Investigation of charge transport in nanofiber based solar cells

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**SCHOOL OF MATERIALS SCIENCE AND
ENGINEERING**

**Investigation of Charge Transport in Nanofiber
based Dye-sensitized Solar Cells.**

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NANYANG TECHNOLOGICAL UNIVERSITY

SCHOOL OF MATERIAL SCIENCE AND ENGINEERING

INVESTIGATION OF CHARGE
TRANSPORT IN NANOFIBER BASED
SOLAR CELLS.

by

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Abstract

Dye sensitized solar cells (DSCs) have garnered a lot of attention owing to their ease of fabrication, low manufacturing costs and good device stability. One of the crucial components of high efficient dye sensitized solar cell is the mesoporous metal oxide nanocrystalline photoanode. High surface area and mesoporous photoanodes are essential for greater adsorption of sensitizer monolayer leading to improved optical density especially for low absorption coefficient sensitizers like Ru based complexes (N719). In order to enhance light harvesting efficiency which is instrumental in boosting the device performance, either thicker photoanode materials or dyes with higher absorption coefficients need to be engaged. Nevertheless utilizing thicker photoanode films leads to poor charge collection. Therefore one dimensional nanostructures are being explored as a replacement for nanoparticles with the aim of improving charge transport by providing a directional path for charge percolation and by reducing the surface traps and density of grain boundaries associated with nanoparticles. One of the simplest yet versatile method to synthesize such 1D nanostructures is by electrospinning. Photoanodes made of electrospun TiO_2 nanostructures with good inter connectivity and high surface area play a critical role in determining the conversion efficiency of dye-sensitized solar cells. High molecular weight polyvinylpyrrolidone polymer when mixed in to the titanium sol-gel precursor solution results in the formation of electrospun fibers with nanofibrillar morphology. This work focuses on the integration of as-spun nanofibrous films with intact fiber morphology as photoanodes in dye-sensitized/perovskite solar cells. One fundamental observation deduced from the photovoltaic measurements is that the nanofibrous based photoanodes always exhibited higher open circuit voltage than the nanoparticle systems. Electrochemical impedance spectroscopy (EIS) measurements indicated that the resultant photoanodes had better charge collection as a consequence of improved charge transport and recombination dynamics compared to previous reports of photoanodes prepared by grinding electrospun nanofibers or by using nanoparticles. This characteristic of the nanofibers is of paramount interest in the solid-state DSCs (ssDSCs) where the charge recombination kinetics is faster than the kinetics observed in liquid DSCs. In this work, the EIS measurements validated that the nanofibers

demonstrated better charge dynamics even in ssDSCs thus showcasing them as potential candidates for highly effective solar cells.

Regardless of the better charge dynamics exhibited by the nanofibrous DSCs, the electrochemical conversion efficiencies are observed to be lower than the nano-particle DSCs. The prime contributing factor for the poor performance of the 1D solar cells is associated with their lower surface area for dye adsorption. This resulted in meager photon harvest thereby yielding appreciable current densities. Consequently this work also focuses on modulating the morphology of electrospun nanofibers to hierarchical nanostructures as well as to sensitize the nanofibrous photoanodes with one or more highly efficient sensitizing materials with the sole purpose of enhancing the light harvesting efficiency. So initially by solvo thermal treatment the nanofibers' morphology was adapted to a hierarchical structure comprising of anatase nanofiber backbone with single crystalline rutile nanorods branching out. The aspect ratio and density of the nanorods was meticulously modulated and investigated by varying the reaction time. The UV-Vis absorption and incident photon to electric conversion efficiency (IPCE) measurements demonstrated that the hierarchical structure enabled higher loading of dye molecules which is essential for improving the current density. Also a high open circuit voltage ensued by the compact packing of dye molecules on the hierarchical nanostructure. It also concurs well with its higher resistance to recombination between the TiO_2 conduction band electrons and the oxidizing species of hole transporting medium measured from EIS. A similar phenomenon of enhancement in current densities and open circuit voltage was observed when an alternative approach of sensitizing the nanofibers with 2 structurally different organic dyes with complementary absorption profiles was introduced. Initially a triphenylamine D35 chromophore with bulky butoxyl groups was employed to sensitize the nanofibers followed by sensitizing them again with a smaller indoline dye called D131. This semi-tandem like co-sensitization process concomitantly improved the light harvesting efficiency and passivated the nanofiber surface by virtue of the condensed packing of both the dye molecules which suppressed the charge recombination with the tri-iodide species of the electrolyte. Having demonstrated the better electron percolation and suppressed recombination and possible routes of improving the current densities marginally, the final work of this thesis focuses on sensitizing nanofibers with high absorption coefficient hybrid organic-inorganic materials like methyl ammonium lead iodide perovskite for dramatic improvement in photon harvesting. On account of the perovskite crystal quality affecting the solar cell performance, significance of porous network of the nanofibers on the percolation of perovskite was demonstrated with respect to a thin perovskite layer.

Thus in this thesis, significance of as-spun nanofibrous photoanodes in DSCs as well as in emerging novel photovoltaic systems was investigated in terms of

processability, light harvesting efficiency and electron dynamics. The as-spun nanofibers have exhibited easier processability, better infiltration of hole transporting material (HTM)/perovskite absorber material, better charge transport and higher charge recombination resistance leading to higher charge collection efficiency even in the ssDSCs in contrast to the screen printed or spincoated nanoparticle films.

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Chapter 1

Introduction

1.1 Background and Motivation

The energy needs of the world are growing exponentially every year and most of these energy requirements are met by oil, coal and natural gas (fossil fuels) as seen in Fig. 1.1. Though these natural reserves can last for quite a long time they will eventually deplete with the expanding population and concomitantly will have adverse effects on global economy and quality of life. The emission of green house gases such as carbon dioxide by combustion of these fossil fuels for energy has been scientifically proven and ascertained that this phenomenon has led to the rising of temperatures globally. This dependence on fossil fuels will inevitably lead the mankind to make a transition to clean and renewable forms of energy which pose little environmental hazards and which can be replenished by themselves. The various forms of renewable energy are solar, wind, tidal, hydroelectric power, biomass, wave and geothermal energy. Among these various forms, the International Energy Agency has reported in 2011 that the investment in solar energy

Figure 1.1: Global consumption of energy is increasing undoubtedly along with the emergence of new forms of energy^[1].

has greater long term benefits globally as they are inexhaustible and can enhance countries' energy security, keep a check over the prices of the fossil fuels and suppress pollution. All these factors contributed to impressive and extensive research in the field of photovoltaics.

As depicted in Fig. 1.2, the solar cells can be broadly classified as (a) multi and single junction cells, (b) crystalline Si cells, (c) thin film and (d) emerging photovoltaics (PV). Though very high solar to electric conversion efficiencies can be attained using Si, GaAs or multi junction solar cells, their high efficiencies are

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Figure 1.2: Best research cell efficiencies^[2].

at the expense of intricate and expensive manufacturing process which results in low performance to price ratio. Whereas solution processed solar cells comprising the family of dye-sensitized solar cells (DSCs), perovskite solar cells, organic cells, quantum dot cells offer several advantages in terms of simple, inexpensive fabrication routes in conjugation with inexpensive precursors. Until 2012, DSCs attracted scientific as well as industrial interests owing to their ease of fabrication, flexibility, high efficiency and low production costs^[3–5]. Titanium dioxide is widely used in DSCs as it is cheap, abundant and can be synthesized by various techniques^[6–11]. Mesoporous layers consisting of nanoparticles are used extensively as support for sensitizers and photon to electron conversion efficiencies of up to 12-13 % have been reported^[12]. The optical density in a DSC is greatly influenced by the type of sensitizer used. Generally Ru based sensitizers were widely used and proved to be the most effective dyes by achieving highest pho-

ton to current conversion efficiencies^[13,14] for films with thickness as high as 15 μm . Few years ago metal free organic dyes have gained significant attention because of their high molar extinction coefficients, facile synthesis and environmental friendliness^[15]. Also the efficiencies of photovoltaic cells sensitized with organic dyes were observed to be higher as compared to the cells sensitized with Ru based dyes when thin (1.6 μm) mesoporous films were used^[16]. The advent of the high absorption coefficient organic dyes paved way for the solid state DSCs where the problems associated with the liquid electrolytes were resolved. In order to further enhance the light harvesting efficiency of the DSCs, several approaches like cosensitization was employed where a red light absorbing sensitizer is co-sensitized with a blue light absorbing dye. The panchromatic behavior achieved by this approach had improved the cell performance considerably^[17]. However, the full potential of organic dyes in achieving high efficiencies is hindered either by their ability to form aggregates or due to scarcity of TiO_2 surface area for adsorption of dye molecules in case of co-sensitization. The formed H or J aggregates lead to quenching of excited states thereby lowering the cell performance. In 2009, the replacement of conventional dyes in liquid DSCs with a high absorption coefficient (10 times higher than that of organometallic dye) hybrid organic-inorganic perovskite namely $\text{CH}_3\text{NH}_3\text{PbI}_3$ yielded a solar to electric conversion efficiency of 3.8 % which upon further optimization increased to 6.5 %^[18]. As these perovskites are highly unstable in the presence of the electrolyte, replacing the electrolyte with a hole transporting material (HTM) and by reducing the TiO_2 film thickness, stable solar cells with efficiencies 9.7 % have been reported^[19]. With an optical bandgap of 1.55 eV, these materials can generate a maximum photocurrent of 24 mAcm^{-2} , assuming that all the photons are con-

verted to electrons.

Figure 1.3: Schematic illustrating effect of morphology on charge transport^[20]. Charge transport for (a) mesoporous nanoparticle film, (b&c) nanofiber longitudinal and cross-sectional views.

In a typical DSC where mesoporous nanoparticles with high surface area constitute the scaffold for the adsorption of sensitizers, the photoinjected electrons are subjected to long and tortuous percolation routes as well as interaction with surface states that affect their transport within the semiconductor film and their collection at the electrode. These nanoparticles have high density of disordered inter particle connections which promote trap-assisted diffusion of charge. Charge transport is facilitated by diffusion as field assisted transport is prevented in DSCs owing to the presence of ions in the electrolyte^[21] as shown in Fig. 1.3(a). However the slow charge transport of these mesoporous systems did not affect the charge collection at the electrode as the recombination kinetics were slower. Nevertheless, this slow transport would pose a problem to thicker TiO_2 films where the film thickness is increased to enhance the optical density. To overcome this problem, efforts have been made to incorporate one-dimension (1D) nanostructures like nanotubes^[21–23], nanowires^[24], nanofibers etc. instead of nanoparticles. The 1D nanostructures facilitate directional charge transport ow-

ing to their higher crystallinity, fewer inter-particle connections and field assisted charge transport. The diameters of these nanorods are larger than the diameters of the nanoparticles thereby facilitating an electric field which will confine the charges within the core thereby reducing recombination. The difference in the mechanism of charge confinement for a nanoparticle and nanofiber is illustrated in Fig. 1.3. For the nanofibers, a radial electric field prevents the accumulation of more charge (Fig. 1.3(b&c)) and thus reduces surface recombination which is reflected as higher open circuit voltage^[20]. However, these nanostructures possess low surface area compared to nanoparticles, thus limiting the total number of adsorbed sensitizer molecules. So fibers with internal structures such as fibrils were synthesized, which exhibited higher surface area compared to the nanoparticles^[25]. These nanofibers can be synthesized by a simple, inexpensive yet versatile route called electrospinning. Electrospinning is a simple tool to synthesize 1D nanostructures like nanotubes, nanowires, nanofibers^[26], nanobelts^[27–29]. Since it involves the use of a precursor solution which undergoes sol to gel transformation, the polymer^[30] and metal alkoxides^[31] critically affect the morphology, strength and stability of the fibers. DSCs with fibrous photoanodes TiO₂ fibers electrospun from a precursor solution containing polyvinylpyrrolidone (PVP) exhibit good interconnectivity and are potential candidates as photoanodes but their poor adherence to the substrates after calcination restricts their application. So elaborate surface treatments to improve surface adhesion or fabrication of layers through screenprinting^[32] or spraying^[33] of ground electrospun fibers have been employed. These methods sacrifice interconnectivity due to the breakage of the long nano fibers into small, randomly oriented nano rods thereby negating the effect of long and interconnected nanofibers on the charge transport. This thesis in-

tends to fabricate DSCs whose photoanodes comprise of long and interconnected electrospun TiO_2 nanofibers and to scale down the process steps by eliminating elaborate paste making or spraying steps. This thesis also focuses on synthesizing nanofibers with good adhesion to the substrate and suitable diameters for highly efficient solar cells as smaller diameters have fewer grain interfacial effects while the larger diameter ones have more grains and light scattering effect^[20].

After investigating the charge transport properties of nanofiber based DSC with respect to nanoparticle, the focus of this thesis work is extended to improve the light harvesting efficiency of the nanofibrous DSCs. The growth of secondary nanostructures on the nanofibers is an interesting concept to enhance the surface area for greater dye loading and light scattering^[34–39]. Initial efforts will be directed towards the synthesis of secondary structures of suitable length and morphology and their integration in solid state DSCs. The role of these hierarchical nanostructures in affecting the dye loading and charge transport properties of a DSC will be investigated by impedance spectroscopy measurements. Another interesting and simpler approach is to co-sensitize the nanofibers with more than one organic chromophore. The rationale behind choosing organic chromophores arises from their higher absorption coefficients in comparison to their Ru counterparts^[16]. However as explained earlier they are infamous for their ability to aggregate leading to quenching of excitons^[40]. So the choice of chromophores with complementary absorption spectra, suitable energy alignment and inability to aggregate is vital for achieving panchromatic behavior resulting in improved photon harvesting. The effect of co-sensitization on the I-V parameters of the co-sensitized nanofiber based DSC will be correlated with the charge recombination and transport resistance measured from electrochemical spectroscopic measure-

ments. Final research focus will be channeled in utilizing the high absorption coefficient $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite material to sensitize the nanofibers and thereby enhance the cell performance by increasing the current densities as these perovskites can generate 25.9 mA cm^{-2} of current density ideally. As the perovskite crystal size and coverage is critical in determining the photon-to-electricity conversion efficiency, the knowledge from the initial studies of nanofiber based DSCs will be implemented to tailor the nanofiber morphology, film thickness and porosity to improve the nanofibrous solar cells' efficiencies.

1.2 Objectives and Scope

The objectives of this thesis which are designed to address the challenges which were described in section 1.1 are outlined below as:

1.2.1 Manifestation of 1D, as-spun, long and interconnected TiO_2 nanofibrillar photoanodes in DSCs.

As in mesoporous nanoparticle films the charge percolation is through a disordered, high density inter-particle connections, transport is touted to be trap-assisted diffusion process. In liquid DSCs, this slow charge transport is not a problem as the recombination kinetics with the oxidized species of liquid electrolyte is slower. But with viscous electrolyte or hole transporting materials like cobalt electrolyte and spiro which are related with poor charge diffusion, porous films with efficient charge collection properties are required. In order to improve the diffusion assisted charge transport, 1D nanostructures with field assisted charge

transport which suppresses surface charge recombination leading to better open circuit voltage are preferred. Though electrospun nanofibers were able to improve the charge transport, they were neither defect free nor were they long and well connected. They were mostly rod shaped as these electrospun nanofibers were ground to make a paste resulting in having fibers with smaller lengths. Then these fibrous paste was screenprinted or sprayed on the substrates to function as photoanodes. Our goal is to synthesize long and well connected nanofibers without compromising on the length. This involves employing pre-treatments like dipping the nanofibrous substrates into DMF to improve the adhesion of the film and to understand the limitations of this system in terms of thickness and porosity.

To achieve this, our first objective is to demonstrate electrospun TiO_2 nanofibers directly on the conducting glass substrate, strategize measures to achieve thick and crack free nanofibrous films and to testify that the nanofibers exhibit enhanced open circuit voltages due to their field assisted electron transport.

1.2.2 Investigating the impact of modulated morphology of 1D nanofibers to 3D hierarchical nanostructures on the I-V parameters in DSCs.

The challenge to harvest maximum photons for comparatively thinner nanofibrous films where the thickness is limited by its adhesion to the conducting substrate needs to be addressed. This arises from the fact that when the nanofibers are electrospun directly onto the conducting substrates, they are amorphous in nature and upon annealing to 450-500° C they become highly crystalline. However in this process due to the annealing process step, the nanofibrous film will undergo

shrinkage which increases as the distance between the conducting substrate increases as a result of difference in the thermal coefficient of the substrate and the nanofibrous film. As such their thickness is limited to 6-7 μm whereas the nanoparticle film thickness ranges from 10-15 μm . Consequently the nanofibers suffer from poor light harvesting efficiency. Thus the intention of this thesis is to enhance light harvesting efficiency of these nanofibers by increasing the surface area for greater dye loading.

Hence the second objective is to study the effect of evolution of low surface area 1D nanofibers to high surface area 3D nanostructures by subjecting the nanofibers to solvo thermal treatment with varying reaction times and the translation of the morphological evolution in terms of device parameters.

1.2.3 To study the effect of cosensitization phenomenon on the photovoltaic performance of a nanofiber based DSC.

The complexity in fabrication of hierarchical nanostructures and its translation in DSCs is still a conundrum. The acidic nature of solvo thermal process has a detrimental effect on the cell performance for thicker nanofibrous films by either causing delamination or cracking of the films or by clogging of pores by the new building blocks leading to poor infiltration of viscous electrolytes or hole transporting materials. This leads to low yield of reproducible cells. A simple approach like employing one or more organic sensitizers with high absorption coefficients, energy alignments favoring efficient charge injection and complementary absorption spectra should be considered.

Therefore the third objective of this thesis is to analyze the development in

optical density of the nanofibrous film by the utilization of two organic sensitizers. Initially, the nanofibers are sensitized with a sensitizer having higher absorption coefficient followed by subsequent sensitization with a chromophore which is structurally different from the first one. The competence of this method is assayed in terms of the device performance.

1.2.4 Investigating the applicability of nanofibrous DSCs to emerging novel photovoltaic systems.

The advent of highly efficient $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite material as a sensitizer is attracting a lot of attention due to the high photocurrents attained by it. The incorporation of this material in solid-state cells has enhanced the cell performance as well as the stability of the device. Owing to its very absorption coefficient, this material requires mesoporous films which are just several nm thick. Also as the state of art of these perovskite solar cells is similar to that of conventional DSC, it is sensible to integrate the nanofibers in these cells.

Hence, the objective of this thesis is to couple the thin, defect free nanofibrous photoanodes with $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite as sensitizer and study the effect of this configuration on the advancement in light harvesting efficiency. In order to achieve this, knowledge obtained from the initial work regarding porosity, thickness and dimensions of the nanofibers will be implemented.

1.2.5 Study of charge dynamics in nanofibrous DSCs in liquid and solid state systems.

Investigating charge dynamics in DSCs is critical for understanding the various parameters that determine the cell performance as well as to design highly efficient solar cells. Vast and extensive studies were performed and well defined theories have been established which have been accepted unanimously. Among the various analytical techniques, EIS has been the most prominent technique to derive charge transport and recombination properties. The attractive feature of EIS is that a working cell which is represented with an equivalent circuit can be directly analyzed to relate the charge dynamics with the device performance.

Therefore the final objective of this thesis is to investigate the charge dynamics of the nanofiber based DSC with respect to the nanoparticle in both liquid as well as in solid state configurations to analyze the morphology effect on the charge collection. It is also imperative to examine the charge dynamics for the nanofiber based solar cells in conjunction with various sensitizers, modes of sensitizing and morphologically altered nanostructures.

1.3 Thesis Organization

This thesis has been organized into 6 chapters.

Chapter 2 will focus on the state of art of DSCs, the underlying principles and parameters which determine the efficiency of the solar cell. The popular sensitizing materials used including the recent advances like perovskite materials will also reviewed in this section. The need and shortcomings of the 1D and 3D nanostruc-

tures will also be briefly explained. Electrospinning and the effect of embedded electrospun nanofibers in DSCs will also be included. A brief introduction about electrical characterization by EIS measurements will be given at the end of this chapter.

In Chapter 3, the experimental details encompassing the synthesis and fabrication of nanofiber based DSCs will be explained. It also describes the various electrical and physical characterizations used in this thesis.

The results of this work comprising of physical and electrical characterization will be disclosed in Chapter 4. To facilitate this Chapter 4 is divided into 5 sections. In the first section, sustainability of the electrospun nanofibers in liquid DSCs and comparison of its device parameters with a nanoparticle based DSC will be demonstrated. The second section will present the developments of structurally modified nanofibers leading to hierarchical nanostructured DSCs while the third section will disclose the developments of cosensitizing the nanofibers with two organic chromophores. In the fourth section the consequence of using $\text{CH}_3\text{NH}_3\text{PbI}_3$ as a sensitizer for the nanofiber based solar cells will be exhibited. The final section comprises of the results obtained from EIS measurements for different morphologies and sensitizing materials for nanofibers.

Chapter 5 will comprise of detailed discussion on the morphological evolution of the nanofibers on the solar cell performance including the charge dynamics study. It will also elucidates the impact of various sensitizing materials on the nanofibers' light harvesting efficiency as well as on their charge recombination dynamics.

Chapter 6 which is the final chapter of this thesis will summarize the salient features of this project. The prospect of continuation of further research in the 1D

electrospun nanofiber based DSC/perovskite solar cell will also be advocated.

1.4 Thesis Contributions

The original scientific contributions achieved during this PhD work are enumerated below:

(1) To the best of our knowledge demonstrating the incorporation of as-spun, 1D, long and inter-connected nanofibrous photoanodes in DSCs with minimum process steps would be amongst the first reports. For liquid DSCs with Ru based sensitizers, synthesis and utilization of high surface area nanofibers ($80 \pm 6 \text{ m}^2/\text{g}$) with nanofibrils has been manifested by incorporating high molecular weight polymers like PVP and accessing the nanofibrils by breaking the outer cladding of the nanofiber by hot-pressing technique. The significance of these high surface area nanofibers on dye loading in DSCs has been shown in comparison with the nanoparticle systems.

(2) Two different approaches have been illustrated to improve light harvesting efficiency: (a) transition of 1D nanofibers to 3D hierarchical nanofibers and (b) cosensitizing the nanofibers with 2 organic dyes leading to panchromatic absorption. The effect of solvo thermal reaction time on the morphological evolution of single crystalline nanorods on the nanofiber scaffold for optimal dye loading has also been elucidated. Furthermore, the suppression in charge recombination by these approaches with the oxidized species has been demonstrated and reasoned to be due to the screening of the electrons by the compact layering of the sensitizer molecules arising from the increased surface area in case of the hierar-

chical nanostructures and from the structural differences of the co-sensitized dye molecules.

(3) From impedance spectroscopy measurements it has been illustrated that in both liquid as well as in solid state DSCs, nanofibers have better charge recombination resistance and charge transport in comparison to the nanoparticle film. These two properties have assigned the nanofibers with better charge collection efficiency. In liquid DSCs, this characteristic of the nanofibers is not utilized completely as the collection efficiencies with the nanoparticles are already good owing to the slow recombination kinetics of the liquid electrolyte which is a two step process. However in ssDSCs due to faster recombination kinetics, the better collection efficiency of nanofibers is beneficial.

(4) The dramatic advancement in the light harvesting efficiency (15.88 mA/cm^2) of the nanofiber based solar cells has been demonstrated by employing $\text{CH}_3\text{NH}_3\text{PbI}_3$ as a sensitizer thereby generating a photoelectrochemical conversion efficiency of 9.82 % at 1 sun. The influence of fibrous film porosity and thickness ranging from 0-1215 nm on the infiltration of perovskite material and its resultant contribution on the photon harvest has been highlighted. The nanofibers complement the high charge transport in perovskites with easy processability and easier loading/conversion of the absorber material.

Chapter 2

Literature Review

This chapter provides detailed description about the modus operandi of DSCs, the parameters which determine their efficiency, the plethora of highly efficient sensitizing materials and the various approaches to incorporate more than one sensitizer to improve photon harvesting. It also elucidates the need and incorporation of one dimensional and hierarchical nanostructures and their synthesis routes. A brief introduction about electrochemical impedance spectroscopy and the parameters extracted from its spectra is also included.

2.1 Dye-sensitized solar cells (DSCs) and photovoltaic properties.

Dye-sensitized solar cells (DSCs) are the prototypes of the third generation cells which are based on mesoporous, interpenetrating and nanocrystalline wide band gap semiconductors in conjunction with light absorbing sensitizers. These devices are promising and have several advantages over the solid-state junction devices.

They offer ease of fabrication, lost-cost production, stability over wide range of temperatures and potential application for large scale production^[13,41]. The mechanisms involved in DSCs are shown in Fig. 2.1 and are explained below:

Figure 2.1: Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell^[13].

2.1.1 Principle of operation of DSCs.

1. Light absorption and generation of excitons by sensitizers.

Various sensitizers like panchromatic sensitizers, organic dyes or quantum dots are used to absorb light and generate excitons upon photoexcitation.

Sensitizers should have a broad absorption in the visible region in conjunction with high extinction coefficients for good light harvest-

ing and secondly, anchoring groups like carboxylates or phosphates to attach firmly to the semiconductor oxide (MO) surface via chemisorption which facilitates effective injection of electron into the conduction band of the oxide. They should also have energetically favorable alignment of their HOMO and LUMO levels with respect to the TiO_2 conduction band and redox potential of the electrolyte or hole transporting material (htm).

For minimal energy losses associated with electron injection, the LUMO level of the excited sensitizer should be higher than the conduction band of the oxide as shown in Fig. 2.1. Whereas the HOMO should be lower than the redox potential of the electrolyte or HOMO of the htm to enable regeneration of the oxidized sensitizer. Other important aspects of the sensitizer that can influence the performance of a highly efficient solar cell are the disability to form aggregates which cause quenching of excited states leading to lower current densities, good compatibility with htm molecules for quicker regeneration, good stability in terms of photo, thermal and electrochemical leading to devices with longer lifetimes^[40].

2. Electron transport through nanocrystalline, mesoporous semiconductor film.

Mesoporous and nanocrystalline films are widely accepted as sensitizer support as they provide high surface area for enhanced light har-

vesting by the sensitizer monolayer, have low inherent conductivity which would otherwise quench the excited sensitizer by energy transfer and facilitate better penetration of electrolyte through the pores which screens the charge of injected electrons thereby having no space charge limitation on the photocurrent^[13,42]. Various wide band metal oxides like TiO_2 , ZnO ^[21], SnO_2 ^[43], Nb_2O_5 ^[44] have been studied, but the prototype cell and the best efficiency cell were the ones with the TiO_2 metal oxide nanocrystalline film as the photoanode^[13,42]. Also efforts are being done in employing higher degree of ordered nanostructures as photoanodes like nanotubes, nanowires, etc with the goal of minimizing surface traps and to enhance the effective electron diffusion coefficient. But these nanostructures suffer from low surface area which is critical for dye adsorption. To answer this dilemma, hierarchical 1D nanostructures have been synthesized which meet both high surface area as well directional charge transport with reduced charge recombination criteria with the goal of improving electron diffusion coefficient^[45–47].

3. Regeneration of the dye by redox electrolyte/ hole transporter.

The redox potential of the dye should be sufficiently higher to facilitate dye regeneration via electron donation from the electrolyte (usually iodide/triiodide couple) as given by eq.2.3. Dye regeneration depends on the concentration of iodine and on the viscosity of the electrolyte. If the viscosity of the electrolyte is high then it will cause significant series resistance and accelerate interfacial charge recomb-

nation^[48].

The iodide is regenerated by the reduction of triiodide (eq.2.4) at the counter electrode with the Platinum (Pt) catalyst enabling this reaction with minimum overpotential^[48]. The circuit is completed by the flow of electron by external load as shown in Fig. 2.1. In case of solid state dye sensitized cells, the dye is regenerated by injecting holes to the hole transmitter (p-type semiconductor/organic material) which are transmitted to the external circuit.

2.1.2 Photovoltaic device parameters

Current density-voltage curve is used to extract the photovoltaic parameters of a solar cell. Fig. 2.2 shows a typical current density-voltage curve with the parameters labeled. Power conversion efficiency is determined by the following three factors (a) Short circuit current density (J_{sc}), (b) Open circuit voltage (V_{oc}) and (c) Fill factor (ff).

1. **Short circuit current (J_{sc}):** When the applied external potential is zero, the measured current density is defined as short circuit current density. In a dye-sensitized solar cell, the J_{sc} depends on the optical absorption of the dye (sensitizer) used. The broader the absorption window of the dye, the higher the short circuit current that is achieved.

Figure 2.2: Current density *vs* voltage plot of a typical solar cell with the device parameters labeled.

2. **Open circuit voltage (V_{oc}):** It is defined as the voltage at which the short-circuit current density becomes zero under illumination. The V_{oc} in a dye-sensitized solar cell is set by the difference in the Fermi level of TiO_2 and the redox potential of electrolyte but is determined by the recombination that occurs in the system.
3. **Fill factor (FF):** The ratio between the maximum power point in the J-V plot and the product of J_{sc} and V_{oc} is defined as the fill factor. It is determined by the "squareness" of the solar cell's J-V characteristics. Mathematically it can be expressed as:

$$FF = \frac{\text{Max.powerpoint}}{J_{sc} \times V_{oc}} \quad (2.5)$$

4. **Power conversion efficiency (PCE) :** The ratio between maximum power that can be attained to the power of the incident radiation is defined as power

conversion efficiency. It is given by the following formula:

$$PCE = \frac{Power_{out}}{Power_{in}} = \frac{J_{sc} \times V_{oc} \times FF}{Power_{in}} \quad (2.6)$$

5. Incident photon to current conversion efficiency (IPCE) : The ratio of electrons that are generated per number of photons that are incident under monochromatic conditions is defined as IPCE. It is given by the following equation:

$$IPCE = \frac{J_{sc} \times 1240}{Power_{in} \times \lambda} \quad (2.7)$$

where J_{sc} is the short circuit current density, $Power_{in}$ is the incident power density of the monochromatic light, λ is the wavelength.

2.2 Organic, inorganic sensitizers and cosensitization approaches.

In DSCs one of the most significant component influencing the cell performance is the sensitizer and the sensitizer can be broadly classified as metal free organic donor-acceptor dyes, metal-organic ruthenium complexes and hybrid organic-inorganic perovskites. The most common sensitizers of ruthenium complexes which yielded 7-11 % solar-to-electric conversion efficiencies under AM 1.5 simulated solar irradiation for liquid DSCs are N3, N719, black dye, Z907, C106^[17,49,50] etc. The general structure of some of these dyes is represented in Fig. 2.3. In these dyes, the charge transfer takes place as an electronic transition from the metal to ligand (MLCT) and the carboxylate groups which are attached to the bipyridyl groups fa-

Figure 2.3: Molecular structures of commonly used Ru based sensitizers.

cilitate the electron injection into the conduction band of the semiconductor^[51,52]. Assigning donor-acceptor moieties to the bipyridine ligand of Ru sensitizers improves the extinction coefficient as well as the wettability at the sensitizer and htm interface^[40]. By enhancing the extinction coefficient of the dyes, the thickness of the mesoporous film can be drastically reduced which effects in lowering the charge transport and recombination losses. Another interesting feature of dyes such as Z907 and C106 is that they have hydrophobic alkyl chains which act as passivating layers disabling the recombination of the photo-injected electrons of TiO_2 conduction band with the oxidized species of electrolyte or holes of htm^[40]. They also reduce the water induced desorption of the dye molecules and therefore improve the stability of the solar cells. In spite of the high efficiencies and high stability, these Ru based sensitizers are highly expensive, involve careful synthesis procedures and have moderate extinction coefficients. In order to satisfy the optical cross-section, the TiO_2 films need to be very thick. Such thick films pose a problem in solid-state cells as the infiltration of spiro through these compact and thick films is incomplete which leads to low conversion efficiencies.

This paves way for the inexpensive, metal free, environment friendly organic dyes whose absorption and electrochemical properties can be tailored by the design of the molecule^[51]. These dyes have been reported to have higher absorption coefficients than the Ru based dyes which makes them a potential candidate for the thin film DSCs^[16]. But they suffer from narrow optical absorption in red light or near IR region of the spectrum, aggregation and unsuitable position of LUMO (lowest unoccupied molecular orbital) level^[42] and the various means to address these drawbacks are explained in the following writeup. There are a plethora of organic sensitizers and their classification and structural details are discussed in great detail in literature reviews^[51,52]. Some of the common ones are squaraines (SQ01, SQ02)^[53,54], triphenylamines (D35)^[55], indolines (D149)^[56] etc. A comprehensive view of the molecular structures of these popular dyes is given in Fig. 2.4. The

Figure 2.4: Molecular structures of some of the metal-free organic sensitizers. (a) squaraines (SQ01, SQ02)^[54], (b) triphenylamines (D35)^[55] and (c) indolines (D149)^[56].

squaraine dyes generally comprise of electron poor four membered core with 2 electron rich donors. This structure of the squaraines imparts them strong absorption in the red region of the solar spectrum^[54]. By designing suitable donors, their

absorption can be extended into the infra-red region as well. However there two main aspects of these sensitizers which needs to be considered. Firstly, differences between the symmetrical (VG1C8) and the unsymmetrical (SQ01) squaraines and secondly the problem of aggregation associated with these dyes^[40]. For symmetrical squaraines, the two donor groups are identical with two anchoring groups whereas for the unsymmetrical ones, there is only one anchoring group and the two donors are different from each other. The unsymmetrical ones have been reported to exhibit superior properties owing to their anisotropic nature where the directional flow of electrons from the donor to the anchoring groups enables better injection of electrons into the semiconductor^[40]. Secondly, the aggregation caused by the orientation of these molecules is also significant in affecting the current densities of a solar cell. When the molecules orient plane to plane with each other, they form H-aggregates which is reflected as blue shift in absorption spectra while they orient head to tail with each other they form red-shifted J-aggregates^[40]. However these type of behavior can be suppressed by using co-adsorbents like chenodeoxycholic acid (cheno, CDCA)^[57]. While it suppressed dye aggregation, it had no effect on the photocurrent but interestingly improved the open circuit voltage of the cell thereby enhancing the overall performance. Another interesting class of dyes which took the DSC world by a storm is the indoline class of sensitizers with D149 yielding 8 % efficiency in conjunction with cheno. D149 dye as seen in Fig.2.4(c), has HOMO delocalized over indoline group whereas the LUMO is delocalized across the rhodanine groups. As a result of the separation of HOMO and LUMO in the compound, the HOMO-LUMO transition is considered to be an intramolecular charge-transfer (ICT) transition^[58]. As more and more research shifted to solid state DSCs, one particular dye gained

a lot of attention by achieving 4.5 % efficiency. This chromophore is named D35 which belongs to the triphenylamine class of organic sensitizers. This dye was designed by Anders Hagfeldt and his co-workers and its structure as shown in Fig. 2.4(b) comprised of triphenyl amine donor group with additional phenyl groups functionalized with p-butoxy moieties^[55]. This unique structure imparts it with steric hindrance to charge recombination resulting in high open circuit voltages. This steric hindrance is attributed to its bulky butoxy chains which eliminates the need for co-adsorbents.

Figure 2.5: Schematic showing co-sensitization and FRET^[40].

Since there are always some drawbacks associated with the synthesis of organic dyes, some innovative approaches to combine the best features of two or more sensitizers and to achieve panchromatic behavior is to employ co-sensitization or Frster resonance energy transfer (FRET). Cosensitization of two or more dyes with complementary absorption spectra and matched energy levels can be done either in a cocktail approach^[59] or in a sequential approach^[17]. In the cocktail approach 2 or 3 dyes will be dissolved in a common solvent and the TiO_2 film will be immersed in the solution for some time till all the three types of dye molecules are adsorbed on to the semiconductor surface. Whereas in a sequential approach,

the mesoporous TiO_2 film will be sensitized first with one dye in immersing it the dye solution and then it will be rinsed to remove unattached dye molecules and then will be immersed in the second dye solution. In the cocktail approach there is a competition between the dye molecules for adsorption on TiO_2 surface whereas in the sequential approach the second dye molecules are forced to occupy those places which are not occupied by the first dye molecules. This approach enables compact packing of all the dye molecules thereby reducing charge recombination which is reflected in the enhanced V_{oc} . For panchromatic behavior, it is common practice to use porphyrins, indolines or phthalocyanines whose absorption is in blue region of visible light in conjunction with squaraines^[40]. In most of the cases, cosensitization approach yields higher efficiency as a result of improved V_{oc} and J_{sc} in comparison to the individual dyes. However it has also been reported that sometimes due to dye aggregations leading to quenching of excited states the overall cell performance may depreciate^[40]. Also when cosensitizing with near infra red dyes, the V_{oc} of the cell was reported to decrease as a result of their small band gaps^[60]. One drawback of cosensitization is that for the anchoring of so many dye molecules, high surface area of the semiconductor film is required. In FRET, the energy relaying dyes (ERD) are placed either inside the electrolyte, inside the semiconductor or attached to the already anchored sensitizers. This approach overcomes the need for high surface area as was required in cosensitization. These ERDs absorb sunlight and transfer energy to the anchored sensitizers non-radiatively and so they need not satisfy the energy alignment condition. The energy transfer occurs through FRET which comprises of dipole to dipole coupling between the sensitizer and the ERDs. An important factor while designing ERDs is that their photoluminescent lifetime should be short to prevent

quenching of charge by the electrolyte/htm. In spite of their very high excitation transfer energies, the only challenge to be addressed is the solubility of all the ERDs in the electrolyte^[60].

Figure 2.6: (a) Perovskite structure^[61] and (b) schematic illustrating the energy levels of TiO₂, CH₃NH₃PbI₃ and spiro-OMeTAD^[19].

Recently a new class of perovskite materials have emerged as the most suitable candidates for high efficiency solid state cells. Perovskite is the name given to the compounds with the chemical formula ABX₃ as shown in Fig. 2.6(a). It consists of cubic unit cell, with the A-cation occupying the 8 corners of the cube, while B cation occupying the body center and the X anion occupying the face center. Examples of typical inorganic perovskites are BaTiO₃ and CaTiO₃. Among the different classes of perovskites, the organic-inorganic hybrid perovskites are the most fascinating to study due to their interesting optical and electrical properties. For example, CH₃NH₃PbI₃ is a 3-D perovskite with an optical bandgap of 1.55 eV (Fig. 2.6(b)). It has been shown that the minimal electron and hole diffusion lengths are in the order of 100 nm^[62]. With the optical bandgap of 1.55 eV, a maximum photocurrent of 25.9 mAcm⁻² can be achieved assuming all the photons are converted to electrons. Optical bandgap can also be tuned by substituting the iodine anion with bromine or by substituting methyl ammonium cation with forma-

dinium cation. First reports on using $\text{CH}_3\text{NH}_3\text{PbI}_3$ as sensitizer was demonstrated by Miyasaka and coworkers in 2009^[18]. In this configuration, liquid iodine/iodide electrolyte was used as redox couple, but the problem was the dissolution of perovskite in the electrolyte. Later on, in 2012 a breakthrough in efficiency and stability of perovskite was obtained by the group of N.G. Park and M. Grätzel who obtained an efficiency of 9.7 % with the following photovoltaic parameters : $J_{sc} = 17.6 \text{ mAcm}^{-2}$, $V_{oc} = 0.888 \text{ V}$ and $\text{FF} = 0.62$ ^[19]. This opened an avenue for further explorations of this ambipolar $\text{CH}_3\text{NH}_3\text{PbI}_3$ in terms of its usage as only hole transporting material, as both sensitizer as well as hole transporting material, with different scaffolds (Al_2O_3 ^[61], TiO_2 particles, TiO_2 nanofibers^[63], ZnO nanorods^[64]) as well as without any scaffold^[65]. With this material, the solid state efficiencies soared to 17.9 % (as shown in Fig. 1.2) which is remarkable and the performance of these cells is highly dependent on the quality of the perovskite crystals. So different approaches to deposit $\text{CH}_3\text{NH}_3\text{PbI}_3$ have been employed which yield cells with high reproducibility. There are two main approaches for depositing $\text{CH}_3\text{NH}_3\text{PbI}_3$. The first approach is to mix all the precursors in a single pot either in solution^[19] form or by vapour^[65] and deposit it on the photoanode while in the second approach lead iodide solution in di-methyl formamide is spin-coated on the photoanode and upon drying it is reacted with methyl ammonium iodide solution in isopropanol either by immersing^[66] or by dropcasting the solution on the lead iodide coated substrate^[67]. Much attention is being directed in understanding the kinetics of charge transfer and recombination in these materials as well as in finding lead free perovskite alternatives for a safer environment. However most of the lead free perovskites are unstable and conscientious efforts must be made to improve the device stability.

2.3 Role of one dimensional and 3D nanostructures as photoanodes in photoelectrochemical solar cells.

Since the mesoporous semiconductor film plays a vital role in providing sufficient surface area for the adsorption of dye molecules resulting in efficient light harvesting and in charge collection, it is vital to consider the beneficial morphologies of the semiconductor material. In conventional liquid DSCs, mesoporous nanoparticle films are used which are about 10 μm and it is widely reported that for such films the electron transport is greatly affected as the electron may get trapped at the surface or defect states^[68]. However in spite of the slow trap-mediated diffusion, the charge collection is faster than the recombination due to the slower multi-electron kinetics of I_3 reduction on semiconductor surfaces^[21]. However in order to improve the light harvesting efficiency of the solar cells, either one should design dyes with absorption at longer wavelengths or increase the optical density by scaling up the film thickness. This would pose a problem for charge collection and calls for the use of single crystalline nanowires. These 1 dimensional (1D) nanowires have better charge collection characteristics than the mesoporous nanoparticle films. Additionally they have an internal electric field which cause band bending at the nanowire surface that enables the confining of the electrons within the core thereby reducing charge recombination^[21]. Hereof, various research groups focused their efforts in synthesizing 1D nanostructures by electrospinning, aqueous seed-growth, hydrothermal treatments etc^[21,25,68]. Though these 1D nanostructures have several advantages over the nanoparticle films, they fail to fully harvest light as they suffer from low surface area required for the adsorption of dyes. In order to address this problem, one of the several approaches

is to transform the 1D nanostructures to three dimensional (3D) nanostructures. This approach not only addresses the surface area criterion required for good photon harvesting but it also enables light scattering which is otherwise achieved in nanoparticle system by the usage of a scattering layer. Most of the hierarchical nanostructures were synthesized by means of solvothermal treatment^[34–39] and they showed remarkable improvement in the overall cell performance as a result of improved current densities.

2.4 Electrospinning

Electrospinning is a very old technique which attracted scientific interest in recent years due to its capability of producing continuous 1D nanostructures from micrometer to nano meter range using a plethora of materials. By electrospinning, 1D nanostructures such as nanobelts, mesoporous nanofibers, nanotubes etc can be synthesized. Fig. 2.7 shows the various 1D nanostructures synthesized by electrospinning. The principle involved in electrospinning is the stretching of the

Figure 2.7: Various 1D nanostructures synthesized by electrospinning. SEM images of (a) electrospun porous poly-L-lactide fibers^[69], (b) porous anatase nanobelts^[69] and (c) anatase nanotubes^[29].

viscoelastic solution by electrostatic forces. Electrospinning setup involves injection of a viscoelastic solution from a plastic syringe with a flat tip metallic needle

which acts as an electrode, a grounded conducting collector/counter-electrode and a high voltage supply. When voltage is applied, the liquid droplet at the end of the needle tip will experience electrostatic forces in addition to surface tension and gravity. Surface tension tries to minimize surface area by pulling the liquid in whereas the gravity and electrostatic forces tend to stretch the liquid down. The charges tend to repel each other thereby increasing the distance between them leading to stretching of the solution. When the electrostatic forces overcome the surface tension of the droplet, a Taylor cone is formed and a thin jet is ejected. As the jet travels towards the collector, it could undergo three types of instabilities - (a) Rayleigh instability, (b) axis-symmetric instability and (c) non-axis-symmetric instability. Rayleigh instability occurs when the surface tension becomes prominent leading to formation of droplets. This can be solved by using strong electric field where the surface tension is subdued by the electrostatic forces. Also the high surface charge density facilitates non-axisymmetric instability which causes bending and thinning of the jet (of our importance). Axis-symmetric instability causes varicose structures^[27] which are not desirable but this is eliminated in the presence of high electric fields. The flow rate of the polymer from the syringe is also critical as it determines the mass of material flowing. On increasing the feed rate, fibers with big diameters and sometimes beads/droplets are produced. In addition to the extrinsic properties like high voltage and flow rate, intrinsic parameters like rheology of the solution, type of polymers used also play an important role in determining the final morphology and diameter of the fibers. If the solution is not viscous enough then fibers can not be spun and droplets/beads are formed on the collector. Viscosity of the solution can be increased by addition of polymers to the precursor solution. Depending upon the rheology of the solution, the diameter

Figure 2.8: Effect of solution rheology on fiber morphology and diameter. SEM images of poly-vinyl-pyrrolidone (PVP) fibers in water and ethanol mixture. (a) Low concentration of polymer gave rise to beads and (b) upon increased concentration beadless fibers were obtained^[69].

of the fibers can be varied. So by increasing the viscosity of the solution, thinner fibers can be obtained but upon reaching a threshold value, the solution becomes too viscous to be spun. So monitoring the viscosity of the solution is very important to meet specific requirements. In Fig. 2.8(a) beads were observed due to the Rayleigh instability becoming prominent whereas in Fig. 2.8(b), by increasing the polymer concentration in the solution the Rayleigh instability was dismissed and smooth fibers were produced. Role of solvents, humidity, temperature etc also have a major role in defining the morphology of the electrospun fibers. Solvents with high rate of evaporation block electrospinning due to the formation of a tiny layer of gel. Whereas when solvents with very low rate of evaporation are used, then formation of flat ribbons or thin film is favored over smooth cylindrical nanofibers^[30]. Solvents with optimal evaporation rate facilitate bonding between the intersecting fibers due to the presence of residual solvent in between the fibers. Also the pores in the fibers are influenced by the solvent because during electrospinning, phase separation occurs and the solvent rich domains form pores upon

solvent extraction. Since solvent evaporation depends on vapor pressure^[30] and according to Clausius-Clapeyron eq which is given as:

$$\frac{d(\ln p)}{dT} = \frac{M\Lambda}{RT^2} \quad (2.8)$$

where p is the vapor pressure, T is the temperature, M is the solvent molecular weight, Λ is heat of vaporisation and R is universal gas constant; the vapor pressure of the spinning area is affected by ambient humidity and temperature. With humidity as high as 60 % fibers do not dry and form entanglements^[26]. Also the drying of the fibers is influenced by the distance between the collector and needle tip. There should be sufficient distance for the jet to travel and to solidify as it reaches the collector. Very short distances do not provide sufficient time for the fibers to solidify and thus result in beaded or wet fibers or flat ribbons. Electrospinning also facilitates collection of fibers in various configura-

Figure 2.9: Fiber alignment depending on the mode of collection. SEM image of (a) uniaxially arranged nanofibers obtained by introducing insulating gap between collectors^[69] and (b) randomly oriented non-woven fibers obtained on a stationary plate collector^[69].

tions. Aligned (Fig. 2.9(a)) or randomly (Fig. 2.9(b)) oriented fibers are possible by manipulating the electric field which is achieved by modulating the shape of

the collector. Instead of using a stationary table to collect the fibers, if a drum or disc is used which rotates at a very high speed, the air flow generated by the rotating drum assists in aligning the fibers in the direction of wind. High speed rotating disc proved to yield higher degree of aligned fibers than the high speed rotating drum due to strong electric field at the edge of the disc. Similarly many setups have been designed to collect fibers with different orientations^[70]. Thus to acquire 1D structures of specific morphology, it is very important to fine tune both intrinsic as well as extrinsic parameters.

2.4.1 Electrospun photoanodes in DSCs

Figure 2.10: High efficiency DSCs using electrospun TiO_2 nanofibrillar structures^[25].

Ever since, highly efficient (11 %)^[25] dye sensitized solar cells were fabricated by electrospinning Ti-n-propoxide along with poly vinyl acetate (PVAc) on FTO substrates to form TiO_2 nanofibers with high surface area (Fig. 2.10), many research groups realized the versatility and simplicity of this field and various experiments are being done to further improve the performance of the cells. As seen in Fig. 2.10, small nanorods on each nanofiber called nanofibrils were formed as

a consequence of phase separation between the high molecular weight polymer rich and inorganic rich phases during electrospinning. These nanofibrils exhibited high surface area ($123 \text{ m}^2/\text{g}$) which facilitated in more dye adsorption yielding current density of $21 \text{ mA}/\text{cm}^2$ which contributed to the high conversion efficiency. The porous structures, high surface areas (by surface treatments) and high directionality of charge transport with minimized charge recombination as compared to the randomly arranged nanoparticles made the electrospun nanofibers potential candidates for photoanodes in DSCs.

2.5 Electrochemical impedance spectroscopy (EIS)

In order to design new materials it is important to comprehend the relation between the material properties and the cell performance. Electrochemical impedance spectroscopy (EIS) is an effective tool to characterize and understand the kinetic processes of DSCs. The advantage of using EIS over intensity modulated photocurrent spectroscopy (IMPS)/ intensity modulated photovoltage spectroscopy (IMVS) is that all the parameters, like chemical capacitance (C_μ), steady state charge transport resistance (R_t), transient diffusion coefficient (D_n) and charge transfer resistance (R_{ct}), can be measured at one time^[71]. For a real working DSC, electron transport/transfer in the mesoporous, nanocrystalline TiO_2 film/at counter electrode, charge recombination at the TiO_2 /electrolyte interface and diffusion of redox species in electrolyte can be investigated from the shape of the impedance spectra. These electronic species are described by a transmission line model which is shown in Fig. 2.11.

The resistances represent the hindrance to charge transport in the materials

Figure 2.11: Equivalent circuit impedance model of DSC^[72]. R_s is ohmic series resistance of the cell, R_{ce} and C_{ce} are the charge transfer resistance and capacitance, total transport resistance of the film is $R_t = r_t L$ with L being thickness of the film, total capacitance of the film is $C_\mu = c_\mu L$, R_{co} and C_{co} are the contact resistance and capacitance at TiO_2/FTO interface, R_{su} and C_{su} are charge transfer resistance and capacitance at electrolyte/FTO interface and Z_D is the mass transport impedance at Pt electrode^[72].

(charge transport in TiO_2 and redox species in electrolyte in the pores) and charge transfer (related to interaction between electrons and I_3^- ions) across the interfaces ($\text{TiO}_2/\text{electrolyte}$) whereas the capacitances represent the accumulation of charge^[72]. Bias potential (V) relates to the electrochemical potential (E_{Fn}) of electrons^[71]. Since photon to electron conversion efficiency is given by^[73] η (%) = $(V_{oc} \times J_{sc} \times FF \times 100) / I$, where V_{oc} is the open circuit voltage, J_{sc} is the short circuit current density, I is the incident light intensity and FF is the fill factor which is the maximum power delivered to external load; it is important to relate the cell performance to the impedance parameters. V_{oc} is defined as the difference between the fermi level of electrons in TiO_2 (in light) and the redox potential. So it is influenced by effective injection of electron and reduced recombination (large R_{ct}) between the injected electrons and I_3^- ions of the electrolyte. This is expressed in terms of electron lifetime (τ_n) which is given by ($\tau_n = R_{ct} C_\mu$) and for high performance cells $\tau_n > 100$ ms at high bias potential was observed^[71]. J_{sc} is determined by the charge transport property, recombination resistance and charge injection from the dye. Diffusion length (L_n) of charge in TiO_2 film is a good in-

indicator for charge collection/extraction^[71] which is calculated from the measured EIS parameters as $L_n = L \sqrt{\frac{R_{ct}}{R_t}}$. Thus impedance measurements can be effective in understanding the performance of the cell and offers scope for improvement.

Chapter 3

Experimental section

This chapter has been classified into three segments. In the first segment synthesis of one dimensional nanofibers by electrospinning is discussed. Also metamorphosis of one dimensional nanofibers to three dimensional nanostructures has been elucidated. The second segment focuses on the physical and optical characterization of these nanostructures. The third segment of this chapter encompasses electrical characterization of dye-sensitized solar cells based on 1D nanofibers and 3D nanostructures photoanodes.

3.1 Synthesis of 1D and 3D TiO₂ nanostructures

3.1.1 Electrospinning of sol-gel precursor sol

Titanium (IV) butoxide (4 g, 97%, ALDRICH), polyvinylpyrrolidone (PVP, 0.8 g, Mw = 1300000, ALDRICH), acetylacetone (1.75 g, ≥99%, SIGMA ALDRICH) were stirred together for 12 h in methanol solvent to make the sol-gel precursor solution. All chemicals were used as received. Fluorine-doped tin oxide (FTO,

<14 ohm/square, 2.2 mm thick, Pilkington) substrates were used for the photo-electrodes as well as for the counter electrodes. Cleaning of the substrates as well as immersing the substrates in TiCl_4 solution was done as reported in literature^[71,74,75]. The sol-gel precursor solution taken in a syringe was injected in the presence of electric field onto the FTO substrates. Fig. 3.1 illustrates the electrospinning setup and the collection of nanofibers directly on the substrate. The electrospinning was done using a commercial setup (NANON, MECC). Voltage of 25 kV and feedrate of 0.3 mL/h was used to obtain a composite mat of randomly oriented nanofibers on the FTO substrates. They were calcined at 450° C for 3 hr at a rate of 2.5° C/min in air to acquire the desired phase.

Figure 3.1: Schematic diagram of electrospinning on FTO.

Effect of rheology of precursor solution

Different rheologies of precursor solutions were investigated by varying the polymer or metal oxide precursors concentration. The ratio in which the Ti:PVP were varied are 4:1, 5:1, 5:2, 5:3, 6:1, 10:1.

Effect of hot-pressing and DMF treatment to the mat of nanofibers

The effect of pressing the composite mat of nanofibers between two metallic plates of STAHL'S Hotronix (STX6) and Teflon sheet on the adhesion of the fibrous film was investigated. The fibrous films were pressed at 125° C for about 10 min. The effect of treating these hot-pressed nanofibrous films with dimethylformamide (DMF, ALDRICH, 99.9%) for 5 s was also studied.

3.1.2 Solvo thermal treatment to electrospun nanofibers

In order to synthesize three dimensional nanofibers which are referred to as hierarchical (HNF), the substrates with the electrospun TiO₂ nanofibers were subjected to solvo thermal treatment. In the solvo thermal treatment, the substrates were immersed in a solution comprising of 20 mL HCl, 20 mL de-ionized (DI) water and a known amount of titanium isopropoxide (Aldrich). This reaction was carried out in a Teflon-lined autoclave.

Effect of reaction time

The Teflon-lined autoclave containing the FTO with nanofibrous film and the precursor solution for hierarchical nanostructures, was sealed and put in to a pre-heated oven at 150° C for different reaction times of 0.5, 1, 2 and 3 h respectively.

3.2 Physical and optical characterization

3.2.1 X-ray diffraction (XRD)

Phase and crystallite size investigation of as-spun electrospun as well as calcined TiO₂ nanofibers and the hierarchical nanostructures grown on the surface of the nanofibers were characterized by X-ray Diffraction (XRD) Bruker D8 Advance. Scans were made from 20-70 using Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$) with grazing incident configuration ($\theta = 1^\circ$, step size = 0.05° and dwell time = 4s) at room temperature.

3.2.2 Field emission electron microscopy (FESEM)

The surface morphology of the as-spun, calcined, hot-pressed, DMF treated nanofibers and hierarchical nanostructures at different reaction times was characterized by FESEM (JEOL, JSM-7600 F, 5 kV). The working distance for imaging was varied between 7-10 mm. For cross-section imaging, freshly cut samples were used. Cutting of the substrates was done by using a diamond scribe. In all the cases, the samples were sputtered with platinum before they were imaged.

3.2.3 Transmission electron microscope (TEM)

Selected area electron diffraction (SAED) and high resolution transmission electron micrographs (HRTEM) were obtained to analyze the crystal morphology, phase and crystallinity using JEOL 2100F operating at 200 keV. Powder samples for TEM were dispersed in ethanol before dropping onto holey-carbon copper grid.

3.2.4 Surface profiler

The thickness of the nanostructured films were measured by a surface profiler (Alpha step IQ) using a step height analysis. The scanning details are as follows: scan length 2000 μm , scan speed 100 $\mu\text{m/s}$, sampling rate 50Hz and sensor range 550 $\mu\text{m}/33\text{ pm}$. The stylus force was manually adjusted to 5-6 mg for scanning of the materials.

3.2.5 Thermo gravimetric analysis (TGA)

The as-spun fibers were characterized by thermogravimetric analysis (TGA, TGA-2950, TA Instruments, USA) to evaluate the decomposition temperature of the composite. The analysis was done in nitrogen gas with a heating rate of 10° C/min upto 700° C.

3.2.6 Brunauer-Emmett-Teller (BET) Surface Area Analysis

BET surface area analysis of the hot-pressed, calcined fibers was done by NOVA 3200e (QUANTACHROME INSTRUMENTS). The powder for BET analysis was acquired by scraping the nanostructures from the substrates.

3.2.7 UV-vis absorption spectroscopy (UV-vis)

The absorption spectra of the nanostructured films on FTO were recorded in the wavelength range of 300-800 nm using UV-Vis-Nir Spectrophotometer (UV3600, Shimadzu) with 282 nm wavelength light source, in absorbion mode. For dye loading experiments, the dye molecules which were anchored to the nanostructured films were desorbed by using TMAH (0.1 M, Sigma Aldrich) solution and

the resultant solutions were inspected via the spectrophotometer. The measurement details are as follows: data interval 1 nm, scan range (300-800 nm), integration time 0.44 s, scan speed 125 nm/min and slit width 1 nm.

3.3 Electrical characterization

The electrical properties of the nanofibrous photoanodes are characterized by incorporating these photoanodes in dye-sensitized solar cells and measuring their I-V characteristics, charge transport resistance, charge recombination resistances and charge diffusion lengths. In case of liquid DSCs, an area of 0.2826 cm² of the TiO₂ nanofibers mat was retained on each FTO to serve as the active layer of the photo anode. This was then immersed in 0.1 M TiCl₄ solution at 40° C for 24 h followed by rinsing with deionized water and ethanol. The FTO substrates were heated at 500° C for 30 min using a hot blower (LEISTER) and on cooling; the samples were dipped in dye solutions for 24 h in case of liquid and for 4 h in case of solid state DSCs. The dyes utilized were N719 (0.3 mM), D102 (0.5 mM)^[16] and D358 (0.5 mM^[16]) respectively. The dye (N719 and D102) solutions were prepared in a solution of acetonitrile (MERCK) and tertiary butanol (SIGMA ALDRICH) by volume 1:1. For D358 dye solution, 0.1 M Cheno (Sigma) was also included. In case of perovskite solar cells, 1M PbI₂ in DMF solution was spincoated on the nanofibrous photoanodes at 6000 rpm for 30 s. Then the films were dried at 70° C for 30 min. Then these substrates were immersed in methyl ammonium iodide solution (8 mg/mL in IPA). Then the perovskite loaded TiO₂ substrates were dried at 70° C for 30 min. Prior to drying at 70° C, the substrates were rinsed with IPA and spincoated at 4000rpm for 30s. In case of

liquid DSCs, cleaned and Pt deposited FTO substrates were used as counter electrodes. The two electrodes were assembled together as given in literature^[71,74,75] and Fig. 3.2 is the schematic diagram of an assembled liquid DSC. The liquid electrolyte used was Solaronix AN 50 (iodine/iodide redox couple). Whereas in case of solid-state DSCs and perovskite solar cells, an organic hole conductor namely spiro-OMeTAD (2, 2', 7, 7'-tetrakis-(N, N-di-p-methoxyphenylaminated) 9, 9'-spirobifluorene) was dissolved in chlorobenzene and spincoated on these substrates. This composition has been referred to as HTM through out this thesis. Additives like Li (CF₃SO₂)₂ N, tert.-butylpyridine and FK102 dopant were added to the above solution^[76]. The counter electrode was formed by depositing gold via shadow masking by using a thermal evaporator. The gold electrode thickness was about 80 nm and an active area was defined by the overlap of TiO₂ and Au measuring at 0.64 cm² (solid-state DSC) and 0.2 cm² (perovskite solar cell). For comparing the characteristic properties of nanofibers with that of nanoparticles, photoanodes with mesoporous P25 nanoparticles were prepared by screen printing the P25 paste to achieve a film thickness which is comparable to that of the nanofibrous film. The nanoparticle film was prepared as given in literature^[71,74,75]. In case of hierarchical photoanodes, after the growth of hierarchical nanostructures on the electrospun nanofibers, an active area of 0.2 cm² was retained on each substrate and the films were treated with 0.1 M TiCl₄ solution at 40° C for 24 h. They were then incorporated into the device as described above.

Figure 3.2: Schematic diagrams of liquid and solid state DSCs based on nanofiber photoanodes.

3.3.1 Photovoltaic measurements

The photovoltaic characteristics of the solar cells so formed were tested using a simulated solar light (San-EI Electric, XEC-301S, AM 1.5, 100 mWcm^{-2}). The current-voltage data under these conditions was obtained using Keithley model 2612A source meter. Different light intensities were obtained by using UV Fused Silica Metallic Neutral Density Filters (Newport Corporation) filters.

3.3.2 Incident photon to charge carrier efficiency (IPCE) measurements

IPCE measurements were performed using PVE300 (Bentham), with dual Xenon / quartz halogen light source, measured in DC mode with no bias light. Incident light intensity was calibrated using a photodiode detector (silicon calibrated detector, Newport). All the measurements were performed in air.

3.3.3 Electrochemical impedance spectroscopy (EIS)

To determine the charge transport properties, electrochemical impedance spectroscopy studies were made under illumination using an automated potentiostat (AutoLab PGSTAT302N). A 10 mV ac signal and frequency ranging from 100

KHz-0.1 Hz were used. The cells were subjected to different bias potentials ranging from 0 V to open-circuit voltage.

Chapter 4

Results and Discussion

In this chapter, the various aspects of the nanofibers will be elucidated in 5 sections. The first section encompasses the synthesis of nanofibers by electrospinning, the various parameters affecting the synthesis, the integration of the nanofibers as photoanodes in solar cells and the factors hindering high performance of the nanofiber based solar cell. In the second section the problem of low surface area of the 1D nanofibers is addressed by altering its morphology to 3D hierarchical nanostructures and the impact of this morphology on the cell performance is explained. Another approach to improve the light harvesting efficiency of the as spun nanofibers without altering its morphology is by sensitizing the nanofibers with two dyes having complementary absorption profiles and the effect of this co-sensitization on cell performance has been elucidated in the third section. The fourth section comprises of achieving high efficiency nanofiber based solar cells by sensitizing the nanofibers with a hybrid organic-inorganic perovskite in solid state cells. The charge transport, charge recombination and charge collection characteristics of the nanofibers is studied in the last section. The study was done with

respect to that of the nanoparticle system as well as with the various configurations of nanofiber based solar cells.

4.1 Incorporation of as-spun TiO₂ nanofibers in liquid DSCs

This chapter has been classified into three segments. In the first segment synthesis of one dimensional nanofibers by electrospinning is discussed. Also metamorphosis of one dimensional nanofibers to three dimensional nanostructures has been elucidated. The second segment focuses on the physical and optical characterization of these nanostructures. The third segment of this chapter encompasses electrical characterization of dye-sensitized solar cells based on 1D nanofibers and 3D nanostructures photoanodes. In this section, synthesis of nanofibers via electrospinning and the incorporation of these nanofibers, which are directly electrospun on FTO substrates, as photoanodes in dye-sensitized solar cells has been illustrated. In the consequent subsections, the formation of high surface area nanofibrils, their physical and optical characterization, effect of hot-pressing and DMF treatment and their effect as photoanodes on solar cell performance has been elucidated. The last subsection summarizes the results of this section.

4.1.1 Synthesis of nano-fibers

Electrospinning TiO₂ nanofibers is via sol-gel route in which metal alkoxides used undergo hydrolysis and condensation reactions^[27] to form a colloid. Titanium butoxide undergoes hydrolysis and condensation reactions in the following manner:

Since transition metal alkoxides are highly reactive with water, they are stabilized by complexing agents like acetyl acetone. Acetyl acetone controls the hydrolysis rate of the alkoxide without formation of colloidal particles^[77,78]. In electrospinning the rate of evaporation of the solvent is very critical^[26,28,30] in affecting the microstructure of the final product. If faster is the evaporation of the solvent then greater is the reduction in jet diameter resulting in thinner fibers, which is the aim of this work. So methanol with optimal volatility (for residual solvent to permit bonding between intersecting fibers) has been used in the synthesis of TiO₂ nanostructures via sol gel route. Polymer acts like a binder and facilitates spinning by controlling the viscosity of the solution and thereby controls the morphology of the fibers. When a thin jet was spun, the metal alkoxides hydrolyze by reacting with atmosphere moisture to form a continuous gel network with the polymer matrix^[69,79]. The fast evaporation of the solvent leads to cooling of the jet resulting in phase separation of organic and inorganic phases^[69,79]. High voltage of 25 kV and small feed rate of 0.3 ml/h were chosen in order to achieve fibers as thin as possible. As reported^[26] high voltage induces higher mass flow from the tip of the needle and thus faster deposition rates leading to thin diameter fibers. As feed rate controls the jet velocity and material transfer rate, low feed rates are preferred to obtain thin fibers^[26]. Low voltage and feed rates of higher magnitude resulted in fibers with larger diameters.

4.1.2 Nanofibril formation

The nanofibers are neither hollow nor solid. Each nanofiber is composed of nanofibrils which were present under the smooth cladding of the fiber and these were exposed on disintegrating the cladding by applying high pressure at 125 °C. Under insufficient load the cladding/ sheath of the fiber does not rupture and the nanofibrils will not be exposed. The good miscibility between TiO₂ and PVP allows slow segregation between the 2 phases during solvent evaporation and are elongated in the liquid phase^[80]. On reaction with atmosphere moisture, the surface of the fiber transforms into gel and solidifies faster than the core and thus forms a sheath. Inside the fiber slow phase separation and solidification takes place resulting in a bundle of fibrils. The diameter of these fibrils varied from 16-20 nm which is comparable to the size of nanoparticles used in conventional high efficiency DSCs. These fibrils are much thinner than the fiber, oriented along the axis of the fiber, retained the porous structure of the web and increased the surface area and roughness of the whole mat of fibers.

4.1.3 Effect of hot-pressing and DMF treatment to nano-fiber film

The as-spun nanofibers suffer from delamination from the substrates after calcination as all the organic binders are removed during this process. This leads to shrinkage of the nanofibers which creates gaps in between the nanofibers resulting in delamination and poor interface contacts between each nanofiber as well as between the nanofiber and the substrate. In order to address this issue, the substrates with the nanofibrous films are subjected to treatments like hot-pressing

and DMF treatment prior to calcination. Hot-pressing is a technique where the substrates wrapped with Teflon sheet are sandwiched between two metallic plates under controlled pressure. The hot-plates are maintained at 125 °C. This technique serves two purposes: one is that it improves the contact between the nanofibers and the substrate by pressing them against each other and secondly, as explained in previous subsection, it exposes the nanofibrils thereby making the nanofibrous film achieve high surface area. Though the hot-pressing technique could address the delamination issue to certain extent, we observed that by after hot-pressing, if the samples are dipped in DMF solution for 5 s and left to air dry, the film has better adhesion and is devoid of cracks as shown in Fig. 4.1^[81].

Figure 4.1: Effect of hot-pressing and DMF treatment on the quality and adhesion of nanofibrous film^[81].

4.1.4 Physical characterization of electrospun nano-fibers

Depending on the wt% of PVP in a composite, the decomposition temperature of the polymer varies^[82,83]. In order to ensure complete removal of the polymer, it is essential to determine its decomposition temperature. As is evident from the thermogram Fig. 4.2) of the composite mat of PVP-TiO₂, the polymer PVP dissociates completely at 389 °C. Based on the TGA analysis, calcination of the fibers at 450 °C was chosen which ensures the complete removal of the polymer

Figure 4.2: TGA thermogram of as-spun TiO_2 /PVP composite^[81].

as well as any organic components present.

XRD was used to determine the phases of the TiO_2 nanofibers at various stages-before calcination, after calcination and after TiCl_4 treatment. The XRD spectra shown in Fig. 4.3 (d) demonstrates that the as-spun nanofibers are amorphous in nature as the spectrum shows no peaks. Whereas the nanofibers which were calcined at 450 °C demonstrate distinct peaks referring to the anatase phase of TiO_2 Fig. 4.3 (b). By treating the nanofibers with TiCl_4 treatment and sintering them at 500 °C, the nanofibers revealed rutile phase in addition to anatase phase Fig. 4.3 (a). The additional peaks in Fig. 4.3 (a) refer to the peaks arising from the

FTO substrate, the spectrum of which is plotted in Fig. 4.3 (c). So the nanofibers which are used as photoanodes are characterized by a mixture of rutile and anatase phases.

Figure 4.3: XRD spectra of (a) nanofibrous substrates treated with 0.1 M TiCl_4 solution and sintered at 500 °C, (b) calcined nanofibers at 450 °C, (c) plain FTO and (d) amorphous as-spun nanofibers.

The morphological evolution of the nanofibers at various stages is characterized by FESEM and TEM. Fig. 4.4 gives the FESEM images of the nanofibers (a) before calcination in the as-spun state, (b) hot-pressed and DMF treated nanofibers, (c) calcined nanofibers and (d) TiCl_4 treated and sintered nanofibers^[81].

As seen in Fig. 4.4 (a), the as-spun composite nanofibers had smooth surfaces and their diameters ranged from 200 to 400 nm. As explained in the previous subsection of hot-pressing and DMF treatment, Fig. 4.4 (b) reveals that the treated nanofibers were pressed against each other. The nanofibers still retain their smooth

Figure 4.4: FESEM images of the nanofibers:(a) before calcination in the as-spun state, (b)hot-pressed and DMF treated nanofibers, (c)calcined nanofibers and (d) TiCl_4 treated and sintered nanofibers^[81].

surface morphology. Upon calcination, due to removal of the organic phases and due to crystallization of the inorganic phases as nanofibrils (as mentioned in the nanofibril formation subsection), Fig. 4.4 (c) reveals that each nanofiber is composed of several nanostructures which are about 16-20 nm. They were much thinner than the fiber, oriented along the axis of the fiber, retained the porous structure of the web and increased the surface area ($80 \pm 6 \text{ m}^2/\text{g}$) of the whole mat of fibers. The surface area of the nanofibers was validated by BET. When these nanofibers were further treated with TiCl_4 solution and sintered, small rutile nanoparticles nucleated on the rough nanofibers as shown in Fig. 4.4 (d). It was reported^[73,84]

that this post treatment is essential for dye-sensitized solar cells as these nanoparticles enhance the surface roughness and dye adsorption^[85], thereby improving the photovoltaic cell efficiency. In order to validate this point, experiments were done by making DSCs without post TiCl_4 treatment. The efficiencies were quite low, whereas under similar experimental conditions for TiCl_4 treated nanofibers, efficiencies improved (Table. 1) due to increased J_{sc} which is attributed to dye adsorption. This treatment was also reported to enhance the necking between the particles resulting in better charge diffusion with reduced charge recombination^[25,86]. The growth of the rutile nanoparticles is inhibited by using a low optimized temperature of 40 °C. It is critical that these nano particles do not grow in size in order to retain the porosity of the fibers which can be controlled by monitoring temperature and duration of the treatment.

Fig. 4.5 shows the TEM bright field images of (a) as-spun fibers as well as that of (b) calcined fibers. In both the cases, stack of long fibrils embedded in a single nanofiber are visible. The inset of Fig. 4.5(a) is the SAED pattern of the as-spun fibers. Prior to calcination the fibers are in amorphous state which is confirmed by the diffusive ring in SAED pattern. The spotty concentric rings in SAED pattern (inset of Fig. 4.5(b)) revealed the polycrystalline nature of the calcined fibrils with $d_{101} = 0.35$ nm, $d_{004} = 0.24$ nm, $d_{204} = 0.15$ nm, $d_{008} = 0.12$ nm emphasized.

4.1.5 Current density-voltage characteristics of electrospun nanofibers as photoanodes

Finally, the electrospun nanofibrous networks were integrated as photoanodes in DSCs. Depending on the electrospinning time, the thickness of the nanofibrous

Figure 4.5: Bright Field TEM images of (a) amorphous TiO_2 nanofibers prior to calcination and (b) hotpressed and calcined TiO_2 nanofibers. The insets are the SAED patterns of (a) and (b) samples respectively.^[81]

photoanode could be controlled. For comparison, mesoporous P25 nanoparticle and electrospun nanofibrous DSCs were fabricated under similar conditions and are designated as P1 and N1 respectively. The average thickness of the mesoporous nanoparticle and nanofiber film was measured to be 3 μm by surface profilometer. The current density-voltage characteristics were tabulated in Table 4.1 and the J-V spectra was shown in Fig 4.6.

Table 4.1: Summary of photovoltaic parameters (J_{sc} , V_{oc} , ff, η , average thickness) of two cells P1 and N1 sensitized with N719 dye.

Sample ID	Avg Thickness (μm)	J_{sc} (mA/cm^2)	ff	V_{oc} (V)	η (%)
P1	3.0	5.20	0.72	0.78	2.90
N1	3.0	8.21	0.67	0.80	4.40

Photon to electron conversion efficiency is given by^[73] η (%) = $(V_{oc} \times J_{sc} \times \text{FF} \times 100) / I$, where V_{oc} is the open circuit voltage, J_{sc} is the short circuit current density, I is the incident light intensity and FF is the fill factor which is the maximum power delivered to external load. As seen from the Table 4.1 and Fig. 4.6, for

Figure 4.6: Current density - voltage curves of nanoparticle and nanofiber based liquid DSCs. NP refers to nanoparticle and NF represents nanofibrous photoanodes respectively^[81]. The dark currents are represented by black and blue curves for NF and NP respectively.

similar thickness, the nanofiber based DSC exhibited higher current density (8.21 mA/cm²) owing to its higher surface area (80 m²/g) whereas the P25 nanoparticle film exhibited only 5.2 mA/cm² current density owing to its lower surface area (50 m²/g). Also the one dimensional nanofibers were reported to exhibit directional charge transport minimum surface states facilitating faster charge collection and reduced charge recombination which was reflected in the higher V_{oc} (0.8 V) of the nanofibers in contrast to the 0.78 V of the nanoparticle film. In case of nanoparticles, the charge carriers are subjected to long and tortuous percolation routes as well as enhanced encounter with surface states that affect their transport and thus the overall efficiency of the cell^[22,68]. However the photoelectrochemical conver-

sion efficiency for the nanoparticle film is lower than the reported high efficiencies (11.9 %) [2], this is because in this work, the films were only 3 μm in comparison to the conventional films used in liquid DSCs which is about 12 μm [25,84]. The reason for choosing such thin films is that the electrospun nanofibrous film cannot be scaled to thicker films as it will result in formation of cracks within the film in spite of the hot-pressing and DMF treatment. As such, electrospinning technique limits the thickness of as-spun photoanodes. So these thin films suffer from incomplete light harvesting i.e for a sensitizer such as N719 dye whose absorption coefficient is $(14000 \text{ M}^{-1}\text{cm}^{-1})$ [87], the photoanode should be considerably thick enough to facilitate complete optical crosssection. So sensitizers with higher absorption coefficient should be employed to improve light harvesting. Recently metal free organic dyes have gained significant attention because of their high molar extinction coefficients, facile synthesis and environmental friendliness [15]. D102 is one such sensitizer. So to improve light harvesting efficiency of the nanofibrous solar cells, nanofibrous photoanodes which were about 3 m thick were sensitized with N719 (Cell N1) and D102 (Cell D1) dye respectively.

Table 4.2: Summary of photovoltaic parameters (J_{sc} , V_{oc} , ff, η , average thickness) of two cells D1 and N1 sensitized with 2 different dyes (D102 and N719) respectively.

Sample ID	Avg Thickness (μm)	Dye	J_{sc} (mA/cm^2)	ff	V_{oc} (V)	η (%)
D1	3.0	D102	6.1	0.64	0.69	2.7
N1	3.0	N719	7.5	0.64	0.80	4.0

The characteristics of these cells were tabulated in Table 4.2. For similar thickness of photo anode without any scattering layer, $\eta = 4.0 \%$, FF= 0.64, $V_{oc} = 0.8 \text{ V}$ and $J_{sc} = 7.5 \text{ mA}/\text{cm}^2$ were achieved for cell N1 whereas $\eta = 2.7 \%$, FF = 0.64, $V_{oc} = 0.69 \text{ V}$ and $J_{sc} = 6.1 \text{ mA}/\text{cm}^2$ were recorded for cell D1(Fig. 4.7 and Table 4.3).

Figure 4.7: Current density - voltage curves of nanofiber based liquid DSCs sensitized with N719 and D102 dyes respectively, at different light intensities. N1 (solid marks) refers to N719 and D1 (hollow marks) represents D102 sensitized nanofibrous photoanodes respectively. Circles denote 1 sun, triangles denote 0.5 sun while diamonds denote 0.01 sun. In the inset the dark currents of both N1 and D1 are shown.

The molar extinction coefficient of dye D102 ($58800 \text{ M}^{-1}\text{cm}^{-1}$) is much higher than that of N719 ($14000 \text{ M}^{-1}\text{cm}^{-1}$)^[87] dye and its high absorptivity is attributed to its larger molecular size^[33,88] as compared to N719 dye. The molecular structures are shown in Fig. 4.8 and Fig. 4.9 gives the absorption spectra of N719 and D102 dyes of same concentration (0.03 mM). The absorption of D102 sensitizer is narrow but higher than that of N719 at $\lambda = 400 \text{ nm}$, whereas the absorption profile of N719 dye is wider and expands till 650 nm wavelength. This suggests that the cell D1 sensitized with high absorption coefficient should have higher efficiency

Results and Discussion

Table 4.3: Comparison between the cells (3 m thick (avg.)) sensitized with N719 and D102 dyes for various light intensities.

Sample ID	Dye	Light power (mW/cm ²)	J _{sc} (mA/cm ²)	ff	V _{oc} (V)	η (%)
D1	D102	100	6.1	0.64	0.69	2.7
		50	2.99	0.66	0.66	1.27
		10	0.68	0.69	0.61	0.29
N1	N719	100	7.5	0.69	0.77	4.03
		50	3.41	0.69	0.75	3.56
		10	0.72	0.69	0.677	3.38

Figure 4.8: Chemical structures of N719 and D102 dye molecules respectively.

for the same thickness as compared to that of N1. But the observed efficiency of N1 is higher than that of D1 at various light intensities as seen in Fig. 4.7 and in Table 4.3. Inspection of the dark currents (inset of Fig. 4.7) revealed suppression of dark current for the working electrode which was sensitized with N719 dye. N719 dye delayed the onset of dark current by screening recombination of electrons at the TiO₂/electrolyte interface^[85]. Owing to its larger molecular size, D102 dye failed to impregnate into the small pores and form a dense covering on the TiO₂ nanofibers^[89]. So the electrolyte comes in contact with the TiO₂ surface and facilitates recombination. This is reflected in the lower V_{oc} value of D1 where as in the case of N1, the N719 dye molecules which are smaller in size were able to percolate and form a dense layer (blocking layer) on the TiO₂ surface and thus

Figure 4.9: Absorption spectra of N719 and D102 dyes of same concentration (0.03 mM). The absorption of D102 is higher than that of N719 at $\lambda = 400$ nm.

reduce the charge recombination.

4.1.6 Summary

DSCs using TiO_2 nanofibers which were directly spun on the substrates have been fabricated. This involves a simple yet effective fabrication process that has a potential for scaling up. The photoanodes made up of as-spun fibers exhibited higher surface area ($80 \pm 6 \text{ m}^2/\text{g}$) than the P25 nanoparticles ($50 \text{ m}^2/\text{g}$) due to its nanofibrillar morphology. The diameters of the nanofibers varied from 200-400 nm while the nanofibrils had a diameter of about 16-20 nm. The as-spun nanofibers were amorphous but upon sintering at 450°C , anatase phase was observed. Upon

TiCl₄ treatment, the nanofibers were covered with rutile nanoparticles. This allows good dye adsorption resulting in higher J_{sc} . For a film of 3.0 μm (avg.), the P25 nanoparticle film yielded 2.9 % while the electrospun nanofibrous photoanode exhibited 4.4 % efficiency. Using N719 and D102 dyes, efficiencies of 4.0 % and 2.7 % have been achieved for films with average thickness of 3.0 μm . In spite of having higher absorption coefficient, D102 sensitized cell exhibited poorer performance due to its poor passivation role which is attributed to its molecular structure.

4.2 Enhancing surface area of the nanofibers by using them as a host scaffold for the growth of hierarchical nanostructures.

In the previous section, it was concluded that to improve photovoltaic performance, one of the possible approaches is to increase the light harvesting efficiency of the nanofibrous photoanodes by using the nanofibers as a host scaffold for the growth of secondary nanostructures giving rise to hierarchical nanostructures. These secondary nanostructures were grown on the electrospun nanofiber scaffold by subjecting the scaffold to solvo-thermal treatment. It was observed that the solvo-thermal reaction time was critical in affecting the morphology of the hierarchical nanostructures.

4.2.1 Physical characterization

Fig. 4.10 shows the FESEM images illustrating the morphological evolution of the nanofibers upon being subjected to solvo-thermal treatment for different reaction times. As seen from Fig. 4.10(a) for a reaction time of 10 min, small nuclei have nucleated on the surface of the nanofibers. These nuclei were formed from the precursor solution and will act as the nucleation centers for the nanorods. Even when the reaction time was increased to 30 min, from the FESEM Fig. 4.10(b) it was observed that still no secondary structures grew on the nanofiber scaffold. The diameter of the nanofibers was measured to be ranging from 150 to 200 nm. However on inspecting the nanofiber surface closely (inset of Fig. 4.10(b)), it was observed that the surface of the nanofibers became rougher which is instrumen-

Figure 4.10: FESEM images illustrating the effect of solvo thermal reaction time on the secondary growth on TiO_2 nanofibers. For reaction times of (a) 10 min, (b) 30 min, (c) 45 min, (d) 1 h, (e) 2 h, and (f) 3 h.. In the insets the magnified images of nanostructures with a scale bar of 500 nm are shown^[39].

tal in reducing the energy barrier for heterogeneous nucleation of nanostructures, thereby assisting in their growth. Upon prolonging the reaction time to 45 min, it was observed from Fig. 4.10(c), that the spherical morphology formed irregular aggregates. For a reaction time of 1 h, it was observed that nanofibers were covered with secondary growth of nanorods (Fig. 4.10(d)). This system of nanorods on the nanofiber scaffold are referred to as HNF throughout this work. These rods provide 80 % surface coverage on the nanofibers. As such they increase the diameter of the HNF to 500-700 nm. This condition was ideal for the HNF structure as it increases the surface area without sacrificing the porosity of the nanofiber network. When the nanofiber scaffold was exposed to the solvo thermal reaction precursors for 2 h, the nanorods grew further in not only length and width but in density as well. This effect was shown in Fig. 4.10(e), where the higher density of nanorods leads to shrinkage of pores between the nanofibers. These nanorods grew in the direction away from the nanofiber and there were tetragonal in shape

with the tip having facets which resemble a square. The length of the nanorod diagonal measured 200-250 nm. By increasing the solvo thermal reaction time to 3 h, it was observed from Fig. 4.10(f) that the nanorods grew further leading to dissolution of the nanofiber scaffold as they grew at the expense of the nanofiber seeding layer. This lead to the formation of flower-like nanostructures which had diameters varying from 240-260 nm. Also it was observed that the tips of the nanorods got tapered. Thus by varying the solvo-thermal reaction time, the morphology of the HNF structures can be tailored in terms of their length, width and density.

Figure 4.11: XRD spectrum of HNF nanostructures for solvo thermal at 150 °C for 1 h^[39].

The XRD spectrum (Fig. 4.11) for the HNF nanostructures reveals that due to the solvo thermal treatment for 1 h at 150 °C, the HNF sample reveals both anatase (JCPDS: 21-1272) and rutile phase (JCPDS: 21-1276). The sharp diffraction peaks in the XRD spectrum denote that the nanostructures were highly crystalline in nature. The crystallite size which was calculated by using scherrer formula was

found to be 26.7 nm while that of NF was 16.1 nm. The scherrer formula is given by $D_{hkl} = K\lambda/(B_{hkl}\cos\theta)$, where D_{hkl} is the crystallite size in the direction perpendicular to the lattice planes, hkl are the Miller indices of the planes being analyzed, K is a numerical factor frequently referred to as the crystallite-shape factor, λ is the wavelength of the X-rays, B_{hkl} is the width (full-width at half-maximum) of the X-ray diffraction peak in radians and θ is the Bragg angle^[90]. Also by using Rietveld refinement model, the weight percentage of each phase was calculated from the XRD spectra (Fig. 4.12) to be 25.31 % anatase and 68.37 % rutile. This suggests that majority of the rutile phase comes from the nanorods grown by solvo thermal method. CIF anatase file [ICSD 9852] and rutile file [ICSD 51940] were used for the Rietveld refinement model. The fundamental parameters peak-shape profile was used; a five-coefficient Chebychev polynomial and 1/x background, zero error, scale factors, unit cell parameters and crystal size were sequentially refined using the TOPAS V3 program. The weight percentage of each phase was calculated based on quantitative phase analysis using the Rietveld method^[39,91,92]:

$$W_{\alpha} = \frac{S_{\alpha}(ZMV)_{\alpha}}{\sum_i S_i(ZMV)_i}$$

where W_{α} is the weight fraction of phase α , S is the Rietveld scale factor, Z is the number of formula units in unit cell, M is molecular mass of formula unit and V is unit cell volume.

In order to study further the morphology and structural details of HNF nanostructures, TEM and HRTEM measurements were done and shown in Fig. 4.13. For comparison and for ease, the TEM and HRTEM images of NF were also included in Fig. 4.13. As explained in previous section, Fig. 4.13(a) shows that the calcined

Figure 4.12: XRD spectra from which the weight percentage of each phase was calculated. The blue spectrum denotes the experimental data, the red spectrum denotes the simulated data and the black spectrum denotes the misfit between the experimental and simulated data.

NF's surface was smoother and nanofibrils were evident from the contrast arising from the varying crystalline density. From the HRTEM image (Fig. 4.13(b)), the distance between adjacent lattice fringes was calculated to be 0.35 nm. And from the SAED pattern (inset of Fig. 4.13(b)), the NF was confirmed to be polycrystalline owing to the presence of concentric rings. Fig. 4.13(c), reveals the TEM image of nanorods grown on the NF for the solvo thermal reaction time of 1 h at a low magnification. As seen from the TEM image, the nanofibers were completely covered with the nanorods and they appear as clusters due to the breakage of the nanostructures during sample preparation. Also it was observed that as the nanorods grew at the expense of nanofiber scaffold, the nanofiber was not visible in the TEM image. From both the FESEM as well as from the TEM images, it was observed that the nanorods grew at an inclined angle with respect to the nanofiber acting as the backbone. The HRTEM image of a single nanorod (Fig. 4.13(d))

revealed that the inter planar spacing between the lattice fringes was 0.23 nm and was indexed to the rutile phase (JCPDS no. 21-1276) possessing tetragonal crystal structure. The SAED pattern was obtained and it revealed that the nanorods were single crystalline and were rutile in nature. It was also inferred from both the XRD and HRTEM data that the nanorods had preferred growth direction in the $[\bar{1}10]$ orientation. Thus, by solvo-thermal reaction single crystalline rutile nanorods were grown on the TiO_2 nanofibers.

The surface area of the HNF and NF was investigated by measuring the adsorption of a sensitizer called D358 on these nanostructures. The molecular structure of this sensitizer is shown in (Fig. 4.14(a)). The reason for using this sensitizer was that the average thickness of these films was about 4 μm and in order to increase light harvesting of such thin films, this sensitizer with molar extinction coefficient of $6.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at $\lambda_{\text{max}} = 532 \text{ nm}$ ^[93] was used. This sensitizer has 2 prominent peaks at 400 nm and 525 nm wavelengths. When the HNF and NF were sensitized with D358 dye under similar conditions, $6.0 \times 10^{-8} \text{ mol/cm}^2$ of dye was loaded on HNF while only $4.25 \times 10^{-8} \text{ mol/cm}^2$ of dye was adsorbed on the NF. This confirms the claim further that the HNF nanostructures have higher surface area by illustrating that the HNF clearly had higher dye loading by 41.17 % than the NF.

4.2.2 Growth mechanism

The growth and formation of these nanorods on the nanofibers was explained by varying the solvo thermal reaction time and was partially illustrated in Fig. 4.10. At the initial stage when the nanofiber based substrates were immersed in the

Figure 4.13: TEM and HRTEM images of NFs and HNFs^[39] (a) and (c) are the TEM images of single nanofiber and nanorods respectively. (b) and (d) are the HRTEM images of NF and HNF respectively. In the inset, respective SAED patterns were given.

solvo thermal reaction precursor solution, the solution consisted of Ti precursor along with chlorine ions (Cl^-). This ratio of Cl^- to Ti in the precursor solution was reported to be critical in the formation of these nanorods by solvo thermal treatment^[94,95]. The Cl^- ions diffused out facilitating the nucleation of Ti precursor on the nanofibers as nuclei which aided in the growth of nanorods for longer reaction times. These nuclei were anatase in phase initially and they grew

Figure 4.14: Dye adsorption study for HNF and NF nanostructures. (a) Molecular structure of D358 dye. (b) Absorption spectra of dye molecules adsorbed on the HNF and NF films respectively. The dashed line denotes the absorption spectrum of pure dye solution.

for certain time. The rough morphology of the NF also facilitated in heterogeneous nucleation of nanostructures as it lead to the reduction of heterogeneous nucleation energy barrier. As the reaction progressed, rutile nuclei formed as it was thermodynamically more stable than anatase phase^[95]. These nanostructures grew into irregular aggregates which eventually scavenged via Ostwald's ripening process and facilitated the growth of nanorods. Rutile nanorods grew epitaxially at the expense of the anatase nanofibers via a dissolution and precipitation process^[96]. Thus these nanorods which were rutile in nature were facilitated by the high acidity of the precursor solution and by the presence of low concentration of Cl^- . Both rutile and anatase TiO_2 have tetragonal crystal structure differing only in the assembly of their octahedral chains^[97,98]. Rutile nanostructures are generally rod-like as it has 42 screw-axes along its crystallographic c-axis and this screw structure promotes the growth of the crystal in an orientation resulting in a morphology dominated by $\{110\}$ faces^[99].

4.2.3 Device characteristics

Since a porous network of nanofibers will aid easy and complete infiltration of Spiro-OMeTAD HTM layer in case of solid-state DSCs (ssDSCs), HNF synthesized for a hydrothermal reaction time of 1 h are apt for solar cell application. These synthesized nanostructures were believed to not only retain the porous network but also display higher anchoring sites for the dye molecules, thereby leading to increased light harvesting. The calcined nanofibers and nanofibers with secondary nanostructures were employed as photoanodes in ssDSCs. Different film thickness of NF and HNF based photoanodes were investigated and tabulated in Table 4.4.

Table 4.4: Effect of NF and HNF film thickness on photovoltaic properties. Photoanodes were sensitized with D358 dye under similar conditions.

Sample ID	Average Thickness (μm)	J_{sc} (mA/cm^2)	ff	V_{oc} (V)	η (%)
NF	1.6 $\pm$ 0.16	0.46	0.49	0.96	0.22
	4 $\pm$ 0.20	3.93	0.43	0.84	1.42
	6.5 $\pm$ 0.18	3.41	0.46	0.84	1.31
HNF	1.6 $\pm$ 0.11	1.06	0.72	0.91	0.69
	4 $\pm$ 0.25	4.05	0.58	0.92	2.14
	6.5 $\pm$ 0.33	3.34	0.54	0.87	1.58

By increasing the electrospinning time, the density of electrospun nanofibers was increased and accordingly the thickness of the films were increased. It was observed that as the film thickness increased, J_{sc} also increased as the number of dye anchoring sites increased. However after 4 μm , the J_{sc} decreased for both the photoanodes. This was attributed to the closed pores due to the overlap of the nanofibers resulting poor permeation of the dye molecules. Also with increasing film thickness, open circuit voltage decreases due to enhanced charge recombination^[56]. This trend has been observed even in HNF case. The optimized film thickness was 4 μm , where the porosity of the films was just optimum for good

J_{sc} , V_{oc} and FF resulting in good photoelectrochemical conversion efficiency. The two cells with the best performance were further studied in terms of light harvesting and charge transport. The J-V and IPCE spectra for the best NF and HNF based cells were given in Fig. 4.15

Figure 4.15: (a) J-V spectra and (b) IPCE spectra and integrated photocurrent of both NF and HNF cells.

The nanorods provided additional dye anchoring sites and as mentioned earlier had higher dye adsorption than the NF which resulted in generating high J_{sc} of 4.05 mA/cm² as compared to the lower J_{sc} of NF which was 3.93 mA/cm². Thus the higher surface area of HNF was beneficial in improving light harvesting by generating more photoelectrons. This was also reflected in the high IPCE observed in case of HNF cell (Fig. 4.15(b)). However it was observed that in the IPCE spectra, there was a dip in the absorption spectrum of HNF at $\lambda = 340-385$ nm but this dip had negligible contribution to the measured J_{sc} as the solar photon flux at this wavelength is quite low. Thus, the short-circuit current density integrated from IPCE spectra was higher (2.6 mA/cm²) for the HNF based solar cell than that of the NF based photovoltaic cell (2 mA/cm²) as shown on the right y-axis of Fig. 4.15(b). The discrepancy in the integrated current density and the

current density measured from the I-V curve could be due to sample degradation during the IPCE measurements and also could arise from the fact that no background illumination was used during the IPCE measurements unlike other research labs. It was also observed from Fig. 4.15(a) that the dark current for HNF based cell onseted at higher voltage signifying that the densely packed HNF blocked the recombination of injected electron with the oxidized species of Spiro-OMeTAD. This was reflected in the higher V_{oc} of the HNF based cell which was 0.92 V.

4.2.4 Summary

The light harvesting efficiency of electrospun nanofibers was successfully improved by a simple, effective and economical approach i.e by solvo thermal treatment. By this technique single crystalline, rutile nanorods were grown all over the nanofiber scaffold thereby increasing the surface area of the nanofibers. These nanorods had a preferred growth orientation in $[\bar{1}10]$ and they enhanced loading of dye by 41.17 % than the plain NF owing to their higher surface area. For the first time they were successfully employed as photoanodes in ssDSCs and they exhibited 2.14 % efficiency with J_{sc} of 4.05 mA/cm² and V_{oc} of 0.92 V.

4.3 Improving the J_{sc} and V_{oc} of the nanofiber based liquid DSCs by co-sensitizing dyes with complementary absorption spectra.

Figure 4.16: Chemical structure of D35 and D131 dyes.

In the previous sections we studied nanofibrous photoanodes with film thickness being 4 μm . In this section nanofibrous photoanodes with thicker films were investigated in liquid DSCs. However instead of a single dye, the effect of combination of two dyes on light harvesting and open circuit voltage will be explored in liquid DSCs. A step-wise approach had been employed to sensitize the nanofibers with the two dyes. As the thickness of the fibers spun directly on FTO substrates is limited by the adhesion of the fiber mat to the substrate, the thickness of these fibrous photoanodes lies in the range of 6-7 μm , which is significantly lower than the nanoparticle photoanodes. The reason for the choice of organic dyes for such

systems was to have higher effective optical cross-section. These organic dyes, whose molecular structure is shown in Fig. 4.16, are structurally different from each other and have advantages specific for individual dye.

Figure 4.17: Absorbance spectra of (a) D35 and D131 dyes respectively and (b) bare TiO₂ nanofiber, D35 sensitized, D131 sensitized and cosensitized nanofiber.

Figure 4.18: (a) Cyclic voltammetry spectra of D35 and D131. (b) Schematic illustrating the energy levels and the various processes occurring at each interface.

For co-sensitization approach, the sensitizers used must have a structure which prevents competitive adsorption among the dyes, suppress dye aggregation and reduce charge recombination with the oxidized species of the electrolyte^[100]. In this work, D131 and D35 chromophores were used for step-wise cosensitization. As seen in Fig. 4.16, D131 chromophore was planar and has no bulky alkyl chains whereas D35 dye had 4 butoxy alkyl chains. The absorption spectra of both the

dyes in ethanol solvent was shown in Fig. 4.17(a) while the absorption spectra of bare TiO₂ nanofiber film, nanofibers sensitized with D131 and D35 respectively as well as the absorption spectra of the fibers sensitized with both the dyes was shown in Fig. 4.17(b). D131 had higher molar extinction co-efficient ($50000 \text{ M}^{-1}\text{cm}^{-1}$) giving rise to a peak at $\lambda = 420.5 \text{ nm}$ (Fig. 4.17(a)) with intensity higher than the intensity of the peak ($\lambda = 438 \text{ nm}$) of D35 dye whose molar extinction coefficient at $\lambda = 445 \text{ nm}$ is $31300 \text{ M}^{-1}\text{cm}^{-1}$ [101]. Another important effect to take note is that for the fibers which were sensitized with both the dyes, the absorbance has increased as a convolution effect of absorbance by both type of the dye molecules. The HOMO and LUMO energy levels of the two chromophores were estimated from cyclic voltammetry and UV-visible spectroscopy measurements and were illustrated in Fig. 4.18(a) and tabulated in Table 4.7. The oxidation onset potentials which correspond to highest occupied molecular orbital (HOMO) energy levels were -5.1 eV for D35 and -5.13 eV for D131. Optical band gaps were calculated from the onset of absorption (Fig. 4.17(b)) and were 1.99 eV for D35 and 2.2 eV for D131 dye. Hence the lowest unoccupied molecular orbital (LUMO) was calculated to be -3.01 eV and -2.93 eV for D35 and D131 dyes respectively. In the energy band diagram (Fig. 4.18(b)); it was evident that the LUMO levels of both the dyes were above the TiO₂ conduction band edge thereby energetically favored electron injection into TiO₂.

Table 4.5: Energy levels of D35 and D131 chromophores.

Dye	$E_{onset} \text{ (ox) (vs } \text{Fc}^+/\text{Fc})$	HOMO (eV)	$\lambda_{onset} \text{ (nm)}$	Optical band gap, E_g (eV)	LUMO (eV)
D35	-5.10	-5.10	620	1.99	-3.01
D131	-5.13	-5.13	566	2.2	-2.93

From Table 4.6 and Fig. 4.19(a), which summarized the current density-voltage

characteristics of the photoanodes sensitized with only D35, with both D35 + D131 and with only D131; it was observed that the fibers which were once sensitized with D35 dye, upon further sensitization with D131 exhibited higher J_{sc} and intermediate V_{oc} resulting in higher photovoltaic efficiency by 25 %. The best efficiency obtained by cosensitizing the nanofibers was 6.22 % with V_{oc} , J_{sc} and FF being 0.79 V, 12.34 mA/cm² and 0.63 respectively. As was evident from the IPCE spectra (Fig. 4.19(b)), the cosensitized cell exhibited higher J_{sc} as a result of the convolution effect from

Table 4.6: Effect of cosensitization of nanofibers on photovoltaic properties. Photoanodes were sensitized with D35, D131 and with both the dyes under similar conditions.

Sample ID	J_{sc} (mA/cm ²)	ff	V_{oc} (V)	η (%)
Fibers sensitized with D35	10.26	0.62	0.73	4.59
Fibers sensitized with D131	8.39	0.66	0.77	4.21
Fibers sensitized with D131+D35	12.41	0.62	0.75	5.77

Figure 4.19: (a) J-V and (b) IPCE spectra of cells sensitized with D35, D131 and D35+D131 dyes respectively.

As discussed earlier, D131 dye was smaller than D35 dye, it formed a close packing and covered the entire surface area of the nanofibers. This close packing prevented the recombination of the TiO₂ conduction band electrons with the oxidized species of the liquid electrolyte. But as was observed from the absorption

spectra of D131 dye, it had a narrow peak 420.5 nm wavelength where the photon flux is lowest which resulted in lowest current with respect to D35 and cosensitized cells. Whereas for the D35 sensitized cell, the current density was higher than the D131 sensitized cell, as its highest absorption peak was slightly towards the higher photon flux area. But because of its bulky structure, it was not able to provide full coverage on the nanofiber surface. There were still some gaps in between the dye molecules which facilitated the recombination and hence loss of electrons which was reflected in its lower V_{oc} . In order to utilize these two unique properties of these two dyes, when the nanofibers were sensitized with both the dye molecules via a sequential approach, the co-sensitized nanofibers exhibited higher photovoltaic performance. For the first dye (D35) soaking process, the long alkyl chains of D35 were reported to render steric hindrance between the dye molecules which prevented the close packing of the dye. This mode of dye adsorption facilitated gaps between each adsorbed D35 molecule thereby leaving scope for the recombination of photo-injected electrons between the electrolyte and metal oxide surface. When such cell was sensitized with D131 which was a simple, planar dye molecule devoid of steric giving alkyl chains, the probability for this dye to squeeze through the gaps of D35 and adsorb onto TiO_2 surface was higher. So the metal oxide surface was covered with more number of dye molecules which acted as a passivating layer, thereby reducing the transfer of electrons from TiO_2 to electrolyte. Also in the dark, as recombination of photo injected electrons from TiO_2 conduction band occurred only with the I^{3-} ions of the electrolyte and not with the oxidized dye, this claim was further confirmed from the observed dark currents in Fig. 4.19(a). In case of the cell sensitized with both the dyes, onset of dark current at higher voltage indicated that the recombination

of injected electrons with the oxidized species of the electrolyte was minimized due to TiO_2 surface passivation by the compact packing of the 2 dye molecules. Also in case of the small structure of the dye D131, due to compact packing of the dye molecules, the onset of dark current was at higher voltage.

4.3.1 Summary

The light harvesting efficiency of the nanofiber based DSCs has been improved considerably by employing a simple technique called co-sensitization. For co-sensitization approach organic dyes with complementary absorption spectra for efficient light harvesting and proper energy alignments for effective electron injection have been chosen. The approach of sensitizing the nanofibers first with D35 chromophore followed by D131 dye yielded DSCs with short circuit current density of 12.41 mA/cm^2 , open circuit voltage of 0.75 V, fill-factor of 0.62 resulting in a conversion efficiency of 5.77 %. These results were higher than those observed for the individual dye sensitized nanofibers (4.59 % for D35 and 4.21 % for D131).

4.4 Coupling $\text{CH}_3\text{NH}_3\text{PbI}_3$ as absorber with 1D electrospun nanofibers for further enhancement of light harvesting efficiency of the nanofiber based solid state solar cell.

In this section TiO_2 nanofibers which were directly electrospun on TiO_2 compact layer were sensitized with a sequentially deposited perovskite and were employed in solid-state cells. As mentioned in previous section, that these nanofibers suffer from poor light harvesting efficiency, there is a need to couple them with high absorption coefficient sensitizers. Since $\text{CH}_3\text{NH}_3\text{PbI}_3$ is one such sensitizer whose absorption coefficient is $1.5 \times 10^4 \text{ cm}^{-1}$ at 550 nm^[19], it was anticipated that coupling of the nanofibers with this perovskite would improve the light harvesting efficiency. However this perovskite is sensitive and is unstable with the conventional liquid electrolytes^[102] and as such the nanofibers sensitized with this perovskite absorber were incorporated in the solid state cells. The effect of different nanofiber film thickness was investigated in terms of perovskite loading to yield best photo electrochemical conversion efficiency.

4.4.1 Fabrication of device

In Fig. 4.20 the device architecture of the nanofiber-based $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite cell was illustrated. The mesoporous nanofibers were used as scaffold for the loading of the inorganic perovskite and the thickness, fiber diameter and porosity were optimized by modulating the electrospinning conditions, such as solution viscos-

ity and deposition voltage.

Figure 4.20: Schematic illustrating the various components of nanofiber based perovskite solar cell^[63].

4.4.2 Physical characterization

Fig. 4.21 depicts the morphology and topography of the nanofibers at different stages of fabrication of perovskite based solid state solar cells. When PbI_2 was spincoated on the nanofibers, they adopted and conformed to the rough and porous morphology of the nanofibers which was evident from the pores observed in between the PbI_2 grains in Fig. 4.21(a). The roughness of the PbI_2 film was evident even from the cross-section image (Fig. 4.21(b)) and it was also observed from Fig. 4.21(b) that the PbI_2 had infiltrated throughout the depth of the nanofiber film. When the nanofibers loaded with PbI_2 were immersed in a solution of IPA contacting $\text{CH}_3\text{NH}_3\text{I}$, the solution permeated through the pores and contacted PbI_2 thereby transforming completely to $\text{CH}_3\text{NH}_3\text{I}$ within the photoanode. The formation of perovskite within the nanofibrous photoanode was shown in the cross-sectional FESEM image as Fig. 4.21(c). It was also observed that the perovskite formed additional crystals on top of the nanofibrous film. The cross-sectional view of the complete nanofiber device was shown in the FESEM Fig. 4.21(d), and

it revealed that the nanofiber film was 413 nm thick. The perovskite had infiltrated completely through the nanofibrous film and also formed an over layer of about 250 nm and the spiro-OMeTAD formed an over layer of another 275-300 nm. A high concentration of spiro-OMeTAD of (120 mg/mL in chlorobenzene) was used to form a thick over layer in order to smoothen the rough surface of the perovskite which originated due to the nanofibers. This prevented the cells from getting short-circuited.

Figure 4.21: FESEM characterization of $\text{CH}_3\text{NH}_3\text{PbI}_3$ loaded nanofibers at different process stages. (a) Top-view FESEM image of PbI_2 loaded nanofibers, FESEM cross-section view of (b) PbI_2 loaded nanofibers, (c) perovskite formation within and crystals on top of nanofibers and (d) complete perovskite based solid state solar cells.

The effect of the porosity of the nanofiber on the infiltration and coverage of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was further investigated and confirmed from the EDX analysis. Fig. 4.22 gives the mapping of the various components throughout the depth of the nanofiber film.

The EDX mapping of the cross-section area as shown in the insets of Fig. 4.22

Figure 4.22: EDX analysis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ loaded nanofibers.

(a & d) demonstrated the distribution of various elements: O, Ti, I and Pb along the nanofiber film thickness. From the EDX mapping it was evident that that PbI_2 infiltrated the entire nanofiber film due to the open pores which was the characteristic feature of the nanofiber network. This easy infiltration of PbI_2 till the base of the film was facilitated by the large pores of the nanofibrous film. Having proved the impact of open pores for the infiltration of lead perovskite, it was essential to investigate the effect of porosity of the nanofiber films.

4.4.3 Effect of different film thickness and porosity

As explained in previous sections, the porosity and film thickness of electrospun nanofibers can be controlled by varying the electrospinning time and other parameters like viscosity and Ti:PVP concentration. Since it was already demonstrated the synthesis of continuous and 200 nm diameter nanofibers using a particular precursor recipe, the same recipe was used for different electrospinning times in order to modify the porosity of the nanofibrous films. Fig. 4.23, shows the FESEM im-

ages illustrating the effect of electrospinning time on the pore-distribution. As evident from Fig. 4.23(a), thinner films of nanofibers exposing the pores in between them were attained for shorter electrospinning times (about 7.5 min). Whereas films with a higher density of nanofibers with greater overlapping and reduction in porosity were observed in Fig. 4.23(b) for longer electrospinning times which was about 15 min. Since perovskite layer was composed of crystals of irregular size, porosity of the scaffold was anticipated to affect the perovskite loading and thus the overall cell performance.

Figure 4.23: Effect of electrospinning time on the pore-distribution of nanofibers^[63].

From Fig. 4.24, it was observed that the amount of light absorbed by the perovskite loaded nanofibrous films depreciated as the films got thicker. This observation correlated well with previous claim made that thickness of the film determined the porosity which in turn affected the loading of perovskite and thus the absorption of light. So thinner films which were 413 nm showed higher absorption of light than the thicker films (1215 nm).

It was clearly evident from the trend that thinner nanofibrous films facilitated higher perovskite loading which would be beneficial for photovoltaic performance and were thus preferred with respect to thicker films. However due to the limitations imposed by electrospinning technique and the diameter of the nanofibers,

Figure 4.24: Effect of nanofiber film thickness on photon absorption^[63].

homogeneous and continuous nanofibrous films which are thinner than 413 nm cannot be synthesized. As such, 413 nm thick nanofibrous film properties were compared to a substrate without any nanofiber scaffold in terms of perovskite loading, coverage and photovoltaic performance in the subsequent subsections.

When PbI_2 was spincoated on the blocking layer alone which comprised of closely packed TiO_2 nanoparticles^[3], as was evident from Fig. 4.25, PbI_2 formed a smooth and compact topography. From the cross-section view of the planar device (Fig. 4.25(b & c)), it was clear that the PbI_2 /perovskite film was thinner than that observed in case of Fig. 4.21(b & c) implying that the amount of perovskite loading was higher when there was a nanofiber scaffold. It was also observed that due to the compact nature of the blocking layer, the formation of lead iodide film was compact and this resulted in incomplete $\text{CH}_3\text{NH}_3\text{PbI}_3$ formation which was due to incomplete infiltration of $\text{CH}_3\text{NH}_3\text{I}$ solution through the compact PbI_2 .

Figure 4.25: FESEM characterization of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on just the blocking layer without any scaffold, at different process stages. (a) Top-view FESEM image of PbI_2 deposited on the blocking layer, FESEM cross-section view of (b) PbI_2 on blocking layer, (c) perovskite formation with the crystals on top of the blocking layer and (d) complete perovskite based planar solid state solar cells.

This observation was supported by XRD characterization of the planar device as shown in Fig. 4.28. The XRD spectra was recorded for samples with the following configuration: FTO/blocking layer/ PbI_2 / $\text{CH}_3\text{NH}_3\text{I}$. The blue squares represented the diffraction peaks which were indexed to PbI_2 peaks that conformed well to the literature data^[76,103]. The diffraction peaks which originated from the FTO substrate were denoted by the open squares and the unmarked peaks were indexed to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite which were observed upon reacting the PbI_2 with $\text{CH}_3\text{NH}_3\text{I}$ in IPA solution. The presence of PbI_2 peaks even after exposure of the PbI_2 coated planar substrate to $\text{CH}_3\text{NH}_3\text{I}$ clearly indicated that the transformation to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite was incomplete. For complete perovskite formation it was necessary to expose the PbI_2 covered planar device to $\text{CH}_3\text{NH}_3\text{I}$

solution for prolonged time but that resulted in the dissolution of the lead iodide in the solution itself. This phenomenon was observed even by Burschka et al^[76]. Fig. 4.25(d) shows the cross-section image of the complete planar device with the following structure: FTO/TiO₂ blocking layer/CH₃NH₃PbI₃/spiro-OMeTAD/Au.

Figure 4.26: XRD spectra of (a) PbI₂ spincoated on a blocking layer and (b) perovskite formed due to interaction of PbI₂ with CH₃NH₃I in IPA solution^[63].

4.4.4 J-V characteristics

The photovoltaic characteristics for different nanofiber film thickness were illustrated in Fig. 4.27 and tabulated in Table 4.7.

From absorption spectra, FESEM characterization and J-V characteristics it was observed that 413 nm was the optimized film thickness for the nanofibrous film to achieve best photoelectrochemical conversion efficiencies. For thicker

Figure 4.27: Effect of nanofiber film thickness on J-V characteristics^[63].

Table 4.7: Effect of nanofiber film thickness on photovoltaic properties.

Film thickness (nm)	J_{sc} (mA/cm ²)	ff	V_{oc} (V)	η (%)
413	15.88	0.63	0.98	9.82
844	6.41	0.66	0.78	3.32
1215	5.14	0.66	0.74	2.49

films such as 1215 nm and 844 nm, the V_{oc} values dropped to 0.74 V and 0.78 V respectively, which was due to a higher recombination rate in the thicker films. The increased recombination was observed for thicker films due to the increase in surface area which resulted in consequent increase of trap assisted recombination in TiO₂ films^[56,103]. From the early onset of dark currents (from Fig. 4.27) for the thicker nanofibrous films, it was further confirmed that the recombination was higher for the thicker films. Another critical observation made was that there was a dramatic reduction in J_{sc} as the film thickness increased. This was in correlation with our previous explanations that with increased film thickness, porosity was decreased leading to reduced perovskite loading which was reflected in the lower

J_{sc} values. Also a comparative study was made by fabricating solid state solar cells with planar devices and 413 nm thick nanofibrous films to investigate the effect of scaffold on photovoltaic performance and their photovoltaic characteristics were shown in Fig. 4.28 and tabulated in Table 4.8 .

Figure 4.28: (a) J-V and (b) IPCE action spectra of 413 nm nanofibrous based perovskite solar cell and planar perovskite solar cell respectively.

Table 4.8: J-V characteristics of nanofiber based and planar solar cells at different light intensities.

Sample details	Light intensity (mW/cm ²)	J_{sc} (mA/cm ²)	ff	V_{oc} (V)	η (%)
Nanofiber	100.0	15.88	0.63	0.98	9.82
	79.4	11.82	0.64	0.98	9.39
	63.0	9.59	0.67	0.97	9.89
	50.1	8.40	0.68	0.97	11.09
	31.6	4.95	0.73	0.94	10.83
	10.0	1.62	0.82	0.89	11.79
Planar	100	4.02	0.73	1.06	3.93
	79.4	2.42	0.74	1.06	2.39
	63.0	2.13	0.73	1.05	2.58
	50.1	2.16	0.72	1.05	3.26
	31.6	1.41	0.72	1.03	3.29
	10.0	0.46	0.68	0.97	3.03

From Fig. 4.28(a) and Table 4.8, it was clearly evident that the nanofiber based solar cell yielded exceedingly higher photoelectrochemical conversion efficiency of 9.82 % at 1 sun in comparison to the planar solar cell with 3.11 %. Though the planar device exhibited higher FFs and V_{oc} s, the performance of the nanofiber device was better due to its higher J_{sc} which was 15.88 mA/cm². The higher J_{sc} values of the nanofiber based cell were due to greater loading of the perovskite as

was witnessed in the FESEM Figs. 4.21 & 4.25. The V_{oc} of the nanofiber devices was only 0.98 V in comparison to 1.06 V of the planar device. This drop in V_{oc} for the nanofiber based solar cell was expected since the trap-assisted recombination was lower for the planar device, and this trend was similar to that observed in the nanofibers devices with different film thickness. It was also reported that due to direct injection of charges from $\text{CH}_3\text{NH}_3\text{PbI}_3$ to the conducting and compact blocking layer, loss in voltage was reduced considerably^[61].

Even from the IPCE spectra shown in Fig. 4.28(b), the higher J_{sc} of the nanofiber based cell can be validated and the J_{sc} integrated from the IPCE spectra which was 15.5 mA/cm^2 conformed well with the J_{sc} (15.88 mA/cm^2) which was observed from the J-V measurements. For the planar device the J_{sc} calculated from the IPCE spectra was 3.93 mA/cm^2 which was also close to the J_{sc} measured in the J-V analysis. Though the shape of the IPCE spectrum for the nanofiber based cell was similar to the ones reported in literature^[76], the shape of the IPCE spectrum of the planar device was deviant from the standard profile of $\text{CH}_3\text{NH}_3\text{PbI}_3$ IPCE spectrum, especially at $\lambda = 350\text{-}650 \text{ nm}$. This feature was attributed to the incomplete transformation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ as was discussed in previous section.

The photovoltaic parameters namely η , J_{sc} and V_{oc} were plotted as a function of light intensities for the nanofiber and planar based perovskite cells and were illustrated in Fig. 4.28(b). It was observed that there was a linear dependence of J_{sc} on light flux which demonstrated that the efficiency of charge collection was independent of light intensity as reported in literature^[21]. Also the nanofiber based cell yielded higher J_{sc} and higher η systematically as compared to that of the planar devices, at all light intensities. At 0.1 sun, the nanofibrous perovskite cell exhibited 11.79 % efficiency while the planar device exhibited only 3.03 %.

Figure 4.29: Efficiency (%), J_{sc} (mA/cm^2) and V_{oc} (V) of nanofiber vs planar solar cells as a function of different light intensities.

4.4.5 Summary

The light harvesting efficiency of the electrospun nanofibers was remarkably improved by coupling them with an inorganic-organic hybrid perovskite namely $\text{CH}_3\text{NH}_3\text{PbI}_3$. When the nanofibers coupled with $\text{CH}_3\text{NH}_3\text{PbI}_3$ were integrated in solid-state solar cells, photo electrochemical conversion efficiencies of 9.8 % at 1 sun and 11.79 % at 0.1 Sun were achieved. The efficiencies were mainly deter-

mined by the porous nature of the electrospun nanofiber network which was varied by tailoring the electrospinning parameters like electrospinning time. It was also shown that a scaffold was necessary in order to achieve good device performance as it will lead to greater perovskite loading resulting in higher current densities.

4.5 Investigation of electrical properties of electro-spun nanofibers with respect to nanoparticles.

4.5.1 Effect on diffusion lengths in liquid electrolyte DSCs.

In the previous sections, the synthesis, physical characterization and incorporation of as-spun TiO₂ nanofibers have been demonstrated. The various approaches employed to enhance the overall performance of the nanofiber based liquid state, solid state and perovskite solar cells. In this section, the charge transport and collection properties of the 1D nanofibers is compared with that of the mesoporous TiO₂ nanoparticle films. In order to investigate these properties, EIS measurements were performed on both the systems (as explained in Chapter 3). The Nyquist plots were fitted with an equivalent electrical circuit^[71,104] which is given in Fig. 4.30 and the parameters fitted from the spectra are shown in Fig. 4.31. From Fig. 4.30, it is evident that there is a convolution of the small semicircle at high frequencies (which represents the resistance and capacitance between the counter electrode and the electrolyte interface) and the large semicircle at intermediate frequencies (which signify the resistance between TiO₂/sensitizer and electrolyte interface). As a consequence of this a very small linear region from which the resistance to charge transport (R_t) is derived. Also it is observed that as the voltage is decreased the large semicircle gets incomplete. As a consequence of this the fitted parameters derived from lower voltage spectra are excluded in this analysis.

The low charge transport resistance of the nanofibers (Fig. 4.31a) is attributed to the directional pathway of the charge through the interconnected nanofibers with low density of grain boundaries or inter particle connections relative to the

Figure 4.30: Nyquist plots of cell N1 at different bias voltages. In the inset, Nyquist plots of N1 at high frequency is shown along with the equivalent circuit used for analyzing the EIS spectra where the sheet resistance of the cell is given by R1, while the distributed element Pt resistance and constant phase element are represented by DX, R2 and CPE respectively.

mesoporous nanoparticulate films with tortuous pathways for the charge^[21,68]. Thus the diffusion coefficient values ($D_n = L^2/R_t C_\mu$)[34] for the nanofibrous system are higher than the nanoparticle system as seen in Fig. 4.31c. Fig. 4.31b reveals that the recombination resistance between the photo injected electrons and the oxidized species of the electrolyte is higher for the nanofiber based cell in comparison to that of the mesoporous nanoparticle film. Hence the nanofiber based cells exhibit lower loss of electrons. This unique behavior of the nanofiber based cells is attributed to the depletion of space charge region^[105]. As observed from the FESEM images of previous sections, each nanofiber is composed of densely packed grains, and as a result band bending^[21,68] occurs which enables the electrons inside the core of the fiber and away from the nanofiber surface thereby

Figure 4.31: Elements of transmission line model plotted against bias voltage for cells N1 (black diamonds) and high efficiency nanoparticle cell NP1 (blue circles). (a) R_t is the electron transport resistance in the nanofibers, (b) R_{ct} is the resistance to interfacial charge recombination, (c) D_n is the diffusion coefficient and (d) collection efficiency is given as $\eta_{collection} = 1/(1 + R_t/R_{ct})$. The control cell thickness is $12 \mu\text{m}$ and is sensitized with N719 dye^[81].

screening the electrons from the oxidized species of the electrolyte. The resulting low charge transport resistance and the high charge recombination resistance of the nanofibrous based cell yielded an improved charge collection efficiency ($\eta_{collection}$) reaching 99 % (Fig. 4.31d) which is quite remarkable. The $\eta_{collection}$ is calculated by the following equation ($\eta_{collection} = 1/(1 + R_t/R_{ct})$). Even the diffusion lengths (L_n) of the nanofibers were calculated to be $100 \mu\text{m}$ implying that the fibers have very good charge transport properties owing to their fewer surface traps enabling better charge collection. Thus the as-spun photoanodes reported in this work displayed lower R_t , lower C_μ , higher R_{ct} and higher L_n as compared to published data of nanorods^[32] synthesized via electrospinning route, emphasizing

the importance of retaining the fiber morphology for better charge transport and charge collection.

Having observed that the as-spun nanofibrous solar cells have benefits over the nanoparticle system in terms of charge collection, further investigation was done on the charge transport and charge recombination characteristics for different configurations of the nanofibrous system. In order to further understand whether the above stated good charge transport properties of nanofibers are dependent on the type of sensitizer used, EIS measurements were performed on nanofibrous solar cells sensitized with D102 (D1) and N719 (N1) dyes respectively (Fig. 4.32). Their performance in terms of I-V characteristics was already explained in the previous section with the D102 sensitized nanofibrous solar cell performing poorer compared to the N719 sensitized nanofibrous cell.

From the Fig. 4.33iii, it is visible that though both D1 and N1 cells were fabricated using the nanofiber photoanode, the diffusion length ($14.5 \mu\text{m}$) of the D1 cell is lower than the diffusion length of N1 cell ($100 \mu\text{m}$). But inspection of charge transport resistance (R_t) plotted in Fig. 4.33(i) revealed that the R_t for D1 cell is only marginally higher than that for N1 cell, suggesting that the discrepancy in L_n is not bottlenecked by the electron transport in the nanofiber. This discrepancy in the L_n values for D1 and N1 cells arose from the charge transfer resistance (R_{ct}) which was observed to be significantly lower for cell D1 as compared to the R_{ct} for cell N1 (Fig. 4.33(ii)). Though L_n for cell D1 is lower than that of N1, it is higher than the L_n reported by Lee et.al.^[45]. The low R_{ct} for cell D1 observed could be due to the catalytic^[106–108] effect of the organic dye which draws I_3^- ions closer to the surface facilitating recombination of the injected electrons with the electrolyte. Whereas the N719 dye reduces

Figure 4.32: EIS spectra of cells using N719 dye (black solid curve) and D102 dye (red dash curve) respectively in light measured at V_{oc} .

the interfacial recombination by screening the oxidized species of the electrolyte from the electrons^[106] thus displaying higher R_{ct} . Larger R_{ct} and C_μ (chemical capacitance, Fig. 4.33(iii)) impart longer electron lifetime ($\tau_n = R_{ct} C_\mu$)^[71] which results in higher V_{oc} . As shown in Fig. 4.34(a), N1 has larger electron lifetime as compared to D1 implying less charge recombination which explains its higher V_{oc} . From Fig. 4.34(b), it appears that the diffusion coefficient ($D_n = L^2/(R_t C_\mu)$) of N1 is higher than that of D1, implying that the charge trapping events in case of N1 are lower. The observed shift in C_μ is probably due to the conduction band shift as different dyes have been employed. It was also observed that the maximum D_n value measured for N1 is $2.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ (at high bias potential) which is

Figure 4.33: Elements of transmission line model plotted against bias voltage for cells N1 (black diamonds) and D1 (red triangles). (i) R_t is the electron transport resistance in the nanofibers, (ii) R_{ct} is the resistance to interfacial charge recombination, (iii) C_μ is the chemical capacitance and (iv) L_n is the electron diffusion length.

similar to the reported values^[71] for nanoparticle system sensitized with Ru based dyes and higher than the ones observed for nanorods^[32]. These results emphasize that in addition to the structural and electrical properties of the sensitizer support, the catalytic or screening properties of the dyes play a significant role in affecting the performance of the cell^[106–108].

Figure 4.34: (a) Electron lifetime and (b) diffusion coefficient plotted against bias voltage which was obtained from the EIS spectra. The black diamonds correspond to cell N1 and the red triangles correspond to cell D1.

Effect of co-sensitization on the charge transport and recombination properties of the sensitized nanofibers.

It is intriguing to investigate the charge transport characteristics of the nanofibers when they are sensitized with 2 different dyes having different absorption spectra. As explained in section 3.3, the nanofibers were sensitized firstly with D35 chromophore and then with D131 sensitizer. For a complete study, the nanofibers were also sensitized with the individual dyes. All these cells were analyzed using EIS and the fitted parameters of charge transport and charge recombination resistance are shown in Fig. 4.35.

The R_t values for all the cells i.e co-sensitized, D35 sensitized and D131 sensitized, are similar as is evident in Fig. 4.35a. This is according to the expectation that the nanofiber scaffold properties were not influenced by the sensitizer and by its mode of adsorption on its surface. The trend in the observed V_{oc} of co-sensitized cell with respect to the individual dye sensitized cell as was observed in section 3.3 is in agreement with the R_{ct} values shown in Fig. 4.35(b). It was ob-

Figure 4.35: (a) Charge transport resistance in the TiO₂ nanofiber vs applied voltage, (b) charge recombination resistance plotted against chemical capacitance obtained from the EIS spectra and (c) schematic illustrating the adsorption of the D35 and D131 dye molecules on the TiO₂ nanofiber surface.

served that for the co-sensitized cell where the two types of dye molecules form a compact monolayer on the TiO₂ surface (as shown in the schematic of Fig. 4.35c), the charge recombination resistance followed the trend of D131 charge recombination. The monolayer formed by the adsorption of both the dyes reduced the recombination of the injected photoelectrons with the oxidized species of the liquid electrolyte similar to the close packing acquired by the small molecule D131 adsorption on the TiO₂ surface. Whereas it was clearly evident from the Fig. 4.35(b), that the D35 sensitized cell exhibited lower charge recombination resistance as a result of the presence of some voids in between the D35 dye molecules when adsorbed on the TiO₂ surface. This validated the lower V_{oc} observed in case of D35 sensitized cell and the higher V_{oc} for co-sensitized and D131 sensitized cells.

4.5.2 Effect on charge collection efficiency for solid state DSCs.

As explained earlier in section 4.5.1 nanofibrous photoanodes exhibited better charge collection owing to its morphology, however the morphological effects of the nanoparticle and nanofiber on charge dynamics are not very critical in liquid DSCs as the charge collection is faster compared to the recombination dynamics

between the photoinjected electrons and the triiodide ions of the electrolyte. The charge recombination is slow because the formation of triiodide is a two electron process. However in the solid-state system, the recombination of electrons in the conduction band of TiO_2 with the holes in hole transporting material is faster as it is a single electron process^[109]. As such the objective of this thesis is to employ 1D nanofibers in solid state DSCs for improving the charge collection by suppressing charge recombination. The charge dynamics of nanofibrous (NS) and nanoparticle (PS) ssDSCs were investigated by EIS and the results are shown in Fig. 4.36.

Figure 4.36: (a) Charge recombination resistance vs applied voltage and (b) charge collection efficiency for nanofiber vs particle ssDSC.

As shown in Fig. 4.36(b), the charge collection efficiency which is dependent on charge recombination resistance and inversely on charge transport resistance (as explained in section 4.5.1) is higher for nanofibrous ssDSC in comparison to the nanoparticle ssDSC. This is attributed to the higher resistance to recombination of injected electrons with the holes of spiro-OMeTAD exhibited by the nanofibrous ssDSC. Due to the band bending associated with the morphology of long and interconnected nanofibers, the confinement of electrons within the core

suppresses charge recombination at the surface. This feature of the nanofibers is beneficial in improving the cell performance.

Impact of morphological alterations of the as-spun nanofibers on the charge collection efficiency of solar cells.

The electrochemical impedance spectroscopy measurements are further performed to investigate the effect of morphological evolution of the 1D nanofibers to 3D hierarchical nanostructures on the charge collection properties. The plain fibers solid-state cell (NF) and the hierarchical based solid-state cell (HNF) are compared with each other in terms of charge recombination resistance, charge transport resistance and charge collection efficiency. The Nyquist plots of NF and HNF cells are shown in Fig. 4.37a.

Figure 4.37: (a) EIS spectra of NF and HNF cells^[39], (b) charge transport resistance and (c) charge recombination resistance plotted against applied voltage derived from the EIS spectra.

As explained earlier, from the fitting of the two EIS spectra the R_t derived for the NF is higher than the R_t of HNF cell (Fig.4.37(b)). This can be explained from the nanofiber structure where the charge has to encounter greater number of grain boundaries arising from the presence of the nanofibrils within each nanofiber. From Fig. 4.37(c), it is evident that the charge recombination resistance of the HNF cell to the oxidized species of HTM is higher than that of

the NF cell. This clearly implies that the densely populated nanorods with higher dye loading provide greater screening between the injected electrons in TiO_2 film and holes in HTM, thereby suppressing the recombination of electrons at the TiO_2 and spiro-OMeTAD interface^[39,110]. In the case of NF - based cell, the pores between the nanofibers are big and the dye coverage is relatively lower, ensuing the recombination of electron hole pair at TiO_2 /spiro-OMeTAD.

4.5.3 Summary

In conclusion, as shown in Fig.4.37, though in liquid DSCs the charge collection is similar for both the morphologies, the nanofibers exhibited better charge dynamics than the nanoparticles in solid state DSCs. As a result of the higher resistance to charge recombination and lower charge transport they facilitate better charge collection and thereby confirm that 1D nanostructures have potential in enhancement of device performance.

Figure 4.38: Summary of charge dynamics for nanoparticle and nanofiber based liquid and solid state DSCs.(a) Recombination resistance vs voltage and (b) charge collection efficiency plotted against voltage derived from the EIS spectra.

Chapter 5

Conclusion and Outlook

5.1 Comprehensive summary & conclusion

The emerging photovoltaics are economical and have avenues for research in terms of effective charge collecting photo electrodes and sensitizing materials. In this thesis, nanofibrous photoanodes with better charge collection ability, tunable porosity and interconnected network were introduced in liquid/solid DSCs and perovskite solar cells. These nanofibers were synthesized by electrospinning a mixture of Ti-n-butoxide, PVP, acetylacetone and butanol in measured quantities. The uniqueness of this work is that the nanofibers were electrospun directly on to conducting substrates without involving any additional process steps. This method of photoanode fabrication facilitated the nanofibers to retain their high length to diameter (90-120 nm) aspect ratio in comparison to other established alternative approaches. Physical characterizations revealed that upon sintering highly crystalline, pure anatase TiO₂ nanofibers which were polycrystalline were synthesized. However due to this sintering step, due to difference in thermal co-

efficient between the substrate and the nanofibrous film, problems like cracking or delamination of the film were observed. Only for films with thickness measuring to 4-7 μm , no defects were observed. When nanoparticle based DSC of similar thickness was compared with the nanofibrous DSC, the J_{sc} and V_{oc} were higher for the nanofibrous DSC. For nanoparticle DSC, the optical density criterion was not satisfied and as a result yielded lower current density. Whereas the nanofiber with its unique morphology comprising of nanofibrils provided more surface area for dye loading and thereby exhibited higher J_{sc} . The higher V_{oc} of the nanofiber based DSC is attributed to its morphology resulting in confining the electrons within the core of the nanofiber thereby suppressing charge recombination. These characteristics of the nanofibers were also in agreement with the EIS data. From EIS it was observed that the nanofibers exhibited lower resistance to charge transport within the TiO_2 film while the resistance to recombination of injected electrons with the oxidized species of the electrolyte was higher which resulted in a charge collection efficiency of 99 %. However, as these films' full potential is bottlenecked by its lower thickness, the low dye loading restricts the attainment of higher solar to electric conversion efficiencies. So for just 3 μm , an electrochemical conversion efficiency of 4.4 % was attained.

In order to increase the photon harvesting efficiency of nanofibers, the morphology was conscientiously modulated to achieve 3D hierarchical nanostructures which comprised of small single crystalline rutile nanorods on the anatase nanofibers. These nanostructures were obtained by solvothermal treatment to the as-spun nanofibrous substrates and they improved the surface area of the electro-spun nanofibers which is beneficial for greater dye loading. For a reaction time of 1 h, nanorods with optimal length, width and density were obtained. These

nanorods were tetragonal having square faceted tips. The hierarchical based DSCs outperformed the nanofiber based DSCs owing to higher J_{sc} and V_{oc} . The higher J_{sc} was attributed to the higher surface area provided by the nanorods shooting perpendicular from the nanofiber base. The higher V_{oc} was explained in terms of higher resistance to charge recombination observed from EIS measurements. The higher V_{oc} observed is because the presence of larger number of dye molecules anchored to the nanorods provided a compact packing thereby screening the injected electrons from recombining with the oxidized species of the hole transporting material.

Owing to the complexity and acidic nature of solvothermal route for the synthesis of hierarchical nanostructures required for enhancing light harvesting, a simpler route of co-sensitization was employed. By co-sensitizing the nanofibers firstly with D35 chromophore followed by sequentially sensitizing them with D131 sensitizer, a photoelectrochemical conversion efficiency of 5.7 %. The efficiency attained with co-sensitization is higher than what was observed for D35 sensitized ($\eta = 4.59\%$) and D131 sensitized ($\eta = 4.21\%$) nanofiber DSC. The improved performance was due to the convolution of absorption by the two chromophores yielding 12.41 mA/cm^2 . The higher V_{oc} was attributed to the assembling of the small D131 dye molecules inbetween the gaps of anchored D35 dye molecules. Such a compact packing of D35 and D131 molecules passivated the TiO_2 surface and thereby prevented the recombination of electrons injected into the conduction band of TiO_2 film with the oxidized species of electrolyte. These results were further confirmed by the charge recombination resistance values obtained from EIS measurements with the co-sensitized cell exhibiting higher resistance to charge recombination. The light harvesting efficiency of the nanofiber

based solar cells was improved dramatically when they were sensitized with an organic-inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite whose absorption coefficient is one order of magnitude higher than the conventional organic chromophores and Ru-complexes. This feature of the perovskite enabled the usage of very thin nanofibrous films (413 nm) which eliminated the problems associated with cracking and delamination of the film from the substrate. J_{sc} of 15.88 mA/cm^2 was acquired for the first time for an as-spun, 1D nanofiber based solar cell which is a remarkable achievement in the 1D nano world. The porosity and nanofiber film thickness was tailored to maximise perovskite infiltration and light harvestation. As the nanofiber film thickness increased, a decline in the performance of the solar cell was observed with decreasing J_{sc} and V_{oc} . The nanofiber film thickness was varied as a function of time. The waning trend in J_{sc} was due to the lower perovskite loading as the percolation of perovskite was obstructed by the closing pores with increased overlapping of the nanofibers for thicker films. Whereas the loss of voltage for thicker nanofibrous films observed was attributed to the increased trap assisted recombination which arises from increase in surface area.

In conclusion, the 1D electrospun nanofibers display good charge collection efficiency in both liquid as well as in solid state DSCs and therefore can be advantageous for devices where charge diffusion and infiltration of viscous components is a challenge. The field assisted charge transport in 1D nanofibers is crucial in improving voltage losses. The poor light harvesting efficiency and challenges associated with the adhesion of the nanofibrous photoanodes are addressed by the utilization of sensitizers with high absorption coefficients like $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$.

5.2 Future Outlook and recommendations

During the planning, execution and analyses of this thesis work, two individual aspects of the nanofibrous photoanodes need to be investigated for providing comprehensive practical and theoretical knowledge for making the electrospun nanofibrous DSCs a viable candidate for highly efficient solar cells. Firstly insight into the physics of light transmission through the nanofibers need to be studied in order to design efficient nanostructured solar cell. Secondly, alternative non-aqueous and economical approaches to synthesize high quality, crystalline one dimensional nanostructures need to be explored.

5.2.1 Investigation of geometry and coverage of electrospun nanofibers on photon propagation for a nanofibrous DSC by finite difference time domain (FDTD) simulation.

Though the light harvesting efficiency of the nanofibrous solar cells has been improved considerably, the effect of the nanofibers' diameters, length, porosity and their distribution on the physics of photon propagation and photon-matter interaction was not scrutinized. With the help of various optical simulation techniques such as the finite element method (FEM), finite difference time domain simulations (FDTD), wavelet methods, finite integration technique (FIT), rigorously coupled wave analysis (RCWA), plane wave expansion methods (PWE), these photo-physical properties can be reviewed^[111]. Among these, FDTD technique is widely popular and used by various researchers to analyze the light propagation, radiation and scattering in nanodevices as it is a faster, accurate and efficient

full wave resolver technique. Using FDTD, three dimensional (3D) Maxwell's time dependent curl equations are resolved to analyze the light-matter interactions where the photon is considered as an electromagnetic wave propagating into a space containing conducting or dielectric structure. By providing the boundary conditions pertaining to the length, diameter and spacing of the nanofibers, the optical properties of these solar cells can be determined. The following nanofiber configurations need to be investigated using FDTD to design device with optimized configuration exhibiting minimum photon losses:

1. Nanofibers with smaller diameter followed by electrospinning of nanofibers with larger diameter: This architecture should combine the advantages of both the diameters of the nanofibers with the smaller ones contributing to dye adsorption while the larger ones contribute to scattering of light within the film. With the help of FDTD simulation, the diameters of the lower and upper layers can be varied and the light propagation can be inspected.
2. Porosity and distribution of nanofibers: Using FDTD simulation, the distance between the overlapping nanofibers can be varied leading to bigger or smaller pores in between the nanofibers. This simulation will enable us to investigate the optimum porosity required for efficient dye loading.

Thus these types of studies are useful in determining and designing the structural features which contribute less to loss of photons either by excessive scattering or shadowing by the larger and overlapping nanofibers.

5.2.2 Alternative approaches for synthesis of single crystalline, 1D nanostructures

As discussed in previous sections, the as-spun electrospun nanofibers exhibited good charge dynamics and the high resistance to charge recombination exhibited was attributed to its morphology causing band bending which confined the electrons within the core of the nanofiber. However these nanofibers are polycrystalline in nature and reproducing nanofibers with similar fiber diameters which are well-connected is highly subjective of the surrounding environmental factors like humidity and vapor pressure. This results in a low yield of good quality nanofibrous photoanodes and poor reproducibility in cell performance. As such other approaches to synthesize single crystalline, anisotropic and high quality 1D nanostructures should be investigated and some of the approaches are listed below.

1. Vapor-liquid-solid growth (VLS): In this approach, a liquid alloy droplet is prepared on the substrate and the substrate is introduced to vapor which adsorbs on to liquid surface and diffuses into the droplet. Then nanowires are grown by the supersaturation and nucleation occurring at the liquid/solid interface. The advantages of synthesizing nanowires through catalyst patterning, controlling the orientation of the nanowires by substrate selection, conforming the morphology by varying temperature and pressure and the feasibility of forming hybrid nanowires make this technique unique and widely accepted. However as this process is carried out in high vacuum, it is not a cost effective approach.
2. Thermal evaporation (TE): TE involves a simple setup where a dual zone furnace is used where the hot end of the furnace is used for evaporating the

material and the cold part where the evaporated particles nucleate and grow. The evaporated particles are transported by carrier gas and the substrates at this end are generally kept at lower temperatures (210-180 °C).

3. Laser assisted growth (LAG): This method is extremely useful in depositing materials with high melting points without the usage of high temperatures for evaporating the materials as the high intensity of the incident laser pulse causes the material to sublime or to form plasma. The target material absorbs the laser pulse energy, evaporates and nucleates on the substrate and grows into high quality nanowires. The deposition can take place either in vacuum or in presence of carrier gases like oxygen to form metal oxide nanostructures.
4. Molecular beam epitaxy (MBE): Another approach to grow high quality nanowires is by MBE where the target materials are heated in separate quasi Knudsen cell and then these gaseous atoms condense on the substrates. The deposition rates are very slow leading to formation of epitaxial nanostructures. As this process takes place in a high vacuum environment the quality of the epitaxially grown nanowires is superior to other approaches but on the other hand, the high vacuum requirement makes it an expensive approach.

Thus with these approaches high quality 1D nanowires with tunable dimensions can be synthesized and the low surface area issue associated with the 1D nanowires can be resolved by sensitizing them with the high absorption coefficient materials like methyl ammonium lead iodide perovskite materials where surface area is not an issue.

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Appendix A

List of abbreviations

DSC(s)	Dye-sensitized solar cell(s)
ssDSC(s)	Solid State Dye-sensitized solar cell(s)
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
IPCE	Incident photon to current efficiency
I-V	Current-voltage
J-V	Current density-voltage
FTO	Flourine doped tin oxide
TiO ₂	Titanium dioxide
PVP	Polyvinylpyrrolidone
CH ₃ NH ₃ PbI ₃	Methyl ammonium lead iodide
Ru	Ruthenium
ZnO	Zinc oxide
SnO ₂	Tin dioxide
Nb ₂ O ₅	Niobium oxide
Al ₂ O ₃	Aluminum oxide
FRET	Frster resonance energy transfer
ERD	energy relaying dyes

List of abbreviations

I ₂	Iodine
LiI	Lithium Iodide
ACN	Acetonitrile
EIS	Electrochemical impedance spectroscopy
SEM	Scanning electron microscopy
FESEM	Field emission scanning electron microscopy
XRD	X-ray diffraction
UV-Vis	Ultraviolet visible
AM	Air mass
AC/DC	Alternating/direct current
R _{ct}	Recombination resistance
C _μ	Chemical capacitance
CDCA	Cheno Deoxy Cholic acid

Appendix B

List of publications

- (1) Sabba Dharani, Hemant Kumar Mulmudi, Natalia Yantara, Pham Thi Thu Trang, Nam Gyu Park, Michael Grätzel, Subodh G. Mhaisalkar, Nripan Mathews, Pablo P. Boix. High efficiency electrospun TiO₂ nanofiber based hybrid organic-inorganic perovskite solar cell, *Nanoscale* 2014, 6, 1675-1679.
- (2) Dharani Sabba*, Anurag Krishna*, Hairong Li*, Jun Yin, Pablo P. Boix, Cesare Soci, Subodh G. Mhaisalkar, Andrew C. Grimsdale. Novel hole transporting materials Based on triptycene core for high efficiency mesoscopic perovskite solar cells, *Chemical Science* 2014, 5, 2702-2709.
- (3) Dharani Sabba, Shweta Agarwala, Stevin S.Chen Shi (Dr) Pramana, Subodh G. Mhaisalkar. A maskless approach towards hierarchical growth on TiO₂ nanofibers for enhanced surface area and suppressed charge recombination in solid-state dye sensitized solar cells, *Nanoscale Res Lett.* 2014, 9(1) 14.
- (4) Dharani Sabba, Nripan Mathews, Julianto Chua, Stevin S. Pramana, Hemant K. Mulmudi, Qing Wang, Subodh G. Mhaisalkar. High-surface-area, interconnected, nanofibrillar TiO₂ structures as photoanodes in dye-sensitized solar cells, *Scripta Materialia* , Volume 68, Issue 7, 2013, 487-490.
- (5) Dharani Sabba, Herlina Arianita Dewi, Rajiv Ramanujam Prabhakar, Tom Baikie, Chen Shi, Pablo. P. Boix, Nripan Mathews, Subodh G. Mhaisalkar. Incorporation of Cl in sequentially deposited lead halide perovskite films for highly efficient mesoporous solar cells, submitted to *Nanoscale*.
- (6) Guichuan Xing, Nripan Mathews, Swee Sien Lim, Natalia Yantara, Xinfeng Liu, Dharani Sabba, Michael Grätzel, Subodh G. Mhaisalkar, Tze Chien Sum. Low-temperature solution-processed wavelength-tunable perovskites for lasing,

Nature Materials 13, 476-480, 2014.

(7) Mulmudi Hemant Kumar, Dharani Sabba, Wei Lin Leong, Pablo P.Boix, Rajiv Ramanujam Prabhakar, Tom Baikie, Chen Shi, Hong Ding, Ramesh Ramamoorthy, Mark Asta, Michael Grätzel, Subodh G. Mhaisalkar, Nripan Mathews. Lead-free halide perovskite solar cells with high photocurrents realised through vacancy modulation, accepted in *Advanced Materials*.

(8) Teck Ming Koh, Dharani Sabba, Hairong Li, Rajiv Ramanujam Prabhakar, Nripan Mathews, Andrew C. Grimsdale, Subodh G. Mhaisalkar. Cobalt dopant with deep redox potential for organometal halide hybrid solar cells, accepted in *Chem Sus Chem*.

(9) Chen Shi, Goh Teck Wee, Dharani Sabba, Julianto Chua, Nripan Mathews, Alfred Huan, Sum Tze Chien. Energy level alignment at the methylammonium lead iodide/copper phthalocyanine, accepted in *APL Mater*.

(10) Mulmudi Hemant Kumar, Natalia Yantara, Dharani Sabba, Michael Grätzel, Subodh Mhaisalkar, Pablo P. Boix, Nripan Mathews. Flexible, low-temperature, solution processed ZnO-based perovskite solid state solar cells, *Chem. Commun.* 2013, 49, 11089-11091.

(11) Loc H. Nguyen, Hemant K. Mulmudi, Dharani Sabba, Sneha A. Kulkarni, Sudip K. Batabyal, Kazuteru Nonomura, Michael Grätzel, Subodh G. Mhaisalkar. A selective co-sensitization approach to increase photon conversion efficiency and electron lifetime in dye-sensitized solar cells, *Phys. Chem. Chem. Phys.* 2012,14, 16182-16186.

(12) Xincun Dou, Dharani Sabba, Nripan Mathews, Lydia Helena Wong, Yeng Ming Lam, Subodh Mhaisalkar. Hydrothermal synthesis of high electron mobility Zn-doped SnO₂ nanoflowers as photoanode material for efficient dye-sensitized solar cells, *Chem. Mater.* 2011, 23 (17), pp 3938-3945.