



## SUSTAINABLE SOLAR ENERGY CONVERSION AND STORAGE BY MODIFIED PHOTOGALVANIC EFFECT OF NILE BLUE A DYE, L-ASCORBIC ACID REDUCTANT AND BRIJ-35 SURFACTANT

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### Abstract:

The study focused on the developing modified photogalvanic cell to increase the conversion and storage of solar energy with enhanced electrical output at least cost. Photogalvanic cell is a photo-electrochemical cell that can be chargeable in solar light by its photogalvanic effect to convert and store solar energy in electrical energy. It is an H-shaped glass tube cell containing two electrodes which were dipped in a multifaceted electrolyte solution of dye-reductant-surfactant-alkali. In this study, an integrated system of Nile blue A (as dye), L-ascorbic acid (as reductant) and Brij-35 (as surfactant) has been developed and used for formulating modified photogalvanic cell for increasing the solar energy conversion and storage capacity. This system by way of variable concentration of chemical components were used to formulate a modified photogalvanic cell. The modified photogalvanic cell indicated significantly improved performance in terms of dark potential (691 mV), open-circuit potential (1087 mV), short-circuit current (2800  $\mu$ A), power (705.60  $\mu$ W), charging time (24 min), half change time (45 min), conversion efficiency (19.67%), and fill factor (0.232). The outcome of various cell formulation parameters was studied for optimization of the cost of formulation variables for the optimal cell performance based on the proposed mechanism.

**Keywords:** Nile blue A; L-Ascorbic acid; Brij-35; Solar energy conversion and storage; Photogalvanic cell; Photo-dye sensitizer.

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## 1. INTRODUCTION

The sustainable energy is the quantitative form of clean energy mainly exploited from the renewable resources of energy for example solar energy and wind energy.<sup>[1-3]</sup> The simultaneous conversion and storage of sustainable energy is an innovative approach that has directed to an cumulative interest in solar energy and photo-electrochemical effect.<sup>[4,5]</sup> The sun is the vital source of sustainable solar energy and it is help to sustain the life on the earth. The solar energy is a clean and abundantly available renewable source of energy for electric power generation.<sup>[6]</sup> There are numerous techniques to harvest solar energy and convert it into electrical energy such as polymer cells, perovskite cells, dye-sensitized cells, photovoltaic cells, photogalvanic cells, etc.<sup>[7,8]</sup> On view of above, photogalvanic cell is most promising and commercially important technique to simultaneously convert and store solar energy with sophisticated electrical output and efficiency, and intrinsic power storage capacity at low cost.<sup>[9]</sup> In photogalvanic cell, solar energy can cause current and potential changes which is define by the photo-electrochemical reactions of the electrolyte solution. The solar energy effect on the current and potential is called photogalvanic effect. It is also known as modified Becquerel effect and Becquerel effect was first developed by scientist Becquerel in 1839.<sup>[10]</sup> Later in 1940, the another scientist Rabinowitch has also been investigated a Thionine-Fe<sup>2+</sup> photogalvanic cell for the efficient conversion of solar energy into electricity.<sup>[11]</sup>

Several reports have been found in literature with various blends of dye-reductant-surfactant. The dye-reductant-surfactant formulas like glycerol-Azur-sodium lauryl sulphate (SLS),<sup>[12]</sup> Indogo carmine-ascorbic acid,<sup>[13]</sup> Brilliant green-ascorbic acid-ammonium lauryl ether sulphate (ALES),<sup>[14]</sup> oxalic acid-Brilliant Cresyl,<sup>[15]</sup> Rhodamine B-fructose-SLS,<sup>[16]</sup> Congo red-formaldehyde-SLS,<sup>[17]</sup> Tropaeline O-oxalic acid-benzalkonium chloride,<sup>[18]</sup> Sudan I-fructose-SLS,<sup>[19]</sup> Indigo carmine-formic acid-SLS,<sup>[20]</sup> Congo red-D-Xylose-Cetylpyridinium chloride,<sup>[21]</sup> Safranin O-EDTA-Cetyltrimethylammonium bromide (CTAB),<sup>[22]</sup> Toluidine blue-oxalic acid-Tween 80,<sup>[23]</sup>

Naphthol green B-fructose-SLS,<sup>[24]</sup> Toluidine blue-arabinose-SLS,<sup>[25]</sup> Malachite green-arabinose-SLS,<sup>[25]</sup> Brilliant Cresyl blue-fructose-SLS,<sup>[26]</sup> Indigo Carmine-formic acid-SLS<sup>[27]</sup> and so forth, have been reported to use in photogalvanic cell by various researchers and found various results. There are some mixed dye-reductant and dye-reductant-mixed surfactant systems has also been reported to use in photogalvanic cells such as Brilliant green+Celestine blue-EDTA and Methylene blue-xylose-SLS+CTAB, and found extraordinary results.<sup>[28,29]</sup> Bhimwal and Gangotri have been studied the comparative performance of photogalvanic cell using Methyl orange, Rose Bengal, Toluidine blue and Brilliant Cresyl blue as dye with D-Xylose and SLS, and initiated that Methyl orange-xylose-SLS system found to have highest solar energy conversion efficiency and storage capacity.<sup>[30]</sup> The literature survey reveals that the photogalvanic system of Nile blue A-L-Ascorbic acid-Brij-35 has not been reported so far for the harvesting of solar energy, and therefore, it can potentially replace the existing chemical systems for conversion of solar energy and its storage in photogalvanic cell.

The present research focuses on the development of modified photogalvanic cell to improve the conversion and storage of solar energy with enhanced electrical output at least cost. The modification of photogalvanic cell by changing the electrode surface area and the replacement of electrolyte solution is not only reduced the cost of fabrication of photogalvanic cell but also at the same time as enhance the photogalvanic effect to a striking conversion and storage of solar energy. Therefore, it is good to achieve the economic viability and ease of commercial application of photogalvanic cell. An integrated system of Nile blue A (as dye), L-ascorbic acid (as reductant), and Brij-35 (as surfactant) has been developed and used for fabricating photogalvanic cell for enhancing the solar energy power conversion and storage capacity. This system with variable concentration of chemical components were used to fabricate a modified photogalvanic cell. The modified photogalvanic cell showed significantly improved performance in terms of dark potential (691 mV), open-circuit potential (1087 mV), short-circuit current (2800  $\mu$ A), power (705.60  $\mu$ W), charging time (24 min),

half change time (45 min), conversion efficiency (19.67%), and fill factor (0.232). The outcome of various cell formulation parameters was studied for optimization of the cost of formulation variables for the optimal cell performance based on the proposed mechanism.

## 2. MATERIALS AND METHODS

**Materials:** In this study, chemical, Nile blue A (Synonym - Basic blue 12; General formula -  $2C_{20}H_{20}N_3O.SO_4$ ; Molecular weight - 732.85  $g.mol^{-1}$ ; Physical state - Blue-to-black powder; Solubility - Soluble in water and alcohol) has been procured from Sigma Aldrich Pvt. Ltd., and L-Ascorbic acid (Synonym - Vitamin C; Assay - >99%; General formula -  $C_6H_8O_6$ ; Molecular weight - 176.12  $g.mol^{-1}$ ; Physical state - White crystalline powder; Solubility - Soluble in water and alcohol), Brij-35 (Synonym - Polyoxyethylene lauryl ether, Polyethyleneglycol lauryl ether; Assay - >99%; General formula -  $C_{58}H_{118}O_{24}$ ; Molecular weight - 1199.56  $g.mol^{-1}$ ; Physical state - White powder; Solubility - Soluble in water and alcohol), and sodium hydroxide (Synonym - Caustic soda; Assay - >99%; General formula - NaOH; Molecular weight - 39.99  $g.mol^{-1}$ ; Physical state - White pellet; Solubility - Soluble in water) has been procured from Loba Chemie Pvt. Ltd.. All the chemicals has been used as received without further purification or chemical modification.

The stock solutions, 0.001M of Nile blue A, 0.01M of L-ascorbic acid, 0.01M Brij-35 and 1M NaOH have been used and all solutions have been prepared in distilled water.

**Characterization and apparatus:** The potential in millivolt (mV) were preliminarily measured by digital pH meter (pH Meter, LMPH-9, Labman Scientific Instruments Pvt. Ltd., Chennai, India; Range -  $\pm 1999$  mV; Accuracy - 0.1%), and current in microampere ( $\mu A$ ) were measured by Micro-ammeter (Micro-ammeter, OM Meter, Ambala Cantt Haryana, India). The artificial sunlight was getting from 200W incandescent tungsten filament bulb and sunlight intensity were measured by light meter (HTC LX-101A Luxmeter; Accuracy -  $\pm 5\%$  of the reading). A carbon pot log 470K device for changing the resistance of the circuit, a copper

(Cu) wires for completing the external circuit key, a brass plug circuit key for closing the circuit, a platinum (Pt) electrode for making negative terminal of the cell, and a saturated calomel electrode (SCE) for making positive terminal of the cell has been used in this study. SCE used as the reference electrode.

**Experimental Methods:** The experimental setup consist of a H-shaped photogalvanic cell equipped with Pt and SCE electrodes, artificial light source, digital pH meter (for measuring potential), micro-ammeter (for measuring current), carbon pot log (for changing resistance of circuit) and circuit keys, which all are connected together in photogalvanic cell set up (see **ESI Fig. S1**).

The H-shaped transparent and cylindrical glass tube was fabricated and filled with an identified amount of aqueous solution of Nile blue A (dye), L-ascorbic acid (Reductant), brij-35 (Surfactant) and sodium hydroxide (Alkali medium). One arm of the tube is darkened and other side is un-darkened to illuminate with artificial light source (200W incandescent tungsten filament bulb). Both SCE and Pt electrodes are submerged in the solution in darkened and un-darkened side arm of the tube, respectively. The area of Pt electrode were reduced to 12.5 times than the reported system for the purpose of reducing the cost of the galvanic cell and it is then placed in front of artificial light source. The terminals of both electrodes were connected to a digital pH meter and micro-ammeter through a key and resistance to measure the photo-potential and photo-current, respectively. According to the experimental setup, every part of the equipment is connected to one another in a circuit manner.

In order to establish a stable potential, the circuit is initially left open and put in a dark environment to obtain the dark potential ( $V_{dark}$ ). The electrolyte solution is then illuminated with artificial sunlight source while the circuit is still open to charge the cell. At various time intervals, the value of photo-potential is noted down. Maximum potential ( $V_{max}$ ) is the highest potential that can be measured during illumination. The cell is then said to be fully charged when it reaches a stable potential value known as open-circuit potential ( $V_{oc}$ ).  $V_{oc}$  is

little lower than the  $V_{max}$ . The cell's illumination is then turned off.

The circuit is then turned off. Maximum current ( $i_{max}$ ) is defined as the largest current obtained immediately after closing the circuit at resistance zero. Short-circuit current ( $i_{sc}$ ) is the result of the current obtained at a quite static value over time.

The potentiometer is used to adjust the circuit's resistance. By changing the current value from  $i_{sc}$  to zero value and noting the corresponding potential value, the  $i$ - $V$  characteristic of the cell is investigated (by altering the circuit resistance, zero current is attained at the greatest resistance). The term "power at power point" refers to the highest product of the current and the matching potential value (maximum power extractable from the cell,  $P_{pp}$ ). Current at power point ( $i_{pp}$ ) and potential at power point ( $V_{pp}$ ) are the abbreviations for the respective current and potential at power point.

The charging time ( $t$ ) is calculated using the following formula:

$$t = \text{Time at which } V_{oc} \text{ is attained} - \text{Time at which illumination is started}$$

The fill factor (FF) and conversion efficiency (CE) have been calculated using the following formula:

$$FF = \frac{(i_{pp} \times V_{pp})}{(i_{sc} \times V_{oc})}$$
$$CF = \frac{(i_{pp} \times V_{pp} \times FF \times 100\%)}{(A \times P)}$$

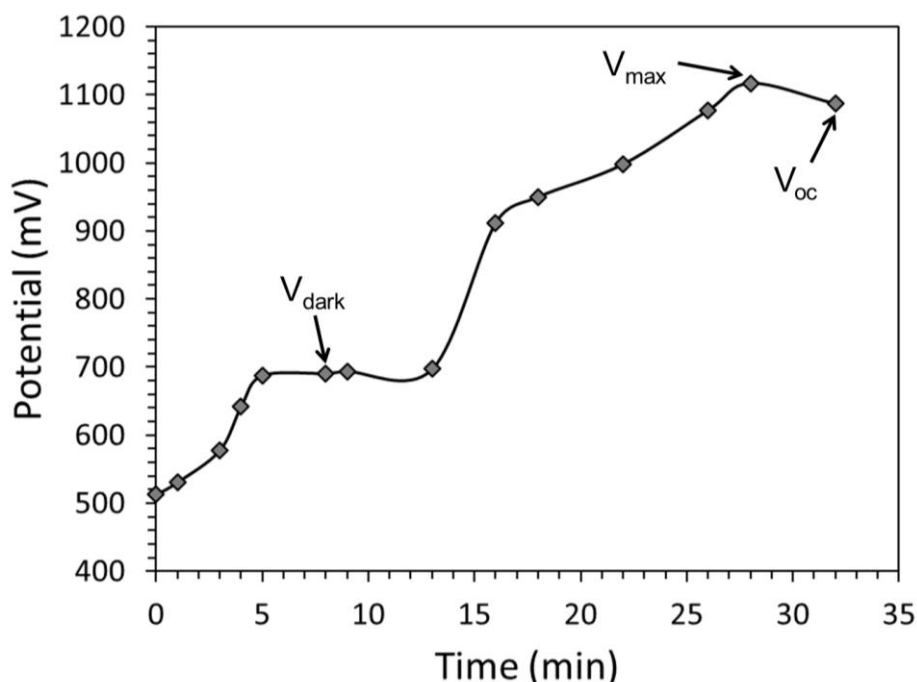
Where "A" stands for Pt electrode area ( $\text{cm}^2$ ) and "P" stands for average artificial solar intensity ( $\text{mWcm}^{-2}$ ), respectively. The half change time ( $t_{0.5}$ ), which is the amount of time it takes for the cell's power to drop to half of its highest level while being extracted from it in the dark at a particular external load, is used to

measure the power storage capacity of a cell (resistance).

### 3. RESULTS AND DISCUSSION

The fabrication of modified photogalvanic cell and improved modified photogalvanic effect (solar energy conversion and storage) have been observed on the variation of working electrode surface area and concentration of dye, reductant, surfactant and alkali compounds. In this study, Nile blue A as dye, L-Ascorbic acid as reductant, Brij-35 as surfactant, sodium hydroxide (NaOH) as alkali medium, and platinum (Pt) electrode as working electrode have been used for the fabrication of modified photogalvanic cell and to improve the conversion and storage of solar energy with enhanced electrical output at least cost. The study of effect of different variables such as concentration of dye, reductant, surfactant and alkali, and surface area of Pt electrode shows that the values of these variables affects the solar energy conversion performance of the modified photogalvanic cell. There is a characteristics value of each variable at which the modified photogalvanic cell shows the highest performance. Therefore, the optimum performance of the modified photogalvanic cell can be obtained by the careful selection of values of various variables. The optimal photogalvanic cell performance have been elucidated in terms of potential, power, photocurrent and charging time. In this modified photogalvanic cell setup, diffusion length ( $D_L$ ) and artificial sunlight intensity were fixed throughout the experiments and the values are 90 mm and  $10.4 \text{ mW.cm}^{-2}$ , respectively.

**Effect of variation of photopotential:** Effect of variation of photopotential has been studied by fabricating a modified photogalvanic cell consisting of  $6.0 \times 10^{-5} \text{ M}$  Nile blue A dye,  $1.6 \times 10^{-3} \text{ M}$  L-Ascorbic Acid reductant and  $1.2 \times 10^{-3} \text{ M}$  Brij-35 surfactant. The other conditions for modified photogalvanic cell are  $\text{pH} = 12.84$ , Pt electrode size (length x width) =  $0.4 \text{ cm} \times 0.2 \text{ cm}$ ,  $D_L = 90 \text{ mm}$ , and sun light intensity =  $10.4 \text{ mWcm}^{-2}$ .



**Figure 1:** Study of change in photopotential with respect to time in modified photogalvanic cell.

On illumination of modified photogalvanic cell, it was found that the photopotential of cell increases fairly exponentially and reached to a highest potential value that is marked as “ $V_{max}$ ”, which then decreases and becomes fairly constant that is marked as “ $V_{oc}$ ” (**Fig. 1**). It is due to the increasing number of excited electrons and increasing number of electrons donating dye molecules during illumination. At  $V_{max}$ , the number of excited electrons and electron donating dye molecules are highest.

**Effect of variation of Nile blue A dye photosensitizer concentration:** Effect of variation of Nile blue A dye photosensitizer concentration has been studied by fabricating five photogalvanic cells having different concentration of dye and rest other factors

remain constant in each cell. Each photogalvanic cell has packed with 25 mL electrolyte solution of dye-reductant-surfactant-alkali and double distilled water (See **ESI Table S1** for composition and concentration of each component of cell with variable Nile blue A dye concentration). The volume of 0.001M Nile blue A dye in all five cells are 0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL and 2.5 mL, and the resultant concentration of dye in each cell is  $2.0 \times 10^{-5}M$ ,  $4.0 \times 10^{-5}M$ ,  $6.0 \times 10^{-5}M$ ,  $8.0 \times 10^{-5}M$  and  $10.0 \times 10^{-5}M$ , respectively. The increasing trends in cell parameters was observed from  $2.0 \times 10^{-5}M$  to  $6.0 \times 10^{-5}M$  concentration of Nile blue A dye and afterward the decreasing trends in cell parameters was observed from  $6.0 \times 10^{-5}M$  to  $10.0 \times 10^{-5}M$  concentration of Nile blue A dye (**Table 1**).

**Table 1:** Effect of variation of Nile blue A dye concentration on the performance of photogalvanic cell.

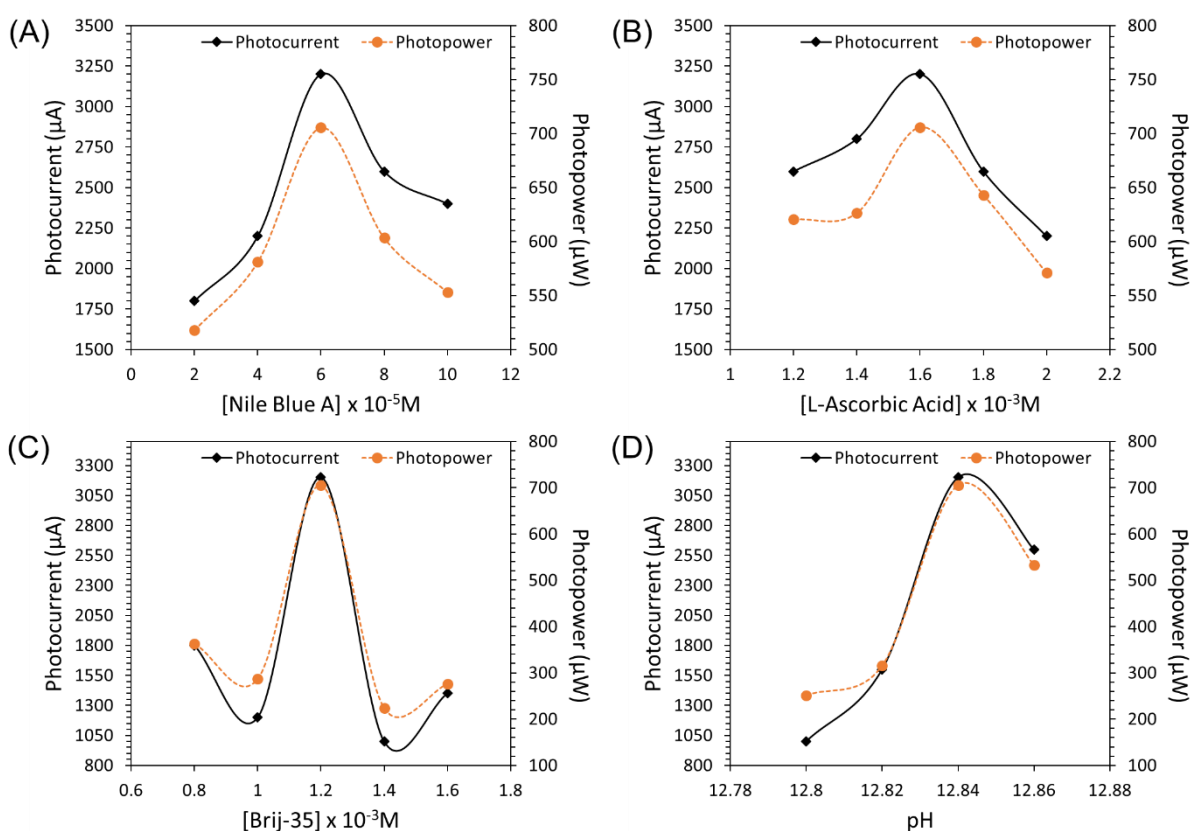
Entry	Cell Parameters (Unit)	[Nile blue A] x $10^{-5}M$				
		2.0	4.0	6.0	8.0	10.0
1	$V_{dark}$ (mV)	560	592	691	562	578
2	$V_{max}$ (mV)	1148	1154	1117	1122	1032
3	$V_{oc}$ (mV)	1117	1128	1087	1078	1017
4	$i_{max}$ ( $\mu A$ )	1800	2200	3200	2600	2400

5	$i_{eq}$ or $i_{sc}$ ( $\mu A$ )	1400	1800	<b>2800</b>	2000	2200
6	$V_{pp}$ (mV)	863	581	<b>504</b>	431	461
7	$P_{pp}$ ( $\mu W$ )	517.8	581.0	<b>705.6</b>	603.4	553.2
8	$i_{pp}$ ( $\mu A$ )	600	1000	<b>1400</b>	1400	1200
9	t (min)	24	33	<b>28</b>	20	16
10	CE (%)	20.60	19.98	<b>19.67</b>	20.29	16.43
11	FF	0.3311	0.2861	<b>0.232</b>	0.2798	0.2472

**Note:** [L-Ascorbic Acid] =  $1.6 \times 10^{-3} M$ ; [Brij-35] =  $1.2 \times 10^{-3} M$ ; pH = 12.84; Pt electrode size (Length x Width) = 0.4 cm x 0.2 cm; Diffusion length ( $D_L$ ) = 90 mm; Sunlight intensity =  $10.4 \text{ mWcm}^{-2}$ .

Thus, a maxima was obtained in  $6.0 \times 10^{-5} M$  concentration of Nile blue A dye and found the maximum electrical output in modified photogalvanic cell. It was happened due to the optimal concentration of Nile blue A dye which absorb appropriate amount of solar energy and donate appropriate number of electrons to Pt electrode and found maximum performance of modified photogalvanic cell. Whereas, higher concentration of Nile blue A dye ( $10.0 \times 10^{-5} M$ )

will not allow the absorption of appropriate amount of solar energy and therefore, a fall was obtained in the performance of modified photogalvanic cell. See **Fig. 2(A)** for graphical demonstration of photocurrent and photopower of modified photogalvanic cell that was fabricated with variable concentration of Nile blue A dye and observed a peak at  $6.0 \times 10^{-5} M$  concentration of Nile blue A dye indicating maximum electrical output and improved performance of modified photogalvanic cell.



**Figure 2:** Graphical demonstration of effect of variables on the photocurrent and photopower of modified photogalvanic cell. (A) Nile blue A; (B) L-Ascorbic acid; (C) Brij-35; and (D) pH.

**Effect of variation of L-Ascorbic acid reductant concentration:** Effect of variation of L-ascorbic acid reductant concentration has been studied by fabricating five photogalvanic cells having different concentration of reductant and rest other factors remain constant in each cell. Each photogalvanic cell has packed with 25 mL electrolyte solution of dye-reductant-surfactant-alkali and double distilled water (See **ESI Table S2** for composition and concentration of each component of cell with variable L-ascorbic acid reductant concentration). The volume of 0.01M L-ascorbic acid reductant in all five cells are 3.0

mL, 3.5 mL, 4.0 mL, 4.5 mL and 5.0 mL, and the resultant concentration of reductant in each cell is  $1.2 \times 10^{-3}\text{M}$ ,  $1.4 \times 10^{-3}\text{M}$ ,  $1.6 \times 10^{-3}\text{M}$ ,  $1.8 \times 10^{-3}\text{M}$  and  $2.0 \times 10^{-3}\text{M}$ , respectively. The increasing trends in cell parameters was observed from  $1.2 \times 10^{-3}\text{M}$  to  $1.6 \times 10^{-3}\text{M}$  concentration of L-ascorbic acid reductant and afterward the decreasing trends in cell parameters was observed from  $1.6 \times 10^{-3}\text{M}$  to  $2.0 \times 10^{-3}\text{M}$  concentration of L-ascorbic acid reductant (**Table 2**). Thus, a maxima was obtained in  $1.6 \times 10^{-3}\text{M}$  concentration of L-ascorbic acid reductant and found the maximum electrical output in modified photogalvanic cell.

**Table 2:** Effect of variation of L-Ascorbic acid reductant concentration on the performance of photogalvanic cell.

Entry	Cell Parameters (Unit)	[L-Ascorbic acid] x $10^{-3}\text{M}$				
		1.2	1.4	1.6	1.8	2.0
1	$V_{\text{dark}}$ (mV)	520	688	<b>691</b>	540	521
2	$V_{\text{max}}$ (mV)	1180	1094	<b>1117</b>	1138	1084
3	$V_{\text{oc}}$ (mV)	1143	1056	<b>1027</b>	1076	1056
4	$i_{\text{max}}$ ( $\mu\text{A}$ )	2600	2800	<b>3200</b>	2600	2200
5	$i_{\text{eq}}$ or $i_{\text{sc}}$ ( $\mu\text{A}$ )	2400	2600	<b>2800</b>	2400	1800
6	$V_{\text{pp}}$ (mV)	517	522	<b>504</b>	536	571
7	$P_{\text{pp}}$ ( $\mu\text{W}$ )	620.4	626.4	<b>705.6</b>	643.2	571.0
8	$i_{\text{pp}}$ ( $\mu\text{A}$ )	1200	1200	<b>1400</b>	1200	1000
9	t (min)	29	24	<b>28</b>	18	16
10	CE (%)	16.86	17.17	<b>19.67</b>	19.25	20.61
11	FF	0.226	0.228	<b>0.2453</b>	0.249	0.300

**Note:** [Nile blue A] =  $6.0 \times 10^{-5}\text{M}$ ; [Brij-35] =  $1.2 \times 10^{-3}\text{M}$ ; pH = 12.84; Pt electrode size (Length x Width) = 0.4 cm x 0.2 cm; Diffusion length ( $D_L$ ) = 90 mm; Sunlight intensity =  $10.4 \text{ mWcm}^{-2}$ .

It was happened due to the optimal concentration of L-ascorbic acid reductant which donate appropriate number of electrons to Nile blue A dye and found maximum performance of modified photogalvanic cell. Whereas, higher concentration of L-ascorbic acid reductant will not allow the absorption of appropriate amount of solar energy by dye molecules and hinder the mobility of dye molecules, and therefore, a fall was obtained in the performance of modified photogalvanic cell. See **Fig. 2(B)** for graphical demonstration of photocurrent and photopower of modified photogalvanic cell that was fabricated with variable concentration of L-ascorbic acid

reductant and observed a peak at  $1.6 \times 10^{-3}\text{M}$  concentration of L-ascorbic acid reductant indicating maximum electrical output and improved performance of modified photogalvanic cell.

**Effect of variation of Brij-35 surfactant concentration:** Effect of variation of Brij-35 surfactant concentration has been studied by fabricating five photogalvanic cells having different concentration of surfactant and rest other factors remain constant in each cell. Each photogalvanic cell has packed with 25 mL electrolyte solution of dye-reductant-surfactant-alkali and double distilled water (See

**ESI Table S3** for composition and concentration of each component of cell with variable Brij-35 surfactant concentration). The volume of 0.01M Brij-35 surfactant in all five cells are 2.0 mL, 2.5 mL, 3.0 mL, 3.5 mL and 4.0 mL, and the resultant concentration of surfactant in each cell is  $0.8 \times 10^{-3}\text{M}$ ,  $1.0 \times 10^{-3}\text{M}$ ,  $1.2 \times 10^{-3}\text{M}$ ,  $1.4 \times 10^{-3}\text{M}$  and  $1.6 \times 10^{-3}\text{M}$ , respectively. The increasing trends in cell parameters was observed from  $0.8 \times 10^{-3}\text{M}$  to  $1.2 \times 10^{-3}\text{M}$  concentration of Brij-35 surfactant and afterward the decreasing trends in cell parameters was observed from  $1.2 \times 10^{-3}\text{M}$  to  $1.6 \times 10^{-3}\text{M}$  concentration of Brij-35 surfactant (**Table 3**). Thus, a maxima was obtained in  $1.2 \times 10^{-3}\text{M}$  concentration of Brij-35 surfactant and found the maximum electrical output in

modified photogalvanic cell. It was happened due to the critical micelle concentration (CMC) of Brij-35 surfactant which create dye-micelle system. This system allow dye molecule to eject electrons from dye-micelle system to aqueous system. The ejected electrons is then attracted by the Pt electrode and therefore got the maximum performance of modified photogalvanic cell. See **Fig. 2(C)** for graphical demonstration of photocurrent and photopower of modified photogalvanic cell that was fabricated with variable concentration of Brij-35 surfactant and observed a peak at  $1.2 \times 10^{-3}\text{M}$  concentration of Brij-35 surfactant indicating maximum electrical output and improved performance of modified photogalvanic cell.

**Table 3:** Effect of variation of Brij-35 surfactant concentration on the performance of photogalvanic cell.

Entry	Cell Parameters (Unit)	[Brij-35] x 10 <sup>-3</sup> M				
		0.8	1.0	1.2	1.4	1.6
1	V <sub>dark</sub> (mV)	430	528	<b>691</b>	583	590
2	V <sub>max</sub> (mV)	1127	1120	<b>1117</b>	1106	1105
3	V <sub>oc</sub> (mV)	1079	1103	<b>1087</b>	1078	1081
4	i <sub>max</sub> (μA)	1800	1200	<b>3200</b>	1000	1400
5	i <sub>eq</sub> or i <sub>sc</sub> (μA)	1600	1000	<b>2800</b>	800	960
6	V <sub>pp</sub> (mV)	605	495	<b>504</b>	590	460
7	P <sub>pp</sub> (μW)	363.0	287.1	<b>705.6</b>	224.2	276.0
8	i <sub>pp</sub> (μA)	600	580	<b>1400</b>	380	600
9	t (min)	36	17	<b>28</b>	19	20
10	CE (%)	9.17	8.98	<b>19.67</b>	7.00	8.82
11	FF	0.210	0.260	<b>0.232</b>	0.260	0.266

**Note:** [Nile blue A] =  $6.0 \times 10^{-5}\text{M}$ ; [L-Ascorbic Acid] =  $1.6 \times 10^{-3}\text{M}$ ; pH = 12.84; Pt working electrode size (Length x Width) = 0.4 cm x 0.2 cm; Diffusion length (D<sub>L</sub>) = 90 mm; Sunlight intensity = 10.4 mWcm<sup>-2</sup>.

**Effect of variation of pH:** Effect of variation of pH has been studied by fabricating four photogalvanic cells having different concentration of NaOH and rest other factors remain constant in each cell. Each photogalvanic cell has packed with 25 mL electrolyte solution of dye-reductant-surfactant-alkali and double distilled water (See **ESI Table S4** for composition and concentration of each component of cell with variable NaOH concentration). The volume of

1M NaOH solution in all four cells are 4.5 mL, 5.0 mL, 5.5 mL and 6.0 mL, and the resultant pH of solution in each cell is 12.80, 12.82, 12.84 and 12.86, respectively. The increasing trends in cell parameters was observed from pH 12.80 to 12.84 and afterward the decreasing trends in cell parameters was observed from pH 12.84 to 12.86 (**Table 4**). Thus, a maxima was obtained at pH 12.84 and found the maximum electrical output in modified photogalvanic cell.



**Table 4:** Effect of variation of pH on the performance of photogalvanic cell at 60°C.

Entry	Cell Parameters (Unit)	pH of Solution			
		12.80	12.82	12.84	12.86
1	V <sub>dark</sub> (mV)	630	641	<b>691</b>	656
2	V <sub>max</sub> (mV)	1140	1098	<b>1117</b>	1104
3	V <sub>oc</sub> (mV)	1098	1026	<b>1087</b>	1029
4	i <sub>max</sub> (μA)	1000	1600	<b>3200</b>	2600
5	i <sub>eq</sub> or i <sub>sc</sub> (μA)	920	1400	<b>2800</b>	2200
6	V <sub>pp</sub> (mV)	503	526	<b>504</b>	533
7	P <sub>pp</sub> (μW)	251.5	315.6	<b>705.6</b>	533.0
8	i <sub>pp</sub> (μA)	500	600	<b>1400</b>	1000
9	t (min)	46	33	<b>28</b>	27
10	CE (%)	7.52	8.33	<b>19.67</b>	15.08
11	FF	0.2489	0.2197	<b>0.232</b>	0.2354

**Note:** [Nile blue A] = 6.0 x 10<sup>-5</sup>M; [L-Ascorbic Acid] = 1.6 x 10<sup>-3</sup>M; [Brij-35] = 1.2 x 10<sup>-3</sup>M; Pt working electrode size (Length x Width) = 0.4 cm x 0.2 cm; Diffusion length (D<sub>L</sub>) = 90 mm; Sunlight intensity = 10.4 mWcm<sup>-2</sup>.

It was happened due to the relationship of alkali with reductant and the optimum pH value increases the availability of reductant in its anionic form and it is come in better condition to donate electrons. Thus, the performance of modified photogalvanic cell was improved at a particular pH. See **Fig. 1(D)** for graphical demonstration of photocurrent and photopower of modified photogalvanic cell that was fabricated with variable pH range and observed a peak at pH 12.84 indicating maximum electrical output and improved performance of modified photogalvanic cell.

**Effect of variation of platinum electrode size and area:** Effect of variation of Pt electrode size and area has been studied by fabricating five photogalvanic cells with variable sizes of Pt electrode and rest other factors remain

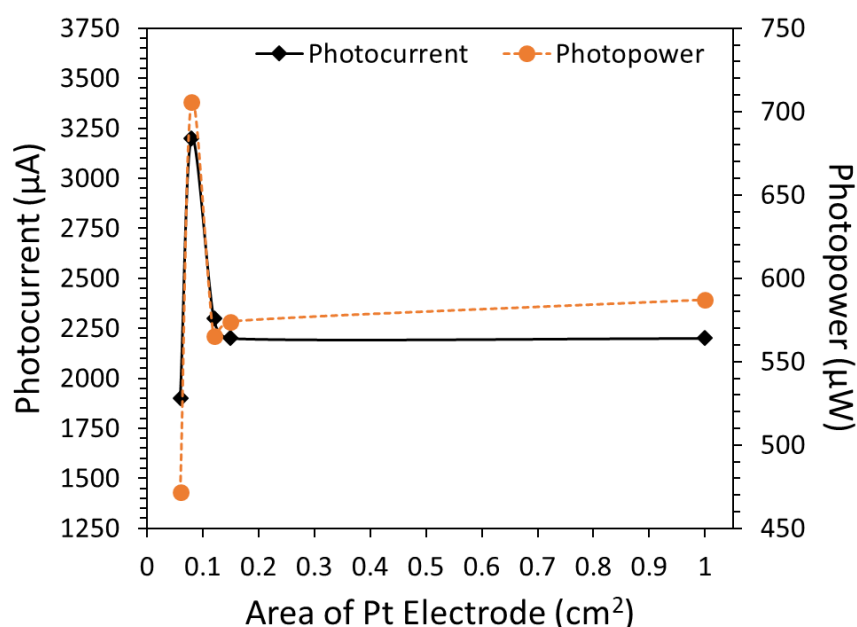
constant in each cell which was optimized previously. The size (length x width in cm) of Pt electrode in all five cells are 0.3 x 0.2, 0.4 x 0.2, 0.4 x 0.3, 0.5 x 0.3 and 1.0 x 1.0, and the resultant area (cm<sup>2</sup>) of Pt electrode in each cell is 0.06, 0.08, 0.12, 0.15 and 1.00, respectively. The highest electrical output was observed in modified photogalvanic cell that was fabricated with Pt electrode of 0.4 cm x 0.2 cm size and 0.08 cm<sup>2</sup> area (**Table 5**). It was happened due to the optimal optimum number of electrons striking to the smaller sized Pt electrode and faster mobility of electrons. The smaller sized electrode containing modified photogalvanic cell was performed well and have highest electrical output (**Fig. 3**). It will help to reduce the cost of fabrication of photogalvanic cell and provide a more economical viable system with higher solar energy conversion and storage capacity.

**Table 5:** Effect of variation of platinum electrode size on the performance of photogalvanic cell.

Entry	Cell Parameters (Unit)	Platinum (Pt) Electrode Size (Length x Width) in cm and Area				
		0.3 x 0.2 (0.06 cm <sup>2</sup> )	0.4 x 0.2 (0.08 cm <sup>2</sup> )	0.4 x 0.3 (0.12 cm <sup>2</sup> )	0.5 x 0.3 (0.15 cm <sup>2</sup> )	1.0 x 1.0 (1.00 cm <sup>2</sup> )
1	V <sub>dark</sub> (mV)	785	<b>691</b>	672	638	622
2	V <sub>max</sub> (mV)	1088	<b>1117</b>	1122	1164	1140

3	$V_{oc}$ (mV)	1069	<b>1087</b>	1109	1130	1114
4	$i_{max}$ ( $\mu A$ )	1900	<b>3200</b>	2300	2200	2200
5	$i_{eq}$ or $i_{sc}$ ( $\mu A$ )	1700	<b>2800</b>	1800	2000	1400
6	$V_{pp}$ (mV)	555	<b>504</b>	471	574.0	587
7	$P_{pp}$ ( $\mu W$ )	471.75	<b>705.60</b>	565.20	574	587
8	$i_{pp}$ ( $\mu A$ )	850	<b>1400</b>	1200	1000	1000
9	t (min)	19	<b>28</b>	27	20	15
10	CE (%)	19.62	<b>19.67</b>	12.82	9.3452	2.124
11	FF	0.2595	<b>0.232</b>	0.2831	0.2451	0.3763

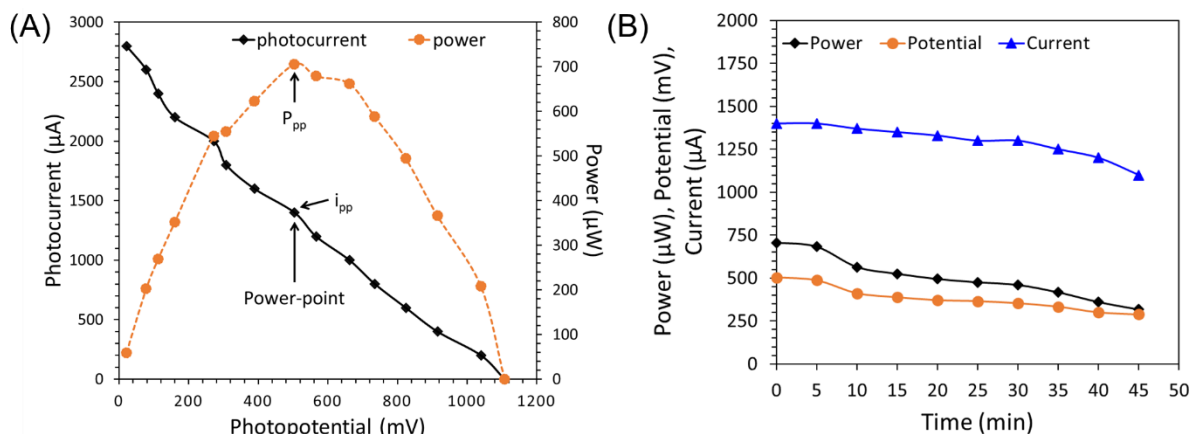
Note: [Nile blue A] =  $6.0 \times 10^{-5} M$ ; [L-Ascorbic Acid] =  $1.6 \times 10^{-3} M$ ; [Brij-35] =  $1.2 \times 10^{-3} M$ ; pH of solution = 12.84; Diffusion length ( $D_L$ ) = 90 mm; Sunlight intensity =  $10.4 \text{ mWcm}^{-2}$ .



**Figure 3:** Graphical demonstration of effect of Platinum electrode area on the photocurrent and photopower of modified photogalvanic cell.

**Photocurrent, photopotential and power characteristics of the modified Photogalvanic cell:** A modified Photogalvanic cell has been studied consists of optimized amount of dye, reductant, surfactant and alkali such as 1.5 mL of 0.001M Nile blue A dye, 4.0 mL of 0.01M L-Ascorbic Acid reductant, 3.0 mL of 0.01M Brij-35 surfactant, 5.5 mL of 1M NaOH alkali and 11.0 mL distilled water to make up to 25 mL total volume. The other specification for this cell are  $D_L = 90$  mm, sunlight intensity =  $10.4 \text{ mWcm}^{-2}$ , optimized Pt electrode area =  $0.08 \text{ cm}^2$ , pH = 12.84, and temperature = 310K.

The photocurrent-photopotential (i-V) characteristics of the modified photogalvanic cell shows that the highest power ( $705.6 \mu W$ ) is extractable from cell at 504 mV photopotential and the photocurrent is  $1400 \mu A$  at this point (**Fig. 4(A)**; **ESI Table S5**). This point is then nominated as power point. The power point power ( $P_{pp}$ ) and photocurrent ( $i_{pp}$ ) are  $705.6 \mu W$  and  $1400 \mu A$ , respectively. Therefore, the cell performance of modified photogalvanic cell has been studied at this stage.



**Figure 5:** Study of modified photogalvanic cell. (A) Photocurrent-power characteristics; (B) Cell performance with respect to time (Time vs Power; Time vs Potential; and Time vs Current).

The cell performance of modified photogalvanic cell shows that the power of cell decreases with time as a result of deactivation of dye molecules in dark (Fig. 4(B); ESI Table S6). The power at power point reduces to its half value in 45 minutes that is called as half change time ( $t_{0.5}$ ). Even after  $t_{0.5}$ , the modified photogalvanic cell continuously supplies the power till its complete discharge.

Cell parameters of this modified photogalvanic cell at specification given above are summarized as  $V_{\text{dark}} = 691$  mV;  $V_{\text{max}} = 1117$  mV;  $V_{\text{oc}} = 1087$  mV;  $i_{\text{max}} = 3200$  μA,  $i_{\text{sc}} = 2800$  μA;  $V_{\text{pp}} = 504$  mV;  $P_{\text{pp}} = 705.60$  μW;  $i_{\text{pp}} = 1400$  μA; charging time ( $t$ ) = 24 min; half change time ( $t_{0.5}$ ) = 45 min; Potential at  $t_{0.5} = 289$  mV; Current at  $t_{0.5} = 1100$  μA; Power at  $t_{0.5} = 317.9$  μW; CE = 19.67%; and FF = 0.232.

#### 4. CONCLUSION

The present research on the development of modified photogalvanic cell for the conversion and storage of solar energy challenges to mitigate the enhanced conversion efficiency, storage capacity, and higher electrical output with reduced cost of fabrication. An integrated system of Nile blue A (as dye), L-ascorbic acid (as reductant) and Brij-35 (as surfactant) has been used for the fabrication of modified photogalvanic cell. The modified photogalvanic cell with optimized concentration of dye-reductant-surfactant showed significantly improved performance. It can be expressed in terms of dark potential (691 mV), open-circuit potential (1087 mV), short-circuit current (2800 μA), power (705.60 μW),

charging time (24 min), half change time (45 min), and conversion efficiency (19.67%). The improved performance has been obtained with the small-sized platinum electrode. It is concluded that the modified photogalvanic cell with optimized concentration of dye-reductant-surfactant and small-sized platinum electrode showed improved performance, and therefore, the researcher has been able to improve the performance of cell at reduced cost of fabrication. Therefore, it is good to achieve the economic viability and ease of commercial application of photogalvanic cell.

#### Acknowledgement

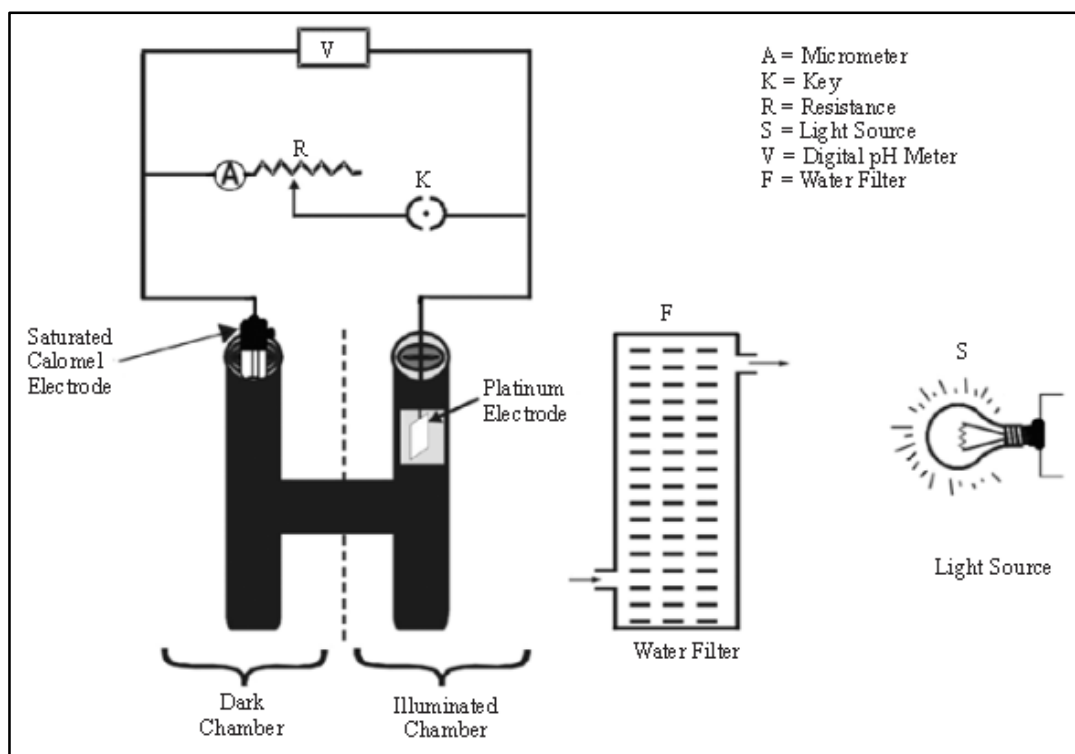
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**Figure S1:** Experimental setup of photogalvanic cell (A = Microammeter; K = Key; R = Resistance; and V = Digital pH meter).

**Table S1:** Study of change in chemical composition of cell of variation of Nile blue A photosensitizer dye.

Entry	Volume of chemical solution used to prepare total 25 mL mixture					Resultant Concentrations			
	0.001M Nile Blue A (mL)	0.01M L-Ascorbic Acid (mL)	0.01M Brij-35 (mL)	1M NaOH (mL)	Double Distilled Water (mL)	[Nile Blue-A] x 10 <sup>-5</sup> M	[L-Ascorbic acid] x 10 <sup>-3</sup> M	[Brij-35] x 10 <sup>-3</sup> M	[NaOH] pH
1	0.5	4.0	3.0	5.5	12.0	2.0	1.6	1.2	12.84
2	1.0	4.0	3.0	5.5	11.5	4.0	1.6	1.2	12.84
3	1.5	4.0	3.0	5.5	11.0	6.0	1.6	1.2	12.84
4	2.0	4.0	3.0	5.5	10.5	8.0	1.6	1.2	12.84
5	2.5	4.0	3.0	5.5	10.0	10.0	1.6	1.2	12.84

**Note:** #Saturated Calomel Electrode as reference electrode; Pt working electrode size 0.4 cm x 0.2 cm; and sunlight intensity 10.4 mWcm<sup>-2</sup>.

**Table S2:** Study of change in chemical composition of cell of variation of L-ascorbic acid reductant.

Entry	Volume of chemical solution used to prepare total 25 mL mixture					Resultant Concentrations			
	0.001M Nile Blue A (mL)	0.01M L-Ascorbic Acid (mL)	0.01M Brij-35 (mL)	1M NaOH (mL)	Double Distilled Water (mL)	[Nile Blue-A] x 10 <sup>-5</sup> M	[L-Ascorbic acid] x 10 <sup>-3</sup> M	[Brij-35] x 10 <sup>-3</sup> M	[NaOH] pH
1	1.5	3.0	3.0	5.5	12.0	6.0	1.2	1.2	12.84
2	1.5	3.5	3.0	5.5	11.5	6.0	1.4	1.2	12.84
3	1.5	4.0	3.0	5.5	11.0	6.0	1.6	1.2	12.84
4	1.5	4.5	3.0	5.5	10.5	6.0	1.8	1.2	12.84
5	1.5	5.0	3.0	5.5	10.0	6.0	2.0	1.2	12.84

**Note:** #Saturated Calomel Electrode as reference electrode; Pt working electrode size 0.4 cm x 0.2 cm; and sunlight intensity 10.4 mWcm<sup>-2</sup>.

**Table S3:** Study of change in chemical composition of cell of variation of Brij-35 surfactant.

Entry	Volume of chemical solution used to prepare total 25 mL mixture					Resultant Concentrations			
	0.001M Nile Blue A (mL)	0.01M L-Ascorbic Acid (mL)	0.01M Brij-35 (mL)	1M NaOH (mL)	Double Distilled Water (mL)	[Nile Blue-A] x 10 <sup>-5</sup> M	[L-Ascorbic acid] x 10 <sup>-3</sup> M	[Brij-35] x 10 <sup>-3</sup> M	[NaOH] pH
1	1.5	4.0	2.0	5.5	12.0	6.0	1.6	0.8	12.84
2	1.5	4.0	2.5	5.5	11.5	6.0	1.6	1.0	12.84
3	1.5	4.0	3.0	5.5	11.0	6.0	1.6	1.2	12.84
4	1.5	4.0	3.5	5.5	10.5	6.0	1.6	1.4	12.84
5	1.5	4.0	4.0	5.5	10.0	6.0	1.6	1.6	12.84

**Note:** #Saturated Calomel Electrode as reference electrode; Pt working electrode size 0.4 cm x 0.2 cm; and sunlight intensity 10.4 mWcm<sup>-2</sup>.

**Table S4:** Study of change in chemical composition of cell of variation of sodium hydroxide (NaOH) and pH at 60°C.

Entry	Volume of chemical solution used to prepare total 25 mL mixture					Resultant Concentrations			
	0.001M Nile Blue A (mL)	0.01M L-Ascorbic Acid (mL)	0.01M Brij-35 (mL)	1M NaOH (mL)	Double Distilled Water (mL)	[Nile Blue-A] x 10 <sup>-5</sup> M	[L-Ascorbic acid] x 10 <sup>-3</sup> M	[Brij-35] x 10 <sup>-3</sup> M	[NaOH] pH
1	1.5	4.0	3.0	4.5	12.0	6.0	1.6	1.2	12.80
2	1.5	4.0	3.0	5.0	11.5	6.0	1.6	1.2	12.82
3	1.5	4.0	3.0	5.5	11.0	6.0	1.6	1.2	12.84
4	1.5	4.0	3.0	6.0	10.5	6.0	1.6	1.2	12.86

**Note:** #Saturated Calomel Electrode as reference electrode; Pt working electrode size 0.4 cm x 0.2 cm; and sunlight intensity 10.4 mWcm<sup>-2</sup>.

**Table S5:** Photocurrent-power (i-V) characteristics of modified photogalvanic cell.

Entry	Photocurrent (μA)	Photopotential (mV)	Power (μW)
1	2800	21	58.8
2	2600	78	202.2
3	2400	112	268.8
4	2200	160	352
5	2000	272	544
6	1800	308	554.4
7	1600	389	622
8	1400	504	705.6
9	1200	566	679.2
10	1000	662	662
11	800	735	588
12	600	824	494.4
13	400	915	366
14	000	1108	0

**Table S6:** Study of performance of modified photogalvanic cell with respect to time.

Entry	Time (min)	Power (μW)	Potential (mV)	Current (μA)
1	0	705.6	504	1400
2	5	681.8	487	1400
3	10	564.44	412	1370
4	15	525.15	389	1350
5	20	494.76	372	1330
6	25	475.8	366	1300
7	30	460.2	354	1300
8	35	417.5	334	1250
9	40	361.2	301	1200
10	45	317.9	289	1100