

**Photovoltaic Performance Analysis of Dye Sensitized Solar Cell
Based on Nanostructured TiO₂ Photoanode**

**Synopsis
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a) Brief introduction on the state of the art of the research topic

Energy is an essential need for the economic development of a nation; besides it is basic for modernization and automation. The United Nations Department of Economic and Social Affairs projected that the global population will reach 9.8 billion in 2050. It corroborates the increase in energy demand. The energy needs are mostly satisfied from fossil fuels, on a long run they are not sustainable and also vulnerable to the ecosystem. One of the alternatives is to avail energy from the renewable energy resources. Sun provides the amount of energy to the earth which is sufficient to cover energy needs for a whole year.

Dye sensitized solar cells (DSSC) are the potential candidates for the replacement of conventional silicon-based p-n junction photovoltaic (PV) devices [1,2]. Metal oxide semiconductors are extensively explored for many applications in photocatalysis, sensors, high speed memory devices [3-6]. Among several semiconductor metal oxides, anatase titanium dioxide (TiO₂) has proven to be the better material for photo-conversion efficiency [7]. Photovoltaic conversion efficiency of DSSC also depends on the factors like quantum confinement of nanostructures, thickness of the layer, coating method, sensitizer, electrolyte and counter electrode [8-12]. For the preparation of TiO₂ nanostructures, a variety of synthesis methods such as hydrothermal, solvothermal, sol-gel, direct oxidation, chemical vapour deposition, electro deposition, sonochemical, and the microwave method have been used [13-20]. In the last two decades, many studies have targeted on fabrication of TiO₂ nanostructures with desired features, but obtaining the desired morphology with a uniform size and distribution is still a challenging task to realize.

b) Definition of the problem

This is an era of artificial intelligence (AI) and internet of things (IoT). Luckily, most of the sensors and transducers require only feeble power for functioning. And most of the devices are installed and used indoors. For this condition, DSSCs can be a potential candidate as it offers better performance, when compared to conventional Si solar cells. But there are factors such as high efficiency, stability, and cost reductions are the challenges for the commercialization. These challenges mainly depend on the working electrode and counter of DSSC. The photoanode should possess high surface area to adsorb more sensitizers to harness photons from the solar spectrum. In addition, it provides a channel for the transport of electrons to reach the current collector.

Most importantly, to increase overall performance of the DSSC devices, the generated charges should be effectively collected from the sensitizer and it should avoid back electron recombination. Investigation on Pt free counter electrodes is also important to bring the cost reduction. Based on the above needed criteria, the investigation started with one dimensional nanostructure for their unidirectional charge transport, three dimensional structures, and higher surface area with cuboidal shapes. For the indoor application, the device should be able to harvest photons from visible light for better performance. In this aspect, graphitic carbon nitride has been chosen for its better visible light trapping ability, tunable bandgap and the cascading alignment of its band gap with respect to TiO_2 makes it act better in photovoltaics. Further, electro active sites present in carbon nitrides were utilized in addition with conventional conductive multiwall carbon nanotubes in the aspect of counter electrode. To improve the overall efficiency, the high electron mobility compact layer was also investigated and focused towards large area DSSC devices.

c) Objectives and Scope of the research work

The main focus of the research work is to fabricate large area DSSC devices with higher efficiency and to enhance the low power consuming devices. The following objectives were intended and achieved.

- To synthesize TiO_2 nanomaterials using the microwave method.
- To conserve the 3D morphology of TiO_2 after annealing process.
- To evaluate the performance of different concentration of SnO_2 compact layers precursor solution based photoanodes for dye sensitized solar cell.
- To study the incorporation of graphitic carbon nitride (g- C_3N_5) on working electrode towards the photovoltaic performance enhancement in dye sensitized solar cell.
- To prepare Pt free counter electrode.
- To fabricate a highly efficient TiO_2 photoanode with Pt and Pt free counter electrode based DSSC devices.
- Finally, large area working electrode has been prepared.

d) Layout of the thesis

Chapter-I

Introduction

This chapter deals with an introduction about working and counter electrodes for the fabrication of DSSC devices. Advantage and disadvantage of the microwave synthesis methods have also been discussed. It also covers the effort taken to achieve morphology conservation. It comprises the effect of compact layers on the performance of DSSC devices. It also deals with various aspects of graphitic carbon nitride materials towards

working and counter electrode performance. Importance and advantage of the screen-printing technique was also covered in this introduction. In addition, the necessities to replace the conventional Pt electrode have also been discussed.

Chapter-II

Review of Literature:

This gives a brief review on synthesis of titanium dioxide using the microwave method. In addition to that, it covers the conservation of 3D morphology of TiO_2 . The parameters of compact layers were also reviewed in detail. The review also focused on graphitic carbon nitride materials preparation, optical properties and band structures. Pt free counter electrode materials and its characterization towards electrocatalytic activity has also been reviewed. Further, it covered large area of DSSC device closed configuration assembly.

Chapter- III

Methodology:

This chapter explains the methodology of TiO_2 nanomaterial synthesis, compact layer formation, synthesis of $\text{g-C}_3\text{N}_5$ composite samples, and preparation of Pt free counter electrode and fabrication of large area devices.

Phase-I

Synthesis of TiO_2 nanomaterial using microwave method: 0.034M of titanium isopropoxide was chosen as a precursor and was added drop wise into 100 ml of glycerol under ultrasonication to make the solution homogeneously clear. The solution was kept in the microwave oven. Obtained precipitate was filtered, washed and dried. Dried powder was annealed at 450°C for 3hrs.

Phase-II

Use of urea as a N-doping and morphology preserving agent for titanium dioxide nanostructures: 0.034 M of titanium isopropoxide was added dropwise into 100 ml of glycerol under ultrasonication. Different concentrations of urea (0.3 mM, 0.6 mM, 1.25 mM, 2.5 mM and 5 mM) were added to the above mixture. The prepared mixtures were kept in a domestic microwave oven at 240W of 2.45GHz until the solution turned to white in colour. The obtained powders were dried at 80°C and annealed at 450°C for 3hrs.

Phase-III

SnO_2 compact layers preparation: 2M of stock solution was prepared by using tin (IV) chloride pentahydrate in water. After that, fluorine doped tin oxide (FTO) substrate was treated with 40, 65 and 90 mM from the 2M of stock solution at 70°C for 30 mins.

Phase-IV

g-C₃N₅ incorporated TiO₂ working electrode: 5-aminotetrazole monohydrate served as precursor for the synthesis of g-C₃N₅ and directly heated at 500°C for 3hrs. Hydrothermal method was performed to obtain TiO₂ nanoparticles. For the preparation of TiO₂@g-C₃N₅, prepared TiO₂ nanoparticles with 5-aminotetrazole monohydrate in different weight ratios were ultrasonicated for 30 mins. Thus, obtained suspension was dried using a water bath at 80⁰ C. The dried powder was calcined at 500⁰ C for 3hrs. And for g-C₃N₅@TiO₂ preparation, hydrothermal method was employed by adding different ratios of prepared g-C₃N₅ with the precursor of TiO₂.

Phase-V

Preparation of Pt free counter electrode: Graphitic carbon nitride (g-C₃N₄) was prepared by simple thermal polymerization of dicyandiamide at 550⁰ C for 2 hrs. Prepared g-C₃N₄ powder was mixed with multiwalled carbon nanotube (MWCNT) in different weight ratios.

Phase-VI

Large area DSSC Device fabrication: Pure TiO₂ and TiO₂@g-C₃N₅ (1:0.02) have been chosen to prepare screen printed photo anode. Compact layer was obtained from 40 mM of SnO₂ precursor solution. MWCNT: g-C₃N₄ (1:1) was chosen as counter electrode.

Characterization: The prepared powders and compact layer thin films were characterized using XRD, FESEM, Raman, UV analysis, BET analysis, XPS analysis, EDAX analysis, PL analysis, hall effect measurements, electrochemical impedance spectra, cyclic voltammetry and current- voltage measurements.

Chapter-IV

Results and discussion

This chapter gives detailed interpretation of results obtained in various characterization techniques.

Phase-I

Effect of microwave power irradiation on TiO₂ nano-structures and binder free paste screen printed dye sensitized solar cells

Titanium dioxide nanostructures (nanorods and nanoparticles) were prepared using a low-cost microwave irradiation method from a polyol medium of glycerol. Titanium glycerolate and TiO₂ powders were obtained in the glycerol medium for the first time with four different power densities (240 W, 480 W, 720 W, 960 W) irradiation using a domestic microwave oven of 2.45 GHz, to understand the impact of power on morphology tuning. The structural and morphological features of the titanium glycerolate and TiO₂ powders were characterized by X-ray diffraction pattern to confirm the phase and crystalline size. Morphology of the

prepared samples were characterized using field emission scanning electron microscopy (FESEM) and raman spectra was used to analyze the vibrational modes of prepared samples. TiO_2 was successfully used in the fabrication of photovoltaic devices and as a proof-of-concept of binder free paste was prepared and successfully employed for photoanode using screen printing on the fluorine doped tin oxide substrate.

Phase-II

Use of urea as a N-doping and morphology preserving agent for titanium dioxide nanostructures towards dye sensitized solar cells

3D morphologies developed using a low-cost microwave synthesis technique found in earlier research were not retained during the transformation of titanium dioxide (TiO_2) by annealing titanium glycerolate (TGy) powder, resulting in low photoelectron conversion efficiencies in dye-sensitized solar cell (DSSCs) devices. This study overcame the challenge, and FESEM imaging showed that 3D morphologies were retained after annealing via the same microwave method and the solvent system by using urea as an aid for a structure-preserving agent. The morphological tuning and N-doping resulted in the 3D hierarchical titanium dioxide nanostructures, including Gomphrena globosa flower-like and blossomed flower of Dahlia pinnata-like morphologies, and other 3D features. The diffusion of N in the TiO_2 matrix was confirmed from XPS and EDX and was also reflected in optical absorption characteristics. The binder-free TiO_2 pastes have been prepared from the synthesized TiO_2 nanopowders that were employed in the screen printing. The screen-printed photoanodes were used to assemble DSSC devices. The output performances of DSSC reveal the influence of nitrogen doping in relation to the undoped TiO_2 -based device. The globosa flower-like TiO_2 nanostructured photoanode exhibited the most pronounced enhancement in short-circuit current density and an increase in the maximum power conversion efficiency, by nearly a factor of 2 compared to pure TiO_2 .

Phase: III

Effect of SnO_2 compact layers in the performance of dye sensitized solar cell

Various concentration of SnO_2 precursor solution was prepared by using tin (IV) chloride pentahydrate in water. After that, FTO substrate was treated with 40, 65 and 90 mM from the 2M of stock solution at 70°C for 30 mins. Then it was annealed at 500°C for 30 mins. For comparison 90 mM of TiCl_4 was treated and annealed at 450°C for 30 mins. Different combinations of photoanode have been prepared using previously obtained SnO_2 compact layers on FTO plate. The prepared substrate was characterized using XRD, the electrical parameters were measured using hall effect measurements. UV transmittance was taken for bare FTO and all compact layer treated substrates. Finally, the highest efficiency of

4.53% was obtained for the SnO₂ compact layer treated from 40mM precursor solution. The pretreatment of SnO₂ as a compact layer enhances the electron transport process and reduces the recombination. The power conversion efficiency is reduced for another obtained compact layer (60mM and 90 mM). It may be due to more trap states. And these trap states tend to block the movement of photoexcited electrons from the TiO₂ layer. Moreover, thicker compact layer reduces optical transmittance and lowers J_{sc} and V_{oc}.

Phase IV:

Effect of incorporation of g-C₃N₅ on working electrode towards the photovoltaic performance enhancement in dye sensitized solar cell

High-efficiency dye-sensitized solar cells have been made by utilizing the opto-electronic characteristics of g-C₃N₅ by preparing TiO₂@g-C₃N₅ and g-C₃N₅@TiO₂ composites. The DSSC device performances are strongly dependent on g-C₃N₅ content. The incorporation of optimum amount of g-C₃N₅ in the composite material enhanced the short circuit photocurrent density, and a decrease in V_{oc} was evidenced. The excess loading of g-C₃N₅ in either composites, when compared to the critical amount of g-C₃N₅ may disrupt the effective connection between TiO₂ nanoparticles and FTO substrate. The noted increase in efficiency of composite samples is due to the presence of g-C₃N₅. This may be due to the cascading of band alignment, which may act as a blocking layer to reduce the loss of photogenerated electron recombination. In addition to that, efficient dye loading and comparable diffused reflectance with respect to pure TiO₂ might also have contributed to the enhancement of device performance.

Phase V:

Performance analysis of Pt free counter electrode

Prepared g-C₃N₄ powder was mixed with multiwalled carbon nanotube (MWCNT) in different weight ratios. MWCNT/ g-C₃N₄ (1:1) counter electrode showed an improved photovoltaic performance with J_{sc} of 13.16 mA/cm², V_{oc} of 0.75V, and FF of 0.54 with an efficiency of 5.41%. The synergetic photovoltaic performances of MWCNT and g-C₃N₄ counter electrode was evidenced because, this optimum content provides a medium for electro-active sites and electron transport. Therefore, MWCNT/g-C₃N₄ (1:1) counter electrodes can be used as an alternative to Pt counter electrodes in DSSC.

e) Paper published

1. Effect of microwave power irradiation on TiO₂ nano-structures and binder free paste screen printed dye sensitized solar cells, **J. Vinodhini**, J. Mayandi, R. Atchudan, P. Jayabal, V. Sasirekha, J.M. Pearce, *Ceramics International*, 2019, 45, 4667-4673.

2. The use of urea as an N-doping 3D hierarchical preserving agent for titanium dioxide nanostructures tailored for dye-sensitized solar cells **Vinodhini Jayapal**, Selvapriya Rangasamy, Sasirekha Venkidusamy, Ragavendran Venkatesan, Jeyanthinath Mayandi, Joshua M. Pearce, International journal of energy research, 2022, 46, 9533-9548.

f) Conclusion

The microwave-driven method was adopted for the synthesis of TiO₂ nano powder. 3D hierarchical flowers like TiO₂ nanostructures have been successfully obtained with urea as a morphology tuning/conserving agent. The different weight ratios of the TiO₂@g-C₃N₅ sample shows lower charge transfer resistance compared to other samples implying better charge transfer and produces a lower electron backward recombination process. Increase in photocurrent density was observed in composite samples which are having the critical amount of g-C₃N₅ content was due to the cascading of band alignment, which may act as a blocking layer to reduce the loss of photogenerated electron recombination. In addition to that, efficient dye loading and comparable diffused reflectance with respect to pure TiO₂ might also have contributed to the enhancement of device performance. MWCNT/ g-C₃N₄ exhibited better performance in the counter electrode by showing two typical pairs of peak current density. SnO₂ compact layer has been prepared using different concentrations of precursor solution. The highest efficiency of 4.53% was obtained for the SnO₂ compact layer treated from 40mM precursor solution. Finally, 10.22 % efficiency was achieved from Pt based counter electrodes and an efficiency of 6.73% was obtained from Pt free counter electrodes. Large area working electrode has been prepared.

g) References

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