Chapter 6

Dye Sensitized Solar Cell based on SnS Nanoparticles

Since the beginning of the recent century, the situation of energy crysis has experienced a serious challenge. Therefore, the demand for energy in the world is increasing rapidly [253-254]. The semiconducting nanocrystals have several important applications in the field of photovoltaic and optoelectronic devices such as light emitting diodes (LED), heterojunction solar cells, dye sensitized solar cell (DSSC), photo detectors, biosensors etc [238,240,255]. Therefore, SnS nanoparticles are significant and promising material in the discipline of optoelectronic devices and technology [256]. Dye sensitized solar cells (DSSCs) are promising due to their light weight, high efficiency, easy fabrication method, pollution-free nature and low cost photovoltaic device used for power invention from non-conventional energy resources [257-258].

Natural dye-sensitized solar cell is a promising alternative PV for economical energy production. Dye-sensitized solar cell (DSSC) is a marvellously idea as like as natural photosynthesis. In photosynthesis process chlorophyll absorbs photons but does not contribute in charge transfer mechanism [259]. These dyes are obtained from extracts of papaya leaves [260], hibiscus [260], red cabbage [262] and red rose [263] etc. The basic principle of dye is to absorb light, transfer electrons into the conduction band of sample, and then collect electrons from the electrolyte solution [263]. Anthocyanins are natural complex which are generally found in flowers, fruits as well as leaves of plants such as blue pea, strawberries, blackberries and Lawsonia inermis leaves [264-266]. Besides, Anthocyanin is a natural as well as water soluble pigment.

DSSCs exchange the photon energy from solar light to the electrical energy. For the fabrication of DSSCs, our main focus is to improve the electron transfer and to reduce recombination rate. Dye-sensitized solar cells usually composed of a dye sensitized photoanode, a redox (iodide/triiodide) electrolyte solution, a transparent conductive oxide coat that assists to transfer of charge from the electrode layer, graphite paint on ITO coated glass which works as a counter electrode (CE). Usually natural dyes are applied in photovoltaic solar cell. Anthocyanin solution which is called natural dye is found in the plants leaves and flowers used as a photosensitizer to enhance the efficiency of the fabricated solar cells. In this work, anthocyanin (natural dye) has been extracted from Acalypha Wilkesiana leaves.

6.1. Fabrication and Characterization of Natural Dye Sensitized Solar Cells based on SnS

Pure SnS, Fe doped SnS and Mn doped SnS have been synthesized by wet chemical precipitation technique to construct an economical dye sensitized solar cells (DSSCs). The research study represents the fabrication and characterizations of SnS, Fe-SnS and Mn-SnS nanoparticles based natural dye sensitized solar cells. Our main target is to increase the power conversion efficiency of the fabricated solar cells. Thus, Acalypha Wilkesiana leaf extract was used natural dye which acts as photo sensitizers. The fabricated solar cells were characterized through J-V study under the illumination of 100 mW/cm^2. Open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) as well as power conversion efficiency (η) were also studied. The power conversion efficiency of SnS, Fe-doped SnS and Mn-doped SnS based natural DSSCs were found to be 1.34%, 1.43% and 1.47% respectively.

6.1.1. Experimental section

6.1.1.1. Preparation of samples

Undoped SnS, Fe-doped and Mn-doped SnS were synthesized by simple wet chemical precipitation method. Tin chloride dihydrate ($SnCl_2.2H_2O$), Sodium sulfide ($Na_2S.\ XH_2O$), Triethylamine [N ($CH_2CH_3)_3$] (TEA), Iron (III) chloride anhydrous ($Fecl_3$), Manganese (II) chloride tetrahydrate ($Mncl_2.4H_2O$) was used to prepare pure SnS, Fe doped and Mn doped SnS at room temperature. The technique of sample preparation and its various characterizations were described in chapter 3.

6.1.1.2. Preparation of natural dye sensitizer

Acalypha Wilkesiana leaves were collected from the garden of Vidyasagar University, West Bengal, India for the preparation of dye solution. These leaves are cleaned and washed with deionised water for few times and situated in a vacuum furnace for 1 hour to dry the leaves. After that the leaves are crushed with a porcelain mortar and pestle. The crushed leaves are dipped into 50 ml ethanol taken into a beaker for 30 minutes. After extraction, the crushed samples are then filtered with filtered paper. Now this is the prepared Anthocyanin solution which is called natural dye used as photosensitizers which may enhance the solar cell efficiency.

6.1.1.3. Fabrication of Dye Sensitized Solar Cells

0.3 gm of pure SnS, 0.3 gm of Fe doped SnS and 0.3 gm Mn doped SnS nanoparticles are added individually with 0.6 mL acetic acid and grinded in mortar to make lump free pestle. A uniform thin layer of pure SnS, Fe doped SnS and Mn doped SnS pastes were deposited on the conducing face of ITO glass. Then these ITO glasses are put on the top of a hot plate and heated at approximately 45 °C for one hour. After that the conductive glasses are allowed to cool to room temperature. The ITO glasses are dipped into the prepared dye solution for 45 minutes. The graphite paint has been used to coat another ITO glass as a counter electrode.

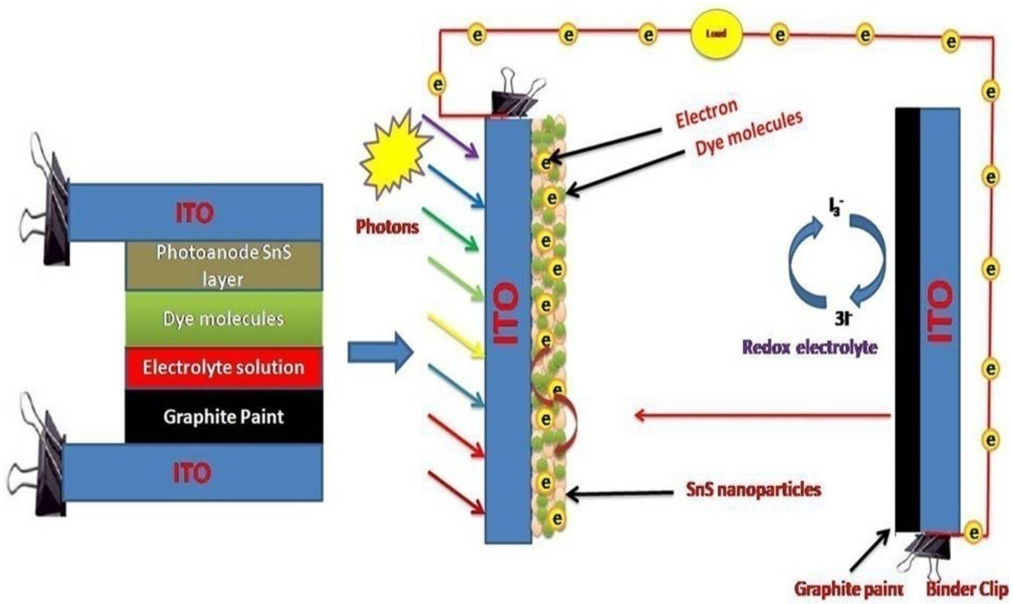

Fig. 6.1.1. Structure of the fabricated solar cell (left) and charge transfer mechanism (right) of fabricated dye sensitized solar cell.

Then the two electrodes are clipped together using binder clips. A redox electrolyte solution has been prepared using 0.3 mol of KI and 0.03 mol of I_2. Finally, few drops of redox electrolyte solution were introduced into the junction of clipped ITO glasses. This redox electrolyte solution was used as charge transfer agent. The structure of the fabricated dye sensitized solar cell is shown in the left side of fig.6.1.1.

6.1.2. Charge transfer mechanism

The fabricated dye sensitized solar cells consist of SnS layer performing as the electron carrier whereas the dye molecules layer acting as the electron generator. This will recuperate to its initial state through the electrons provided by the electrolyte KI solution. When the photons from sunlight falls on the fabricated Dye sensitized Solar Cell (DSSC), then the dye molecules absorb the incident photons. Hence absorbed dye molecules get stimulated from their initial state to an excited state (dye*). Then excited high energetic dye molecules are quickly oxidized and split the surface of SnS layer. The excited state of the dye can be thought of as an electron-hole pair. The excited dye transfers an electron to the semiconducting SnS layer (electron injection) and a hole to the electrolyte. This separates the electron-hole pair leaving the hole on the dye (dye^{*+}). Therefore, the electrons travel without any barrier through the SnS layer and reach at the collector of the anode (ITO) by a sequence of interparticle steps. Then the electrons flow through an external circuit to reach at the counter electrode (CE). After that, the electrons are transported to the electrolyte KI solution where they reduce the oxidant dye agent with the help of catalyst. Therefore, the created reducing agent reduces the stimulated dye molecules (dye*) to the initial state (dye) through a complete cycle. The transferred electrons in the photoanode then recombine with the oxidized dye molecules before the reproduced of dye or the redox pair can stop to transfer an electron from the photoanode before the collection of electrons. The reaction mechanisms within the DSSCs are described as follows [267]:

$$\text{Dye} + h\nu \rightarrow \text{Dye}^*$$

$$\text{Dye}^* + \text{SnS} \rightarrow \text{SnS}^{\bullet} + \text{Dye}^{+}$$

$$SnS^{\bullet} + CE \rightarrow SnS + CE^{\bullet} + Energy$$

$$Dye^{+} + I^{-} \rightarrow Dye + I_3^{-}$$

$$I_3^{-} + CE \rightarrow I^{-} + CE$$

Generally: hν (photon) → Energy

(CE is the counter electrode)

The schematic diagram as well as charge transfer mechanism of the fabricated solar cell is also described in the right side of the fig. 6.1.1.

6.1.3. Material characterization

Fe-doped SnS, Mn-doped SnS and pure SnS paste was uniformly deposited on the conducing surface of ITO glass. Graphite paste has been used as an ohmic contact to coat another ITO glass for J-V study. Finally, the current density-voltage (J-V) data of the fabricated dye synthesized solar cells (DSSCs) were recorded with a keithley electrometer (6514) under illumination with white light of intensity 100 mW/cm^2.

6.1.4. Results and discussion

6.1.4.1. Performance of DSSCs

The fabricated SnS, Fe doped SnS and Mn doped SnS DSSC solar cells have been sensitized using Acalypha Wilkesiana leaf extract as a photo sensitizer. Current density (J) vs. voltage (V) as well as power density (P) vs. voltage (V) graph was performed under visible light radiation to characterize the fabricated solar cells. The electrical parameters such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and maximum power density (P_{max}) were calculated from the current density (J) vs. voltage (V) characteristics curves of the fabricated DSSCs under illumination. Fig. 6.1.2 (a) shows the variation of current density (J) with the applied voltage (V) of the fabricated undoped as well as doped DSSCs under visible radiation. It is seen that the current density of the fabricated Mn doped SnS DSSC is greater than the pure as well as Fe doped SnS NPs based DSSCs and therefore increased in efficiency. The small value of current density of the fabricated pure SnS as well as Fe doped SnS based DSSCs can be thought of recombination of charge carrier at the grain boundaries and the existence of sulfur ion vacancies [268].

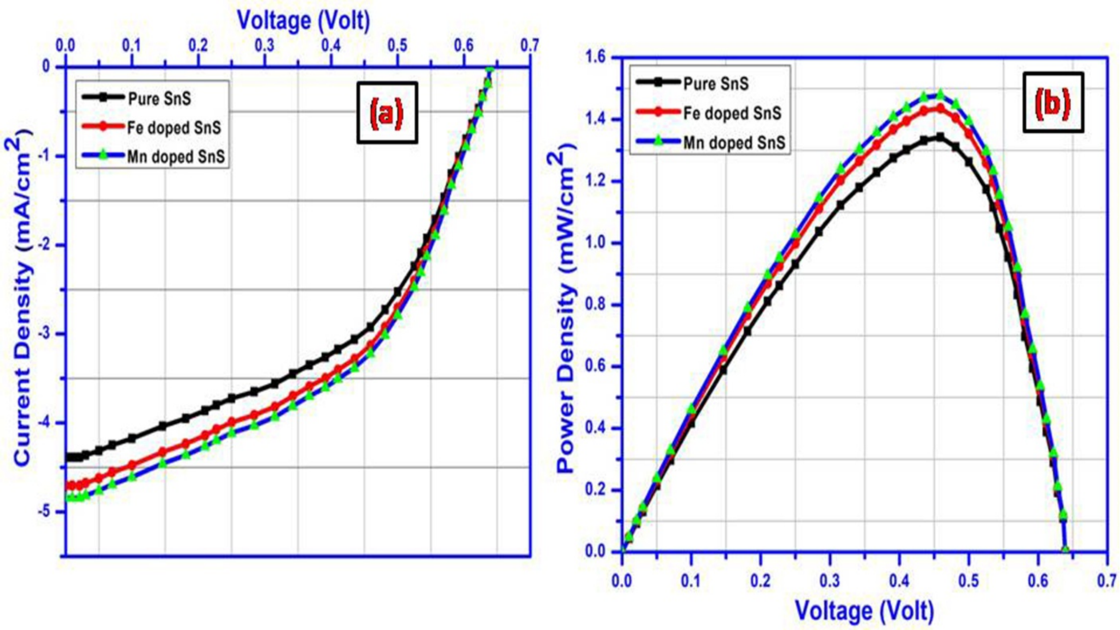

Fig. 6.1.2. (a) J-V study of pure SnS and doped SnS based DSSCs (b) Variation of power density with applied voltage of pure SnS and doped SnS based DSSCs.

The increase in current density of Mn doped SnS based DSSC is due to the increase in particle size. With increase in crystal size, the surface states decrease which increases the current density. The increase in current density of Mn doped SnS based DSSC is probable due to production of large number of electron-hole pairs. Therefore, the Mn doping with SnS NPs could enhance the light to power conversion efficiency by establishing localized bands which assist the development of charge transfer [268]. The graphical presentations of power (P) vs. applied voltage (V) of pure as well as doped samples are shown in fig. 6.1.2(b). The fill factor and the power conversion efficiency can be calculated from the following relations

$$FF = \frac{V_{mp}J_{mp}}{V_{oc}J_{sc}} \qquad (6.1.1)$$

$$\eta = \frac{J_{sc}V_{oc}}{P_{in}}FF \qquad (6.1.2)$$

Where, V_{mp}, J_{mp} are the voltage and current density at maximum power respectively. V_{oc}, J_{sc} are the open circuit voltage and short circuit current respectively. P_{in} is the incident power. η is the power conversion efficiency. The power conversion efficiency (η%) of pure SnS, Fe doped SnS and Mn doped SnS were found to be 1.34%, 1.43% and 1.47% respectively. A comparison of electrical parameters of the fabricated DSSCs with other reported work is described in the table 6.1.1.

Table: 6.1.1

Comparison of electrical parameters of the fabricated natural DSSCs with other reported work

Sample Name	Dye Solution	V_{max} (V)	J_{max} (mA/cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (FF)%	Efficiency (η)%	References
TiO_2	Red cabbage	-	-	0.47	4.38	36	0.73	[262]
TiO_2	Blue pea	-	-	0.45	4.16	35	0.67	[262]
TiO_2	Red rose	-	-	0.48	4.57	36	0.81	[263]
ZnO	Jamun	-	-	0.58	1.56	58	1.23	[267]
TiO_2	Lawsonia inermis leaves	-	-	0.61	1.870	58	0.66	[266]
ZnS	Acalypha wilkesiana	-	-	0.293	0.025	54	0.29	[269]
ZnS	Gerbera Jamesonii	-	-	0.13	0.011	68	0.05	[269]
CdTe	Hibiscus mutabilis	0.50	2.407	0.609	2.966	66.63	1.20	[168]
Zn-doped CdTe	Hibiscus mutabilis	0.57	2.724	0.692	3.264	68.76	1.55	[168]
CdSe NRs	Ixora chinensis petals	0.472	3.239	0.671	4.145	54.96	1.52	[270]
Pure SnS	Acalypha wilkesiana	1.347	0.9973	0.638	4.377	48.07	1.34	This Work
Fe-doped SnS	Acalypha wilkesiana	1.441	0.9975	0.638	4.686	48.06	1.43	This Work
Mn-doped SnS	Acalypha wilkesiana	1.483	0.9976	0.638	4.829	47.94	1.47	This Work

6.1.5. Conclusions

Pure SnS, Fe-doped SnS and Mn-doped SnS were prepared by simple chemical precipitation method to fabricate dye sensitized solar cell in a cost effective way. The leaf extract of Acalypha Wilkesiana as a natural dye was used in the fabrication of low cost dye sensitized solar cell. The anthocyanin present in the leaf extract was used as photosensitizer which can enhance the efficiency of the fabricated solar cells. The current density (J) vs. voltage (V) characteristics of the fabricated device was performed under visible light radiation. The power conversion efficiency of Mn doped SnS is greater than the pure as well as Fe doped SnS. The increase in efficiency of Mn doped SnS nanoparticles is influenced by short circuit current density (J_{sc}). Thus the small increase in power conversion efficiency of Mn doped SnS is probably due to the reduced rate of recombination of the photogenerated carriers. Therefore, the Mn doping with SnS NPs could enhance the light to power conversion efficiency by establishing localized bands which assist the development of charge transfer.

6.2. Fabrication and Characterization of Dye Sensitized Solar Cell based on Green Synthesized SnS Nanoparticles

The green synthesis of the semiconducting nanoparticles has been suggested as an eco-friendly, non-toxic, environmentally safe over the chemical and physical technique [271-273]. The synthesis of nanocrystals using the plants is a green chemistry technique that relates nanotechnology through plants. The plant leaf extracts have been employed as a capping agent is more and more environmental friendly [274-275]. This is reliable and cost effective method also. The extracts of plants can be thought of a best choice for the growth of nanoparticles. Therefore, the plants are called nature's chemical factories. They are cost effective and needed to low maintenance [276].

Chemically grown SnS and green synthesized SnS nanoparticles were prepared by simple and cost effective method. Gymnema Sylvestre leaf extract has been used as capping agent for the preparation of green synthesized SnS NPs. These samples have been applied for fabrication of natural dye sensitized solar cell. A comparative study between the efficiencies of the DSSCs fabricated with green synthesized as well as chemically grown SnS NPs has been discussed. Acalypha Wilkesiana leaves extract was used as natural dye. Open circuit voltage (V_{oc}), short circuit current (J_{sc}) of the fabricated dye sensitized solar cells have been studied. Fill factor (FF) as well as power conversion efficiency (η) were also determined. Low cost as well as efficient dye sensitized solar cells has been fabricated and characterized by J-V study under white light with intensity of 100 mW/cm^2. The J-V characteristics study of the fabricated DSSCs show that the power conversion efficiency of ~ 1.63 % for the green synthesized SnS NPs based solar cell and 1.39 % for chemically grown SnS NPs based solar cell.

6.2.1. Experimental section

6.2.1.1. Preparation of samples

Chemically grown SnS and green synthesized SnS nanoparticles were prepared by simple hydrothermal method. Tin chloride ($SnCl_2.2H_2O$) and Thiourea (CH_4N_2S) were employed to prepare SnS nanoparticles. The preparation methodology, collection, extraction of plant samples and its structural as well as optical properties are described in details in chapter 3.

6.2.1.2. Preparation of natural dye sensitizer

Acalypha Wilkesiana leaves were collected from the garden of Vidyasagar University, West Bengal, India. After that, these leaves are cleaned and washed with deionised water with several times and positioned in a vacuum furnace for 1 hour. Next, the leaves are crushed with a porcelain mortar and pestle. The crushed sample is then dipped into 50 ml ethanol taken into a beaker for few minutes. After extraction, the crushed samples are then filtered with filtered paper. Now this is the prepared Anthocyanin solution, extracted from Acalypha Wilkesiana leaves, which is called natural dye, used as photosensitizers.

6.2.1.3. Fabrication of DSSCs

At first, the chemically grown SnS and green synthesized SnS paste have been prepared using acetic acid. These prepared SnS paste were deposited carefully on the conducing side of ITO coated glasses and dried at 45 °C for one hour. Acalypha Wilkesiana leaves extract treated as natural dye has been prepared. This is the prepared Anthocyanin solution. Now, the dried ITO coated glasses were dipped for 45 minutes in the prepared dye solution. Another ITO glasses are coated with graphite paint have been used as counter electrodes. Then the two electrodes are squeezed in together using binder clips. The prepared KI redox electrolyte solution was injected into the junctions of two cells to supply charge carriers in between the electrodes.

6.2.2. Sample characterization

Chemically grown SnS and green synthesized SnS paste were uniformly deposited carefully on the ITO coated glasses. Graphite paste has been used as counter electrode for the study of J-V measurements of the fabricated solar cell. The current density-voltage (J-V) characteristics of the fabricated dye synthesis solar cells (DSSCs) based on chemically grown and green synthesized SnS NPs were studied. Acalypha Wilkesiana leaves extract, used as natural dye, employed for the fabrication of solar cell. The current density-voltage (J-V) data of the fabricated DSSC were recorded under white light illumination condition (intensity of light 100 mW/cm^2) using two multimeters and a Keithley electrometer (6514).

6.2.3. Results and discussion

6.2.3.1. Characteristics of Dye Sensitized Solar Cells

The photovoltaic performances of the fabricated Dye Sensitized Solar Cells (DSSCs) have been studied by analyzing the current density (J) vs. applied voltage (V) characteristics curve under the visible light radiation of 100 mW/cm^2. Here, we have used Acalypha Wilkesiana leaf extract as a natural dye photo sensitizer to sensitize the fabricated DSSCs. The current density (J) vs. voltage (V) graph of the prepared DSSCs is shown in fig. 6.2.1(a). The increase in current density of DSSC based on green synthesized SnS nanoparticles is probably due to the decrease in electron-hole recombination as depicted in fig. 6.2.1(a) [277-278]. With the absorption of visible light radiation by the dye molecules large numbers of electron–hole pair are generated. This verifies the light absorption character by Acalypha Wilkesiana leaf extract. Hence, the efficiency of the fabricated green synthesized SnS nanoparticles based dye synthesized solar cell is slightly higher than the efficiency of the chemically grown SnS nanoparticles based dye sensitized solar cell. Fig. 6.2.1(b) shows the power graph of as fabricated DSSCs. Different photovoltaic parameters such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), maximum power density (P_{max}), Fill factor

(FF) and the photon to electrical energy conversion efficiency (η) have been determined from the current density (J) vs. voltage (V) as well as power density (P) vs. voltage (V) graphs. This parameters are presented in table 6.2.1.

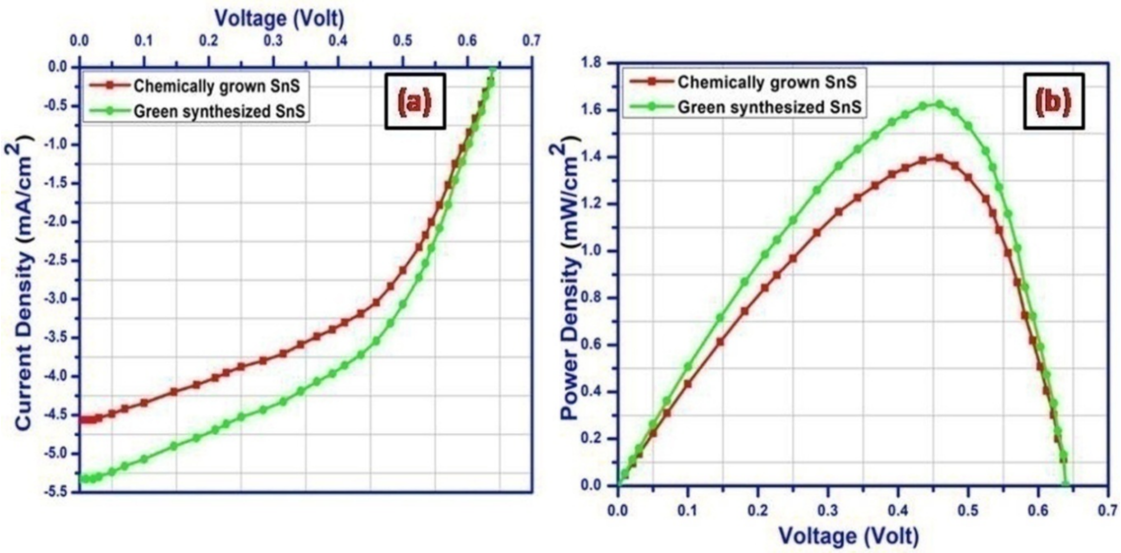

Fig. 6.2.1 (a) Current density (J) vs applied voltage (V) characteristics of chemically grown SnS and green synthesized SnS DSSC; (b) Variation of power density (P) with applied voltage (V) of chemically grown SnS and green synthesized SnS DSSC.

The fill factor and the power conversion efficiency were calculated using the following relations

$$FF = \frac{V_{mp}J_{mp}}{V_{oc}J_{sc}} \qquad (6.2.1)$$

$$\eta = \frac{J_{sc}V_{oc}}{P_{in}} \times FF \qquad (6.2.2)$$

Where, V_{mp} and J_{mp} are the voltage and current density at maximum power. V_{oc} and J_{sc} are the open circuit voltage and short circuit current respectively. P_{in} is the incident power radiation. η is the power conversion efficiency. The power conversion efficiency of ~ 1.63 % and 1.39 % were obtained in the DSSCs fabricated with green synthesized as well as chemically grown SnS NPs respectively. Therefore, high short circuit current density (J_{SC}) of ~ 3.596 mA/cm^2, open circuit voltage (V_{OC}) of ~ 0.638 V and power density (P_{max}) of ~ 1.63 mW/cm^2 are measured in fabricated DSSC based on green synthesized SnS NPs. Hence the greater carriers trapping ability [278] of green synthesized SnS NPs is mainly responsible for the enhancement of the short circuit current density (J_{SC}) and therefore the power conversion efficiency (η).

Table: 6.2.1

Comparison of solar cell parameters of the fabricated natural DSSCs with other reported work

Name of sample	Name of plant/ /leaves/ seed extract	Used dye solution (Chemical/Natural)	V_{max} (V)	J_{max} (mA/cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (FF)%	Efficiency (η)%	References
ZnO	Tilia Tomentosa	N719	-	-	0.65	6.26	48.5	1.97	[279]
TiO_2	Bixa orellana	N719	-	-	0.68	2.00	73	1.03	[280]
CuO	Calotropis gigantean	N719	-	-	0.676	8.13	62	3.4	[281]
ZnO	coffee powder	N719	-	-	0.593	7.54	69.8	3.12	[282]
ZnO	Amorphophallus paeoniifolius tuber	Terminalia catappa	-	-	0.47	4.9	68.3	1.58	[283]
CdTe	Thevetia peruviana leaf extract	Thevetia peruviana leaf extract	0.55	3.83	0.695	4.38	69.2	2.106	[132]
TiO_2	-	Red rose	-	-	0.48	4.57	36	0.81	[263]
ZnS	-	Acalypha wilkesiana	-	-	0.293	0.025	54	0.29	[269]
SnS	-	Acalypha wilkesiana	0.452	3.084	0.638	4.552	48.0	1.39	This work
SnS	Gymnema Sylvestre	Acalypha wilkesiana	0.453	3.596	0.638	5.326	47.94	1.63	This Work

6.2.4. Conclusions

The green synthesis was fruitfully utilized to prepare SnS NPs by the Gymnema Sylvestre leaves extract. The leaves extract of Gymnema Sylvestre plant have been employed as an efficient capping agent for the synthesis of SnS NPs. The Acalypha Wilkesiana leaves extract used as natural dye for the fabrication of natural dye sensitized solar cell. The fabricated dye sensitized solar cell is efficient and cost effective. The fabricated solar cell based on green synthesized SnS and chemically grown SnS nanoparticles have been characterized through current density vs. voltage (J-V) study. The J-V study on the solar cells indicate that the efficiency of the fabricated green synthesized SnS nanoparticles based dye synthesized solar cell is slightly higher than the efficiency of the chemically grown SnS nanoparticles based dye sensitized solar cell. This increase in power conversion efficiency of the fabricated green synthesized SnS nanoparticles based DSSC is due to the decrease in recombination of the electron-hole pairs. Therefore, the novel green synthesis of SnS NPs from the Gymnema Sylvestre leaves extract is a pollutant free, low cost and eco-friendly synthesis method. The biosynthesized SnS NPs have been utilized for the production of efficient DSSC with high short circuit current density, high power density and therefore high performance.