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Investigation of bacterial pigment from Serratia nematodiphila as a sensitizer for a nanostructured solar cell

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Dye sensitized solar cells have proven its potential as affordable, green method of turning solar energy into electrical energy. This article presents an extensive comparative study on dye sensitized solar cells with two types of transport layers made of ZnO nanorods and TiO_2 mesoporous film, wherein bacterial pigment extracted from microorganism *Serratia nematodiphila* strain B2 is employed as a sensitizer. For performance enhancement via the plasmonic effect, Ag nanoparticles have been deposited onto conducting glass and used as counter electrode (CE). The efficiency and fill factor (averaged over 3 readings) are found to be approximately 2% and 43%, respectively, with TiO_2 mesoporous film and 0.4% and 25%, respectively, with ZnO nanorod in the designed DSSCs. Experiments have been conducted with TiO_2 film for ten weeks to evaluate the stability of the pigment. The findings suggest that bacterial pigments may possibly replace dyes, creating a new category of solar cells known as biopigment-sensitized solar cells.

Keywords: Bacterial pigment, DSSC, Biopigment-sensitized solar cells, Biopigment-sensitized solar cells

Global population growth, combined with rising living standards, has resulted in a rapid rise in overall energy consumption. To meet the ever-increasing worldwide demand for energy, a technology that is both safe and green is of utmost necessity. If the sun's energy radiated on earth in an hour is successfully absorbed, it can meet the world's energy needs for a year[1]. Solar energy is the most effective way to meet a large portion of the world's energy needs because it is clean, free and never ending.

Owing to simplicity of manufacturing and decreased production costs, Dye Sensitized Solar Cell (DSSC)s are regarded as attractive addition to the class of future generation solar cells (SCs). A great variety of experimental studies have been conducted on DSSCs. In this work, a semiconducting mesoporous film is created upon a Transparent Conducting Oxide (TCO) and bacterial pigment is adsorbed onto it to produce the photoanode. The incorporation of mesoporous nanostructures improves solar photon conversion because the greater surface area offered by nanostructures allows for higher usage of sunlight by allowing more dye molecules to be coupled to the surface, which absorbs energy from the photons. Thicker structures can also yield higher photon absorption, but they obstruct the gathering of photo-generated carriers. As a result, the DSSC thickness is an important metric to optimize. A solar cell with an optically thick yet physically thin architecture is highly desirable, that could be accomplished by integrating plasmonic nanoparticles (NPs). Plasmonic NPs provide an additional light trapping mechanism, resulting in increased photon absorption. Pigment based SCs are getting attention in the area of environment friendly SC design. Mejica et al. worked with anthocyanin pigments based SCs with improved pH-dependent photovoltaic properties and reported efficiency of 0.1021% [2]. A detailed review of alternative sources of natural pigments for DSSCs is presented by Orona-Navar et al.[3] where, photoconversion efficiency of 0.004 to 1.67% for bacterial pigment based sensitizers are reported.

In this work, experimental results on biopigment-sensitized solar cell (BSSC)s based on pigment extracted from bacteria with photoanode based on

rutile TiO_2 mesoporous films and ZnO nanorod films deposited (or grown) on conducting glass is reported. Fluorine doped Tin Oxide (FTO) was used as conducting glass for the design of the SCs. Since TiO_2 films[4,5] and ZnO nanorods[4,6] are widely used in nanotechnology based SCs, that's why they are selected for the design of the BSSCs. Microorganism *Serratia nematodiphila* strain B2 (NCBI accession No.MH634699.1) was isolated from the gut of tree borer Neurozerraconferta and was maintained on Nutrient agar (NA) plate maintained at 30°C for 24 h.

Experimental Section

Extraction of the bacterial pigment

The 24 h grown bacterial culture was transferred from NA plates to a conical flask holding 100 mL nutrient broth (NB) which was then maintained at 30°C for 24 h at neutral pH. Conical flask with 250 mL capacity containing 150 mL of NB was taken and 1 mL of the 24 h grown bacterial culture from the broth was transferred, which was maintained at 30°C for 72 h for maximum pigment production. After 72 h incubation time period, the bacterial cultures then centrifuged for 10 min at a rate of 12,000 rpm. The bacterial pellets were extracted from the centrifuged solution and re-suspended in organic solvent (ethanol), for the extraction process. The bacterial samples were vortexed for two minutes and were left for overnight extraction after that the solution centrifuged again for 10 min at a rate of 12,000 rpm. The coloured supernatant was collected carefully in fresh tubes and the pellets were discarded. The crude extract was evaporated in a water bath heated to 70°C, and the dried pigment was redissolved in the appropriate solvent[7].

Preparation of photoanode

Two types of photoanodes were experimented with. One with TiO_2 adsorbed on conducting glass and the other with ZnO nanorods films grown on the conducting glass. In both the cases, conducting side of the TCO glass was used as substrate for photoanode.

For TiO_2 based photoanode, the substrate was cleaned first with deionized water and acetone where mesoporous TiO_2 thin film was formed. The procedure started with addition of five drops of white vinegar to 0.5 g rutile TiO_2 nanopowder to form a slurry. To ensure that the TiO_2 slurry adheres to the conductive glass, addition of two drops of liquid detergent to the slurry was done. A rectangular portion of 1×1 cm^2 of the substrate was prepared with duct tape for TiO_2 mesoporous film deposition. Through doctor blading, two drops of the slurry were applied to the prepared area of the substrate. Duct tape was removed after even distribution of the slurry on the substrate. Then the slurry coated substrate was heated in hot air oven for half an hour at 400°C. Thus a mesoporous TiO_2 coating was deposited on to the substrate. The TiO_2 coated substrate was then submerged in the pigment solution for 10-20 min to allow the pigments to permeate into the mesoporous layer. Next, the substrate was removed from the pigment solution and rinsed in deionized water to eliminate leftover debris. After then, room temperature desiccation of the photoanode was performed and the pigment hue was taken up by the TiO_2 mesoporous film.

In case of ZnO nanorods based photoanode, the nanorods were grown on (1×1) cm^2 area of the substrate using hydrothermal technique[8]. The ZnO grown substrate was then submerged in the pigment solution for 10-20 min to allow the pigment to permeate into the nanorod thin film and then the glass slide was rinsed in deionized water to remove loosely adsorbed materials. Finally, it was dried in a desiccator at room temperature.

Preparation of redox couple (RC)

High solubility and appropriate redox potential of the iodide/tri-iodide electrolyte makes it ideal as the redox pair. It also regenerates dye quickly and absorbs only a little amount of light[8]. 127 mg of crystal iodine and 830 mg of potassium iodide is mixed with 10 mL of ethylene glycol solution under constant stirring to produce the RC. The solution looked yellowish brown colour.

Concentric Electrode (CE) preparation and design of the SC

Plasmonic NPs can be used to increase solar cell absorption. The presence of plasmonic NPs enhance the absorption of light because of the increased path length through scattering in SCs and intensified near field around the plasmonic NPs[9]. The presence of plasmonic NPs can also help in increasing the short circuit current through decay of plasmon resonance by exciting electron hole pairs[9]. Al, Au, and Ag NPs have all been investigated as plasmonic nanomaterials, with Ag having the highest quality factor[10].

Ag NPs are used as a plasmonic nanomaterial on the CE in this study. To create plasmonic effect in CE, Ag NPs were adsorbed on conducting glass. Ag NPs were synthesized using silver nitrate ($AgNO_3$)

and trisoduim citrate ($Na_3C_6H_5O_7$) solution where deionized water was used as solvent [11]. Then, using the dip and dry approach, a coating of Ag NPs was deposited onto the conducting glass to fabricate the CE. After the preparation of photoanode, RC, and CE, the BSSC was built and the schematic of the designed BSSC is shown in Fig. 1. Fig. 1(a) shows the schematic of the TiO_2 mesoporous based BSSC and Fig. 1(b) shows the ZnO nanorod film based BSSC.

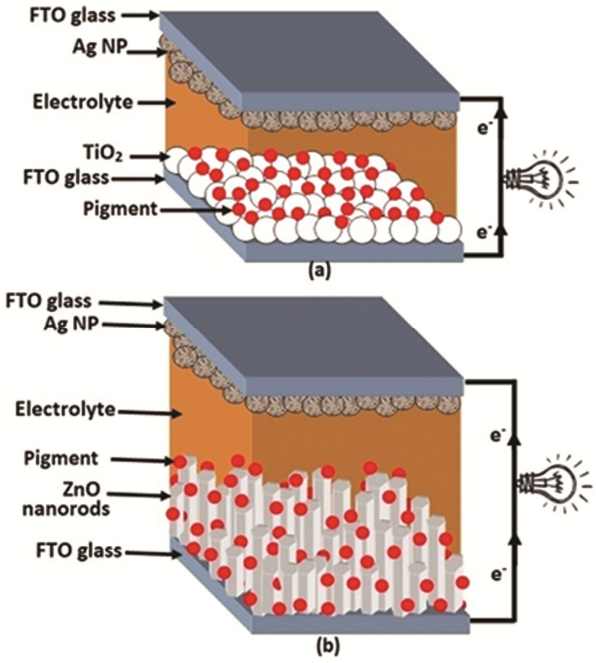

Fig. 1 — BSSC schematic, where photoanode and CE sandwiches a RC. The BSSCs are designed with (a)TiO_2 based photoanode, where pigments are adsorbed onto TiO_2 mesoporous film deposited on conducting side of FTO glass (b)ZnO based photoanode, where pigments are adsorbed onto ZnO nanorod film grown on conducting side of FTO glass

Results and Discussion

Isolation, maintenance of the microorganism and bacterial pigment extraction

The *Serratia nematodiphila* strain B2 bacterial culture was maintained by growing the bacteria in solid nutrient agar media (Fig. 2(a)) and nutrient broth (Fig. 2(b)). The optimum growth condition for that bacterium was found to be at 30°C in pH 7. Serial sub culturing was done to maintain bacteria in laboratory condition.

The bacterial pigment was extracted in organic solvent (ethanol) as shown in (Fig. 2(c)), and was analyzed by scanning the absorbance with a UV-visible spectrophotometer. The addition of the organic solvent disrupts the biological structure and releases pigments into the solution, thereby changing the spectrum of the pigment. The absorbance peak was observed at 536 nm as shown in (Fig. 2(d)), which corresponds to the pigment prodigiosin in which are secreted by *Serratia* spp. as reported earlier[12].

Characterization of TiO_2 mesoporous, ZnO nanorod films and Ag NPs

The deposited films and synthesized NPs were characterized for validation before fabricating the SCs. The SEM micrograph (Fig. 3(a)) of TiO_2 deposited

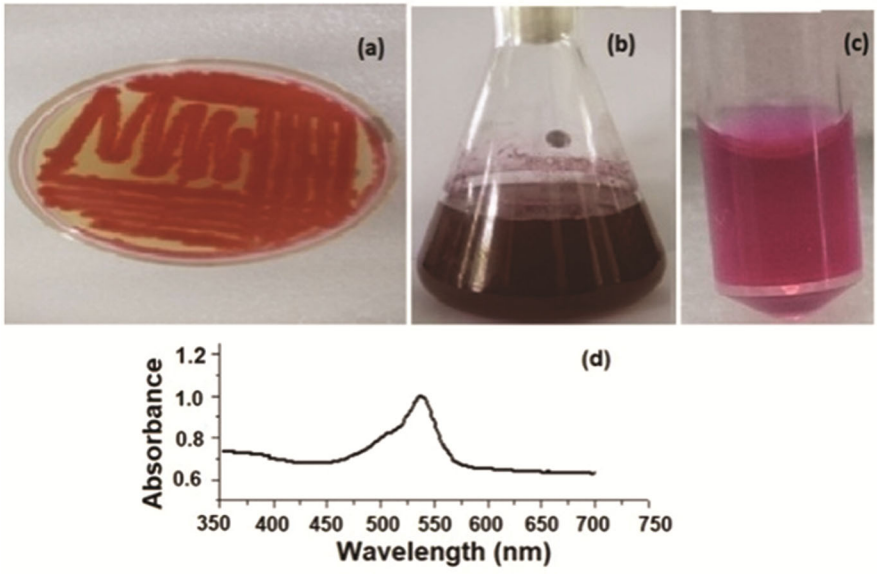

Fig. 2 — *Serratia nematodiphila* culture maintained at 30°C in pH7 (a) nutrient agar (b) nutrient broth (c) bacterial pigment extracted in ethanol and (d) UV-visible spectra of the extracted pigment

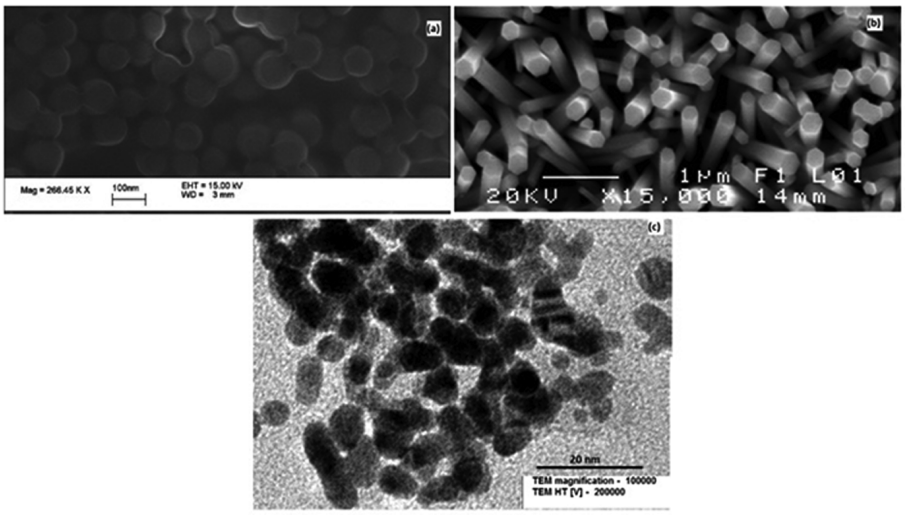

Fig. 3 — Characterization: (a) SEM micrograph of TiO_2 mesoporous film, (b) SEM micrograph of ZnO nanorod film and (c) TEM image of Ag NPs

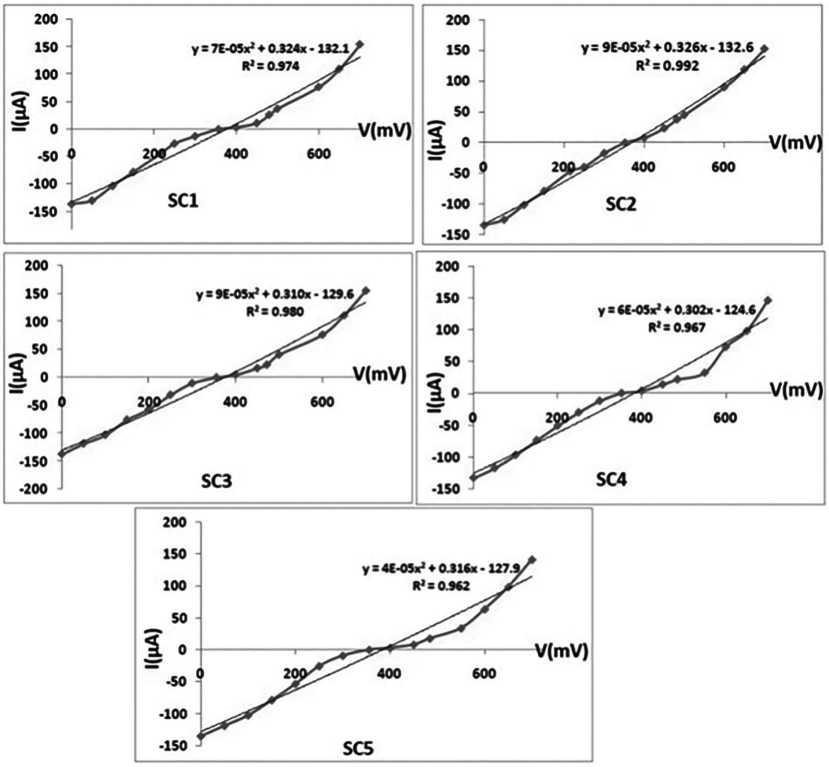

Fig. 4 — I-V characteristics of the DSSCs with ZnO nanorod film

substrate confirms the formation of mesoporous thin film with particle size of about 50 nm and the SEM micrograph (Fig. 3(b)) of the ZnO nanorod grown on the substrate confirms the growth of the nanorods with diameter roughly about 150 nm and length of about 1000 nm. The TEM image of the produced silver NPs in Fig. 3(c) shows that the particles are roughly in between 10 nm to 15 nm in size.

Device performance

Initially two sets of SCs with ZnO nanorod film and rutile TiO_2 mesoporous film were designed each with five BSSCs. The I-V characteristics of the SCs with ZnO nanorod film and that with TiO_2 mesoporous film is shown in Fig. 4 and Fig. 5 respectively.

A comparative analysis of the various important parameters is presented in Table 1, where I_{sc},V_{oc}, I_m ,

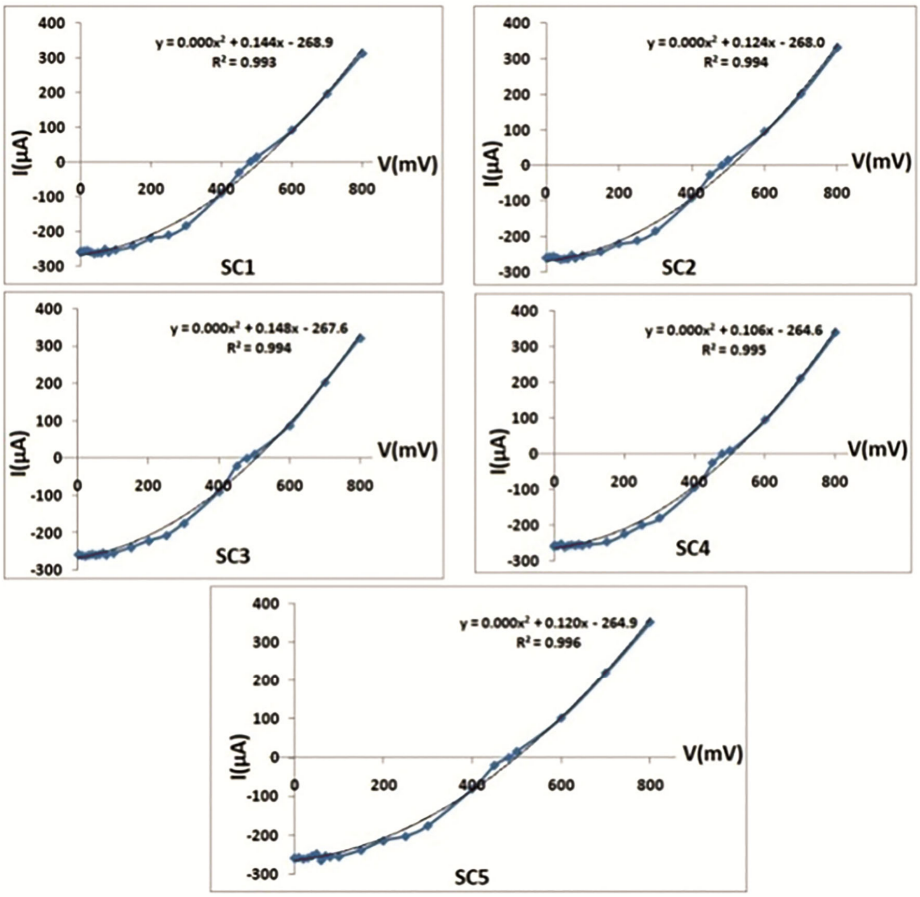

Fig. 5 — I-V characteristics of the DSSCs with TiO_2 mesoporous film

Table 1 — Comparative analysis of the performance of SCs with TiO_2 mesoporous film and ZnO nanorods

Solar cells	I_{sc} (μA)		V_{oc} (mV)		I_m (μA)		V_m (mV)		FF(%)		Ƞ(%)	
	TiO_2	ZnO	TiO_2	ZnO	TiO_2	ZnO	TiO_2	ZnO	TiO_2	ZnO	TiO_2	ZnO
SC1	262.2	135.9	483	357	184.2	77.6	300	150	43.63	23.99	1.97	0.41
SC2	257.4	134.3	478	352	174.2	78.5	300	150	42.47	24.91	1.87	0.42
SC3	261.1	137.3	481	356	178.8	57.3	300	200	42.71	23.44	1.91	0.41
SC4	259.5	132.9	478	352	179.3	73.8	300	150	43.36	23.66	1.91	0.39
SC5	257.9	135.3	482	356	175.4	78.7	300	150	42.33	24.51	1.87	0.42

V_m, FF and η represents short circuit current, open circuit voltage, current at maximum power, voltage at maximum power, fill factor and efficiency respectively.

From Table 1, it is evident that SCs with TiO_2 mesoporous film performed better than that with ZnO nanorod film which may be caused due to better adsorption of pigments on TiO_2 mesoporous film as compared to ZnO nanorod film. The maximum values of I_{sc}, V_{oc}, I_m, V_m, FF and η obtained with TiO_2 mesoporous film based SCs are 262.2 μA, 483 mV, 184.2 μA, 300 mV, 43.63% and 1.97%, respectively, whereas SCs with ZnO nanorod film provided maximum values for the same as 137.3 μA, 357 mV, 78.7 μA, 200 mV, 24.91% and 0.42%, respectively. It is therefore observed that, SC with TiO_2 performed better. Percentage relative standard deviation (%RSD) of the performance parameters are calculated as per the Eq. (1) to check the repeatability of the fabrication method.

$$\%RSD = \frac{100}{\bar{x}}\left[\frac{\sum_{i=1}^{N}(x_i-\bar{x})^2}{N-1}\right]^{\frac{1}{2}} \quad \ldots(1)$$

Where, $\bar{x}$ is the mean of x, specific performance parameter value, N is the total number of fabricated solar cells and i=1, 2, 3, 4, 5.

%RSD (given in Table 2) of the performance parameters is found to be very small for each set of SCs which confirms good repeatability of the fabrication method used.

After the initial study, it is found that TiO_2 mesoporous film perform better as compared to ZnO nanorod film. Therefore, to study the stability of the pigments, experiments were conducted with freshly designed SCs with TiO_2 mesoporous film once in every week for ten consecutive weeks. The extracted pigments were stored in a parafilm capped test tube at around 15 ℃. A new SC was fabricated with the stored pigment every week and performance parameters were analyzed. The combined I-V characteristics of SCs designed every week is shown in Fig. 6. It is observed that the I-V curves are overlapping with one another which indicate good stability of the extracted pigment.

Table 2 — %RSD of the performance parameters

Material	V_{oc}	I_{sc}	V_m	I_m	FF	η
TiO_2	0.79	0.48	0	2.19	1.33	2.19
ZnO	0.68	1.23	13.97	12.43	2.5	2.6

The change in the performance parameters (Fig. 7) of the designed SCs is also not significant. %RSDs (Fig. 8) of the variation of performance parameters over 10 weeks are low which show that the performance parameters are almost intact. Therefore, it may be inferred that the pigment extracted from *Serratia nematodiphila* bacteria did not degrade and remained stable within the period of experiments.

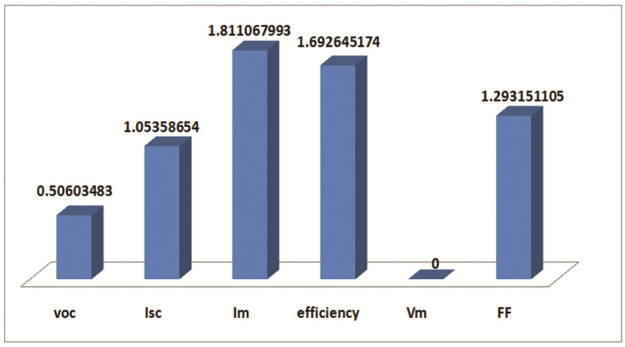

Fig. 8 — Percentage RSD of the variation of performance parameters over 10 weeks

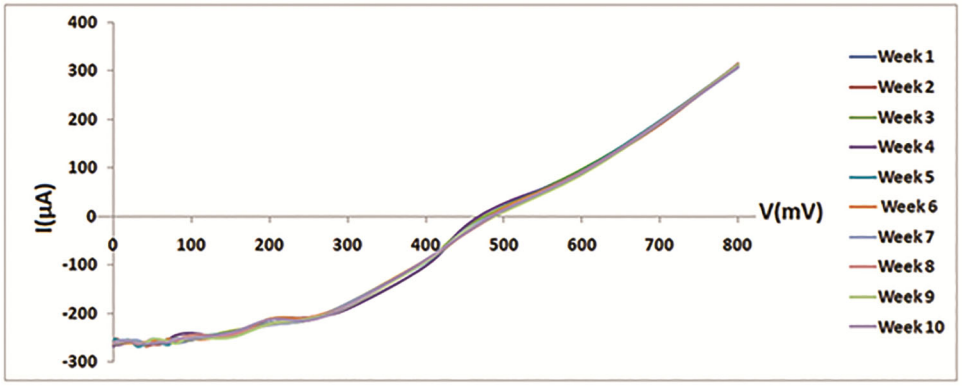

Fig. 6 — I-V characteristics of the SCs designed for 10 consecutive weeks. Overlapping of the curves indicates higher stability of the pigments

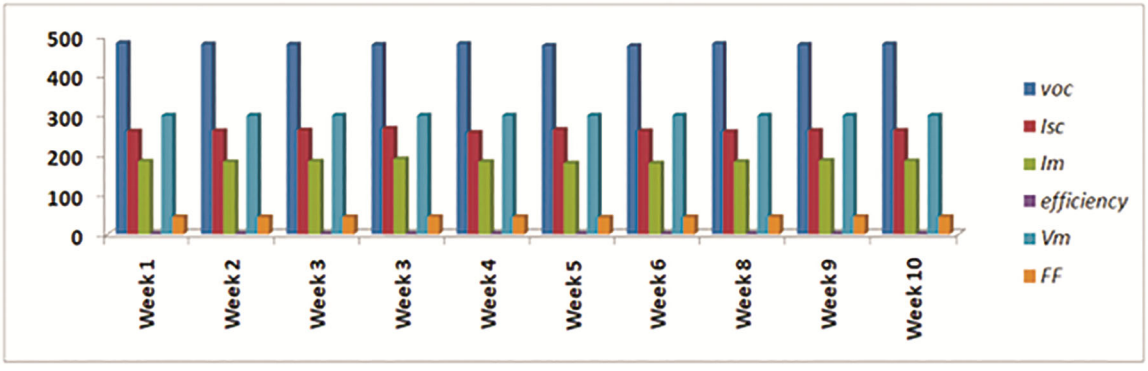

Fig. 7 — Performance parameters of the SCs designed for 10 consecutive weeks. It is observed that performance parameters of the design BSSCs are persistent indicating good stability of the extracted pigments

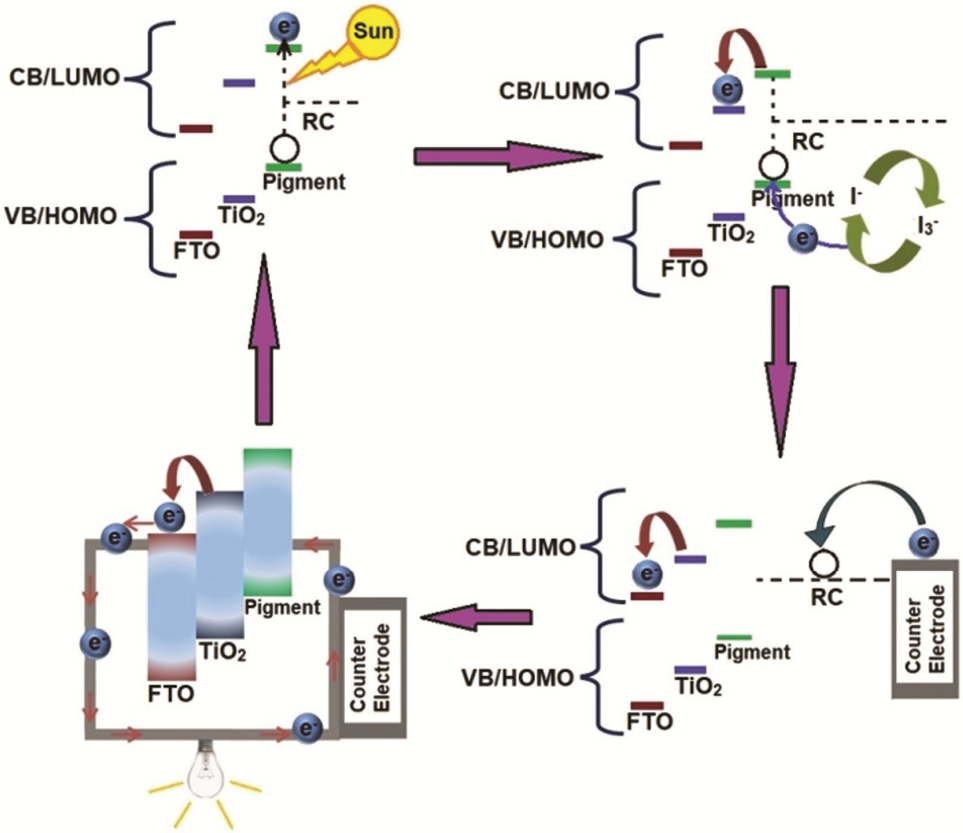

Fig. 9 — Schematic of electron hole pair generation and their transportation through the load using energy band diagram

Working mechanism of the BSSC

Under illumination, electron-hole pair is generated at the interface between the photoanode and RC. The photo-excited electrons get quenched either by recombination or it leaps to the conduction band of the transport layer (TiO_2 mesoporous film or the ZnO nanorod film) which deliver the electron to the conducting glass. The electron then travels through the load and the CE to the RC where it completes the circuit. Fig. 9 shows the schematic of electron hole pair generation and their transportation through the load using energy band diagram. Upon exposure to light, the electron generated at the interface of the photoanode and the RC occupies the lowest unoccupied molecular orbital (LUMO) of the pigment extracted from bacteria and the hole stays there at the highest occupied molecular orbital (HOMO) of the pigment. The electron moves from LUMO of the pigment to the conduction band (CB) of TiO_2 and then to the CB of the FTO. The hole generated interacts with RC and the iodide/tri-iodide electrolyte attains the oxidizing state. The electron from the FTO travels through the load and CE and interacts with the RC and reduces the oxidizing state of the electrolyte and completes the cycle.

Conclusion

Pigment extracted from microorganism *Serratia nematodiphila* strain B2 was tested for possible replacement of dyes in a typical DSSCs. Two sets of SCs were fabricated, one with TiO_2 mesoporous film and the other with ZnO nanorod film as transport layer. It is found that SCs with TiO_2 gave better FF and efficiency as compared to that of the ones with ZnO. The maximum FF and efficiency obtained with TiO_2 is 43.63% and 1.97% respectively. Since SCs with TiO_2 resulted in better performance as compared the ones with ZnO, so to evaluate the longevity of the extracted pigments, TiO_2 based SCs with stored bacterial pigments were experimented for ten consecutive weeks and performance parameters are analyzed. It is found that if the pigment is stored at a temperature around 15°C, the change in the performance is insignificant which makes the bacterial pigment an attractive candidate for use as sensitizers in a new class of solar cells which can be

termed as biopigment-sensitized solar cells. Further work on improving the electron transfer efficiency through various physisorption techniques may pave the way for highly efficient low-cost solar cells with appreciable fill factor.

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