Recent trends in mesoscopic solar cells based on molecular and nanopigment light harvesters

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Mesoscopic solar cells are one of the most promising photovoltaic technologies among third generation photovoltaics due to their low cost and high efficiency. The morphology of wide-band semiconductors, sensitized with molecular or nanosized light harvesters, used as electron collectors contribute substantially to the device performance. Recent developments in the use of organic–inorganic layer structured perovskites as light absorbers and as electron or hole transport materials allows reduction in the thickness of photoanodes to the submicron level and have raised the power conversion efficiency of solid state mesoscopic solar cells above the 10% level.

Introduction

In this modern era, rising living standards of a growing world population can no longer be satisfied through conventional means. Depleting oil sources and ecological factors force us to find alternative energy sources. It has been estimated that by 2050 the energy gap will be around 15 TWh. The majority of today’s energy is produced from fossil fuels. The consequence of the growing dependence on fossil fuels has created an augmentation of the greenhouse effect and resulted in global warming. Solar energy is a clean, reliable and renewable source of energy responding to future demands. As a source of alternative energy supplies solar cells are the best choices due to the abundance of uncaptured solar energy on the earth. More solar power strikes the surface of the earth in one hour than the energy provided by the fossil fuels that are currently consumed globally in one year. Over the past two decades Silicon technology has dominated the domain of PV cells using flat single layer p–n junction diodes; however, now-a-days this photovoltaic technology is facing a strong challenge from third generation PV technologies.

The sensitization of semiconductor materials using dyes started already in the late 1960s [1] but the breakthrough for dye-sensitized solar cells (DSC) came in 1991 with the use of mesoporous titania film for sensitization [2]. The mesoporous titania film increases the surface by 1000 times compared to flat surfaces, enhancing enormously the surface area for dye absorption. Great interest has developed among scientists about this technology as a possible alternative to the conventional silicon solar cells. In the development of third generation photovoltaic technology (3G PV) sensitized mesoscopic solar cells (typically DSC) have a leading edge over other technologies due to their lower cost, simple fabrication methods and high power conversion efficiencies. In silicon solar cells charge separation and charge transfer take place in the same material, whereas, in the case of DSCs, charge separation occurs at the interface of the sensitized electron transport material. The fact that charge separation and electron transport take place in two different materials allows ample scope for the development of novel materials to enhance device performance. The photo conversion process of a sensitized mesoscopic solar cell is analogous to natural photosynthesis; hence, it is also known as ‘artificial photosynthesis’. A schematic diagram of the DSC’s operating principles is shown in Fig. 1. The highest record efficiency of 12.3% was reported with a CoII/III(bpy)3 complex based electrolyte in conjunction with a donor acceptor zinc porphyrin dye [3].

TiO2 nanostructured materials as photoanodes

A commonly used semiconductor material in sensitized mesoscopic solar cells is wide bandgap titanium dioxide (TiO2), which is a non-toxic, biocompatible, cheap and abundant material. TiO2 is a well-known n-type semiconductor, which contains crystal defects of oxygen vacancies and exists in three different crystalline forms, that is, rutile, anatase and brookite. The nanocrystalline TiO2 film used in DSCs is made of anatase due to its larger bandgap (3.2 eV) compared to rutile (3.0 eV). In a sensitized mesoscopic solar cell a dye adsorbed TiO2 film is used as a photoanode to
In a typical DSC the particle size of TiO\textsubscript{2} anatase is in the range of 10–25 \textmu m and a porosity of around 60% to ensure a large internal surface area for adsorbing dye molecules [34]. The nanocrystalline film can be considered to be a network of bulk crystals with a band of extended electronic states arising from the high surface area of the nanocrystals. As smaller TiO\textsubscript{2} particle size films are transparent, part of the visible light will be transmitted through the film. To circumvent this problem a double layered structure of TiO\textsubscript{2} films is generally utilized in DSCs fabricated by depositing a second layer of 250–400 nm particulate TiO\textsubscript{2} film on top of the transparent film [35,36]. The larger particulate layer contributes only a small amount to the dye adsorption, its main contribution being the beneficial light scattering effect. Even though the double layer structure has the advantage of producing more light reflection, due to the increase in the film thickness following its utilization the electron diffusion length is augmented contributing to a higher recombination rate. Kim \textit{et al.} synthesized nanoporous TiO\textsubscript{2} spheres to enhance the device performance by increasing the light scattering [37]. In this case the electron diffusion coefficient within a single spherical structure is highly favorable; however, the drawback of this structure is the difficulty of electron transfer between neighboring structures due to the small contact area. TiO\textsubscript{2} beads-based films have been employed in place of standard mesoporous transparent TiO\textsubscript{2} films to enhance the light harvesting capability without compromising the dye loading [38]. The morphology of the screen-printed TiO\textsubscript{2} beads’ film is shown in Fig. 2. The larger size of the beads is primarily responsible for the light scattering effect. At the same time the mesoporous structure of the beads and densely packed nanocrystals inside the core shell with multiple contacts between the neighboring crystals will provide sufficient surface area for dye adsorption as well as faster electron diffusion in these films leading to higher power conversion efficiencies. Using the same concept, highly crystalline TiO\textsubscript{2} nanocathaheda and agglutinated mesoporous TiO\textsubscript{2} microspheres were synthesized and utilized for high efficiency sensitized mesoscopic solar cells [39]. Even though the one-dimensional structured TiO\textsubscript{2} materials have excellent properties, the DSC devices containing nanocrystalline TiO\textsubscript{2} structured films outperformed these alternative film structures, obtaining record PCEs. 

**Developments in liquid redox electrolytes**

In addition to the photoanode, the electrolyte provides a substantial contribution to the overall sensitized mesoscopic solar cell device performance. Iodide/triiodide-based redox electrolyte has been the most widely used and efficient electrolyte for liquid DSCs. The minimum requirements needed to formulate an efficient redox electrolyte are that the solubility and ionic mobility of the redox couple are high enough in the organic solvent employed. Essentially there should be enough driving force for the dye regeneration process and fast electron transfer kinetics at a minimal overpotential at the counter electrode. The energy level of the iodide/triiodide redox electrolyte is fixed at approximately 0.4 V versus NHE, depending on the concentration of iodide and triiodide species present in the electrolyte. One of the disadvantages of the iodide/triiodide redox electrolyte is that the redox energy level is not tunable to a greater extent. The open-circuit potential ($V_{oc}$) of DSCs stems from the difference in the energy level of redox electrolyte and the quasi-Fermi level of TiO\textsubscript{2}. Hence, the use of iodide/triiodide redox electrolyte limits the $V_{oc}$ due to an excessive loss of voltage during the dye-regeneration process.
In order to enhance the device performance the design and understanding of iodide free electrolytes has become a recent focus in DSC research [40]. One-electron outer sphere redox couples, based on cobalt complexes, have shown promising results as redox electrolytes especially in combination with donor-π-acceptor metal free dyes [40]. Judicial design in and use of donor-π-acceptor (D-π-A) zinc porphyrin dye (YD2-ο-C8) co-sensitized with Y123 D-π-A dye [41] allows light absorption over the entire visible region of the solar spectrum (Fig. 3b, IPCE spectra), and when combined with a CoIII/II (2,2’-bipyridine)3 based redox electrolyte yields an amazing DSC device performance of over 12% efficiency [3]. The I–V curves of co-sensitized devices are shown in Fig. 3a. The absorption spectra of YD2-ο-C8 and Y123 dyes are complementary to each other; the co-sensitization concept of these two dyes allows absorption over the full visible spectrum as shown in the incident photon-to-conversion efficiency (IPCE) spectra of Fig. 3b. The advantage obtained by using a higher redox energy level cobalt-based electrolyte (0.57 V versus NHE) is the attainment of 965 mV of open-circuit voltage (Voc) in the above-mentioned record efficiency DSC device.

Solid-state dye-sensitized solar cells

Earlier research efforts, which are well documented in recent reviews, have focussed on the development of sensitized mesoscopic solar cells which utilize liquid electrolytes through optimization of the electrolyte composition, including introduction of different redox shuttles, as well as investigations on photoanode materials and dyes [40–47]. However, only a relatively small amount of work has been done on the solid-state dye sensitized solar cells (ssDSC). The difference between the liquid DSC and the ssDSC is that the liquid redox electrolyte is replaced by a solid organic hole transport material (HTM). The operating principle of the ssDSC is that the liquid redox electrolyte is replaced by a HTM for hole transfer and dye regeneration. The ssDSC is composed of a thin layer mesoporous TiO2 film deposited on top of a compact layer used as a blocking layer on a transparent conducting oxide (TCO) glass substrate. A thinner photoanode substrate is required in solid-state devices due to eventual pore-filling problems and to ascertain an acceptable diffusion length, thus avoiding facile recombination. The blocking layer prevents direct physical contact between the TCO and the HTM and reduces the recombination at this interface. In case of iodide/triiodide-based electrolytes the reduction of triiodide on TCO is a sluggish two-electron process and, thus, the effect of a blocking layer would be small. A monolayer of sensitizer is adsorbed on top of the mesoporous titania film and then infiltrated (normally by spin-coating) with a HTM solution.
Infiltration of the HTM into the pores of the TiO₂ film is a pivotal step to obtain high performance of the solid-state sensitized mesoscopic solar devices. If the pores of the TiO₂ film are not completely filled then all the dye molecules adsorbed inside of the pores are not able to transfer their holes, formed following electron injection into the TiO₂ film, to the HTM, limiting the device performance. The thinner the TiO₂ film is the easier it is to fill all pores with HTM. The thin layer of organic HTM is capped with a metal (Au or Ag) counter electrode deposited under vacuum. In ssDSCs the most in-depthly investigated and efficient HTM to date is 2,2'-7,7'-tetrakis(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (spiro-MeOTAD). The first efficient ssDSC device, using spiro-MeOTAD as HTM, was reported in 1998 and obtained 0.74% PCE under conditions of full sunlight (100 mW cm⁻², AM 1.5) [48].

Contrary to liquid electrolyte containing sensitized mesoscopic solar cell devices, various nanostructured TiO₂ materials such as nanotubes, nanowires, nanofibers, etc., have been less studied as photoanodes in fabrication of ssDSCs. One of the advantages of applying these one-dimensional structures is to circumvent the pore-filling problem. Highly ordered, vertically oriented titania nanotube (NT) arrays were prepared by anodization of the titanium on FTO-glass substrate and applied to the ssDSC devices for the first time [49]. SEM images of the TiO₂ NT arrays (Fig. 4) show that the pore diameter and wall thickness are 40–50 nm with a flat top layer. A flat top layer is of importance for proper functioning of a ssDSC so as to have a good contact with the HTM and the gold counter electrode. Under 1.5G full sunlight intensity, using C203 (D-π-A) dye [50] as sensitizer and spiro-MeOTAD as HTM, power conversion efficiencies (PCE) of 1.68% and 3.8% were obtained on a NT arrays’ film and a nanocrystalline TiO₂ film-containing device, respectively. One of the origins of poor performance of the NT arrays film device is that the blocking underlayer is not as efficient as the one prepared by spray pyrolysis in the nanocrystalline ssDSC devices. The blocking layer appeared to be destroyed during the anodization procedure used to create NT arrays’ films. In addition, as pointed out previously, the absorption cross-section of the NT sensitized film is smaller than that found in the mesoporous sensitized film, like wise contributing to lower device performance.

The record PCE of liquid electrolyte DSCs is reported to be over 12%. The ssDSC efficiencies have been lagging behind; PCE = 7.2% under standard AM 1.5 one sun light intensity [51].
Perovskite compounds of the general formula \( \text{CH}_3\text{NH}_3\text{MX}_3 \) where depending on the size of the metal ion and the organic cation. They form a MX6 octahedral geometry having M at the center and halides at the corners. The MX6 octahedral extends to form a three dimensional perovskite structure in the orthorhombic \( \text{Pnma} \) space group. As shown in Fig. 5 the cross sectional SEM images of these cells shows that CsSnI3 homogeneously permeates deep into the nanoporous TiO2 substrate. The penetration of CsSnI3 deep into the mesoporous TiO2 film facilitates the charge separation and hole removal, and, in addition, its large hole mobility is primordial for obtaining good device performance. The device exhibited the best photovoltaic performance when the CsSnI3 was doped with 5% of F and SnF2.

Recently, a ssDSC employing \( (\text{CH}_3\text{NH}_3)\text{PbI}_3 \) perovskite nanosheets as light absorber and spiro-MeOTAD as a HTM was reported [85]. The \( (\text{CH}_3\text{NH}_3)\text{PbI}_3 \) was prepared in situ by dissolving equivalent amounts of PbI2 and \( \text{CH}_3\text{NH}_3\text{I} \) in \( \gamma \)-butyrolactone solution. The \( (\text{CH}_3\text{NH}_3)\text{PbI}_3 \) sensitized TiO2 films were coated with spiro-MeOTAD solution using the spin-coating technique [85]. The valence band and conduction band of \( (\text{CH}_3\text{NH}_3)\text{PbI}_3 \) perovskite was determined to be \(-5.43\) eV and \(-3.93\) eV, respectively [78]. Since the conduction band energy of TiO2 is \(-4.0\) eV, there is a small driving force for electron injection. On the other hand photo-induced hole injection in the hole conductor contributes to interfacial charge separation.

This perovskite-based solid-state mesoscopic solar cell device exhibited a PCE of 9.7% under standard AM 1.5G sunlight (Fig. 6). As shown in Fig. 6b the IPCE spectrum shows a maximum of 65% at 450 nm and above 50% up to 750 nm. The detection of \(-17.6 \text{mA cm}^{-2} \) current density with a submicron (0.6 \( \mu \text{m} \)) TiO2 film is remarkably high, and materialized due to the large optical cross section of \( (\text{CH}_3\text{NH}_3)\text{PbI}_3 \) (1.5 \( \times 10^4 \) at 550 nm [86]). The linear response of photocurrent density with light intensity indicates that there is no space charge limitation at the heterojunction associated with only small differences in electron and hole mobilities in this ssDSC device (Fig. 6c). The use of perovskite materials as light absorbers in solid-state sensitized mesoscopic solar cells has opened up a new direction for the use of submicron thin mesoporous TiO2 films without sacrificing device performance. This experimental result attained through the use of thinner TiO2 films in the fabrication of a high performance solid-state sensitized...
mesoscopic solar cells avoids the pore-filling problems associated with HTMs and opens the avenue to use a variety of HTMs to replace spiro-MeOTAD by other conducting oligomers and polymers.

Snaith et al. reported the use of CH$_3$NH$_3$PbI$_2$Cl perovskite as absorber on top of a mesoporous TiO$_2$ film, employing spiro-MeOTAD as a solid HTM, obtaining 8% PCE under full sun illumination [87]. Replacing the TiO$_2$ semiconductor by an insulator, Al$_2$O$_3$, acting as a scaffold in a device coined as mesoporous super-structured solar cell (MSSC) for coating the perovskite layer, they found that the electron transport through the perovskite layer was much faster than through the n-type TiO$_2$ film. The combination of a mixed halide perovskite (CH$_3$NH$_3$PbI$_2$Cl) as a light absorber on top of Al$_2$O$_3$ film gave a record PCE of 10.9% for a

![Cross-sectional SEM image. Thickness is ~10 μm.](image1)

**(a)** Cross-sectional SEM image. Thickness is ~10 μm. **(b)** Elemental mapping by energy dispersive spectroscopy for the rectangular area indicated by a blue box in (a), showing homogeneous infiltration of CsSnI$_3$ into nanoporous TiO$_2$. **(c)** Back-scattering cross-sectional SEM image, showing no discernible contrast difference. **(d)** Cross-sectional HRTEM image taken near the bottom of the cell. (A) CsSnI$_3$ and TiO$_2$ overlapped; (B) high (h k l) index area showing unclear lattice fringes; (C) TiO$_2$. **(e)** Left panel, experimental electron diffraction pattern, indicating TiO$_2$ (ring patterns) and CsSnI$_3$ (spots indicated by white arrows between ring patterns); right panel, theoretical calculation of anatase TiO$_2$. Reprinted by permission from Macmillan Publishers Limited: Ref. [84]. Copyright 2012.

![Photovoltaic characteristics of (CH$_3$NH$_3$)$_2$PbI$_3$ perovskite sensitized solar cell.](image2)

mesoporous super-structured single junction device. It was reported that the $V_{oc}$ obtained with the alumina-based devices is 200 mV higher than that found using titania-based devices. In these devices the electrons are transported through the perovskite layer and the holes are transported through the spiro-MeOTAD layer. The mixed halide perovskite has good spectral response over the visible and near-infrared spectrum compared to the pure halide, CH$_3$NH$_3$PbI$_3$ perovskite. It is interesting to note that the perovskite layer can function both as a light absorber as well as n-type semiconductor for transporting electronic charges out of the device.

In a recent publication it was demonstrated that CH$_3$NH$_3$PbI$_3$ perovskite can act both as an efficient light absorber and as a hole transporter in CH$_3$NH$_3$PbI$_3$/TiO$_2$ heterojunction devices [88]. A ssDSC device was fabricated using CH$_3$NH$_3$PbI$_3$ on top of TiO$_2$ (anatase) nanosheets with exposed (0 0 1) facets without an additional hole transport material, achieving a PCE of 5.5% under standard AM 1.5 solar light of 1000 W m$^{-2}$ intensity. The IPCE of the device shows an excellent photocurrent response up to 800 nm with a maximum of 90% between 400 and 540 nm. When a mesoporous TiO$_2$ film was used in place of the (0 0 1) facet nanosheets the PCE diminished to 2.8% at one sun intensity. The difference in the PCE of the two different structured TiO$_2$ films is attributed to the higher ionic charge of (0 0 1) facets. This is attributed in strengthening the attachment of the perovskites to the titania and enhancing charge screening.

In this relatively new domain utilizing perovskites in mesoscopic solar cells it has been shown by the examples cited above that perovskites of differing chemical composition can be used in multiple functions such as p-type hole transport materials, as light absorbers in a ‘typical’ SSDSC (utilizing spiro-MeOTAD as organic hole transport material) devices, as both light absorber and electron transport material in MSSC, and can serve dual functions as light absorber and hole transport material in non-classical SSDSC type devices. Extremely thin photoanodes or ‘scaffolds’ can be employed circumventing conventional pore-filling problems.

**Summary and outlook**

In the past couple of years there has been tremendous progress in the advancement of mesoscopic solar cell performance. Record PCEs were reported for liquid based DSCs following the development of cobalt complexes as alternative redox electrolytes used in combination with newly designed donor-acceptor zinc porphyrins as sensitizers. Even a modest shift in the absorption onset of the dye would result in further substantial augmentation of the short circuit photocurrent. Thus, a 50 nm red shift is expected to increase the $J_{sc}$ by 3 mA cm$^{-2}$ augmenting the PCE to nearly 15%. At the same time designing new redox couples having sufficient driving force suitable for rapid dye regeneration will boost the device $V_{oc}$ leading to further enhancement in PCE. For ssDSC devices the use of perovskites as a light harvester sparked a jump in the PCE. These values are now approaching those of their counterpart liquid electrolyte-based DSCs. Only a limited number of perovskites were investigated thus far as light absorbers, leaving the field wide open to the discovery of new efficient materials for reaching record PCEs in solid-state sensitized mesoscopic solar cells. It has also been demonstrated that various perovskites can be used as light harvesters and as electron/hole transporting materials. The combination of two different perovskites, as light absorbers and as HTM, will pave a new direction toward all solid inorganic mesoscopic solar cell devices, likely delivering higher device performance and long-term stability. The combination of light absorbing perovskite materials with different conducting oligomers or polymers containing high hole mobility materials is another attractive option. All of this progress may be achieved with submicron mesoporous semiconducting films enabling large reductions in material cost.

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**References**
