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Sustainable Development through Sensitized Solar Cells

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Abstract

Solar energy is considered to be a perfect key to requirement of renewable and economical energy sources for future. Moreover, it embodies the principle of sustainable development as it is available abundantly and does not produce any waste and has no adverse effects on the environment. Especially, solar cells that lead to direct photo-conversion of solar energy to electrical energy by using photovoltaic technology are promising devices. Currently, the commercially available solar cells are made largely from highly purified crystalline silicon but these incur higher manufacturing costs. Therefore, researchers are seeking new inexpensive alternatives based on nanocrystalline materials generally referred as third generation solar cells. The emergence of DSSCs, that used mesoporous nanocrystalline TiO2 sensitized with the ruthenium-based dye molecule, marked the beginning of third generation of solar cells. Since then noteworthy progress has been made in sensitized photovoltaic technology through evolution of the sensitizers from organic dye in DSSCs to inorganic quantum dot in QDSSCs and hybrid organic-inorganic perovskite in PSCs. All these solar cells are very promising as they are less expensive, flexible, compact, lightweight and efficient. The present review, highlights the recent developments in the sensitized solar cells, especially focused on envisaging new, cost effective, efficient, highly stable and eco-friendly sensitizers.

Keywords: Dye sensitized solar cells, sensitizers, perovskites and quantum dots.

Introduction

There is an urgent need for an affordable, sustainable, and carbon-free energy resource to meet global challenging issues such as depleting fossil fuels, looming energy crisis, global warming and climate change. Amongst all the alternative renewable energy sources, solar energy has been regarded as very promising because it is available abundantly and is free of cost and can support the energy requirements of the global population for a few hundreds of generations. It is considered to be an ideal clean and green energy as harnessing the solar energy does not produce any waste, cause no pollution, no noise pollution, and no adverse effects on the environment. Hence, solar energy is considered to be the perfect key to requirement of renewable and economical energy sources for future. Moreover, it embodies the principle of sustainable development as it is available abundantly and does not produce any waste and has no adverse effects on the environment. In this context, direct photo-conversion of solar energy to electricity by using photovoltaic technology or solar cell technology is increasingly recognized as a viable solution to the growing energy challenge.

Photovoltaic (PV) is one of the fastest growing renewable energy technologies and it is expected to play a major role in the future global electricity generation. Photovoltaic solar cells are electronic devices that convert sunlight directly into electricity. The history of development of PV cells or solar cells can be broadly classified into three generations (Fig. 1) depending on the time and the categories of materials which are used for their fabrication. The efficiencies, merits and limitations of each generation of solar cells are listed in the Table I. Currently, the commercially available solar cells are made largely from highly purified crystalline silicon (the first-generation solar cells), but these incur higher manufacturing costs. Despite complicated and difficult processing and high cost, the first-generation solar cells continue to rule in the commercial market (more than 80% of the global solar cell market) due to their high efficiency and good durability.

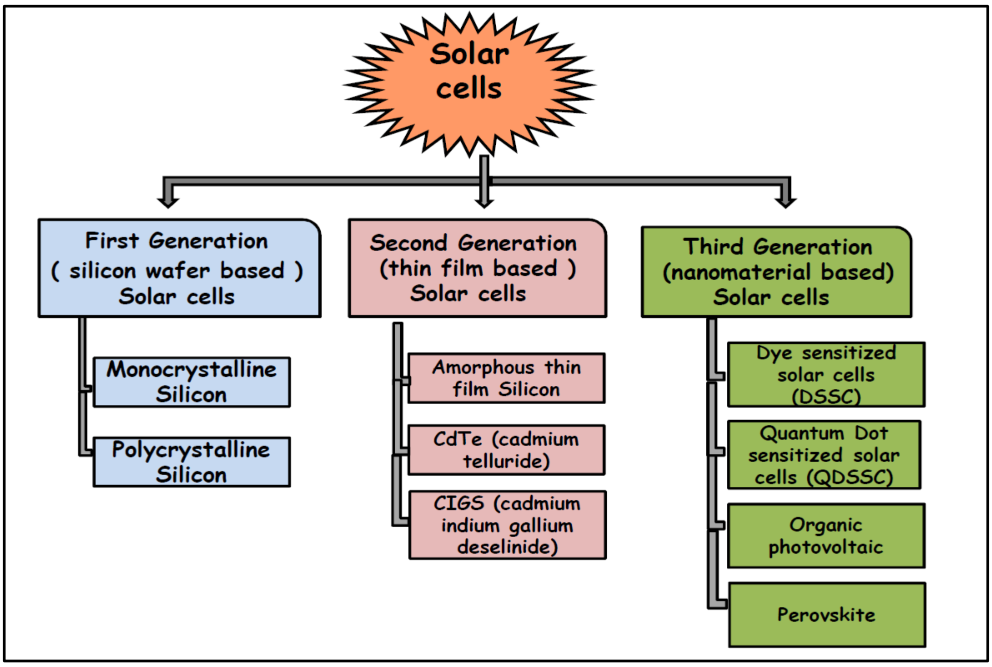
The second-generation solar cells are comparatively less expensive but are not popular due to low durability and stability.

Table 1: Efficiency, Merits and Limitations of Various Generations of Solar Cells

Type of Solar Cell	Efficiency	Merits	Limitations
First Generation Solar Cells	20 -25%	-High stability and durability -High efficiency -Commercially viable	-High cost due to requirement of high purity Si crystals -Complex fabrication processing -Efficiency is limited by the Shockley-Queisser limit
Second Generation Solar Cells (i) a-Si (ii) CdTe (iii) CIGS	 13% 17% 20%	- Flexible -Low cost fabrication resulting in significant reduction in cost per watt	-Low stability and durability -Lower conversion efficiency than 1st generation
Third generation Solar cells (i) Dye sensitized solar cells (DSSCs) (ii) Quantum dot sensitized solar cells (QDSSCs) (iii) Organic solar cells (iv) perovskite solar cells (PSCs)	 11.9% 8.5% 11.0% 20.1%	-Overcome the Shockley-Queisser limit -Lower processing costs -Minor environmental impact and shorter energy payback times -Cheap to produce -simple to manufacture	-Still in research stage, not commercially proven yet.

The third generation of solar cells, which encompasses all emerging photovoltaic technologies based on nanomaterials, are promising but are still in research stage and not commercially proven yet.Thus, a brisk research is required to envisage new materials and improve the technology so as to develop devices capable of harnessing solar energy efficiently and cost effectively. This has motivated researchers to seek new inexpensive, efficient and durable alternatives to crystalline silicon. In this context, the third-generation solar cell or nanomaterial based solar cells are very promising as they are less expensive, flexible, compact, lightweight and efficient.

Fig.1:



Classification of solar cells

Objective of the Study

The present-day sensitized solar cells are the most efficient representatives of third generation photovoltaic cells. While the dye sensitized solar cells (DSSCs) and the perovskite solar cells (PSCs) provide light-to-electricity conversion of up to 11% and 20 % respectively, significant further improvement is envisaged through optimized materials and novel cell and module architectures so as to achieve commercial scale production.This review paper intends to provide an overview of recent developments in sensitized solar cells, especially intended to develop sensitizers with inexpensive and abundant metal centers having good stability and high potential to enhance the device efficiency.

Literature Review of Sensitized Solar Cells

Invention of DSSCs byO' Regan and Gratzel [1] in 1991, marked the beginning of sensitized photovoltaic technology based on completely distinct type of solar cells mimicking the process of photo-synthesis. These solar cells are less expensive, flexible, compact, light weight and efficient, which not only open a way to their applications in the field of wearable or portable electronics but also make them extremely useful in the field of building integrated photovoltaics (BIPV) [2].A further strength of sensitized solar cells lies in their extremely high performance in indoor conditions under artificial light compared to other photovoltaic technologies.

The Gratzel cells are photo-electrochemical devices that use mesoporous nanocrystalline TiO2 sensitized with the ruthenium-based dye molecule. The usage of photostable semiconductors like TiO2, ZnO, or SnO2 instead of crystalline silicon reduces the cost of sensitized solar cells considerably. However, because of their wide band gaps, these semiconductors are insensitive to the visible solar spectrum. Hence, a sensitizer having strong absorption in visible and IR regions is adsorbed on semiconductor nanoparticles to harvest the solar energy. The sensitizer on photoexcitation gets oxidized and injects electron into the nanocrystalline semiconductor photoanode [3]. The electron then passes through external circuit to perform electrical work until it reaches the counter-electrode (CE), from where it diffuses into electrolyte to reduce redox couple. Finally, the redox couple reduced the oxidised dye completing the circuit and regenerating the dye. In first- and second-generation solar cells quality of materials has to be high in order to avoid defects promoting recombination of charges. Unlike conventional solar cells, sensitized solar cell technology separates charge generation (occurring at dye-semiconductor interface) from charge transport (done by the semiconductor and the electrolyte). Since the photo generated charge is quickly injected into two different transport media and each medium only transports a certain type of carriers, chances of recombination are decreased. This allows the high standards for the quality of materials to be relaxed and therefore manufacturing costs to be reduced.

Sensitizer--One of the crucial components of Sensitized Solar cells

A sensitizer determines the light absorption properties, electron transport and the composite device performance. As such envisaging new, cost effective sensitizers with improved efficiency and good stability is an important research field.As research progresses, record efficiencies of several technologies are likely to continue growing. Some of the emerging photovoltaics reported to exhibit remarkable efficiencies include (i) Dye Sensitized Solar Cells (DSSCs), (ii)Quantum Dot Sensitized Solar Cells (QDSSCs) and (iii) Perovskite Solar Cells

(PSCs). Noteworthy progress has been made in sensitized photovoltaic technology through evolution of the sensitizers from organic dye in DSSCs to inorganic quantum dot in QDSSCs and hybrid organic-inorganic perovskite in PSCs [4]. Following sections highlight the recent developments in these solar cells with reference to various materials used as the sensitizers and discuss their future prospects.

Dye Sensitized Solar Cells

For DSSCs applications complexes of ruthenium[5,6], platinum [7], iridium [8]and osmium [9] are reported to have good sensitizing efficiency.Among these ruthenium polypyridyl complex dyes have been investigated extensively and are reported to have the highest efficiency of about 11%. Ruthenium dyes like N719 [5] and N749 [6] (often referred to as “black dye”) are considered as the “benchmark dyes” or “champion dyes”. Despite good efficiency, commercialization of ruthenium based DSSCs is hindered because use of rare and toxic ruthenium sensitizer is against the principles of sustainable development.This has motivated researchers to explore the possibility of using complexes of the first-row transition metals as inexpensive, abundant and non-toxic sensitizers in DSSCs.

The metalloporphyrin form a major series of potential photosensitizers, put forward as an alternative toruth enium complexes due to advantages such as the diversity of their molecular structures, high molar extinction coefficient, simple synthetic route, low cost, and environmental friendliness.Gratzel in 2011 reported Zn (II) porphyrin complexes YD@ [10] and YD2-o-C8 [11] with conversion efficiency of 11.2% and 12.7% respectively, as an alternative to Ru dyes. There is scope of further improvement in solubility as poor solubility of these dyes poses difficulty in film formation on the surface of the TiO2.The absorption coefficients of YD2-o-C8 and its derivatives, still considered low [12], need to be enhanced by suitable modifications in the ligands.

Several copper(I), Iron (II) and nickel (II)based dyes have been recently investigated as sensitizers with great potential. Cu(I) bis (diimine) complexes [13-16] have been reported to possess photo-physical properties similar to that of Ru (II) diimine complexes. Investigations on a number of heteroleptic phenanthroline- and bipyridine-based copper(I) complexes have led researchers to the conclusion that these dyes have very good light harvesting efficiency (LHE) but overall photoconversion efficiency (PCE) is low due to undesirable charge transfer directionality resulting in inefficient electron injection into TiO2 [16]. This suggests that focusing efforts on increase the driving force for electron injection into the semiconductor conduction band by structural modifications of ligands may improve the efficiency of copper sensitizers.

Iron complexes, are very interesting due to the vast abundance of the metal and its non-toxicity. However, the studies on Fe (II) polypyridyl complexes reveal that iron complexes unlike their ruthenium counterparts sensitise TiO2 very inefficiently despite an intense MLCT absorption. This may be attributed to extremely short-lived photoactive MLCT state. Thus extending the lifetime of MLCT state in iron complexes is an importantstrategy for improving efficiency of Fe(II) sensitizers, which has been explored recently by different research groups [17-19] with considerable success. Similarly, the efficiency of Ni sensitizers observed to be quite low, despite satisfactory light harvesting, due to short-lived excited state [20]. Thus, extending the lifetime of the excited state by suitable molecular design is an important strategy for improving efficiency of these complexes.

Quantum Dot Dye Sensitized Solar Cells

QDSSCs are similar to DSSCs in operation but use QDs as sensitizers in place of dyes to sensitize TiO2 nanoparticles.Quantum dots have band gaps that are tunable across a wide range of energy levels by changing the dots' size, which means different wavelength of solar spectrum can be captured by just varying size. Moreover, QDs are capable of harvesting multiple portions of the solar spectrum due to multiple exciton generation (MEG). Also, the use of QD is a cheaper option in comparison to most of the efficient dyes.

Many kinds of light-harvesting binary QDs such as CdSe, PbS, CdS, and Bi_2S_3, have been used to sensitize wide-band-gap semiconductors and their photoelectrochemical properties have been investigated since 1984 [4]. The first landmark in QDSCs was achieved by Toyoda and co-workers in 2007 [21] with reported PCE over 2% with CdSe QDs. Through the exploration of the superior colloidal QD sensitizers and interface modification engineering, the highest PCE of QDSCs has been improved from 5% (with Mn doped CdS/CdSe QD sensitizers) [22] in 2012 to nearly 12.75% (with ZCISe-CdSe QD sensitizers) [23] in 2018. To tune the electronic and photophysical properties of QDs, various strategies have been adopted such as use of core-shell QDs (CdS/CdSe [24], ZnSe/CdSe [25], $CuInS_2$/ZnS [26]), doped QDs and alloyed QDs ($CdSe_xTe_{1-x}$ [27], $CuInS_2$ [28], $CuInSe_2$ [29]). Among these, I–III–VI group alloyed QDs such as $CuInS_2$ (CIS) and $CuInSe_2$ (CISe), are considered as ‘‘green’’ sensitizers as they do not contain toxic elements like Cd or Pb. In addition, these QDs have a high absorption coefficient and narrow band gap, which makes them excellent sensitizer. In recent years, Zhong et al. explored an alloyed Zn–Cu–In–Se (ZCISe) [30] QD sensitizer possessing a narrow band gap and high conduction band edge achieving a record PCE of 11.61%. Thus, the I–III–VI group alloyed QDs possess great potential to promote the further development of QDSCs in the near future.The carbon QD (CQD)[31] composed of black graphene is also a low-cost and eco-friendly sensitizer but has a low efficiency. An intensive investigation in CQD as sensitizer is, therefore the need of the hour.

Perovskite Solar Cells

The latest trend in photovoltaics has been perovskite solar cells (PSCs) in which the sensitizing material is a hybrid organic inorganic perovskites (HOIP). Perovskite for a solar cell has a simple structure with a chemical formula of ABX_3 , where A is occupied by organic such as $CH_3NH_3^+$ (MA) or inorganic material like Cs^+, and B site is occupied by a divalent metal cation (eg : Pb^{2+} or Sn^{2+}) and X by a halide anion [32] .The field has grown immensely in the past few years and efficiencies rapidly surpassed those of all other organic or hybrid solar cells. First PSC was reported by Miyasaka et al. in 2009 [33] with electrolyte as transporting medium.In 2012,a solid hole transport layer was substituted for the liquid electrolyte to develop all-solid-state PSCs which revolutionized the field of photovoltaicsdue to their enhanced efficiency [34]. The recorded efficiency of PSCs has grown progressively from 3.8% in 2009 to25.2% ,reported recently with all inorganic halide perovskites (AIHP) of CsPbX3 [35], which is comparable to conventional silicon solar cells. However, their sensitivity to moisture, oxygen and extreme temperature and light makes them highly unstable that restricts their commercialization. Moreover, the most efficient PSCs are composed of highly toxic and carcinogeniclead halides. Global emphasis on sustainable development has shifted the focus of research in material chemistry to lead free all-inorganic halide perovskites (LFAIHP) materials for solar cells. The manufacture of these materials on a quantum scale (LFAIHP QDs) has also received considerable attention due to the quantum confinement effect [36].

Several LFAIHP QDs such as Sn based [37], Cu based [38], trivalent metal cation (Bi, Sb) based halide perovskites [39, 40] and double perovskites (DP) [41] have been proposed, recently. 2D halide perovskite materials with formula Cs2CuX4 [38] also represent a green alternative to conventional perovskites but the research on this material is limited and requires intensive investigation to understand the optical and electrical properties in order to reveal their potential.

In recent four years, double perovskites (DP) with $A_2B(I)B(III)X_6$ structure have received great attention inrecent four years due to their tunability and excellent stability in moisture, heat and light [42]. In double perovskites, two divalent cations of Pb^{2+} are replaced by one monovalent cation B(I)and one trivalent cation B(III) where ($A=Cs^+$, Rb^+, $B(I)= Na^+$,K^+, Li+, Ag^+,Cu^+, $B(III)=In^{3+}$, Sb^{3+},Bi^{3+} , X=Cl, Br or I). Among the various double perovskites, Cs2AgBiX6 [42]and Cs2 AgInX6 [42] are regarded as the most suitable alternative for the Pb-based halide perovskite QDs. Research in double perovskites for solar applications is in its nascent stage and there are many challenges ahead. For practical applications more research needs to be conducted to understand the exact optoelectronic properties and improve their quantum yield by various techniques like doping, alloying, ligandcontrol, and encapsulation

Conclusion and Future Prospects

Currently a lot of solar research is going on in material science to probe into some new innovations, which can empower the discovery of novel active nano materials capable of improving the solar PCE drastically and thus paving the way for commercially viable sensitized solar cells. Improvement in solar cell materials to enhance the device efficiency must be in accordance with the principles of sustainable development. With this view this work focuses on the recent developments in non-toxic, abundantly available, ecofriendly and efficient sensitizing materials for sensitized solar cells such as dye sensitized solar cells (DSSCs), quantum dot sensitized solar cells (QDSSCs) and perovskite sensitized solar cells (PSCs). To further promote the development of sensitized solar cells, the photo conversion efficiency (PCE) and the stability and the toxicity of various constituent materials should be taken into consideration simultaneously and improved to a new satisfactory level.

For DSSCs, the sensitizers with Iron or copper (I) complexes are very promising alternative to ruthenium dyes due to cheap, abundantly available nontoxic metal center. But these sensitizers have an average efficiency and an intensive research is required to make them commercially viable.The use of heteroleptic copper(I) bis diimine complexes is certainly at its early age but it has potential to spark the developments of new systems for DSSCs.

The development of lead based QD sensitizers has contributed to huge enhancement of the PCE of QDSCs in recent years. However, for the sustainable development highly toxic Cd- or Pb-containing QD materials must be replaced by “green materials”. In recent years, Pb-free I–III–VI group QDs such as CuInS2 and CuInSe2 have emerged as an attractive “green” alternative and have been demonstrated to be capable of obtaining a higher efficiency. However, to scale up QDSSCs to a commercial level, there is still a great need to explore more superior QDs possessing high PCE, good stability environmentally friendly nature, and low cost.

Research in lead free all inorganic halide perovskites quantum dots (LFAIHP QDs) is the latest trend and holds a great potential as ‘green’ sensitizer. Among these double perovskites QDs of Cs2AgBiX6 and Cs2AgInX6 have emerged as excellent materials with good stability and high tunability. To fabricate practical LFAIHP QD-based solar cells, continuing efforts are required towards increasing the stability and enhancing the quantum yield through various techniques like doping or alloying.With so much research work oriented towards developing a methodology and envisaging green materials that can create a scalable and efficient photovoltaic device, the field of sensitized solar cells holds great future prospects.

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