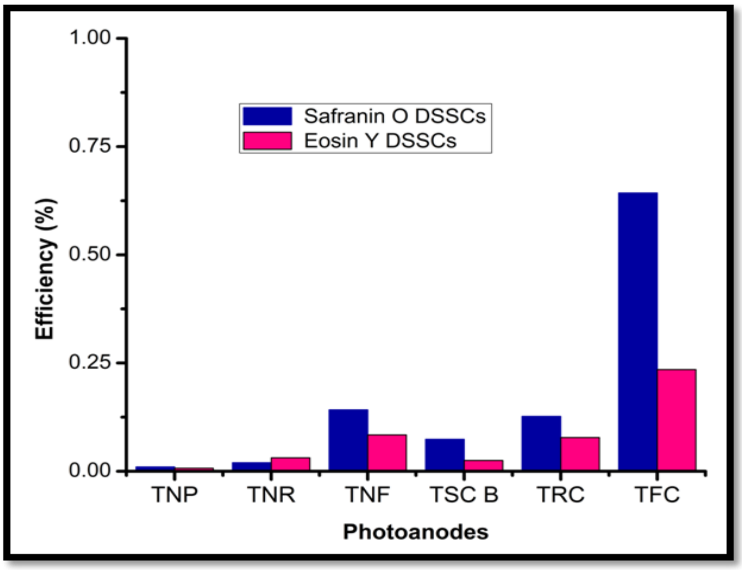
Chapter V- CONCLUSIONS AND FUTURE DIRECTIONS

This chapter presents the concluding remarks of the research work highlighting the important findings made. Further, our outlooks of the future scope of research in advancement of highly proficient TiO_2 based photoanodes for cost-effective dye-sensitized solar cells, is also presented herein.



5.1 Conclusions

In recent years, extensive research well focused on the development of photovoltaic devices with equitable efficiency has been undertaken. The Dye Sensitized Solar Cells (DSSCs) is considered as a promising and viable energy solution as it is an eco-friendly, simple and cost-effective technology for solar energy conversion. The main objective of the present work was to fabricate a simple and low cost DSSC using organic dyes based on multidimensional TiO_2 nanostructures. The experimental section of the research work was designed accordingly and the results thus derived were presented and discussed elaborately in the thesis. Thus, the research work undertaken could be termed as an exploration in pursuit of the key contributory factors influencing the performance of TiO_2 based DSSCs. The study was further extended in order to understand and elucidate the role of each of these parameters in improving cell performance by determiningthe desired optimization values.

- TiO_2 nanoparticles and TiO_2/Cu-SnO_2 nanocomposites were synthesized via a facile sol-gel method. FESEM investigations of the TiO_2 based nanostructures were done to identify the evolved morphology. It was found that TiO_2 nanoparticles are formed in the nano regime consisting of large agglomerates. However, on forming composite using 1 wt % Cu doped SnO_2 with different molar ratios, the samples occurred with nanoparticle nature of lesser agglomeration and reduced particle size. The sample with highest percentage of SnO_2, exhibited poradic rod or triangular shaped nanoparticles with almost nil agglomeration. This clearly depicts that the introduction of SnO_2 has had a marked morphological impact on the TiO_2 nanoparticles. One and three dimensional nano architectures were synthesized using hydrothermal method. 1D TiO_2 nanostructure formation was established with rod formation on ITO substrates with rod diameters in the nanoscale range, whereas 3D nanostructures reveal a flower-like architecture comprising of rods with lengths in micro scale. A sheet like layer formed over the 1D and 3D nanostructures was evident in the FESEM images in the case of TiO_2/SnO_2-Cu nanocomposite wherein the composite layer was obtained by spin coating.

- EDAX analysis suggested that in the case of all multidimensional nanostructures under study, such as 0D, 1D and 3D structures only Ti and O elements are present. For the TiO_2/SnO_2-Cu nanocomposites with different molar ratios, constituents such as Ti, Sn, O and Cu were present and the same result was observed in the nanorod and nanoflower architectures coated with plasmon mediated SnO_2. All the samples evidenced high level of purity and no traces of impurities were detected.

- HRTEM characterization was performed for an insight into the microstructural properties of the synthesized nanostructures at an atomic scale. It is well evident from the figures that TiO_2 nanoparticles and composites were formed in more or less in a spherically agglomerated nature and their particle sizes were concurrent with the XRD results. Nanorod and nanoflower structures were clearly evident in the TEM images and at higher magnifications each nanoflower is seen to consist of nanorods growing evenly and radially from the center.
- The XRD pattern of TiO_2 confirms the formation of anatase phase and the results are in excellent agreement with a reference pattern (JCPDS 21-1272) of titanium dioxide. The average crystallite size was found to be 15 nm using Scherrer's equation. Compared with pristine TiO_2, the as-prepared Cu supported TiO_2/SnO_2 samples exhibited characteristic peaks of both TiO_2 and SnO_2. Peaks characteristic of Cu could not be detected inthe composite samples due to its low concentration (1 wt%). It was further observed that upon introduction of SnO_2 nanoparticle in the pure TiO_2 system, the anatase phase of TiO_2 was replaced with rutile phase. 1D nanorod and 3D TiO_2nanoflower structures confirmed the presence of tetragonal rutile phase which is consistent with the JCPDS card no (89-4920). Cu supported TiO_2/SnO_2 nanorod and nanoflower structures evidenced the existence of rutile phased peaks of both TiO_2 and $SnO_{2.}$

- The average crystallite and particle size calculated from both XRD and FESEM investigations revealed that on plasmon incorporation, the grain sizes reduced, thus paving the way for an enhanced surface area, which would in turn favor better dye absorption and thereby improve the sample's light harvesting properties.
- XPS measurements were performed to analyze the surface composition and chemical structure of the synthesized samples. The survey spectra of the TiO_2 nanostructures presented signals originating from O, Ti and C elements, whereas metal oxide supported samples exhibited additional peaks corresponding to Sn element. A shift is observed in the binding energies of the as-synthesized samples owing to their variantstructures.
- The photovoltaic activity of nanoparticles is highly related to their surface properties. BET analysis indicated that all the synthesized samples exhibited type IV isotherm patterns with distinct hysteresis loop, confirming the presence of mesopores in the samples according to the IUPAC nomenclature. The BET surface area of the unmodified TiO_2 was found to be about $37 m^2/g$, and for TiO_2/SnO_2-Cu nanocomposite obtained with 1wt% Cu in SnO_2, the surface area initially enhanced enormously to 87 m^2 /g, and gradually fell to 61 m^2 /g and 13 m^2 g with increasing concentrations of SnO_2. BET surface area was calculated as 4 m^2/g and 8 m^2/g from the adsorption curves of nanorod and nanoflower

morphologies respectively. With further coating (Cu/ SnO_2) of one and three dimensional TiO_2 nanostructures, the surface area increased to 8.12 m^2/g and 11 m^2/g for nanorod and nanoflower morphologies.

- The optical behavior of the as-synthesized samples was determined using UV- Diffuse reflectance spectroscopy. The absorption edge of TiO_2 sample occurred around 380 nm in the UV region which is the characteristic of TiO_2 owing to its intrinsic band-band transitions. The diffuse reflectance spectra of all the composite samples showed increased absorption edge in the range of 300 nm to 370 nm. It is also seen that Cu doping in SnO_2 resulted in better absorption across the visible spectrum indicating enhanced photon absorption due to the SPR effect and also an increased probability of electron transition due to the addition of SnO_2 to TiO_2.
- The Kubelka–Munk (K-M) function is used to calculate the band gap of all the prepared samples. We observed a linear increase in band gap energy values from 0D to 1D to 3D nanostructures. Nevertheless further coating or composite formation leads to decrease in their energies. This essentially suggests that band gap narrowing has occurred and therefore the probability of charge carrier generation and transportation is found to be more in the composite architectures.

- By analyzing the optical properties of multidimensional TiO_2 nanostructures, we could anticipate that the nanoflower morphology irrespective of additional coating would increase the solar cell performance by replacing conventional nanoparticulate films because of its excellent light scattering ability.
- FTIR spectrum analysis confirmed the formation of metal oxide (TiO_2) in the bare, composite and plasmon supported SnO_2/TiO_2 nanostructured samples. The shoulder observed at 690 cm^{-1} may have been due to the vibration of the Ti–O–O bond. A strong band in the range of 900 cm^{-1} and 500 cm^{-1} was associated with the characteristic modes of Ti-O-Ti bond confirming the presence of TiO_2 phase. The absorption occurring at 600-620 cm^{-1} corresponds both to (Ti-O and Ti-O-Ti) and to (Sn-O and Sn-O-Sn) stretching thereby confirming the formation of TiO_2/SnO_2 nanocomposite in the composite samples. Visible changes in positions, sizes and shapes of the composite samples' peaks evidenced the incorporation of Cu/ SnO_2 in the TiO_2 host lattice.
- The field dependent dark and photoconductivity of the samples under study exhibited a linear increase with applied electric field in both dark and photocurrents representing the ohmic nature of the samples. In all cases the photo currents were observed to be higher than the dark currents suggestive of the photo responsive phenomenon which is essential for

photovoltaic applications. Among the multidimensional TiO_2 nanostructures, nanoflower morphology exhibited the highest photoconducting behavior.

- Composite nanostructured samples possessed better dark and photocurrents than the bare TiO_2 nanostructures, and the results strongly suggested that the plasmon activated composite nanoflower morphology facilitated the formation of extra-large textural mesopores providing more efficient transport channels thereby improving cell efficiency. Further, they have served as effective light scatterers for the incoming light source thereby ensuring better photovoltaic performance.
- Twelve different prototypes of Dye Sensitized Solar Cells were fabricated using bare TiO_2 multidimensional nanostructures and SnO_2/Cu activated TiO_2 multidimensional nanostructures using two different organic dyes - Safranin O and Eosin Y dyes and their I-V characteristics were tested. The efficiencies of the fabricated solar cells were determined using the parameters measured from I-V characterization.
- In both S3 and E3 sensitized DSSCs, plasmon activated nanoflower composite (TFC) photoanode DSSC showed higher efficiency than the other nanostructured photoanodes. On comparison, Safranin O dye sensitized DSSCs employing TiO_2/SnO_2-Cu nanoflower photoanode were considered to be highly efficient, exhibiting a record efficiency of 0.64%

in laboratory conditions and hence emphatically establishing the status of TiO_2/SnO_2-Cu nanoflower as adept photoanode systems in DSSCs.

5.2 Future Directions

The research work in the present thesis has demonstrated appealing strategies to achieve superior electron collection efficiencies of dye sensitized solar cells using cost-effective organic dyes. In the current work, diverse nanostructures of bare and nanocomposite TiO_2 were successfully synthesized by hydrothermal method and were employed as photoanodes in dye sensitized solar cell applications and their efficiencies were recorded.

Based on the preliminary investigations, it is recommended that the following research work could be up taken:

- ❖ Utilization of Ruthenium based dyes in DSSCs is a subject of concern owing to its high cost and environmental hazards. Use of low cost organic and natural dyes as sensitizers would be an interesting alternative to these ruthenium complexes.
- ❖ Co-sensitization by various dyes capable of absorbing in various regions of solar spectrum is another way which could be employed to advance the performance of DSSCs. Also co-sensitization using Quantum dots and Perovskites is a possible option that may offer some explicit advantages.

- ❖ Doping of noble metals was also demonstrated to be an appealing strategy to achieve higher efficiencies for DSSC. The effect of transition and rare earth metal dopants on performance of DSSCs could be investigated.
- ❖ Nanocomposites of various metal oxides (Cu_2O, Bi_2O_3, V_2O_5, HfO_2 etc.) and non metal oxides ($CaCO_3$) could be coupled with TiO_2 and their coupling properties could be examined and compared with their bare counterparts, for DSSC applications.
- ❖ Various hierarchical nanostructures of TiO_2 could be explored and their morphological impact on DSSC performance could be examined.
- ❖ Efficiency and photoanode properties could be well tested using characterizations such as Electron Impedance Spectroscopy (EIS), FT-Raman Spectroscopy, Surface Plasmon Resonance Spectroscopy (SPR), Incident Photon to Current Conversion Efficiency test (IPCE) etc.
- ❖ Efforts can be made to develop efficient photoanodes using flexible plastic and metal substrates without compromising the DSSC efficiency and stability.

Thus, it is proposed to progress the future research work in the direction of optimizing the properties of different components of the DSSCs and their successful correlation to produce high performance photovoltaic devices and other applications extending to gas sensing, photo-catalytic activity and biomedical processes.