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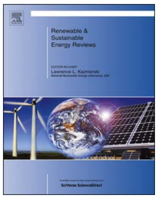

Dye sensitized solar cells: From genesis to recent drifts

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ABSTRACT

Of late, photovoltaics have achieved enormous growth as sustainable energy source. It is witnessed that solar cells being the renewable and pollution free source of electrical energy can easily replace the traditional fossil fuels. This communication overviewed the basic role of various components of dye sensitized solar cells (DSSCs) and the use of nanomaterials to enhance their efficiency. Furthermore, recent trends and future prospects of DSSCs are emphasized.

1. Need of photovoltaics

In this century, the energy and the fuel crises are certainly the major global concerns. With modernization the energy demand is exponentially escalating day by day. The fossil fuels resources are rapidly depleting and many nations worldwide have no other option but to raise the domestic oil prices. Thus, there is a critical need of sustainable energy resources. Solar energy being environmental friendly is the novel alternative with unlimited potential to tackle this problem [1,2]. The clean, abundant, and renewable nature of solar energy is prospective for the diversification of the energy supply, improvement of the air quality, reduction of the fossil fuels dependence, and economic growth [3,4]. Besides, photovoltaics (PVs) have demonstrated the potential to solving the problem of climate change [5]. Research revealed that by covering 0.1% of the Earth's surface with solar cells having efficiency of 10% would gratify the present requirements globally [6]. Currently, the cost of major solar energy systems are more than the energy options like grid electricity available to consumers. Therefore, the cost and efficiency of solar systems need substantial improvement in order to compete in the energy markets [7].

2. Types of photovoltaics

The PV devices that convert the solar energy into electricity are called solar cells, which have undergone three generations so far [8]. The existing PV market consists of wafer-based silicon (Si) and varieties of thin-film technologies. In the first-generation (1G) PV, the production is dominated by single-junction solar cells based on Si wafers including single crystalline Si (c-Si) and multi-crystalline Si (mc-Si). Despite much progress 1G PV costs around US$4/W, which is still roughly four times more expensive for truly competitive commercial fabrication. The 1G technology is comprised of these types of single-junction and silicon-wafer devices.

In the second-generation (2G) PV, efforts are made towards the reduction of $/W by removing the unnecessary material from the cost equation and using thin-film devices. The 2G technology involves single-junction devices that exploit less material but maintain the efficiencies of 1G PV. The 2G solar cells employ amorphous-Si (a-Si), $CuIn(Ga)Se_2$ (CIGS), CdTe/CdS(CdTe) or polycrystalline-Si (p-Si) deposited on low-cost substrates such as glass. These technologies are greatly promising because CdTe, CIGS and a-Si absorb the solar irradiation much more efficiently than c-Si or mc-Si and use only 1–10 mm of active material. Moreover, poor material reproducibility and lack of uniformity over large areas creates a gap between lab efficiencies (above) and the best module efficiencies of 10.7% for CdTe and 13.4% for CIGS. Actually, PVs based on CdTe and CIGS are slow to scale up. Eventually, even 2G technology progressively reduces the active material cost with thinner films and low-cost substrate but higher efficiency need to be maintained to achieve $/W cost-reduction. Thus, third-generation (3G) PV devices has emerged in its own right as future solution.

The 3G solar cells exceed the limits of single-junction devices and lead to ultra-high efficiency for the same production costs of 1G/2G PV, driving down the $/W [9]. Yet, the 3G solar cells still exhibit relatively low efficiencies despite the use of nanostructures in their fabrication. Conversely, the 1G and 2G solar cells based on conventional semiconductor materials display conversion efficiencies as much as 20–

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30%. However, the 3G solar cells have announced countless particularities superior to the 1G and 2G PVs. This supremacy of 3G PV is majorly attributed to their compatibility with flexible substrates and low cost of materials as well as manufacturing [8]. The nanostructured solar cells are advantageous due to the incorporation of new physical mechanisms, which allow to attain an efficiency greater than that of a single-junction solar cell. Nanostructured solar cells offer several notable benefits including the capability to exceed single-junction solar cell efficiency by implementing new concepts, the ability to overcome practical limitations in existing devices such as tailoring the material properties or using nanostructures to overcome constraints related to lattice matching, and the prospect for low-cost solar cell structures using self-assembled nanostructures [10].

The development of dye-sensitized photo electrochemical solar cells (PESCs) is an eventual alternative to the conventional Si based solar cell technology. PESCs having large surface area of nanoparticles are advantageous to increasing the light harvesting capacity and maximizing the number of dye molecules, thereby broaden the spectral response of these cells [11]. The emergence of 3G solar cells based on nanocrystalline and conducting polymers films dominates over the inorganic solid-state junction devices by recommending the prospect of very low cost fabrication thus makes market entry easy. By replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid a PEC cell can be formed. Thus, it becomes possible to quit completely from the traditional solid-state junction device [12]. Fig. 1 illustrates the evolution of world-record efficiencies of laboratory cells. Particularly, the Si cell efficiency can be divided into four stages, with each stage corresponding to new solutions in technology or cell structure [10]. Despite all such advancements in PV technology the tradeoff among cost lowering and efficiency enhancement remain challenging.

3. Cost effectiveness of DSSCs

Presently, the mainstream solar cells are silicon-based because of their high stability and energy conversion efficiency. The big challenge is to reduce the cost of solar panels to promote the extent to which PV generation is used in the future. The c-Si solar cells are widely used despite their fluctuating cost factor and poor energy conversion efficiency. However, the development of non-Si compound semiconductors faces few essential problems including resource depletion and long term toxicity [14]. Although PV cells are attractive due to low-carbon energy supply but remain expensive relative to other technologies. Greatly enhanced penetration of solar cells into global energy markets requires an expansion from designs of high efficiency devices to those that can deliver considerably lower cost per kilowatt hour.

In the past few decades, incredible research efforts have been dedicated to dye-sensitized solar cells (DSSCs) owing to their cost-effectiveness and resource-unlimited attributes [15]. It is worth noting that the current state-of-the-art DSSCs have efficiencies that rival their solid-state counterparts because the initial argument for DSSCs is very convincing. Another advantage of DSSCs is that they can operate well in lowlight conditions [16]. On top, the key materials of DSSCs manufacturing are more environmentally affable and energy-saving than conventional Si technology [14,17,18]. The c-Si wafer technology would not be able to meet the low-cost targets, whereas thin-film technologies offer a foreseeable viable alternative [10]. The organic solar cells owing to their lightweight and flexibility are meritorious than conventional c-Si PVs. Nevertheless, DSSCs are most efficient and cost-effective than all the organic solar cells [19,20].

DSSCs fabrication being devoid of any vacuum process can very easily produce low cost panels in open air. By using the dye both colored and transparent cells can be produced. Flexible thin films solar cells can be formed by aggregates of fine particles of photoelectric conversion materials. Besides, plastic substrates can be used to reduce the weight of solar cells and panel. These prominent advantages allow DSSCs to be installed in locations where appearance is important and other solar cells are hardly applicable. For instance, at the glass panes, the inner and outer walls of a building, the sunroof and outer panels of an automobile, and the cover of a cellular phone [14]. In short, DSSCs are exceptional as compared with almost all other types of solar cells because every task including electron and hole transport as well as light absorption is controlled by different materials in the cell [21]. Unlike to the p-n junction type solar cell, in DSSC the strict requirement of high

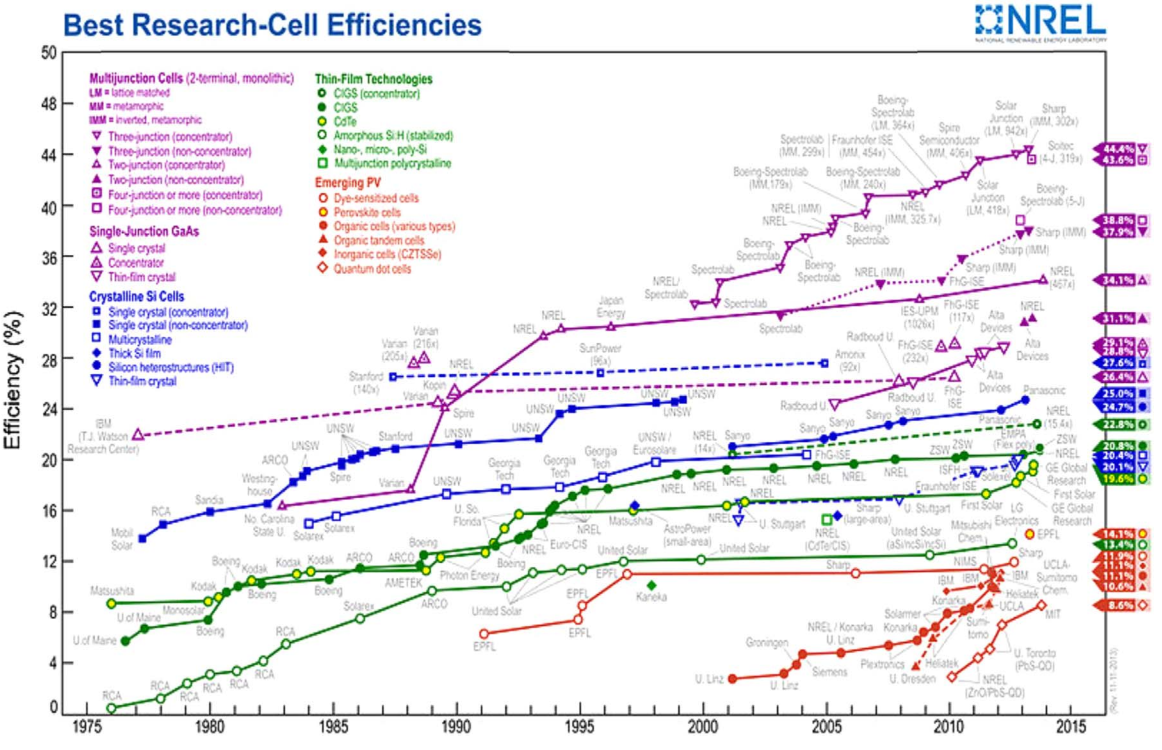

Fig. 1. Evolution of the conversion efficiencies of various types of PV cells [13].

purity materials with anticipated lower cost of unit power production can be relaxed. Furthermore, the improvement of DSSCs efficiency is correlated with the optimization of each section of the cell including the structure of the photo-anode [22].

4. Working principle of the DSSC

The DSSC functioning depends mainly on three processes including charge carrier generation, charge collection, and electron transportation. It consists of a transparent anode ITO/FTO (Indium/Fluorine Tin Oxide glass), a mesoporous oxide layer (generally ZnO/TiO_2) on the anode for activating electronic conduction, monolayer charge transfer dye covalently bonded to the surface of the mesoporous oxide layer to enhance light absorption, an electrolyte and a cathode to facilitate the collection of electrons. The performance of DSSC that is evaluated in terms of cell efficiency (η) and fill factor (*FF*) yields:

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}}$$

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100$$

where J_{sc} is the short-circuit current density ($\mathrm{m\,A\,cm^{-2}}$), V_{oc} the open-circuit voltage, and P_{in} is the incident light power. J_{max} and V_{max} correspond to the maximum current and voltage values, respectively. The maximum output power is displayed in the $J–V$ curve.

Under illumination, the maximum voltage generated in the cell is determined by the difference between the quasi-Fermi levels of the TiO_2 layer and the electrolyte redox potential [23]. In DSSC, the electrons from the photo-excited dye are received by photo-anode which is thereby oxidized and oxidizes the mediator (a redox species dissolved in the electrolyte). By the circulation of electrons through the external circuit, the mediator is regenerated by the reduction at the cathode (generally Pt) [6,12]. Low cost and highly stable DSSCs can be achieved by replacing the photo-anode and counter electrodes of DSSCs with carbon-based materials. However, DSSCs with a pair of carbon-based electrodes face problems. For instance, CNT and graphene exhibit very good conductivity but their catalytic activity is inferior to low-conductive carbon black for the counter electrodes. Moreover, when carbon-based materials are used as the working electrodes then the recombination is expected due to their catalytic activity to the redox reaction.

Fig. 2 depicts the schematics of FTO/ITO and Pt-free DSSC device. Here the working electrode is made with conductive transparent CNT films modified with titanium sub-oxide ($TiOx$) to subduing the charge transfer kinetics. To improve the catalytic activity and the conductivity, thick carbon black layers along with CNT films are used as counter electrode which enhanced the DSSCs performance. It is customary to explain the role of semiconducting oxide films as sensitizer in DSSCs.

5. Semiconducting oxide film

The overall performance of DSSCs is decided by the wide band gap semiconductors assisted sensitization process [25]. In DSSCs, the semiconductor oxides including TiO_2, ZnO, etc. serve as the medium of electron transfer to the conducting substrate. So far, TiO_2 became the most excellent option for DSSC because of its low-cost, market abundance, non-toxicity and biocompatibility. It also exhibits higher performance than other semiconductor oxides. Semiconducting TiO_2 films (band gap ~3.2 eV) are deposited on the conducting substrate by using the sol gel method followed by autoclaving at temperatures up to 240 °C [26].

Among numerous oxides semiconductor, ZnO being the wide band material (band gap ~3.37 eV) is considered to be the best because of its large exciton binding energy (~60 meV). It is already established that antimicrobial effects of ZnO nanoparticles are significantly higher than other metal oxide nanoparticles. Diverse nanostructures of ZnO such as nanorods, nanowires, nanorings, nanobridge, nanocombs, nanocages, nanobelts, etc. have been reported. All of them are potential in fabricating efficient nanoelectronics devices [27]. Nanostructured ZnO can be used as an alternative to TiO_2 as electron conductor in DSSC. The wide band gap of ZnO offers electron mobility better than that of anatase TiO_2. In the fabrication of DSSC photo-anode, a thin layer of ZnO deposited on FTO substrate can be used as blocking layer. The mechanical stability and adherence of ZnO layer can be improved by using ZnO nanorods [22]. Single crystalline ZnO nanowires, core-shell structures and quasi-ordered arrays of TiO_2 nanotubes can enhance the fast and efficient electron transport. Dye adsorption as well as the fast and effective movement of electrons to the collection electrode can be increased. In addition, the recombinations can be suppressed by the use of nanowires in DSSCs, which leads to improved conversion efficiencies. The fabrication of DSSCs with electro-spun ZnO fiber mats also results in higher solar conversion efficiency [28].

It is demonstrated that hierarchically-structured ZnO particles would support light scattering through the presence of secondary colloidal spheres. Consequently, it enhances the photon absorption to increasing the short-circuit current density and the overall light conversion efficiency [30]. Due to the similarity in their conduction band energy levels and the superior electronic mobility of ZnO it is expected to be a comparable active material to TiO_2. By increasing the effective surface area of the ZnO electrode the photocurrents can significantly be improved. Yet, the overall light-to-energy conversion

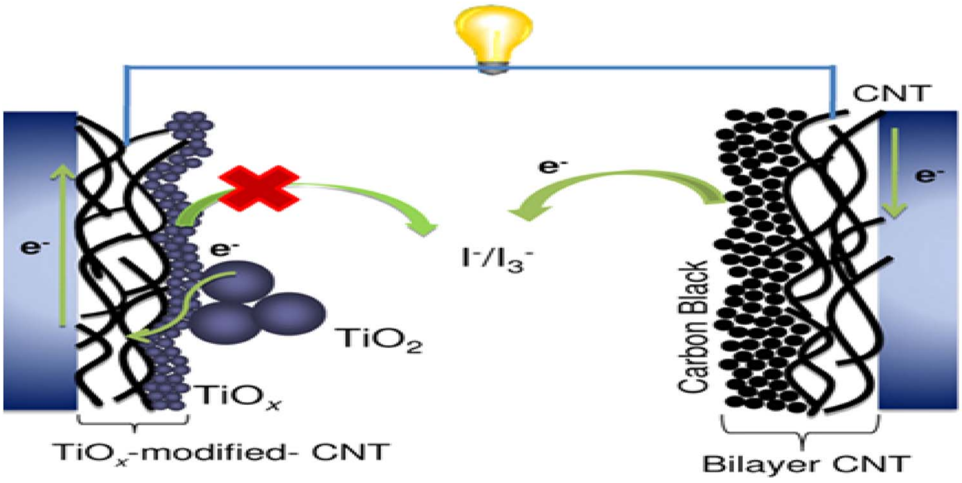

Fig. 2. Schematic of DSSC with a pair of carbon-based electrodes [24].

efficiencies of ZnO-based DSSCs have been poorer than those of TiO_2-based cells. Thus, improving the ZnO-based DSSC performance remains challenging. The incorporation of MWCNTs in the ZnO electrodes provides significant improvement of the photocurrent and conversion efficiency of DSSCs [18]. Owing to their conductive electronic structure, the semiconductors and chalcogenides generally act as sensitizers to facilitate redox processes after illumination [23]. For photo-anode, the choice of metal oxides is made after considering their conduction band energies.

The conduction band of metal oxide should be lower than the LUMO energy level of sensitizer for the photo-excited electrons to be injected from dye to metal oxide [24]. Some materials such as ZnO, SnO_2 and Nb_2O_5 can be used as a photo-anode because their conduction band edge energy is lower than the LUMO of N719 and higher than the redox electrolyte potential for N719 as well as iodide/triiodide electrolyte material [3]. The better performance of DSSC devices depends upon several factors. One of the most important factors which affect the conversion efficiency of DSSCs is the electron transport across a TiO_2 electrode. It is established that the greater electron mobility the higher is the DSSCs efficiency. Besides, the charge recombination processes that generally inhibit the injected electrons from TiO_2 to the conducting glass substrate can diminish the performance of DSSCs. Therefore, to ensure a higher conversion efficiency of DSSC, the fast photo-induced electron transport in the working electrode (TiO_2), and the suppression of charge recombination processes are prerequisite [18].

Due to photo-corrosion, photo-electrodes made of Si, GaAs, InP, and CdS materials get rapidly decomposed under irradiation in solution as compared to the oxide semiconductor materials especially TiO_2. Apart from non-toxicity and low-cost, TiO_2 possesses good chemical stability under visible irradiation in solution. Furthermore, the preparation of TiO_2 thin-film photo-electrode is a very simple process, where TiO_2 colloidal solution (or paste) is coated on a TCO substrate followed by sintering at 450–500 °C. This process produces a TiO_2 film about 10 µm in thickness. The film comprises of nanoporous structure due to the presence of TiO_2 nanoparticles of mean size 10–30 nm. So the actual surface area of TiO_2 film enlarges as compared to its apparent surface area because the roughness factor (rf) is greater than 1000, meaning 1 cm^2 of TiO_2 film having 10 µm thick has an actual surface area of 1000 cm^2. The dye is considered to be adsorbed as a monolayer on the TiO_2 surface. Thus, the amount of dye adsorbed on the film surface can significantly be increased (on the order of 10^{-7} mol cm^{-2}) in case the nanoporous TiO_2 film encloses high rf. An increase of LHE that is near to 100% at the peak absorption wavelength of the dye as compared to the surface of single-crystal and polycrystal materials, where the amount of adsorbed dyes is quite small that is only 1% LHE even at the peak wavelength.

The semiconductor film should also be porous because the electrolyte containing the redox ions must be capable to penetrating the film efficiently to suppress the rate-determining step via diffusion of redox ions into the film. The porosity of TiO_2 colloidal solution or paste up to 50–70%, can be controlled in the sintering process by the addition of a polymers such as polyethylene glycol (PEG) and ethyl cellulose (EC) [29]. In Grätzel cell the photo-electrode is made of porous structure of nanoparticles of TiO_2 to support dye absorption. Light confinement effect along with light scattering from star-shaped particles of TiO_2 can be obtained by stacking their layers (different particle sizes) to provide a cell conversion efficiency of above 10%. Using $TiCl_4$ treatment on the surface of niobium oxide coated on TiO_2, a boost of the conversion efficiency over a wide range of wavelengths is reported which suppressed the electron leakage from the TiO_2 to the electrolyte solution [14].

In case of anatase TiO_2, the best efficiency could be achieved by treating nanocrystalline anatase TiO_2 electrodes with diluted aqueous $TiCl_4$ solution. By comparing the J-V characteristics of dye-sensitized rutile and anatase films (11.5 µm) it is observed that the open-circuit voltages are almost the same (730 mV). However, the J_{SC} of the rutile-based solar cell (10.6 mA cm^{-2}) is roughly 30% lower than that of the anatase-based cell (14 mA/cm^2). Thus, the achieved energy conversion efficiencies of the rutile and anatase-based cells are 5.6% and 7.1%. The difference in values of J_{SC} between rutile and anatase-based cells is obtained because of different amount of dye adsorbed on TiO_2 surface. The surface area of the rutile film is approximately 25% lower than that of the anatase film as confirmed by SEM measurements [3]. Carbon nanotubes are also included in an inorganic TiO_2 sol–gel matrix as reported by Vincent et al. It observed that the PV properties of DSSCs fabricated with anatase and rutile TiO_2 are comparable at one-sun intensity (100 m W cm^{-2}). The light-scattering properties of r-TiO_2 are better than anatase TiO_2 due to its higher refractive index. Besides, r-TiO_2 is cheaper to produce and chemically more stable. It is acknowledged that the electron transport in the rutile layer is slower than in the anatase layer due to the inter-particle connectivity with particle packing density. The intensity-modulated photocurrent spectroscopy and scanning electron microscopy analysis authenticate such observation [30].

So far, the maximum reported efficiency of TiO_2 based DSSC is 12.3%, which is appearing a potentially cost-effective substitute to Si-based PV technology. A main component of a DSSC is the TiO_2 nanoparticle film, which serves as the medium for electron transport and high surface area support for sensitizers (dye molecules). Thus, the performance of the device is strongly influenced by the charge transfer between the sensitizer and TiO_2 as well as electron transport in TiO_2 electrodes. However, several strategies are adopted to increase the electron transfer between dye-sensitized TiO_2 electrode, redox mediator and Pt counter electrode. One of the methods to tackle this problem is to combining a highly electrical conductive material like graphene or carbon nanotubes with TiO_2 nanostructure networks [32]. Because this synergism has great transparency and good conductivity to absorb a large amount of sun-light and to easily donate the captured electrons from dye molecules to the outer surface of the semiconductor film with low resistance (only 10^{-6} Ω cm/sheet).

It is further realized that absorption of graphene is very small in the visible range, only 2.3% of incident white light. However, in the UV range (towards longer wavelengths) the enhanced absorption of graphene integrated TiO_2 is prospective to acting as a UV stabilizer. Table 1 enlists the efficiency of TiO_2-graphene based solar cells as a function of concentration of graphene in semiconducting oxide layer. In high haze condition, implementation of TiO_2 electrodes improves the efficiency of DSSCs. Until now, the maximum recorded DSSC efficiency is about 11.1% as confirmed by Advanced Industrial Science and Technology (AIST). The AIST (Japan) independently measured the I–V characteristics (under standard AM 1.5 sunlight 100 mW/cm^2) using a black metal mask with an aperture area of 0.219 cm^2 and recorded an overall conversion efficiency of 11.1%, which is the highest efficiency established by a public test center [33].

Photo-anodes based on TiO_2 nanotubes opened a renewed opportunity to be used in the near-infrared region of the solar spectrum with improved electron transfer. The aligned geometry of nanotubes has ability to serve as current collectors and transporters [34]. Power conversion efficiency and the stability of the DSSCs can be improved via the incorporation of multi-wall carbon nanotubes to anatase TiO_2 (nanostructured) photo-anodes. It allows the photo-generated elec-

Table 1
Graphene concentrations dependent efficiency and fill factor of TiO_2 based solar cell [32].

Samples	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor	Efficiency
TiO_2	0.77	8.69	0.66	4.42
Graphene (1.0 wt%)-TiO_2	0.68	12.89	0.69	6.05
Graphene (5.0 wt%)-TiO_2	0.71	11.15	0.66	5.22
Graphene (10.0 wt%)-TiO_2	0.70	6.75	0.70	3.31

trons to transport to the back contact without crossing through the TiO_2 layer (where they are expected to recombine with holes) [31]. The development of composite nanostructures imparted further impetus to enhancing the conversion efficiency of CNTs/TiO_2 system by improving the charge separation. CNTs have also been introduced into conjugated polymers to produce organic PV devices [35]. Literature hinted some methods to obtaining long TiO_2 nanotube arrays having lengths in the range 10–100 µm on ITO/FTO (indium/fluorine doped tin oxide) glass substrate as photo-anodes. Vertically aligned TiO_2 nanotubes are produced on Ti substrate by a controlled anodization technique in large scale. The created TiO_2 nanotubes showed narrow diameter (~80 nm) distribution with an average thickness of ~1·5 µm. The existence of a wide multi-modal lateral spacing distribution (LSD) between the tubes has demonstrated a good lateral spacing between these nanotubes, which is found to be beneficial to strengthen the dye–TiO_2 interaction [34].

Due to the 1D nature of the conduction electron states, well-spaced and symmetric structures (van Hove singularities) found in the local density of states of single-walled CNTs (SWNTs). All of the bands of CNTs have a direct band gap, which is inversely proportional to the tube diameter and the fundamental energy gap is of the order about 0.5 eV in semiconducting nanotubes and is zero in the metallic nanotubes. Multiple bands can participate in optoelectronic events for a single CNT, spanning a wide range of energies. It is possible to obtain a continuous response over a broad spectral range by combining CNTs of different diameters and chiralities, correspondingly, different band gaps. TiO_2 particles anchored on CNT are capable to inject electrons from its excited state, which can improve the charge separation and promote the charge flow.

Recently, DSSCs are also made with TiO_2/MWNTs composite electrodes. It is acknowledged that by adding MWNTs with an optimum amount (0.1–0.3 wt%) in the electrode, the physicochemical properties, the electron lifetime and the roughness factor have been considerably improved. Such combination leads to higher adsorbed dye quantities and photo current, thereby improves the cell efficiency. Furthermore, a composite film of MWNT/ poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) has been used as the counter electrode in a DSSC. The performance of such DSSC is discerned to be very close to the devices that used conventional Pt counter electrode. Similarly, the graphene/PEDOT-PSS composite films deposited on ITO have also been used as counter electrodes for DSSCs [36]. Briefly, the efficiency of DSSCs with TiO_2–MWCNTs composite films as the working electrode has been largely enhanced as compared to that of conventional DSSC.

The role of MWCNTs in the solar energy conversion enhancement of the entire fabricated cells is inspected using the electrochemical impedance analysis. Both the electrical double layer capacity and the conductivity at the electrolyte TiO_2/MWCNTs interface are remarkably improved at low MWCNTs concentrations up to 0.025%wt. However, the observed degradation of the DSSC performance at higher MWCNTs loadings at the composite electrode is attributed to the MWCNTs aggregation and optical absorbance enhancement of the composite electrode. Therefore, double-layer capacity, optical absorption and electrical conductivity is found to play a significant role in the enhancement of the energy conversion efficiency of the MWCNTs incorporated DSSCs. Furthermore, the surface area of TiO_2 is not considerably modified due to the incorporation of MWCNTs [18,36]. Similarly, the incorporation of 0.5 wt% nafion-functionalized graphene sheets into commercial TiO_2 (P25) nanoparticles is found improve the overall energy conversion efficiency by 59% as compared to that of pure P25 photo-anode [32]. It is established that the performance of DSSC can be improved by increasing the electrical conductivity of TiO_2.

Lately, hydrogenation has been proven to be a useful method to enhancing the donor density and performance of TiO_2 photo-anodes for photo electrochemical water splitting. This is achieved through the restricted introduction of shallow donors, including oxygen vacancies, and hydrogen impurities. These effects are also observed in ZnO nanowires. Remarkably, the DSSC device with hydrogen-treated TiO_2 electrodes revealed greatly enhanced solar conversion efficiency as compared to raw TiO_2 electrodes. A maximum solar conversion efficiency of 9.30% is achieved for DSSCs with N3 dye sensitized hydrogen-treated P25 photo-electrode under 1sun illumination. This is equivalent to the best values reported for the N3 dye based DSSCs. Fig. 3 displays the I–V characteristics of the TiO_2 nanowire based DSSC devices under illumination with simulated solar light (100 mW/cm^2 AM 1.5G) [31]. In brief, research exploration with synergistic approaches is in continual progression to improve the solar conversion efficiency of DSSCs, hoping that today's fiction is tomorrow's reality!.

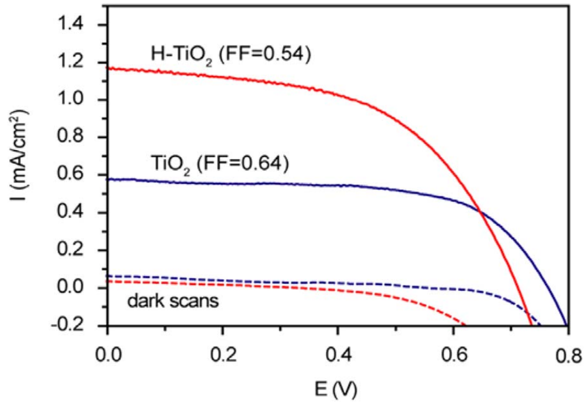

Fig. 3. I–V characteristics for TiO_2 and H-TiO_2 nanowire based DSSC [31].

6. Transparent conducting substrate

The most commonly used conducting substrates are Indium-tin-oxide (ITO), indium-zinc-oxide (IZO) and fluorine or antimony doped tin oxide (FTO, ATO). Both ITO and SnO_2 are prepared on glass substrate using the method of chemical vapor deposition, electron beam evaporation, spray pyrolysis, sputtering, and oxygen ion beam assisted deposition. These transparent conducting substrates must have low electrical resistivity and high transparency in visible spectral region. The resistivity of glass-ITO electrodes can be increased significantly after thermal treatment, which results an increase in the series resistance in the DSSC and reduces the performance of the device. Transparent electrodes based on FTO are more efficient for application in DSSC than ITO electrodes.

Although ITO-glass and FTO-glass electrodes are commercially available but they can easily be grown using spray pyrolysis technique. In this technique, a methanol solution of precursor containing the dopant is sprayed on heated glass. Fluorine acting as an electron donor contributes in the conduction mechanism of the n-type semiconductor [26]. The conventional ITO and FTO based transparent conducting oxide are widely used despite certain drawbacks such as high cost of the rare earth element indium, limited transparency in the near-infrared region, sensitivity to heat treatment, pH of environment, and mechanical brittleness. In solid state DSSCs, ultra thin graphene films have also been used as an alternative to ITO and FTO. Though such grapheme films exhibit a transmittance more than 70% over 1000–3000 nm, high conductivity (550 S/cm) but the cell efficiency is much lower (0.26%) than that of FTO-based cells. Truly, graphene is a promising candidate for solar cells due to its ultra smooth surface with tunable wettability, outstanding chemical durability and thermal stability [23].

7. Counter electrodes

The function of counter electrode (CE) in DSSC is to catalyze the iodine redox couple and close up the electric loop. Generally, the platinum-coated FTO glass is used as the counter electrode. Despite its sturdiness the corrosion of Pt in the form of PtI_4 through the reaction with tri-iodide containing electrolyte are detrimental for cell performance unless inhibited. Thus, the replacement of Pt by an alternative material remains a major concern in DSSCs development. In this regard, the noteworthy features of carbonaceous materials such as high electronic conductivity, high reactivity for tri-iodide reduction, corrosion resistance towards tri-iodide and lower cost make them reasonably smart to replace platinum [16,37,38]. As well, their excellent reduction capacity to tri-iodine ions in electrolyte carbon materials is regarded as outstanding substitutes of Pt. Intensive researches on different types of carbon such as activated carbon, graphite, CNT, carbon black and hard carbon spherules are carried out to get superior counter electrode. These carbon materials have been proven to be competitive with Pt as CE used in flat DSSCs due to their extraordinary merits including high electrical conductivity, chemical stability and large surface area [39].

By introducing CNTs with carbon black it is feasible to fabricate high catalytic activity counter electrode at lower cost [16,37,38]. Both the roughness factor and the electrical resistance of the carbon counter affect the photocurrent–voltage characteristics of DSSC. The activated carbon powder can also be used as counter electrode. It is demonstrated that V_{OC} value can be enhanced with the carbon electrode. The apparent rate for the $I^{3-}=I^{-}$ redox reaction per unit of geometrical surface area of the carbon electrode is found to increase with increasing roughness factor of the carbon electrode. Meanwhile, the roughness factor of the carbon electrode becomes larger when an activated carbon powder with larger surface area is used. In this case, the reaction species (I^{3-}ions) must move into the activated carbon pores and get reduced inside the pores [40].

It is needless to mention that the newly emerged carbon nanostructures such as CNTs, graphene, and ordered mesoporous carbons (OMCs) have distinctive structural properties which are greatly advantageous for DSSCs. OMC–CNT nanocomposites have an exceptional structure in which the key particles of the OMC are interconnected via the CNTs, thus forms a medusa-like morphology. Therefore, the OMC–CNT nanocomposites amalgamate the meritorious properties of both OMC and CNTs. The occurrence of high surface area in OMCs provides numerous catalytically active sites for iodine reduction whereas their interconnected three dimensional (3D) mesoporous structure allows the superficial movement of ions and electrons. Additionally, CNTs act as electrical bridges that intersect separated OMC primary particles, thereby make fast electrical networks. Therefore, using the OMC–CNT-based CE in DSSCs it is possible achieve excellent cell efficiency as compared to the DSSC cell with a conventional Pt-based CE. In addition, the DSSC with the OMC–CNTs-based CE demonstrated distinguished stability in a long-term efficiency test [41].

In DSSCs, the implementation of nanocomposite counter electrodes of MWCNT/graphene has been demonstrated to be a viable and low cost method to improve the overall efficiency. Hitherto, the highest performing DSSCs of these types can attain power conversion efficiencies more than 11%. The extension of the counter electrode segment in DSSCs emphasizes the placement of the graphene that acts as a conducting link and as a space to promote the pointed atomic edges for catalysis [42]. On top, large scale production of graphene oxide (GO) and graphene powders (GPs) through chemical and thermal reduction revealed substantial industrial prospects. It is produced by the chemical oxidation of graphite. A broad range of pure or composite GP films can be made because GO is companionable with wet-based or polymer-based coating processes.

Recently, chemically and thermally reduced GP films are used to make flexible and transparent electrodes for DSSCs and organic solar cells. The solar power conversion efficiencies of DSSCs (0.84%) and organic solar cells (1.1%) with conductive GP films are found to be low. This problem can be overcome using partially reduced GO, which can be both insoluble in water and hydrophilic in nature. These properties are useful for devices with electrolytes such as DSSCs. The solar power conversion efficiency of DSSC PGO is determined to be better than that of DSSC FTO and other kinds of PV cells that employ conductive graphene electrodes. This superiority is primarily ascribed to the ion conduction property of the PGO film throughout the PV process [43].

8. Polymer counter electrode

The breakthrough finding in solar cells is the Windows/back electrode grown from CNTs used for collecting current from the front surface of thin-film solar cells, where transparent thin films containing bulk metallic CNTs are used for providing lateral electrical conductivity. Double-walled CNT (DWNT)/n-Si hetero-junctions have also been developed in solar cell applications due to their high conductivity and transparency. A device with notable increase of V_{oc} (up to 1 V) and J_{sc} is attained using the ITO/PEDOT:PSS/P3OT-CNx-functionalized MWNTs/LiF/Al configuration. Researches confirmed that CNT films can also be used as effectual top or back electrodes in organic solar cells. Upon combining the MWNT film with ITO in the top electrode the photocurrent is found to get double than that of single ITO or single MWNT device, thereby boosted the overall efficiency to 2% at AM 1.5.

To act as window electrodes, these carbon films must have excellent conductivity, ultra-smooth surface with tunable wettability, fine transparency in visible and near-infrared region as well as high thermal and chemical stabilities [35,43]. Nowadays, as an alternative of a costly platinum sputtered FTO glass, the PEDOT:PSS covered FTO glass is used as a counter electrode to catalyze the reduction of I^{3-} to I^{-} in the redox electrolyte. It is affirmed that by adding a liquid organic compound such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), or tetrahydrofuran into the PEDOT:PSS aqueous solution, the conductivity of PEDOT:PSS film can remarkably be improved. The preference of preparation method is also significant for depositing conducting polymers onto the conducting glass because this in turn determines the efficiency of DSSCs. To achieve optimum conversion efficiency, methods such as spin coating and chemical polymerization have been employed to deposit conductive polymers on the counter electrode. Both of them offered excellent electrochemical stability. Lee et al. [30] further customized the counter electrode using MWCNTs due to their capacity to replacing the expensive Pt electrode at the expense of little alteration in the solar cell efficiency. Nonetheless, overall stability of DSSCs remains a major concern for wide spread realization.

9. Temperature and radiation effects on DSSCs stability

Certainly, the long-term stability of DSSCs is critically decided by the ambient temperature variation because the solar cells may attain a temperature as much as 60 °C under full solar irradiance. Thus, under natural conditions the DSSCs must maintain the overall energy conversion efficiency without compromising its stability. It is worth mentioning that the limitations involving the liquid electrolytes process sealing often hinders the practical applications and enduring performance of DSSCs. Research revealed that the implementation of quasi-solid-state electrolytes and solid-state electrolytes may be the best alternatives to liquid electrolytes. To surmount the volatilization and leakage problems of liquid electrolytes, various quasi-solid-state electrolytes ionic liquids including 1-propargyl-3-methylimidazolium iodide, 1-ethyl-1-methylpyrrolidinium, bis(imidazolium) iodide and polymer gels like poly(ethylene oxide), poly(vinylidinefluoride) and polyvinyl acetate are exploited. Yet, via careful sealing treatment the quasi-solid-state electrolytes based DSSCs has achieved a maximum PCE of 8–9% only at high temperature surroundings. Undoubtedly, the development of solid-state electrolytes based DSSC is the major research aim for future commercialization [44].

Earlier, Omar et al. performed an enduring (1000 h) stability tests on the flexible cells depending on various water-based electrolytes under continuous illumination at 1 sun. Irrespective of the nature of water-based electrolytes, the *J*sc revealed a small increase in the first 200 h and stabilized thereafter. Furthermore, these water-based flexible cells displayed insignificant dye desorption (~0.8% loss) after 1000 h under high temperature (60 °C) soaking [45]. Otakwa et al. inspected the influence of temperature and irradiance intensity on a DSSC module performance in a temperate tropical area. A better relative efficiency is achieved at lower irradiance intensities than that of higher one. Moreover, open circuit voltage is increased with increasing irradiance intensity up to 850 $\mathrm{Wm^{-2}}$, which is attributed to the thin film nature of module's cells as well as the high injection levels originated from the closeness of the injection to the collection. This led to a fast build-up of charges and responsible for initial exponential increase of V_{OC} as well as attainment of stability with the further increase of irradiance intensity. The observed stability of V_{OC} for irradiance intensities greater than 850 $\mathrm{Wm^{-2}}$ is interpreted in terms of equilibrium state that aroused somewhere between photo-generation and recombination processes. Meanwhile, the observed reduction of Jsc as well as fill factor at high irradiance intensities is ascribed to the high levels of electron recombination through the electrolyte along with the collection at the transparent conducting oxide and large series resistance of the module, respectively. However, the maximum power is enhanced with increasing irradiance intensity and module temperatures. The temperature insensitiveness of V_{OC} and fill factor clearly demonstrated the superior stability of such module against high temperature that could influence the J_{SC} value. In short, DSSC modules possess relatively better efficiencies at low irradiance intensities [46].

10. Commercialization and competitiveness of DSSCs with existing technologies

Upon outdoor installations the energy production for DSSCs is discerned to increase by 10% in sunny days and 20% in cloudy days as compared to pc-Si modules with the similar nominal power. This increase in energy output is majorly attributed to the small real efficiency of pc-Si at normal operating cell temperature (NOCT). Thus, by considering roughly 5% rise in the effective performance the DSSCs per watt peak installed with respect to conventional technologies, the comparable efficiency of the DSSCs would rise to 10.3% for a nominal 9.9% module. This efficiency is equivalent to the CdTe panels at NOCT. Besides, DSSCs can capture small incidence angle and diffuse sunlight. This enhances the effective energy production hours together with an advanced performance in cloudy days [47].

The fabrication of DSSCs with flexible plastic substrates or metal substrates in different combinations is beneficial because metal can withstand with high temperature variation. Nonetheless, this configuration is somewhat different from usual DSSCs assembly having the counter electrode on the top and photo electrode at the bottom. When metal is used as counter electrode then the low temperature paste required to be coated on the plastic photo electrode. The other advantage of DSSCs is related to their lower cost of manufacturing tools. Consequently, DSSCs fabrication on light weight flexible substrates and roll-to-roll production offer huge cost reductions. On top, the DSSCs exhibit more relative performance under low light conditions than Silicon based solar cells. These notable merits of flexible DSSCs make them prospective for daily uses including traveling bags, battery charging of mobile phones and clothes [48].

The conventional Si solar cells need enormous amount of solar irradiation for its startup operation, which amounts to 200–300 $\mathrm{Wm^{-2}}$ and increases to 800–900 $\mathrm{Wm^{-2}}$ at highest performance level. Conversely, DSSCs reveals working potential along with transparency even under low light conditions, which allows their installations in shaded regions, building corners in therefore and thus increasing their operation periods. In a comparative study, Dyesol Ltd. revealed that these dye solar modules deliver up to 65–300% higher power output on cloudy days than Si as well as thin film solar cells. However, the photo-conversion efficiency of DSSCs is still lower than the ubiquitous single crystalline Si solar cells or CIGS. Definitely, several attractive features of DSSCs such as working ability under diffuse light conditions, transparency, flexibility, better performance in indoor light and easy incorporation in buildings as solar windows will allow them to penetrate the global market [49].

Researches revealed that the photo-conversion efficiency of DSSCs can further be pushed to 19% or even more by elevating the light harvesting capacity up to near infra-red region (920 nm), incorporating strongly absorbing sensitizers and well matching the energy levels at the boundaries of photo-anode/sensitizer/electrolyte. In fact, this is the standard at which DSSCs can compete with market leaders so called thin-film photovoltaic devices [44].

11. Future use of metamaterials in solar cells

Recent development of fake electromagnetic structures so called “metamaterials” created permittivity (ε) and permeability (μ) values that are not attainable in nature. Metamaterials are metallic or semiconducting substances whose properties depend on their newly designed inter-atomic structures rather than on the compositions of the base materials. Certain metamaterials exhibiting negative refractive index can bend visible light rays in the opposite sense from traditional refractive media. Their smart and exotic properties get originated from exact shape, morphology, geometry, size, orientation and atomic arrangement. These unusual properties can be exploited to manipulate electromagnetic waves (blocking, absorbing, enhancing, or bending) to achieve advantages that surpass the capacity of conventional materials.

The main bottleneck in the design of a highly efficient solar cell is related to the selection of the appropriate semiconductor materials with suitable energy gaps that match the solar spectrum. Optimization of their optical, electrical, and structural properties, extra effective charge collection, and improved utilization of the solar spectrum through single as well as multi-junction approaches is underway. However, both approaches are not able to utilize the whole solar spectrum concurrently from IR to UV, thereby limited the solar cell efficiency. To surmount such lacking the exploitation of metamaterials is realized. These materials being insensitive to the light polarization can be used to control the pathway of visible light irrespective of the polarization. Thus, by making the antireflective layer of solar cell using metamaterial with refractive index 1, it is possible to inhibit the reflection entirely and enhance the cell efficiency dramatically without any polarization effect. To utilize of whole solar spectrum and to increase the cell efficiency, the band gap can be tuned by using saw-tooth arrangement in the second layer of metamaterial solar cell [50].

Fig. 4 depicts the typical future multi-junction solar cell. These cells have an anti-reflecting cover followed by a coating of metamaterial of saw-tooth configuration. Besides, the anti-reflective layer is made of the metamaterial having refractive index 1 which is identical to that of the

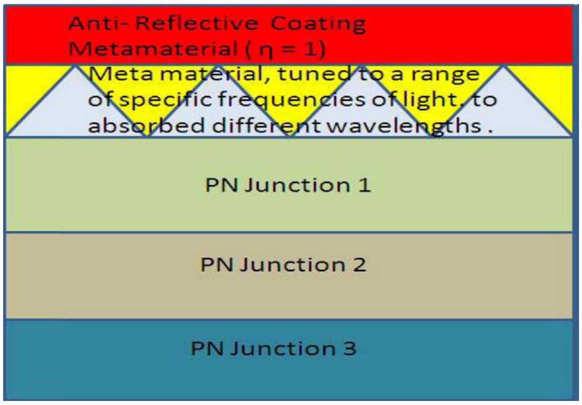

Fig. 4. Future metamaterial based solar cell with P-N junction made of usual or composite metamaterial [50].

air. The anti-reflective coating (first layer) is applied to diminish the losses because the glossy n type semiconducting layer may drive photons bouncing away. This choice of the anti-reflective layer (having refractive index 1) must be transparent to the incident light thus no reflection can occur to reduce the efficiency. Meanwhile, the application of anti-reflective coating on glass cover would avoid solar cell from dust, temperature variation and other natural hindrances. The second layer is the metamaterial of saw-tooth arrangement, where each saw-tooth has a dissimilar negative refractive index.

By altering the metamaterial's refractive index any value of band gap can be achieved because the band gap and refractive index are inversely related. Therefore, the complete solar spectrum −0.5–2.9 or 0–4 eV can be harvested using this saw-tooth configuration [51]. On top, it is found that a planar structure having an ultra-thin semiconducting coating topped with a solid nanoscopically perforated metallic film followed by a dielectric interference film can highly absorb (super-absorber) the electromagnetic radiation in the whole visible range, thereby turns into a platform for highly efficient solar cells. The ultra-thin absorber and perforated metallic film in this broad band outline is indeed a metamaterial effective film, which negatively refracts light in a wide frequency range. These simulations reveal that optimized structure based solar cells exceed the energy conversion efficiency ~12% than that of a single-junction amorphous silicon solar cell.

12. Summary

We deliver a panoramic overview on DSSC by creatively encompassing its humble past, present excitement and future promise. The role of nanomaterials and metamaterials in enhancing the conversion efficiency of DSSCs are emphasized. It is realized that the efficiency of DSSCs can be improved by incorporating nanomaterials in their design, which may open up new avenues in solar cells research. The economic aspect of DSSCs has been discussed in terms of their efficiency and future market entry prospects. A critical evaluation has been made on the use of different semiconducting oxides and nanomaterials to achieve good efficiency of solar cells. Currently, although solar energy exploitation via solar cells is an expensive source of energy but with use of high efficiency solar cells with innovative design concepts the field of photovoltaic can definitely be accelerated. The outstanding performance of DSSCs in diffuse light, working ability on wider angle and easy printing on glass as well as flexible substrates make them promising photovoltaic technology in the near future. Despite intensive research to improving the laboratory scale DSSCs the development of large area solar modules (1% research part contributes towards these modules as compared to lab DSSCs) is seldom focused. Thus, the efficiency of these modules has not been improved much since their introduction in 1996. In addition, solid state electrolytes would be the possible substitutes to the traditional liquid ones with small compromise with efficiency. Yet, stability of DSSCs is a major concern. The low stability of DSSCs has made their entry difficult into practical applications. It is worth to develop nonvolatile electrolytes, sensitizer dyes, nanoporous semiconducting photoanode as well as cheaper counter electrode so that DSSCs can receive its market share in the future solar cell markets. This all-inclusive and edifying communication is hoped to serve as taxonomy for navigating and understanding the research advancements towards DSSCs.

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