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Dye Sensitized Solar Cell: A Summary

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Abstract

Dye sensitized solar cell (DSSC) devices incorporating organic and inorganic materials have found a host of applications. The search for low-cost, high efficient and flexible devices has lead to a remarkable increase in the research and development of solar cell. The current review, describes the constitution components of DSSC in a detailed manner and their development and challenges are also discussed. We focused on various structural modifications in wide band gap nano-crystalline semiconductor materials for an efficient electron transfer to reduce the recombination rate. Fruitful attempts have been made to design new molecular dyes for the wide range of absorption in the visible region. Co-Sensitization is an appropriate technique to enhance the absorption range of dye molecules and to increase the efficiency of solar cell. Moreover hole transport materials, there are the efficient tool to replace redox couple based liquid electrolyte and it produce stable solid state DSSC. The successful modification of counter electrode with different morphology promotes the rate electron transfer into electrolyte. This review also covers the update technology to construct efficient, stable and flexible dye sensitized solar cell.

Introduction

Dye sensitized solar cell (DSSC) is a pillar of modern technology particularly in solar cell due to it's low cost with high efficiency and its flexible device application. Solar energy is the perfect key to sustainable development for future energy requirements. Especially, solar cells are promising devices to generate clean energy. DSSC is a type of photoelectrochemical cell looking like a sandwich structure, whose working principle is based on photovoltaic effect [1]. DSSCs are alternative photovoltaic devices for commercial silicon solar cell. The origin of DSSC was first introduced by Vogel et al (1870) by using silver halide in gelatin medium which are photo active in UV region [2], and then Vogel (1873) silver halide sensitized with dye molecule to make photo activity in visible region [3]. Followed by Hishiki (1965) and Gerisher (1968) sensitized rose bengal and cyanine dyes [4, 5] with zinc oxide. Daltrozzo and Tributch investigated the Rhodamine B dye on ZnO [6]. By the various studies in 1977 Spitler and Calvin replaced ZnO by using TiO_2 [7]. For last few decades Ruthenium dye sensitized with TiO_2 semiconductor was widely used for DSSC which was introduced by Gratzel at 1990. DSSC was first designed by Gratzel and O Regon in 1991; it was a millstone in solar cell research. They introduced large surface area of TiO_2 nanoparticles act as photoanode and an iodine based redox couple was used as a electrolyte to achieve 7.1% efficiency under AM 1.5 G condition [8]. Recently liquid electrolyte based cobalt redox couple achieved 12.3% which is the highest efficiency [9]. But the liquid electrolyte restricts the potential and stability of the system by arising leakage, solvent evaporation and corrosive properties. Solid electrolytes are substituted by liquid electrolyte to achieve good stability with poor

efficiency of DSSC. More efforts are made by many researchers to improve the both efficiency and stability of solar cell. Efficiency and stability of dye sensitized solar cell are enhanced in an effective manner by modifying their molecular structure of dye, counter electrode, electrolyte, structural morphology of semiconductor metal oxides and conducting flexible transparent material. In recent days it is possible to make flexible devices on large scale by printing on flexible substrate materials followed by roll to roll production and its purification processes are also be cost effective. In this review, we focused on updated knowledge and current developments on constitution component of DSSC.

Structure and working process

DSSC have unique structural properties compared with other photovoltaic cell, because it consist nanomaterials and molecular devices. A simple photo-electrochemical cell like DSSC is a photo-electrode which combines semiconductor material (TiO_2) and sensitized dye molecule. The photo-electrode and catalytic counter electrode are deposited on transparent conducting material. Electrolyte is the combination of organic and inorganic material (inorganic salts, redoxcouple, n-type semiconductor, conducting polymers). Electric energy generated from photo-electrode, dye molecules are act as a sensitizer and it absorbed the photon from incident light then its attains the excitation state followed by fast electron injection to the conduction band of semiconductor which sensitizer anchored with TiO_2 semiconductor material. Then transparent conducting material transports the electron to counter electrode among outer circuit. The dye should be oxidized at ground state which again regenerates through the electrolyte. The role of electrolyte is reduction by the oxidized dye molecule for continuously electron production and electrolyte regenerate itself getting electron from outer circuit along with (in the way) counter electrode.

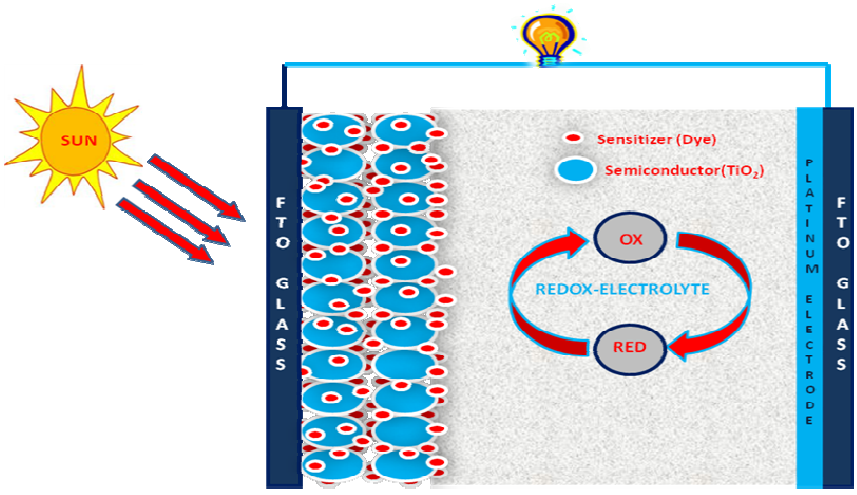

Fig. 1 Schematic representation of dye-sensitized solar cell.

The constitution components of DSSC are transparent conducting material, semiconductor material, sensitizer, electrolyte and catalytic electrode. Schematic diagram Fig. 1 shows constitution components of DSSC. Fig. 2 shows the working process of DSSC.

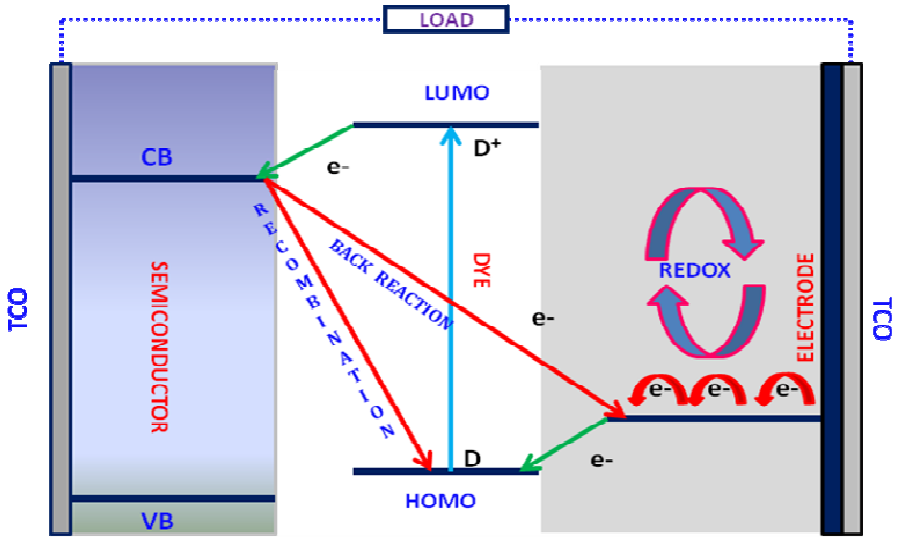

Fig. 2 Various process obtained in dye-sensitized solar cell

Transparent Conducting Oxide

Generally transparent conducting oxides are n-type wide band-gap semiconductors with a relatively high concentration of free electrons in the conduction band and also have high optical transmission and electrical conductivity. Transparent conducting oxide (TCO) like indium doped tin oxide (ITO) and fluorine doped tin oxide (FTO) [10, 11] are desirable to DSSC applications. Transparent conducting oxide ITO & FTO film are coated and estimated on glass, plastic & stainless steel material. High charge mobility and thermally stable transparent conductive oxides are enhancing the optoelectronic properties. Hence it attracts more attention due to their low cost and simple preparation process. Indium doped tin oxide (ITO) are used as transparent electrode in solar cells due to its high optical transparent properties and good electrical conductivity at visible region [12, 13]. The change in electrical properties with respect to temperature will play an important role and the temperature above 350˚C will increase the electrical resistance as three times as compare at ambient temperature. The reason for this at high temperature ITO bonded with atmospheric oxygen hence reducing conductivity [14]. The indium free fluorine doped tin oxide (FTO) is thermally stable and it can also be reliable to use in hydrogen containing environments. The glass based FTO is widely used in dye sensitized solar cells.

Glass-Transparent Conducting Oxide

Glass TCO based DSSC exhibits more efficiency with high optical property. Fluorine doped tin oxide and indium doped tin oxide double layers are coated on glass plates by spray pyrolysis method to enhance the transparent properties and achieved an efficiency of 3.7% .This double layer deposition was to avoid oxidation of ITO at high temperatures [14].Triple-layered transparent conducting oxide film included Indium doped tin oxide (ITO), Antimony-doped tin oxide (ATO) and Titanium dioxide (TiO_2) were developed by magnetron sputtering technique. TiO_2 layer was influenced by photocurrent efficiency of dye sensitized solar cell and also investigated efficiency with TiO_2 and without TiO_2 layer. Triple-layered transparent oxides exhibit high photoconversion efficiency than FTO [15]. DSSC with FTO photoelectrode was more efficient than that ITO based photoelectrode [16].The investigation of fluorine doped tin oxide and indium doped tin oxide under same conditions reported photocurrent efficiencies upto 9.6% and 2.24% respectively. The resistivity of ITO at room temperature is 18 Ω/sq and its resistivity increases upto 52 Ω/sq by

sintering at 450 ^{0}C with decrease in efficiency. But the FTO resistivity was stable at both room and high temperatures [17]. Recently an optical property of ITO was enhanced by localized surface plasmon effect when the gold nanostructure fabricated on ITO surface [18].

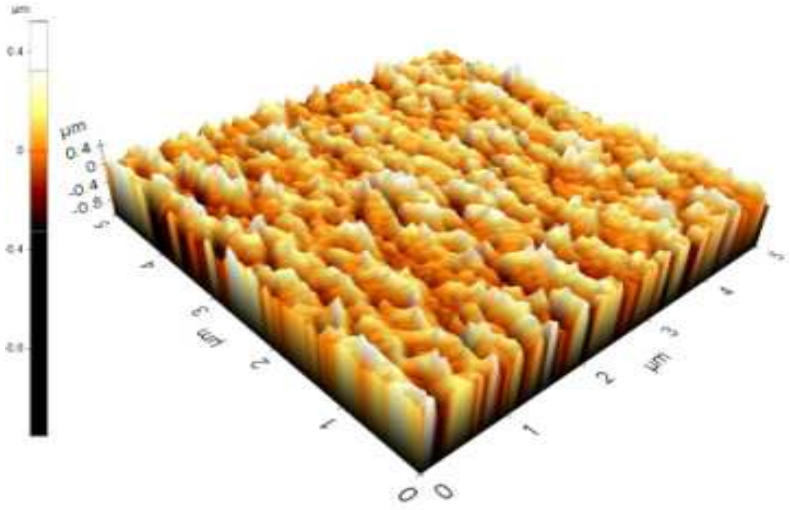

Fig. 3 Atomic Force Microscopy (AFM) image of FTO glass [Adapted from Ref: 19]

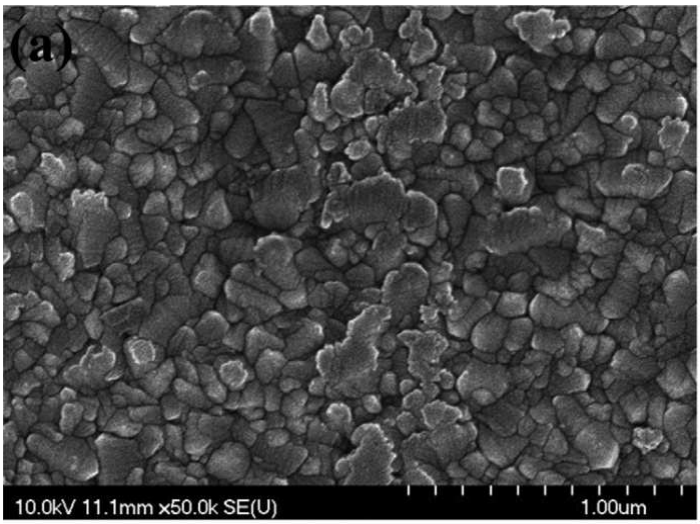

Fig. 4 Field Emission scanning electron microscopic image of FTO glass-top view [Adapted from Ref: 20].

Plastic Transparent Conducting Oxide

A substitution of polymer material instead of a glass material is the appropriate way to increase flexibility and reduce weight. The conducting oxide layer coated on transparent polymer materials like PET (poly ethylene terephthalate) & PEN (poly ethylene naphthalene) produces flexible electrode as well as flexible DSSC. The flexible DSSC was designed in different shapes and applied to different surfaces. Flexible transparent materials are unstable at high temperatures. As a solution to this problem various low temperature methods are developed to fabricate TiO_2 semiconductor on a plastic substrate. Mostly used low-temperature methods are ball-milling, press method, lift-off method, electrodepositing and chemical sintering.

Press method was introduced by Hagfeldt et. al. The photoelectrode which is an oxide semiconductor is deposited on a plastic conducting material by press method [21, 22] at low temperatures. Durr et. al. developed lift-off method. In this method TiO_2 is coated on a gold layer which is coated over a glass plate. TiO_2 layer was subjected to sintering process and then collected from glass plates by dissolving gold layer in suitable solvent. Subsequently semiconductor TiO_2 film transferred on ITO-PET substrate by applying high pressure and is reported to have a photocurrent efficiency of 5.8% [23]. Flexible DSSC was constructed with platinum ITO-PEN counter electrode and titanium metal sheet photoelectode. Platinum is coated on ITO-PEN by electrodeposition method; the light is illuminated on counter electrode surface to produce photocurrent efficiency of 7.2% [24].Temperature free press method produce plastic photo-electrode and hence attained a photo-conversion efficiency of 7.4% under 100mW/cm^2, air mass 1.5G condition [25]. ITO-PEN substrate based mesoporous TiO_2 photoelectrode was developed by doctor blade method in low temperature condition below 130 ^{0}C. Photo-electrode made by binder free condition achieves 6.4% efficiency [26]. The plastic photo-electrode was developed by low-temperature preparation method used with binder free TiO_2 and ITO-PEN. The adhesion property was enhanced between TiO_2 and polymer conducting material by TiO_x buffer layer. It showed photocurrent efficiency 6.31% with ruthenium based SJW-E1 sensitizer [27]. Nanocrystalline TiO_2-P25 was fabricated on plastic transparent conducting material by ball milling method, without used binder and high temperature process. The flexible DSSC sensitized with N719 dye obtained efficiency of 4.2%. Milling methods was produced to prevent the agglomeration because TiO_2 nanoparticles were well dispersed in the paste. So increased film strength and surface area to enhance dye absorption on TiO_2 surface also produced good contact between TiO2 and plastic TCO [28]. Press method produced high efficient plastic substrate dye sensitized solar cells and hence achieved an efficiency of 8.1%under one sun condition. UV-O_3 treatment was carried out to titanium dioxide coated on ITO-PEN film material [29]. Platinum coated on plastic conducting substrate ITO-PEN by electrodeposition method used as counter electrode. The surface morphology and formation of platinum cluster on flexible substrate deposition were shown by the SEM and HR-TEM results .The flexible DSSC with nanocrystalline TiO_2/Ti photoelectrode attained an efficiency of 6.35% [30].

Transparent Conducting Oxide -Stainless steel

In DSSC by reducing internal resistance of stainless steel based counter electrode, it can improved fill factor and conversion efficiency [31]. The SiO_x-sputtered stainless steel material fabricating with nanocrystalline TiO_2 electrode achieved a photocurrent efficiency of 4.2%, then the advantage is that the stainless steel electrode can be sintered to high temperature [32]. The titanium dioxide was deposited on stainless steel material with various thicknesses by electro-synthesis method and further investigated the effect of TiO_2 film thickness on photocurrent [33]. The industrial metal sheet like stainless steel and carbon steel used as counter electrodes were reported to have a photo-conversion efficiency of 3.6% and 3.1% with iodine redox couple electrolyte [34]. Flexible stainless steel substrate based mesoporous TiO_2 photo-electrode controls dark current density and achieved efficient photovoltaic performance of 8.6 % [35].Stainless steel foil with polymer material polypyrrol combination as counter electrode with N719 dye and iodine electrolyte was reported of an efficiency 2.36 % [36].

Semiconductor

Wide band-gap metal oxide semiconductors are ideal materials for DSSC photo-electrode since it produces large surface cross section area to anchored light harvester. The essential aspects for nano-crystalline metal oxide should be high surface area, good structural arrangement, high electron

transfer, chemical stability, low cost and environment friendly. A semiconductor undergoes modification of their morphologies, porosities and film thicknesses to enhance rate of charge transfer and prevent back reaction.

Titanium dioxide

Nanocrystalline semiconductor, titania have attained huge interest in DSSC because of their high surface area large amount of dye could be absorbed following the increase in amount of light absorption [37]. It has to exhibit high photo absorption cross section value among the available semiconductor material in above band-gap of 3.0 eV. Titania exhibits three different structural morphology, those are rutile (tetragonal, Eg ~ 3.05 eV), anatase (tetragonal, Eg ~ 3.23 eV) and brookite (orthorhombic, Eg ~ 3.26 eV). The rutile is thermodynamically stable and also favor to solar cell application, although rutile phase TiO_2 is not widely applied in DSSC. The anatase TiO_2 has high electric conductivity. Hence it has a high electron diffusion coefficient and large dye absorbing capacity than rutile photelectrode [38-40. Anatase photoelectrode is widely used in DSSC because it produces high open circuit current than rutile TiO_2. Rate of the electron transfer speed depends upon the structural morphology of nanocrystalline semiconductor materials. So the structure of semiconductor electrode was designed properly [41]. The spherical TiO_2 nanoparticle was arranged periodically to produce high open circuit current, less recombination rate and high efficiency [42]. TiO_2 with high surface area and uniformly arranged nanocrystalline structure attribute to high light to current conversion efficiency [43]. Several groups developed composition of nanoparticle and nanowires to increase charge mobility of mesoporous film material [44, 45]. Nanorods produce large surface area, higher roughness factor and increases electron life time. One dimension nanorods compared with spherical nanoparticle produces higher conversion efficiency [46]. Titania nanoparticles are also investigated in 1-D shape such as nanorods, nanotubes and nanowires, which increases the electron transporting speed along with the nanocrystalline semiconductor to transparent conducting material. Several methods are available to prepare one dimensional TiO_2 nanoparticle. Few methods are two step sol-gel (gel-sol) process [47], non-hydrolytic sol-gel reaction [48], sono-chemical methods [49], reverse micelle method [50] and hydrothermal method [51] and produce well structured nanoparticles.

High surface area anatase phase TiO_2 nanorods photoanode with gel polymer electrolyte to fabricate a dye-sensitized solar cell which produce efficiencies of 2.8% and 4.4% under illumination of 100 mW/cm^2 and 10 mW/cm^2 [52]. Single-crystalline rutile phase TiO_2 nanowires photoelectrode undergoes $TiCl_4$ treatment to improve photocurrent efficiency with initial conversion efficiency of 1.2% and after $TiCl_4$ treatment the efficiency is 2.9% [53]. The effect of $TiCl_4$ treatment is increases the roughness effect on semiconductor surface and hence the high amount of dyes loaded [54]. Metal and non-metal doped metal oxides semiconductor photoelectrodes have been examined in DSSC. The rare earth oxide $Y2O_3$: Eu^{3+} doping with TiO_2 semiconductor with N-719 sensitizer was reported of an efficiency of 6.52% [55]. Trilayered nanocomposite TiO_2 photoelectrode incorporated with nanoparticle, nanotube, and submicron particle films are coated on FTO by doctor blade method. Nanocomposite TiO_2 improved photocurrent density and achieved an efficiency of 9.36 % [56]. Highly ordered TiO_2 nanotubes was prepared by anodization process. These nanotubes are applied on Ti substrate used as photoelecrode [57]. The Au nanoparticles deposited TiO_2 based photoanode shows better solar energy conversion efficiency in solid-state DSSC due to the effective interfacial charge transfer process [58]. Recently highly ordered TiO_2 nanotubes was developed on Titanium foil sheet (anodic oxidation method) and Transparent conducting glass material (rf-sputtering method). Thick layered TiO_2 nanotubes were grown on

titanium foil which produces high short circuit current density under back side illumination. Thin layer TiO_2 nanotubes were grown on TCO glass with produced low short circuit current density under front side illumination [59].

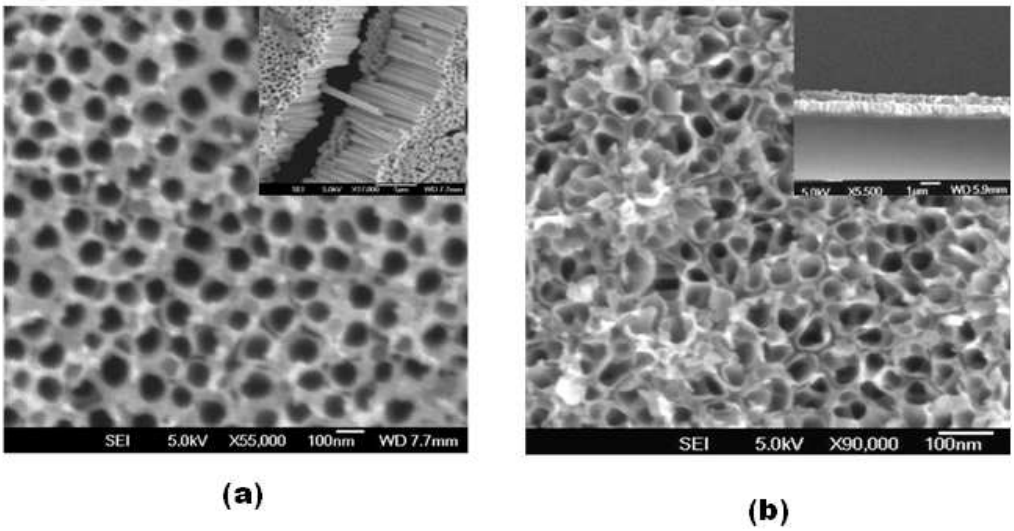

Fig. 5 SEM images of TiO_2 nanotube arrays grown on (a) titanium foil and (b) titanium film coated on conducting glass. (a) nanotube pore diameter 130 nm and length 6 μm, (b) nanotube pore diameter 60 nm and length 400 nm [Adapted from ref: 59].

Zinc oxide

Zinc oxide is alternative to titania semiconductor because the electron transporting rate ZnO is slightly slower than TiO_2. Dye on ZnO sensitization is handled with noticeable attention because of dye adsorption on ZnO and dye can form complexes with zinc anion, then Zn-dye-complex may play a major role in charge generation process. Implying new sensitizer with non–acidic group attached need to be developed to avoid this zinc-dye complexation. Hierarchically–structured ZnO particle prepared with size should be approximately 22 nm and achieved efficiency upto 3.5 % with iodine based liquid electrolyte under condition AM 1.5 and 100mW /cm^2 [60]. ZnO nanorods array coated on FTO surface and the nanorod ZnO film was prepared by RF magnetron sputtering method, in which nanorods array produces fast electron transfer and showed the structural morphology of nanorods in Fig. 6 [61].

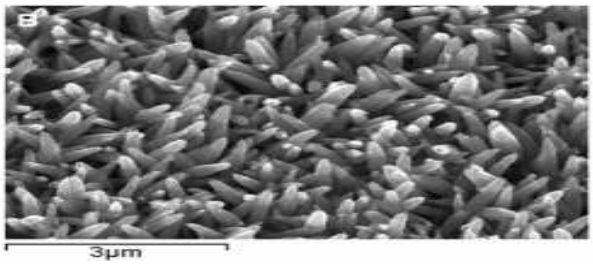

Fig. 6 SEM image of ZnO nanorods [Adapted from ref: 61].

DSSCs fabricated with ZnO nanowires photoelectrode produced large surface area, a high amount of Ruthenium based dye loaded on ZnO under 100mW/cm^2 produced photo conversion efficiency ~1.5% [62]. ZnO nanosheet based photoanodes produced good surface area and fast electron transfer. Evans blue dye sensitized with ZnO nanosheets shows 1.5-fold enhanced photo-conversion efficiency then ZnO nanoparticle [63]. Wurtzite structured ZnO nanorods (ZnONRs) and spherical nanoparticles were synthesized through sol–gel method to apply as photoelectode in DSSC. The

band-gap of ZnONRs and ZnONPs was calculated as 3.09 eV and 3.12 eV and achieved efficiency of 0.89% and 0.35% under 1.5 and 100mW /cm^2 [64]. Sheaf-like hierarchical ZnO-Ag photoelectrode enhance photocurrent efficiency of DSSC due to large surface area and also reduced charge recombination rate [65].

Other metal oxides

SnO_2 nanowire shows high open circuit current because of the surface properties of nanowires [66]. Zinc modified SnO_2 photoelectrode was applied to solar cell application and achieved efficiency up to 3.4%, short circuit current and fill factor are increased with increase in the zinc concentration [67]. Microstructure Nb_2O_5, 6µm thickness film sensitized with ruthenium based dye showed photocurrent conversion efficiency of 5.0 % [68]. Recently, molecular design rules reported to elaborate a new generation of better performing ruthenium polypyridine sensitizers with NiO [69].

Sensitizer

The sensitizer (dye) plays an important role in photo conversion efficiency of DSSC. Especially the performance of DSSC depends upon HOMO and LUMO energy level of dye and rate of electron transfer between dye and nanocrystalline semiconductors material. Metal organic dye and metal free organic dyes are applied as sensitizers. Metal organic dyes have been widely investigated in DSSC application because of wide absorption range and desirable photovoltaic properties. Especially, several ruthenium polypyridyl complexes based dyes were achieved more than 10% efficiency, due to the efficient photophysical and photoelectrochemical properties. Recently metal organic based zinc porphyrin complexes were reported more than 12 % efficiency and it is the highest reported efficiency of DSSC organic dye. Even as several metal free organic dyes like indoline, thiophene and triphenyl amine based dyes are also achieved more than 9% efficiency and it has also close efficiency to metal organic dye.

In designing the new efficient dyes, dyes have to exhibit following essential properties; dye should have high absorption in whole visible region and near IR region with higher molar extinction coefficients. Dye should have good energy level alignment, LUMO level of the dye should be higher than CB of semiconductor and HOMO level of the dye should be lower than the redox potential of electrolyte. Dye has to be stable against aggregation an irradiation of light and should have hydrophophic nature .Dye should exhibit more oxidation value than electrolyte oxidation value for minimizing the charge recombination. If a dye is metal organic, it should exhibit anchoring groups such as –SO_3H and COOH. Dye should be stable in thermal, optical and chemical condition. Dye should have simple preparation procedure, less hazardous and dye (low cost) should be raw material cheep cost. Schematic diagrams show the energy level alignment of dye and semiconductor of possible and not possible charge transition (Fig. 7 and 8).

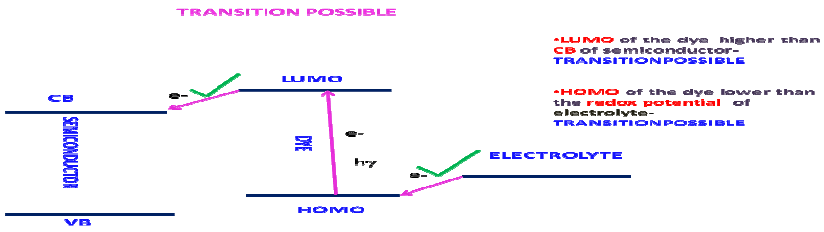

Fig. 7 Energy level position of feasible charge transition in dye-sensitized solar cells

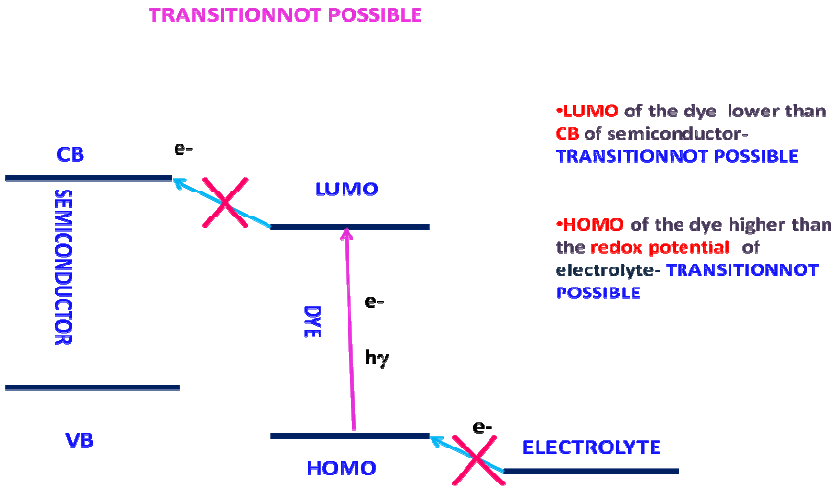

Fig. 8 Energy level position of non-feasible charge transition in dye-sensitized solar cells

Metal organic Dye

Commonly metal-complexes based sensitizer shows central metal ion with anchoring ligand and at least one ancillary ligand. Metal complexes sensitizers when absorb the incident light it takes place metal to ligand charge transfer (MLCT). The d^6 metal porphyrin complexes exhibit this type of charge transition due to extensively used as sensitizer. Anchoring ligand of metal sensitizer attached with semiconductor surface and ancillary ligand do not contact with semiconductor material which exhibit chromophore groups. Ruthenium complexes contains different chromospheres groups in their organic framework so can tune absorption get high broad spectrum through achieved high extinction coefficient. So many modifications carried out on ancillary ligand of ruthenium sensitizer to improve light harvesting. Still date Ruthenium polypyrindine complexes, Zinc porphyrin complexes, Cobalt porphyrin complexes, Gallium phthalocyanine complexes have investigated as a metal sensitizer in DSSC. The widely used anchoring groups in metal organic dyes are carboxylate, catecholates, phosphanate, hydroxamates and acetylacetonate. Advantages of metal organic dyes are stable, exhibit wide range of absorption in visible to near IR (NIR) region and it incorporated the different light absorbing groups in their organic structure which can tune the broad absorption spectrum range to achieve high molar extinction coefficient value. Limitations of metal organic dyes are in Ruthenium polypyridyl complexes because of ruthenium are expensive, should be synthesis carefully and difficult steps follows to purification. Metal organic dyes achieves maximum efficiency as 10.39%, 10.40%, 10.57%, 10.7%, 11.4% &12.3%. Ruthenium based dye achieved maximum efficiency 11.4% but recently zinc porphyrin based dye achieved 12.3% efficiency. Here we discuses several metals that contain more efficient dye.

Gratzel group was recently reported zinc porphyrin (YD2-0-C8) dye cosensitized with metal free Y123 was achieved photocurrent efficiency of 12.3%. The YD2-0-C8 dye was capable with long chain alkoxy group and dye absorption covered with full visible region. Zinc complex integrated with octyloxy group was improved photon-induced charge separation of DSSC using cobalt bipyridyl redox couple based electrolyte [9]. Heteroleptic polypyridyl ruthenium sensitizer (C106) produced efficiency 11.4 % under AM1.5G at 30^{o}C. Hexylthiothiophene conjugated bipyridine ligand to enhance the optical absorbtivity properties of sensitizer. The molar coefficient value 18.7×10^3 M^{-1} cm^{-1} and charge transfer at 550nm, power conversion efficiencies also examined at different temperature conditions [70]. Ruthenium polypyridyl (N719) dye achieved 11.2 %

efficiency with iodine based redox couple [71]. TF1 dye which Ruthenium (II) sensitizers incorporate with both 4, 4', 4''-tricarboxy-2,2':6,2''-terpyridine and 2,6-bis(5-pyrazolyl) pyridine ligands with TiO_2 photoanode thickness of 15 micrometer and the efficiency achieved is 10.7 % under 100 mW/cm^2. It is a thiocyanate free ruthenium sensitizer applied in DSSC [72]. Ruthenium based N945 dye anchored with TiO_2 semiconductor achieved high photocurrent density 18.84 mA/cm^2 and efficiency 10.82 %, which exhibited efficient harvesting of visible light. Heteroleptic ruthenium complex based bipyridine with2,2'-bis(3,4-ethylenedioxythiophene) (C107) sensitizer exhibited very high molar coefficient $27.4 \times 10^3\ M^{-1}\ cm^{-1}$ at 559 nm and achieved the photocurrent density 19.18 mA/cm^2 and efficiency10.7%. The low density dye molecules deposited on TiO_2 leads to faster charge recombination was produce low open circuit current [73, 74].

Ruthenium based cyclometalated ruthenium sensitizers (JK-206) were incorporated with CNN ligand and 2, 20-bipyridine ancillary ligand. JK-206 dye with iodine redox couple liquid electrolyte reported efficiency 10.39%, another case JK-206 dye with polymer gel electrolyte reported efficiency of 7.14% with excellent stability under light 60 ^{0}C for1000 h. Cyclometalated ruthenium complex with the CNN ligand and the broad and red-shifted absorption property reason for the high efficiency and excellent stability of JK-206 [75]. Ruthenium sensitizer (Z-910) with 3-methoxystyryl auxiliary ligands based dye has an efficiency of 10.2% get attractive stability. The black dye (N749) which consist Ruthenium with three thiocyanate ligand and one terpyridine ligand with three anchoring carboxylic acid group its absorption range from visible to near IR upto 930 nm achieved maximum efficiency 10.4% achieved over 80 % IPCE. The N719, Z-907 and N749 dye have exhibit low molar coefficient when dye coated on TiO_2 surface during the illumination of light and dye should be aggregation increases on their surfaces. Other d^6 metal complexes osmium complexes [76,77] and Iron(II) complexes [78] are successfully investigated in DSSC.

Metal free-organic dye

Currently metal free organic dyes have been getting more attraction since metal free organic dyes are quite inexpensive and we can design suitable molecular structure through this can tune absorption and electrochemical properties during high extinction coefficients. All organic donor-acceptor dyes are attained high extinction coefficient from their structural properties relationship known from basic dye chemistry [79]. Metal free organic dye that achieved maximum efficiency is 9.0%, 9.1% and 9.5%.

Indoline based dye D205 with CDCA has reached photo efficiency of 9.52% and current density 18.56 mA/cm^2 under one sun condition, AM 1.5G. Reproducible efficiencies were reported in range of 9.3% to 9.5%, when examined with and without CDCA. The chenodeoxycholic acid (CDCA) was used as an anti-aggregation reagent to prevent dye aggregation and enhance the photovoltaic performance [80]. Thiophene derivative based cyclopentadithiophene-cyanoacrylic acid dyes with arylamine electron donors of dihexyloxy substituted triphenylamine dye (DHO-TPA, C218) with cobalt redox couple electrolyte attained an efficiency of 9.3%. Dye exhibits strongest electron donor and electron-donating capacity followed by high dye regeneration. Followed by C218 dye absorbing red-shifted light and showed a high open circuit current [81]. The organic dye TA-St-CA contains p-conjugated oligo-phenylenevinylene unit with an electron donor–acceptor transfer and a carboxyl group anchoring unit. IPCE value reached maximum of 80% between 400 to 550 nm region. When investigated with standard N719 dye, TA-St-CA has strong absorption in visible region above 600nm and reached photoconversion efficiency of 9.1% [82]. Indoline based indoline

dye with liquid electrolyte and chenodeoxycholic acid used as co-adsorbent attained a photocurrent density of 18.50 mA/cm^2 and efficiency 8.0% [83].

Natural sensitizer

Nature dyes are easily available low cost sensitizer, substituted to expensive organic based DSSC. Fruits, flowers and leaves extracts of plants contain pigments. Pigments interacting with sunlight are a chemical reaction, employing them as natural photosensitizers. The plant materials that provide pigments extensively are carotenoid and flavonides. Familiar anthocyanins dye is a major constituent of flavonides group, which provides various sensitizing performance and their performance vary with respect to the derived type of plants. Natural dyes provide non-toxic to environment, easy preparation and more availability. Negative aspects in natural sensitizer are poor efficiency. Betaline pigments contain red turnip which is reported with a highest efficiency of 1.70% [84] even after searching new efficient natural sensitizers. Several more efficient natural sensitizers are shisonin 1.01% [85], mangosteen pericarp 1.17% [86], Rhoeo spathacea 1.49% [87], sebania grandifolara and Hibiscus rosinesis 1.02%.

Co-sensitization

Co-sensitization is a promising technique to enhance the absorption range of dye. To find and improve the efficiency of DSSC, the single dye should exhibit large absorption in both from visible to NIR region (350-950 nm) and is very complicated. Better way to improve the efficiency of DSSC is reduce the energy level (HOMO and LUMO) gap of dye molecules and large amount of light will be absorbed at visible and NIR region (650-950 nm). Simplified structure design of dye may allow negative dipole moment of dye. So dye close to TiO_2 surface raised CB of semiconductor achieved high Voc and also enhances efficiency. NIR dyes and Energy relay dyes are ideal material to co-sensitization. When the dye absorption range of NIR is maintained around 940 nm, light harvesting in this region can raise current conversion efficiency upto 40% [88].

The absorption molar coefficient is inversely related to spectral width of dye. Absorption coefficient of dye means measuring the rate of decrease in intensity of incident light as it passes through a dye molecule. In DSSC when absorption coefficient increases, width of spectrum decreases and vice versa. Usually organic dyes have high molar extinction coefficient than inorganic Ru-complxes dye. Low molar coefficient Ru-based dyes are requires thick layer coverage on TiO_2 surface to all incident light photon absorption. Organic dyes having high molar extinction coefficient requires thin layer coverage on TiO_2 surface to make co-sensitization.

NIR dyes

Aswani et al recently reported that co-sensitization enhanced the photocurrent efficiency but does not prevent recombination rate of their system. Y123 dye is absorbed in visible region 550 nm (Fig. 9) followed by Jsc increases but Voc slightly decreases [9], so NIR (absorption >700nm) dyes are better to co-sensitization to enhance the efficiency also prevent recombination rate. Some NIR dyes have good charge injection; less recombination in greater Voc and low over potential enough to regenerate of dyes. It is a challenge to maintaining Voc greater, and when it reduces the recombination will increase because of low band gap [89].

Co-sensitization of metal contain zinc porphyrin dye YD2-o-C8 with Y123 dye with cobalt based redox couple instead of iodine redox couple was achieved 12.3% efficiency under 99.5 mW/cm^2, Jsc 17.66, Voc 0.93 mV [9]. Thiophene based JK2 dye co-sensitized with squaraine based SQ1 dye achieved efficiency of 6.4% with binary ionic liquid as a solvent under 100mW/cm^{-2}, AM 1.5G in visible region 400-700nm (Fig. 9 and 10). Individual dye absorption of JK2 and SQ1 dyes are 530 and 650 nm both peaks are complementary absorption [90] .

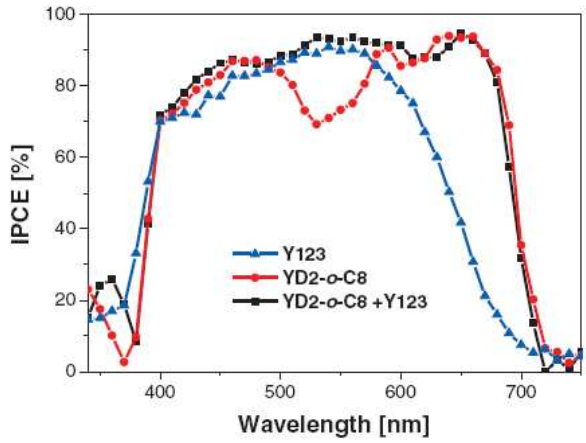

Fig. 9 YD2-o-C8 co-sensitized with Y123 [Adapted from ref: 90]

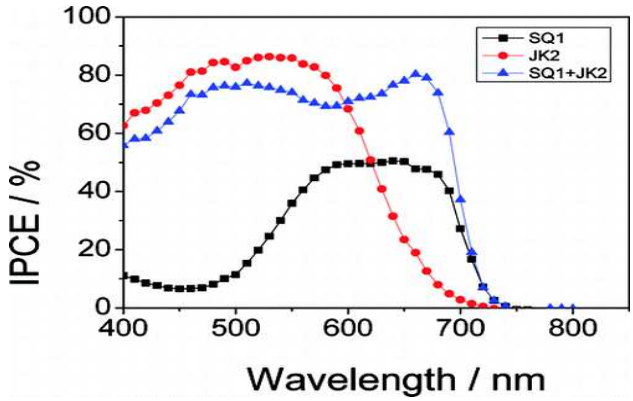

Fig. 10 JK2 dye co-sensitized with SQ1 dye [Adapted from ref: 90].

The effect of co-sensitization of dyes and their aggregation behavior and photosensitization was also investigated from co-sensitization of pentamethylcyanine dye derivative and trimethylcyanine dye derivative deposited on nanocrystalline. TiO_2 showed photoelectric conversion efficiency of 3.4%. Co-sensitization of three organic dyes sensitizing on nanocrystalline TiO_2 electrodes with liquid electrolyte has an overall power conversion efficiency of 6.5% under AM1.5, 80 mW/cm^2 [91]. The mechanism of co-sensitization derived from time resolved spectroscopy by squarylium dye coadsorbed with N3 dye, squarylium to N3 dye electron transfer speed is 300ps, studied among resolved spectroscopy and photoconversion efficiency achieved more than 10% [92]. Co-sensitization of metal contain and metal free dye like thiocyanate free Ruthenium sensitizer (SPS-01) with thienylfluorene (JD1)) was reported 8.30 % efficiency with iodine based electrolyte and also reduce the recombination rate [93].

Electrolyte

Electrolyte is a crucial component in the DSSC, which transfers electron from counter electrode into photoelectrode then the electrolyte should be efficient regeneration itself. Electrolyte should be fully reversible should not show any absorption in the visible region. The electrolyte determines the long time stability of DSSC and durability. Most frequently iodide/triiodide redox couple electrolyte was investigated in DSSCs. Whether decrease redox potential of electrolyte to increase open circuit current. The maximum power conversion efficiency generally related to mass transport of charge carrier occurs in electrolyte by diffusion of ions to semiconductor. A present challenge is enhance the long term stability of the cell based on either solid electrolytes or quasi solid-state electrolyte.

Liquid Electrolyte

Redox couple based liquid electrolyte is widely used in DSSC especially the iodine redox couple based liquid electrolytes have been produced high photocurrent efficiency. Major components of liquid electrolyte are redox couple, organic solvent and additive. Liquid electrolyte has exhibit high dielectric constant organic solvent or low viscous ionic liquid as a solvent medium. The dielectric constant value, donor number and viscosity of organic solvent are influenced performance of liquid electrolyte. The open circuit current was increased when number of donor atom of solvent increased in liquid electrolyte. The liquid electrolyte contains redox couple reported in DSSC are TEMP/TEMPO^{+} [94], T_2/T^{-} [95], $SeCN^{-}/(SeCN)_3^{-}$ [96], Br^{-}/Br_3^{-} [97], Hydroquinone/Benzoquinone [98], Ferricyanide/Ferrocyanide [99], $Co(dtp\text{-}bpy)^{2+/3+}$[9], $Co(bpy)^{2+/3+}$, $Cu(SO(mmt)]^{0/-}$,$Cu(dmp)_2]^{2+/+}$, $Cu(phen)_2]^{2+/+}$ and $Cu((SP)(mmt)]^{0/-}$, ferrocene/ ferocenium(Fc/Fc^{+}). Recently Aswani et al was reported liquid electrolyte with cobalt(II/III) tris bipyridyl redox couple co-sensitized along to the dye showed efficiency of 12.3% under 99.6 mV/cm^2 [9], which is leading efficiency in DSSC. Major problem of redox couple based liquid electrolytes producing huge potential problem, hence recent research focused on alternate material to liquid electrolyte.

Soli- state electrolyte

The solid-state DSSC have been utilized hole transporting materials which are ideal tool to replacing the liquid electrolyte because it don't undergoes corrosion and volatile. Solid-state, hole transporting materials (HTMs) referred as p-type semiconductor. Inorganic HTMs, Organic HTMs and solid state redox couple are widely used charge carrier in solid state DSSC. The first solid-state electrolyte based DSSC was reported efficiency less than one percent efficiency [100]. Last few decades organic HTMs achieved efficiency 7.1 % [101]. Recently, inorganic HTMs based $CsSnI_{3-x}F_x$ compounds was reported efficiency of 10.2% [102]. Solid electrolytes are more advantage compared with the liquid and gel electrolytes, it has achieved more efficiency and stability achieved than gel electrolyte. Further so many efforts making to design the high efficient solid-state DSSC.

Quasi solid-state electrolyte

The quasi solid electrolyte prepared by composition of liquid electrolyte with low molecular weight gelator or nanoparticle or polymer matrix. The nanoparticles with either organic solvent based liquid electrolyte or ionic liquid based liquid electrolyte composite produces the quasi solid electrolyte. This composite of quasi solid electrolyte is exhibits by gels state. The polyacrylonitrile based composite gel was first introduced gel electrolyte which attained efficiency of 4.4 %. Thermo plastic gel electrolyte was reported better efficiency of 7.22% [103].

Counter Electrode

Counter electrode is a catalytic material that is coated on transparent conducting material and it also exhibits efficient reduction properties. The function of counter electrode is the transfer of incoming electron from outer circuit to electrolyte followed by redox reaction occurring at electrolyte. Counter electrode should exhibit superior catalytic activity and high electrical conductivity for efficient electron transport [104]. In DSSC, counter electrode may be classified into two types and they are Pt- counter electrode and Pt-free counter electrodes. Pt-counter electrode consists of Pt film coated on transparent conducting material. Pt-free counter electrode is based on a number of varieties materials such as carbon materials, conductive polymers, transition metal carbides, metal oxide, and quaternary chalcogenides when applied as counter electrode in DSSC.

Platinum

Platinum based counter electrodes exhibit superior catalytic activity to produce efficient electron transfer in DSSC. Several efficient methods available to make platinum counter electrode are spin coating, screen printing and sputtering methods [105]. Drawbacks; Platinum is a noble metal and expensive hence it covers the 40% total manufacture cost of DSSC; another is involving corrosion with contact of iodine liquid electrolyte which is needed for low cost Pt-free material. Platinum ink

electrode used for DSSC application is the conventional technique for the preparation of Pt electrodes by electrochemical deposition, sputtering and thermal decomposition. The platinum ink nanoparticle loaded on FTO has a surface resistance ~8.08 Ω/sq and the efficiency achieved is 5.03%. Electrochemical method is attracted by preparation of platinum counter electrode at room temperature [106] exhibiting high conductivity because to improve the interface of adhesive properties between electrode material and conductive substrate.

Carbon materials

Carbon materials based counter electrodes are very attractive due to its excellent catalytic activity, low cost, low electric resistance and anti corrosive. Carbonaceous materials based counter electrodes including graphite, carbon nanotubes and carbon black showed efficient solar energy conversion efficiency in DSSC. Low charge transfer resistance of carbon nano-particle/fiber is produced efficient counter electrode for DSSC. The graphite and carbon black counter electrodes are produced with continuous non-vacuum process by simple printing techniques [107] and this flexible carbon material showed low resistivity and high conductivity [108]. Carbon nanotubes (CNTs) counter electrode was prepared by two different methods; screen printing and chemical vapor deposition (CVD). The CVD method showed higher photocoversion efficiency (10.04 %) than the screen printing methods [109].

The carbon aerogel [110] and carbon nanoparticle powder [111] modified counter electrodes showed a high power conversion efficiency of 9.06 % and 6.73 %, respectively. Nanosized carbon materials used as the counter electrode achieved efficiency of 7.56 % [112]. Porous carbon counter electrodes have been fabricated at low temperature by carbon slurry coated on FTO conducting glass, achieved efficiency as high as 6.1 %. The carbon slurry was prepared by ball-milling, a dispersion of start carbon in aqueous SnCl4 solution [113]. Yong Zhang et al were reported with green approach preparation based carbon black showed efficiency of 7.4 % [114]. Carbon black coated on FTO-glass showed efficiency 9.1 % due to decrease in the charge-transfer resistance (R_{ct}) of the electrode with the thickness of the carbon layer. MWCNT counter electrode showed efficiency of 7.7 % [115]. SWCNT/graphene nanosheets composite counter electrode prepared by simple doctor blade method which achieved efficiency of 4.0%. Combination of carbon/TiO_2 composite counter electrode fabricated by spin coating method and shows R_{ct} value of 14.75 Ωcm^2 leads to the 5.5 % efficiency [116]. Joshi et al was reported 5.5 % efficiency with carbon nanofibres counter electrode under the condition 91.5 mW/cm^2, AM 1.5G [117].

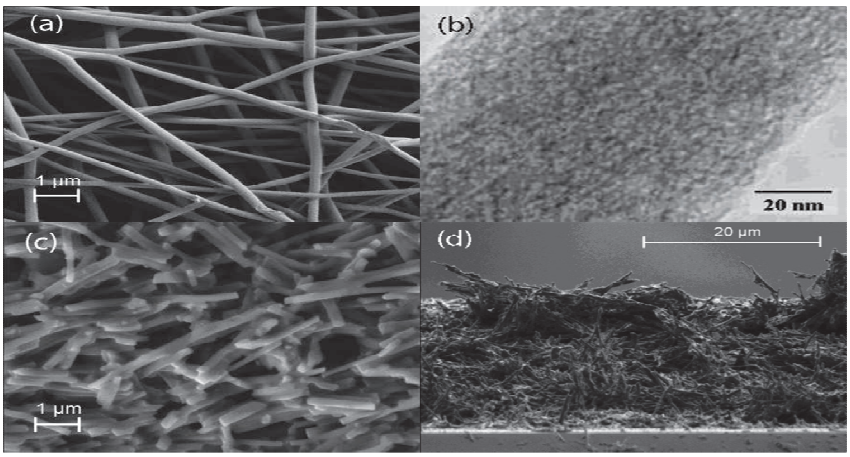

Fig. 11 (a) SEM image of electrospun carbon nanofiber film; (b) TEM image of a typical single carbon nanofiber; SEM image of (c) top-view and (d) cross-section of carbon nanofibercounter electrode. [Adapted from ref 117]

Metal oxides

Tungsten dioxide (WO_2) nanorods based counter electrode coated on FTO surface, which proved efficient catalytic activity to the reduction of iodide based electrolyte. It showed high energy conversion efficiency of 7.25% 100 mW/cm^2 AM 1.5G [118].

Conducting polymer

Conducting polymers has dual role in DSSCs and it act as electrolyte and catalytic electrode materials. Electrochemically developed flexible polyaniline nanofibers on graphitized polyimide carbon films have used as a counter electrode and it has high catalytic activity and low charge transfer [119]. Polypyrrole /functionalized MWCNT nanocomposite modified counter electrode achieved efficiency of 7.02% and 4.04% [120]. Polystyrene sulfonate doped poly (3, 4-ethylenedioxythiophene) with graphene /PEO composites electrode attained efficiency 4.5% [121].

Transition metal carbides

Transition metal carbides materials are employed as effective catalytic materials for counter electrode of DSSCs. Many transition metal carbides including molybdenum carbide (MoC), tungsten carbide (WC), ordered mesoporous carbon (OMC), MoC embedded in OMC (MoC-OMC), and WC embedded in OMC (WC-OMC) are used as catalytic materials of counter electrodes and achieved significant improvement in the device performance. The porous MoC and WC modified counter electrodes are proposed as alternatives to platinum based counter electrode. These electrodes have proved higher energy conversion efficiency than platinum based device [122]. The platinum free porous WC electrode showed excellent solar conversion efficiency of 7.01 % with TiO_2 based photoanode [123]. DSSCs with carbon and carbides counter electrodes showed efficiencies in the range of 4.50–6.81%.

Conclusion

This article reviews focused constitution components of DSSC such as the transparent conducting materials, nanocrystalline semiconductor film, sensitizing dye, electrolytes and catalytic electrode of DSSCs. More reliable methods are proposed to improve energy conversion efficiency, stability and sustainability of DSSCs by changing the components. The metal-free organic dyes are promising alternative to metal complex based inorganic dyes for DSSCs. They offer less cost, less pollutant, simple synthesis procedure and easy energy-gap engineering. Co-sensitization with NIR dyes techniques are further improve the cell efficiency and minimizes the charge recombination process. Physical nature and composition of electrolyte are still problematic. At present, HTMs based solid- state electrolyte is a potential alternative material to the liquid electrolyte and it shows very impressive solar energy conversion efficiency. We have also discussed recent efforts to enhance sustainability, efficiency and stability by modifying the components of DSSC. This summary effectively address the recent progress and update development as well as challenges of constitution component of DSSC.

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