Ionic liquid	14.4	0.76	0.69	7.6
JK 53	0.6 M 1-hexyl-2,3-dimethylimidazolium iodide, 0.05 M I$_2$, 0.1 M LiI, and 0.5 M tert-butylpyridine in CH$_3$CN	6.37	0.70	0.74	3.31 (Baik et al., 2009)
Jk54	0.6 M 1-hexyl-2,3-dimethylimidazolium iodide, 0.05 M I$_2$, 0.1 M LiI, and 0.5 M tert-butylpyridine in CH$_3$CN	7.52	0.71	0.75	4.01
JK2	0.6 M 1-hexyl-2,3-dimethylimidazolium iodide, 0.05 M I$_2$, 0.1 M LiI, and 0.5 M tert-butylpyridine in CH$_3$CN	14.0	0.75	0.77	8.01
JK52	0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.05M iodine, 0.1 M LiI and 0.5 M 4-tert-butylpyridine in acetonitrile	15.56	0.68	0.70	6.88 (Kim et al., 2009)
Jk51	0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.05M iodine, 0.1 M LiI and 0.5 M 4-tert-butylpyridine in acetonitrile	17.43	0.68	0.71	8.42
Mercurochrome		3.1	0.63	0.56	1.1 (Guillen et al., 2008)

reducing ability of the electrolyte. The electrolyte used in DSSC is divided into three types: liquid electrolyte, quasi-solid state electrolyte and solid electrolyte. Liquid electrolyte could be divided into organic solvent electrolyte and ionic liquid electrolyte according to the solvent used. Organic solvent electrolytes were widely used and investigated in dye sensitized solar cells for their low viscosity, fast ion diffusion, high efficiency, easy to be designed and high pervasion into nanocrystalline film electrode (Shi et al., 2008; Baik et al., 2009; Kim et al., 2009; Cerneaux et al., 2008). Ionic liquid electrolytes (Guillen et al., 2008; Kuang et al., 2008; Kawano et al., 2007) have a better chemical and thermal stability than organic solvent electrolytes.

The composition of the electrolytes includes organic solvent, redox couple and additive. The commonly used additive in the electrolytes for dye-sensitized solar cells contained 4-tert-butylpyridine (TBP) and N-methylbenzimidazole (NMBI). The addition of these additives could suppress the dark current and improve the photoelectric conversion efficiency. Organic solvent used in organic liquid electrolyte include nitrile such as acetonitrile, valeronitrile, 3-methoxypropionitrile and esters such as ethylene carbonate (EC), propylene carbonate (PC) and γ-butyrolactone (Kong et al., 2007). One important limitation to DSSC is the volatility of the electrolyte containing I^-/I_3^- redox couples well as problems in encapsulation of the liquid electrolyte. Possible advantages of the I^-/I_3^- redox couple include the fact that the charge carrier is negatively charged, thereby reducing the likelihood of recombination reactions with electrons injected into the TiO$_2$ (Nogueira et al., 2001). Some attempts have been made to overcome the problem of volatility and encapsulation. Colbalt II (Co(II)) and Colbalt III (Co(III)) were investigated for replacing I^-/I_3^- redox couple (Cameron et al., 2004), though the performance was not as good as that of I^-/I_3^- redox couple. Solidifying the liquid electrolyte to form quasi solid electrolyte either by using polymeric or gel materials (Bhattacharya et al., 2009; Chittibabu and Hadjikyriacou, 2002; Wang et al.,

2004; Biancardo, 2006; Thavasi et al., 2008) is another option. Some of the early studies on the use of poly electrolytes were on lithium chlorate- poly (ethylene oxide) complexes which were shown to have tendency to crystallize at room temperature (Armand et al., 1979). Further research led to the development of polymers that could retain their ability to solvate and conduct ions but remain amorphous at room temperature (Armand et al., 1979; Gazotti et al., 2000) as higher ionic mobilities and thus conductance occur in the amorphous regions of polymers. Bhattacharya et al. (2009) reported the preparation of a series of solid polymer electrolytes with different cations. They chose a poly (ethylene oxide) (PEO)- poly (ethylene glycol) PEG blend (40:60 w/w) and complexed it with LiI, NaI, KI, NH_4I, 1-ethyl-3-methylimidazolium iodide (EMII) and 1- hexyl-3-methylimidazolium iodide (HMII) with the same ion to monomer ratio. They concluded that the cell performance of the DSSC fabricated with the systems used showed strong dependence on the cation radii and that the concept of ion intercalation and surface adsorption used for liquid electrolyte systems can be extended to the polymer electrolytes. Chittbabu et al. (2002) prepared the gel electrolyte by cross-linking polymeric material like poly (4-vinylpyridine), employing metal ion and specifically lithium ion. The performance of the gel electrolyte incorporated DSSC were essentially similar to ionic liquid electrolyte containing lithium ion incorporated dye-sensitized solar cells. Wang et al. (2004) employed poly (vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) and silica nanoparticles to solidify 3-methoxypropionitrile based liquid electrolytes containing an ionic liquid, 1-methyl-3-propylimidazolium iodide, as iodide resource and the conversion efficiency was close to 7%. De Paoli et al demonstrated that a polymer electrolyte comprising a poly (epichlorohydrin-co-ethyleneoxide) elastomer, sodium iodide (NaI) and I_2 as mobile redox carriers was an effective hole transporter in dye-sensitized nanocrystalline solar cells (Nogueira et al., 2001). They showed that unsealed devices employing this polymer electrolyte achieved solar to electrical energy conversion efficiencies of 1.6% under one sun, increasing to 2.6% at 1/10th of a sun. Park et al. (2009), designed honey-comb like structure on a dye TiO_2 coated electrode and introduced the liquid electrolyte into the pores of the structure which immobilized the liquid forming a quasi solid electrolyte. A conversion efficiency of about 8% was obtained with the cell.

Another alternative which offers itself to confront the sealing problem is replacement of the redox electrolyte with solid state hole conductors. Some of the hole conductors which have been used are CuI, CuSCN, spiro-OMeTAD, AV-DM, AV-OM and aniline oligomers (Senadeera and Kobayashi, 2005; Grätzel, 2003; Shozo et al., 2009; Kim and Wamser, 2006). One of the major differences between these liquid state (LS) and solid state (SS) is the nature of the charge transport. While the

ionic transport controlled by diffusion prevails in the LS, the electronic transport influenced by conductivity and charge transport mobility plays the deciding role in SS. Though the efficiencies of quasi state (QS) or SS based cells have not surpassed the cells based on liquid electrolytes, the results so far are promising and with more research, there is hope that high efficiencies will be achieved in the nearest future.

Counter electrodes

The task of the counter electrode is the reduction of the redox species used as a mediator in regenerating the sensitizer after injection or collection of the holes from the hole conducting material in a solid state DSSC. At present, several kinds of counter electrodes, CEs have been introduced, and they are platinized transparent CEs (Baik et al., 2009; Kim et al., 2009; Jun et al., 2008), carbon CEs (Kay and Gratzel, 1996; Lee et al., 2008) and conductive polymer CEs (Sommeling et al., 1998). The standard catalyst on the CE in most of the publications is platinum because of the high catalytic activity and high corrosion stability against iodine in the electrolyte and the deposition methods commonly used are electrochemical and thermal deposition methods (Sommeling et al., 1998; Baik et al., 2009; Kim et al., 2009; Jun et al., 2008). Wang et al. (2004) used a Ti plate as the substrate to prepare the counter electrode instead of the fluorine-doped tin oxide glass and found that the fill factor, conversion efficiency and the current density were higher than that of SnO_2: F doped glass. This was found to be due to a decrease in the internal resistance of the cell. Ngamsinlapasathian et al., (2006), compared using double layer of Indium Tin oxide ITO and Tin dioxide ITO/SnO_2 with using only ITO and found that the double layer proved to be a better substrate than the single ITO for higher solar cell performance. To improve not only the electro-catalytic activity by increasing the active surface of the platinum but also the adhesion on the substrate, Kim et al. (2006) used a platinium-nickel oxide (Pt-NiO) biphase electrode for a counter electrode. This was prepared by means of an RF magnetron co-sputtering system on fluorine-doped SnO_2. The short circuit current density increased from 0.44 to 0.61 mA/cm^3 while the cell efficiency increased from 3.2 to 4.3%. Metals like steel and nickel could also be used as substrates for counter electrodes but because the I^-/I^-_3 redox couple in the electrolyte corrode these metals, it is difficult to employ them as substrates. However, if their surfaces are covered completely with anti-corrosion materials such as carbon or fluorine-doped SnO_2, it is possible to employ these materials as the substrate of the CE (Murakami and Grätzel, 2008). Carbon nanotubes have also been proposed for use as counter electrodes, though result of using such is yet to be published as at the time of this report.

Conclusion

Basically, DSSC is based on conduction by electron injection from the dye to the semiconductor and redox reaction to reduce the dye. Since Grätzel his research group reported high efficiency in dye sensitized solar cell more than ten years ago, different efficiency records have been announced by various groups. Several of these efficiencies obtained were by varying the key components of DSSC; ranging from the semiconductor oxide, the conducting substrates and the dye sensitizer to the electrolyte. Researchers in a bid to increase the efficiency of DSSC are incorporating ionic salts known as green solvents with a view to preventing evaporation and the consequent reduction in efficiency. Roll to roll manufacturing process by fabricating the DSSC on plastics are being developed. The maximum efficiency obtained in laboratory so far is only 11%, which is competitive but it drops when extrapolated to an industrial scale. The main technological challenges are the volatility of the I^-/I_3^- redox electrolyte, the inflexibility of glass substrates and the problem of cell degradation when organic dye is used since organic dyes can be degraded by the action of sunlight, with the consequent reduction in useful life compared to silicon cells. However, if flexible substrates are used, their properties of flexibility and variety of colours and shapes can be employed and such cells can be used as decoration in coloured windows that not only allow light through but use this light to generate electricity. Although currently less efficient than the silicon based solar cell, DSSC is more cost efficient due to the low cost of the materials than the silicon solar cells. Hence more research should be focused on producing more stable, flexible, environmental resistant, lower cost and higher efficient DSSC.

REFERENCES

Armand MB, Chabagno JM, Vashisha P (1979). Polyethers as Solid Electrolytes. In Fast Ion Transport in Solids Electrodes Electrolytes, Proc Int. Conf.; Vashishta, P., Mundy. JN and Shenoy, GK, Eds.; Elsevier North: Amsterdam, p. 131-136.

Bach U, Tachibana Y, Moser JE, Haque SA, Durrant JR, Gratzel M, Klug DR (1999). Charge Separation in Solid-State Dye-Sensitized Heterojunction Solar Cells. JACS, 121(32): 7445-7446.

Baik C, Kim D, Kang MS, Kang SO, Ko J, Nazeeruddin MK, Grätzel M (2009). Organic dyes with a novel anchoring group for dye-sensitized solar cell applications J. Photochem. Photobiol. A: Chemistry, 201(2-3): 168-174.

Bhattacharya B, Lee JY, Geng J, Jung HT, Park JK (2009). Effect of cation size on solid polymer Electrolyte based Dye- sensitized solar cell. Langmuir, 25(5): 3276-3281. DOI: 10.1021/1a8029177.

Biancardo M (2006). Incorporation of gel electrolyte in dye-sensitized solar cells could widen applications. SPIE Newsroom, DOI: 10.1117/2.1200609.0394.

Cameron PJ, Peter LM, Zakeeruddin SM, Grätze M (2004). Electrochemical studies of the Co(III)/Co(II)(dbbip)₂ redox couple as a mediator for dye-sensitized nanocrystalline solar cells. Coordination Chem. Rev., 248(13-14): 1447–1453.

Cerneaux SA, Zakeeruddin SM, Gratzel M, Yi BC, Spiccia L (2008). New functional triethoxysilanes as iodide sources for dye-sensitized solar cells. J. Photochem. Photobiol. A: Chemistry, 198: 186–191.

Charoensirithavorn P, Yoshikawa S (2006). High-Efficiency Dye-Sensitized Solar Cell Based on ZnO Nanorod Arrays Electrode. MRS Proceedings, 974, 0974-CC07-10 DOI:10.1557/PROC-0974-CC07-10.

Chittibabu KG, Hadjikyriacou S, Li L (2002). Ionic liquid based gel electrolyte compositions for dye sensitized solar cells. Materials Research Symposium Proceedings, 736: 245-250.

Doh JG, Man G K, Nam GP, Kang JK (2011). Enhanced photocurrent and photo voltage of dye sensitized solar cells with TiO₂ film deposited on Indium –doped zinc oxide substrate" Available at: http://www.electrochem.org/dl/ma/202/pdfs/0897.PDF, as at 8/01/11.

Energy Business Daily (2009). Dye sensitised solar cell. Global Energy Industry Market News and Analysis April 2009, http://energybusinessdaily.com/power/dye-sensitized-solar-cell accessed 26/11/2009.

Fortage J, Séverac M, Houarner-Rassin C, Pellegrin Y, Blart E, Odobel F (2008). Synthesis of new perylene imide dyes and their photovoltaic performances in nanocrystalline TiO₂ dye-sensitized solar cells. J. Photoche. Photobiol. A: Chemistry, 197: 156-169.

Gazotti WA, Spinaec MAS, Girotto EM, De Paoli MA (2000). Polymer electrolytes based on ethylene oxide–epichlorohydrin copolymers. Solid State Ionics, 130: 281-291.

Grätzel M (2004). Conversion of sunlight to electric power by nanocrytalline dye-sensitized solar cells. J. Photochem. Photobiol. A: Chemistry, 164: 3-14.

Grätzel M (2006b). Photovoltaic performance and long-term stability of dye-sensitized meosocopic solar cells. Comptes Rendus Chimie, 9(5): 578-583.

Grätzel M, Durrant JR (2008). Dye-Sensitised Mesoscopic Solar Cells In: Mary D Archer & Arthur J (eds.) Series on Photoconversion of Solar Energy -Vol. 3: Nanostructured and Photoelectrochemical Systems for Solar Photon Conversion, Imperial College Press, Nozik, pp. 503-536.

Grätzel M (2003). Dye Sensitized Solar Cells. J. Photochem. Photobiol. C: Photochem. Reviews. 4: 145–153.

Grätzel M (2006a). The magic world of nanocrystals from batteries to solar cells. Curr. App. Phys. 651: e2-e7. DOI: 10.1016/j.cap.2006.01.002.

Greg PS, Gratzel M. (1998). Demonstrating electron transfer and nanotechnology: A Natural Dye–sensitized Nanocrystalline Energy Converter. J. Chem. Edu. 75: 752-756.

Guillen E, Casanueva F, Anta JA, Vega-Poot A, Oskam G, Alcantara R, et al (2008). Photovoltaic performance of nanostructure zinc oxide sensitized with xanthene dyes. J. Photochem. Photobiol. A: Chemistry, 200: 364-370.

Guyot-Sionnest P (2007) Quantum Dots: An Emerging Class of Soluble Optical Nanomaterials. Materials Matters: Chemistry Driving Performance, 2(1): 10-12.

Haiying W (2004). Dye Sensitized Solar Cell. Literature Seminar, Department of Chemistry, University of Alabama Nov. 23rd. Available at: http://www.docstoc.com/docs/26772993/Dye-Sensitized-Solar-Cells

Ismaila HZ (2006). Hydropower Resources in Nigeria. 2nd Hydro Power for Today Conference, International Centre on Small Hydro Power, April 22-25, Hangzhou, China. Available at: http://www.unido.org/fileadmin/import/52413_Mr._Ismaila_Haliru_Zarma.pdf

Ito S, Murakami TN, Comte P, Liska P, Grätzel C, Nazeeruddin MK, Grätzel M. (2008). Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. Thin Solid Films, 516 (14): 4613-4619.

Jun Y, Son JH, Sohn D, Kang MG (2008). A module of a TiO₂ nanocrystalline dye-sensitized solar cell with effective dimensions. J. Photochem. Photobiol. A: Chemistry, 200(2-3): 314-317.

Kavan L, Gratzel M (1995). Highly efficient semiconductor TiO₂ photo electrodes prepared by aerosol pyrolysis. Electrochimica. Acta., 4(5): 64-652.

Kavan L, O'Regan B, Kay A, Gratzel M (1993). Preparation of TiO₂, (anatase) films on electrodes by anodic oxidative hydrolysis of TiCl₃. J. Electroanal. Chem., 346(1-2): 291-307.

Kawano R, Nazeeruddin MK, Sato A, Grätzel M, Watanabe M (2007). Amphiphilic ruthenium dye as an ideal sensitizer in conversion of light to electricity using ionic liquid crystal electrolyte. Electrochem.

Commun., 9: 1134–1138.

Kay A, Gratzel M (1996). Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder. Solar Energy Mater. Solar Cells,, 44: 99-117.

Kim D, Song K, Kang MS, Lee JW, Kang SO, Ko J (2009). Efficient organic sensitizers containing benzo[cd]indole: Effect of molecular isomerisation for photovoltaic properties. J. Photochem. Photobiol. A: Chemistry, 201(2-3): 102-110.

Kim HS, Wamser CC, (2006). Photoelectropolymerization of aniline in a dye-sensitized solar cell. Photochem. Photobiol. Sci., 5: 955–960.

Kim SS, Park KW, Yum JH, Sung YE (2006). Pt-NiO nanophase electrodes for dye sensitsed solar cells. Solar Energy Mater. Solar Cells, 90(3): 283-290.

Kong FT, Dai SY, Wang KJ. (2007). Review of Recent Progress in Dye-Sensitized Solar Cells. Advances in OptoElectron. Vol. 2007, Article ID 75384, doi:10.1155/2007/75384

Kuang D, Klein C, Snaith HJ, Humphry-Baker R, Zakeeruddin SM, Graetzel M (2008). A new ion-coordinating ruthenium sensitizer for mesoscopic dye-sensitized solar cells. Inorganica Chimica Acta., 361: 699-706.

Law M, Greene LE, Johnson JC, Saykally R, Yang P (2005). Nanowire dye-sensitized solar cells. Nat. Mat., 4: 455-459. DOI:10.1038/nmat1387.

Lee WJ, Ramasamy E, Lee DY, Song JS (2008). Performance variation of carbon counter electrode based dye-sensitized solar cell. Solar Energy Mater. Solar Cells, 92(7): 814-818.

Li X, Lin H, Li JB, Wang N, Lin CF, Zang LZ, (2008). Chemical sintering of graded TiO_2 film at low temperature for flexible dye sensitized solar cells. J. Photochem. Photobiol. A: Chemistry, 195: 247-253.

Lin SC, Lee,YL, Chang CH, Shen YJ, Yang YM (2007). Quantum- Dot – sensitized solar cells: Assembly of CdS-quantum-dots coupling techniques of self assembled monolayer and chemical bath deposition. Appl. Phys. Lett., 90: 143517.

Linda F, Amy H, Shanks K, Bruecken P, Goates W (2008). Nanocrystalline Solar cell Kit: Recreating Photosynthesis. Institute for Chemical Education Madison, WI (1998). Available at: http://www.solideas.com/solrcell/cellkit.html, accessed 23/12/2010.

Longo C, De Paoli M (2003). Dye-sensitized solar cells: a successful combination of materials. J. Braz. Chem. Soc., 14(6): 898-901.

Lukas SM, Gratzel M (2006). TiO_2 pore-filling and its effect on the efficiency of solid-state dye-sensitized solar cells. Thin Solid Films, 500: 296-301.

McCall KL, Jennings JR, Wang H, Morandeira A, Peter LM, Durrant JR, Yellowlees LJ, Woollins JD, Robertson N (2009). Novel ruthenium bipyridyl dyes with S-donor ligands and their application in dye-sensitized solar cells. J. Photochem. Photobiol. A: Chemistry, 202: 196-204.

Murakami TN, Gratzel M (2008). Counter electrodes for DSC: Application of functional materials as catalysts. Inorganica Chimica Acta, 361: 572–580.

Ngamsinlapasathian S, Sreethawong T, Suziki Y, Yoshikawa S, (2006). Double layered ITO/SnO_2 conducting glass for substrate of dye sensitized solar cell. Solar Energy Mater. Solar Cells, 90(14): 2129-2140.

Nogueira AF, Durrant JR, De Paoli MA (2001). Dye- sensitized Nanocrystaline Solar cells: Employing a polymer Electrolyte. Adv. Mater., 13(11): 826-830.

Nogueira AF, Spinace MAS, Gazotti WA, Girotto EM, Paoli MA (2001). Poly(ethylene oxide-co-epichlorohydrin)/NaI: a promising polymer electrolyte for photoelectrochemical cells. Solid State Ionics, 140(3-4): 327-335.

Pagliaro M, Palmisano G, Ciriminna R (2009). Working principles of dye-sensitised solar cells and future applications, Photovoltaics Int., 3: 47-50.

Park JH, Nho YC, Kang MG (2009). Dye-sensitized solar cells containing polymer film with honey-comb like morphology. J. Photochem. Photobiol A: Chemistry, 203, (2-3): 151-154.

Senadeera GKR, Kobayashi S (2005). Versatile preparation method for mesoporous TiO_2 electrodes suitable for solid–state dye sensitized photocells. Bull. Mater. Sci., 28: 635-641.

Shi D, Pootrakulchote N, Li R, Jin Guo J, Wang Y, Zakeeruddin SM, Gratzel M, Wang P, (2008). New efficiency records for stable dye-sensitized solar cells with low-volatility and ionic liquid electrolytes. J. Phy. Chem: C, 112: 17046–17050.

Shozo Y, Yukyeony K, Youhai Y, Kazuhiro M (2009). Nanocrystalline TiO_2 solar cells fabricated using Aniline oligomers as hole conductors. Hybrid and Organic Photovoltaic Conference, Book of Abstracts Paper OG7, Grand Hotel Bari, Benidorm, Spain, 10-13 May 2009.

Sommeling PM, O'Regan BC, Haswell RR, Smit HJ, Bakker NJ, Smits JJT, et al. (2006). Influence of a $TiCl_4$ Post-Treatment on Nanocrystalline TiO_2 Films in Dye-Sensitized Solar cells. J. Phys. Chem. B, 110: 19191-19197.

Sommeling PM, Späth M, Van Roosmalen JAM, Meyer TB, Meyer AF (1998). Dye-Sensitized Nanocrystalline TiO2 Solar Cells on Flexible Substrates. Proceedings of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, pp. 288-291.

Thavasi V, Jose R, Ganga K, Allakhverdier SI, Ramakrishna S (2008). Non liquid based electrolytes for dye molecules sensitized solar cells. J. Qafqaz University, 23: 34-42.

University of Washington (2008). Solar Energy: Popcorn-ball design doubles efficiency of dye-sensitized solar cells. ScienceDaily. Retrieved June 25, 2010, from http://www.sciencedaily.com /releases/2008/04/080410140451.htm.

Wang GQ, Lin RF, Wang M, Zhang CN, Lin Y, Xiao XR et al. (2004). Low sheet resistance counter electrode in dye sensitized solar cell. Chinese Chem. lett, 15 (11): 1369-1372.

Wang P, Zakeerudidn SM, Gratzel M. (2004). Solidifying liquid electrolytes with fluorine polymer and silica nanoparticles for quasi-solid dye-sensitized solar cells. J. Flu. Chem., 125: 1241–1245.

Wikipedia (2009). Dye sensitized solar cell. The Free Encyclopedia, http://en.wikipedia.org/wiki/Dye-sensitized_solar_cell, Assessed 12/06/2009.