Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2014

Photogalvanic cells: Comparative study of various synthetic dye and natural photo sensitizer present in spinach extract

Pooran Koli*, Department of Chemistry, Jai Narain Vyas University

Jodhpur – 342033, Rajasthan, INDIA

1. Method

1.1. Chemicals

The chemicals, Sudan-I of (>95 % Assay-Purity, HIMEDIA, Mumbai, INDIA) as photosensitizer, Rhodamine B (90 % Assay-Purity, Ases Chemical Works, Jodhpur, INDIA) as photosensitizer, Fast Green FCF (LOBA Chemie Pvt. Ltd., Mumbai, INDIA) as photosensitizer, Brilliant Cresyl Blue (Ases Chemical Works, Jodhpur, INDIA) as photosensitizer, Naphthol Green B (LOBA Chemie Pvt. Ltd., Mumbai, INDIA) as photosensitizer, aqueous Spinach Extract as source of natural photo-sensitizers, Fructose (99.8 % Assay-Purity, Ases Chemical Works, Jodhpur, INDIA) as reductant, Sodium lauryl sulfate-NaLS (94 % minimum Assay-Purity, Ases Chemical Works, Jodhpur, INDIA) as surfactant, NaOH (98 % Assay-Purity, Ases Chemical Works, Jodhpur, INDIA) as alkaline medium, and Oxalic Acid (99.5 % Assay-Purity, RANKEM, New Delhi, INDIA) for standardization of NaOH with Phenolphthalein (Merck Specialities Pvt. Ltd., Mumbai, INDIA) as indicator have been used.

Tel. & Fax +91 2912614162,E-mail:poorankoli@rediffmail.com,poorankoli@yahoo.com

Characteristics of Sudan-I (SUD) dye are M.F. $C_{16}H_{12}N_2O$, M.W. 248.28, λ_{max} 476 nm, and Color Index No. 12055.Where, λ_{max} is wavelength of irradiation at which absorbance of dye is highest.

Characteristics of Rhodamine-B (RHD) dye are M.F. $C_{28}H_{31}Cl\ N_2O_3$, M.W. 479.02, λ_{max} (nm) 543,□ (dm^3 mol^{-1} cm^{-1}) 60000.0, and Color Index No. 45170.Where, □ is molar absorptivity of Rhodamine-B dye (defined as equal to absorbance of solution having one molar concentration and one centimeter thickness).

Characteristics of Fast Green FCF (FGF) dye are M.F. $C_{37}H_{34}N_2\ Na_2O_{10}S_3$, M.W. 808.84, λ_{max} (nm) 622-626(high intensity band) and 427(low intensity band) in C_2H_5OH 50%,60 g/l solubility in water at 20°C, 5 g/l solubility in alcohol at 20°C and Color Index No. 42053.

Characteristics of Brilliant Cresyl Blue (BCB) dye are M.F. $C_{17}H_{20}ClN_3O$. 0.5 $ZnCl_2$, M.W. 385.96, λ_{max} (nm) 622, UV-Visible Spectrum [at Conc. 0.005 g/l in 50% Ethanol, E 626(+/-3 nm) >/= 40,000; E 250 (+/- 3 nm) >/= 15,000; E238 (+/- 3 nm) >/= 15,000], Solubility 1 mg/ml H_2O (Clear to opaque, blue solution) and Color Index No. 51010.

Characteristics of Naphthol Green B (NGB) dye are M.F. $C_{30}H_{15}FeN_3Na_3O_{15}S_3$, M.W. 878.46 g/mol, λ_{max} (nm) 714 in water (1 cm,1 %, Aldrich) (315, 690 Gurr), (CAS number 19381-50-1 ,Color Index No. 10020, color Green. Naphthol Green B is the sodium salt of Naphthol Green Y (C.I. 10005). It can be solved in water, however not in ethanol. As an anion, it acts as acid dye.

Aqueous Spinach Extract (SPE) was used as source of natural photo-sensitizer(s). Aqueous Spinach Extract was obtained as (i) Fresh spinach leaves were washed with water, (ii) the washed and wet leaves (50 gm) were crushed in presence of a little water (10 ml) in a Jar of electric mixer, (iii) then crushed matter was filtered with a ordinary filter paper, (iv) filtrate was left undisturbed for some time to allow sedimentation of fibrous and other matter, and (v) the transparent liquid above sediment was used as aqueous Spinach Extract for photosensitization of solution in photogalvanic cell.

Fresh spinach is convenient source of Chlorophyll a & b. The absorption band of chlorophyll-a is at 660 nm (in red region) & 430 nm (in blue) in diethylether. The absorption band of chlorophyll-b is at 650 nm (in red region) & 453 nm (in blue) in diethylether. Under the present experimental conditions, the absorption bands of crude spinach extract were observed at 680 nm (in red region) & 435 nm (in blue). Chlorophyll absorbs radiation almost over the range particularly in the blue-violet (470 nm) and red (650 nm -700 nm). The chlorophyll is the green photosynthetic pigment present in chloroplasts which provides the energy necessary for photosynthesis. The intense green color of chlorophyll is due to its strong absorbencies in the red and blue regions of the electromagnetic spectrum, and because of these absorbencies the light it reflects and transmits appears green.

The solutions, Sudan-I (SUD) dye (M/500, i.e., concentration is five hundredth part of one molar), Rhodamine-B (RHD) dye, Fast Green FCF(FGF), Brilliant Cresyl Blue (BCB) dye, Naphthol Green B (NGB), Aqueous Spinach Extract-SPE (as source of natural photosensitizers), Fructose (M/100,i.e., concentration is one hundredth part of one molar), NaLS (M/10, i.e., concentration is one tenth part of one molar), NaOH (1M, i.e., concentration is one molar) and Oxalic Acid (1M, i.e., concentration is one molar) have been used. All the solutions except Sudan-I have been prepared in single distilled water, and kept in amber colored containers to protect them from sunlight. Solution of Sudan-I has been prepared in ethyl alcohol.

1.2. Basis for chemical composition of various cells

The individual photosensitizers based Photogalvanic cells are thought to use only narrow solar spectrum for solar power generation and storage. The use of narrow spectrum (and failure to absorb broader spectrum) is cited as one of the reason for lower solar power out put of these cells. So, with aim of using relatively wider part of solar spectrum, mixed photosensitizers having λ_{max} in different spectral regions have been used. The various used photosensitizers with λ_{max} (in nm) for mixing are NGB (714 nm), FCF (622 nm), BCB (622 nm), SPE (435 nm & 680 nm), RHD (543 nm) and SUD (476 nm). First, individual photosensitizer based cells were studied to use narrow solar spectrum for solar power generation. Among them one was NGB (714 nm) based cell for use of narrow spectrum (i.e., radiations near 700 nm). Thereafter, photogalvanic cells based on mixed photosensitizers were studied with aim of use of wider solar spectrum for solar power generation. The mixing of photosensitizers was done starting from NGB (λ_{max} 714 nm) side.

The NGB (714) based Photogalvanic cells are thought to use relatively narrow spectrum (700-800 nm). The NGB (714 nm) + FCF (622 nm) +BCB (622 nm) based Photogalvanic cells were studied for using relatively broader spectrum (i.e., radiations ranging from 800-700 to 700-600 nm) for solar power generation. The NGB (714 nm) + FCF (622 nm) + BCB (622 nm) + SPE (435 nm & 680 nm), based photogalvanic cells were studied for using relatively broader solar spectrum (i.e., radiations ranging from 800-700 to 700-600, 500-400 nm). On same pattern, some more cells were fabricated. Finally, a cell based on

NGB (714 nm) + FCF (622 nm) + BCB (622 nm) +SPE (435 nm & 680 nm) + RHD (543 nm) + SUD (476 nm) was studied for using almost whole visible region (i.e., 800-700 to 700-600 to 600-500 to 500-400 nm) for solar energy conversion and storage.

The electrical cell parameters for various individual and mixed photosensitizers are summarized in **Table 2** and **Fig. S5 (a,b)**.

1.3. Experimental set up

The experimental set up consists of a H-cell (photogalvanic cell), natural sunlight, digital pH meter-Systronics Model:335 (for measuring potential in millivolt-mV), microammeter-OSAW (for measuring current in microampere-µA), a carbon pot log 470 K device (for changing the resistance of circuit), and a circuit key, which are connected together as shown in photogalvanic cell set –up (**Fig.S7**).

The photogalvanic cell is made of glass tube of H-shape whose wall is externally blackened, but a window is left in one arm. The arm with window acts as illuminated chamber and other arm without window act as dark chamber[13]. This tube is filled with known amount of the solutions of photosensitizer, reductant, NaLS and Sodium hydroxide. The total volume of the solution is always kept 25 ml making up by singly distilled water. A platinum electrode (as negative terminal) is dipped in illuminated chamber against window and a Saturated Calomel Electrode-SCE of combination electrode (as positive terminal) is immersed in dark chamber. The terminals of the electrodes are connected to a digital pH meter.

Table S1. Variation of potential with time.

Cell No.	Photosensitizer(s) with λ_{max} (nm)	Variation of potential (mV) with time(min.)						
1.	NGB (714)	Time	0	11	26	63	65	70
		Potential	582	625	644	738	938 V_{max}	925 V_{oc}
2.	FCF(622)	Time	0	37	56	72	80	85
		Potential	585	625	643	650	971 V_{max}	960 V_{oc}
3.	BCB(622)	Time	0	10	20	30	33	38
		Potential	613	624	687	701	1045 V_{max}	1040 V_{oc}
4.	SPE(435 & 680)	Time	0	34	37	59	68	75
		Potential	596	634	636	642	950 V_{max}	938 V_{oc}
5.	RHD(543)	Time	0	17	22	28	30	35
		Potential	521	559	578	899	1012 V_{max}	1007 V_{oc}
6.	SUD(476)	Time	0	14	18	20	21	26
		Potential	596	616	620	928	1020 V_{max}	1014 V_{oc}
7.	NGB(714),FCF(622)	Time	0	10	40	48	53	57
		Potential	572	587	633	695	1007 V_{max}	1000 V_{oc}
8.	NGB(714),FCF(622), SPE (435 & 680)	Time	0	12	25	40	44	55
		Potential	550	575	606	725	980 V_{max}	973 V_{oc}
9.	NGB(714),FCF(622), RHD(543)	Time	0	15	35	40	45	50
		Potential	556	573	592	611	975 V_{max}	970 V_{oc}
10.	NGB(714),FCF(622), BCB(622),SPE(435& 680),RHD(543), SUD(476)	Time	0	5	9	12	15	22
		Potential	541	560	602	657	1057 V_{max}	1040 V_{oc}
11.	NGB(714)	Time	0	5	13	39	44	50
		Potential	520	524	575	723	1040 V_{max}	1040 V_{oc}
12.	NGB(714),FCF(622), BCB(622)	Time	0	15	25	35	38	42
		Potential	591	640	692	744	1055 V_{max}	1052 V_{oc}
13.	NGB(714),FCF(622), BCB(622),SPE(435 & 680)	Time	0	13	28	30	31	32
		Potential	570	595	645	937	1002 V_{max}	999 V_{oc}
14.	NGB(714),FCF(622), BCB(622),SPE(435& 680),RHD (543)	Time	0	16	43	44	48	52
		Potential	517	574	612	992	1067 V_{max}	1060 V_{oc}
15.	NGB(714),FCF(622), BCB(622),SPE(435& 680),RHD(543), SUD(476)	Time	0	7	10	16	23	26
		Potential	492	584	927	981	1008 V_{max}	1004 V_{oc}

Table S2. Change of power with time (Study of cell performance)

Cell No.	Photosensitizer(s) with λ_{max} (nm)	Study of cell performance [Change of current (µA), potential (mV) and power(µW) with time]						
1.	NGB (714)	Time	0	40	120	140 $t_{0.5}$	147	152
		Current	420	440	440	435	300	300
		Potential	486	363	325	314	339	321
		Power	204.1	159.7	156.2	136.5	101.7	96.3
2.	FCF(622)	Time	0	10	15	27 $t_{0.5}$	34	38
		Current	420	350	340	310	300	300
		Potential	443	399	345	312	309	298
		Power	186	139.6	117.3	96.7	92.7	89.4
3.	BCB(622)	Time	0	15	30	45	63 $t_{0.5}$	68
		Current	450	430	400	360	320	320
		Potential	482	427	361	349	334	309
		Power	216.9	183.6	144.4	125.6	106.8	98.8
4.	SPE(435 & 680)	Time	0	10	20	30	44	50 $t_{0.5}$
		Current	600	570	530	490	450	450
		Potential	440	411	349	313	302	291
		Power	264	234.2	184.9	153.3	135.9	130.9
5.	RHD(543)	Time	0	5	9	15	26 $t_{0.5}$	31
		Current	600	570	550	490	430	410
		Potential	454	440	410	357	313	310
		Power	272.4	250.8	225.5	174.9	134.5	127.1
6.	SUD(476)	Time	0	6	12	18	30 $t_{0.5}$	34
		Current	600	570	530	480	430	410
		Potential	528	486	411	304	251	233
		Power	316.8	277	217.8	145.9	107.9	95.5
7.	NGB(714),FCF(622)	Time	0	8	12	15	17 $t_{0.5}$	22
		Current	520	550	540	510	420	340
		Potential	518	416	402	381	315	240
		Power	269.3	228.8	217	194.3	132.3	81.6
8.	NGB(714),FCF(622), SPE (435 & 680)	Time	0	6	54	84	125 $t_{0.5}$	128
		Current	520	425	400	390	320	300
		Potential	478	523	465	455	370	350
		Power	248.5	222.2	186	177.4	118.4	105
9.	NGB(714),FCF(622), RHD(543)	Time	0	5	10	20	30 $t_{0.5}$	34
		Current	540	540	530	500	380	370
		Potential	470	440	389	370	329	318
		Power	253.8	237.6	206.1	185	125	117.7

10.	NGB(714),FCF(622), BCB(622),SPE(435& 680),RHD(543), SUD(476)	Time	0	4	9	14	19 $t_{0.5}$	24
		Current	660	630	580	510	470	460
		Potential	460	400	367	303	320	301
		Power	303.6	252	212.8	155.8	150.4	138.4
11.	NGB(714)	Time	0	40	100	180	260 $t_{0.5}$	270
		Current	800	780	760	610	560	560
		Potential	528	493	423	411	376	363
		Power	422.4	384.5	321.4	250.7	210.5	203.2
12.	NGB(714),FCF(622), BCB(622)	Time	0	14	25	35	51 $t_{0.5}$	60
		Current	850	780	710	640	600	580
		Potential	511	467	401	379	361	341
		Power	434.3	364.2	284.7	242.5	216.6	197.7
13.	NGB(714),FCF(622), BCB(622),SPE(435 & 680)	Time	0	10	22	26	32 $t_{0.5}$	37
		Current	1000	930	860	810	710	680
		Potential	464	422	385	332	323	319
		Power	464	392.46	331.1	268.9	229.3	216.9
14.	NGB(714),FCF(622) ,BCB(622),SPE(435 & 680),RHD (543)	Time	0	4	8	10	14 $t_{0.5}$	19
		Current	850	800	730	680	600	580
		Potential	477	436	401	342	333	313
		Power	405.4	347.2	292.7	232.5	199.8	181.5
15.	NGB(714),FCF(622) ,BCB(622),SPE(435 &680),RHD(543), SUD(476)	Time	0	5	12	20	31 $t_{0.5}$	0
		Current	750	690	610	560	530	750
		Potential	463	422	377	345	326	463
		Power	347.2	291.1	229.9	193.2	172.7	347.2

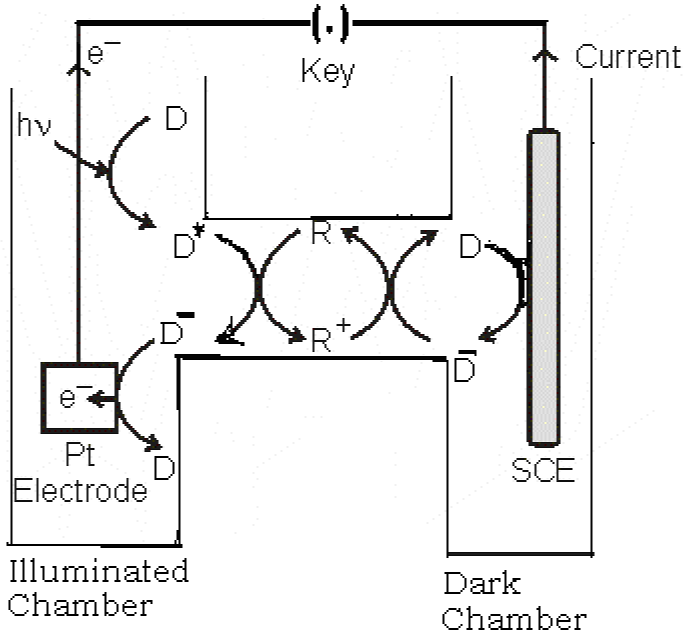


Fig. S 1. Mechanism of photogeneration of current in photogalvanic cell. SCE, Saturated Calomel Electrode; D, Dye (Photosensitizer); D^{+}, Oxidized form of Dye; R^{+}, Oxidized form of reductant ; e^{-}, Electron.

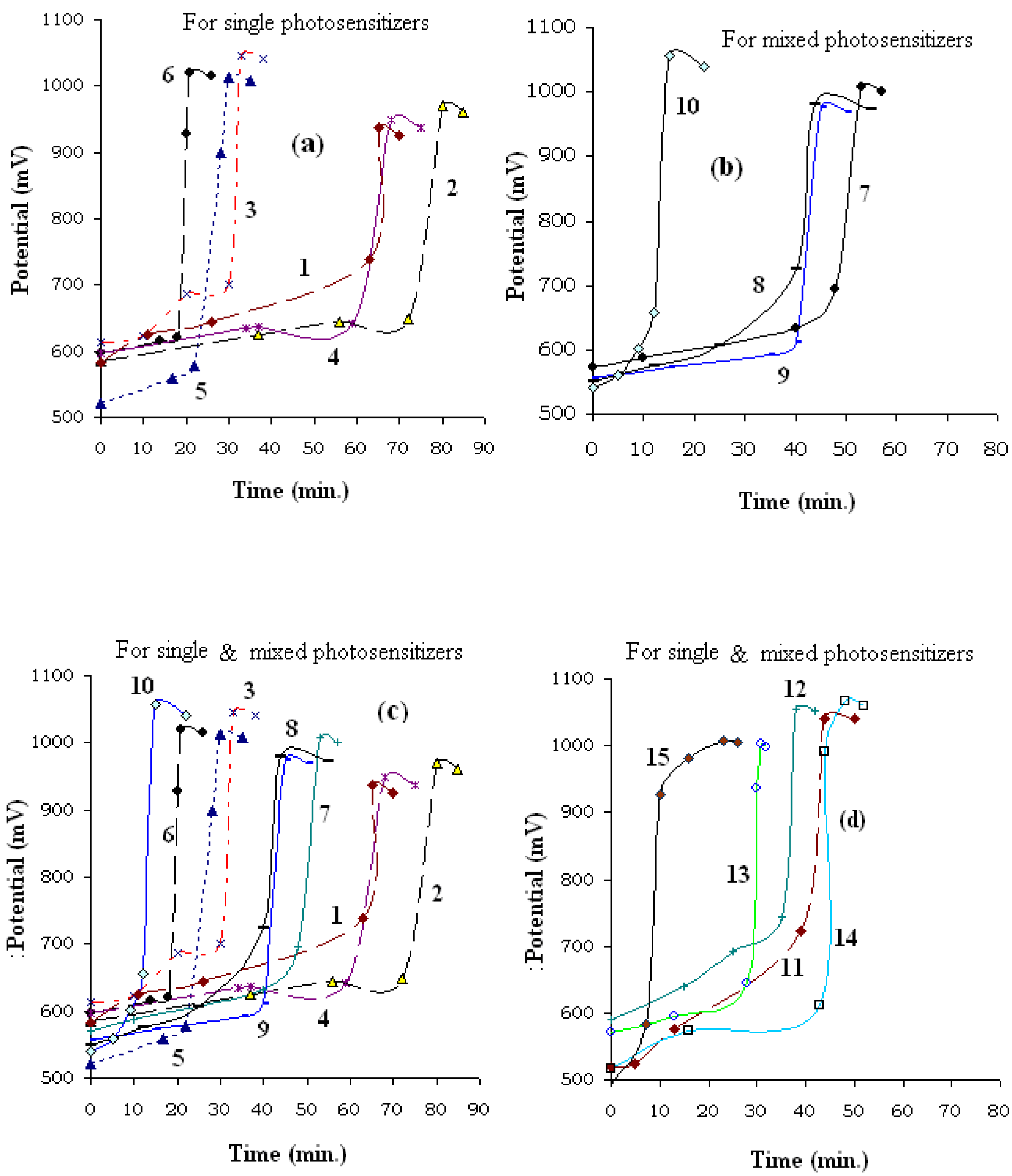
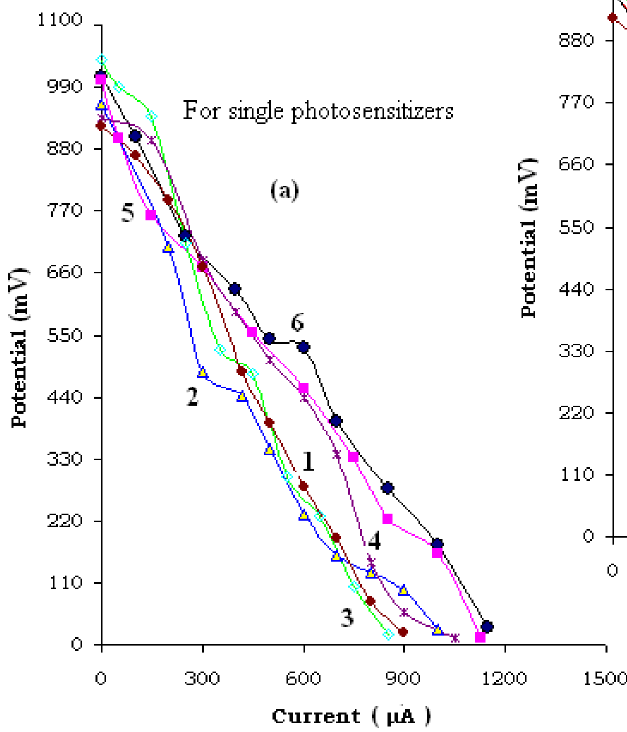


Fig. S2(a,b,c,d).Variation of potential with time,1.NGB (714 nm),2.FCF(622 nm),3. BCB(622 nm),4.SPE(435 nm & 680 nm),5.RHD(543 nm),6. SUD(476 nm),7. NGB,FCF,8.NGB,FCF,SPE,9. NGB,FCF,RHD ,10. NGB,FCF,BCB,SPE,RHD, SUD,11.NGB,12.NGB,FCF,BCB,13.NGB,FCF,BCB,SPE,14.NGB,FCF,BCB,SPE,RH D,15. NGB,FCF,BCB,SPE,RHD,SUD.



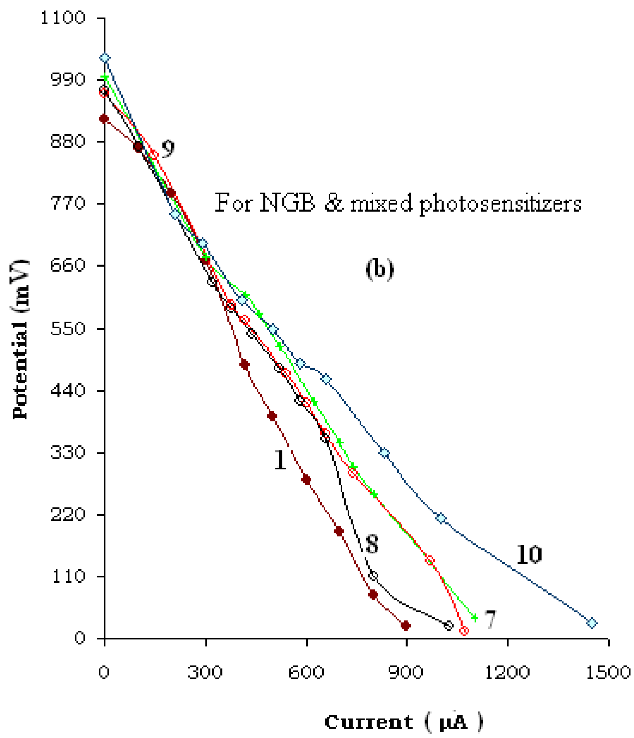


Fig. S3(a,b)Variation of potential with current(i- V characteristic of the cell), 1.NGB (714 nm),2.FCF(622 nm),3.BCB(622 nm),4.SPE(435 nm & 680 nm),5.RHD(543nm),6.SUD(476nm),7.NGB,FCF,8.NGB,FCF,SPE,9.NGB,FCF,RHD, 10.NGB,FCF,BCB,SPE,RHD,SUD,11.NGB,12.NGB,FCF,BCB,13.NGB,FCF,BCB,SPE,14.NGB,FCF,BCB,SPE,RHD,15. NGB,FCF,BCB,SPE,RHD,SUD.

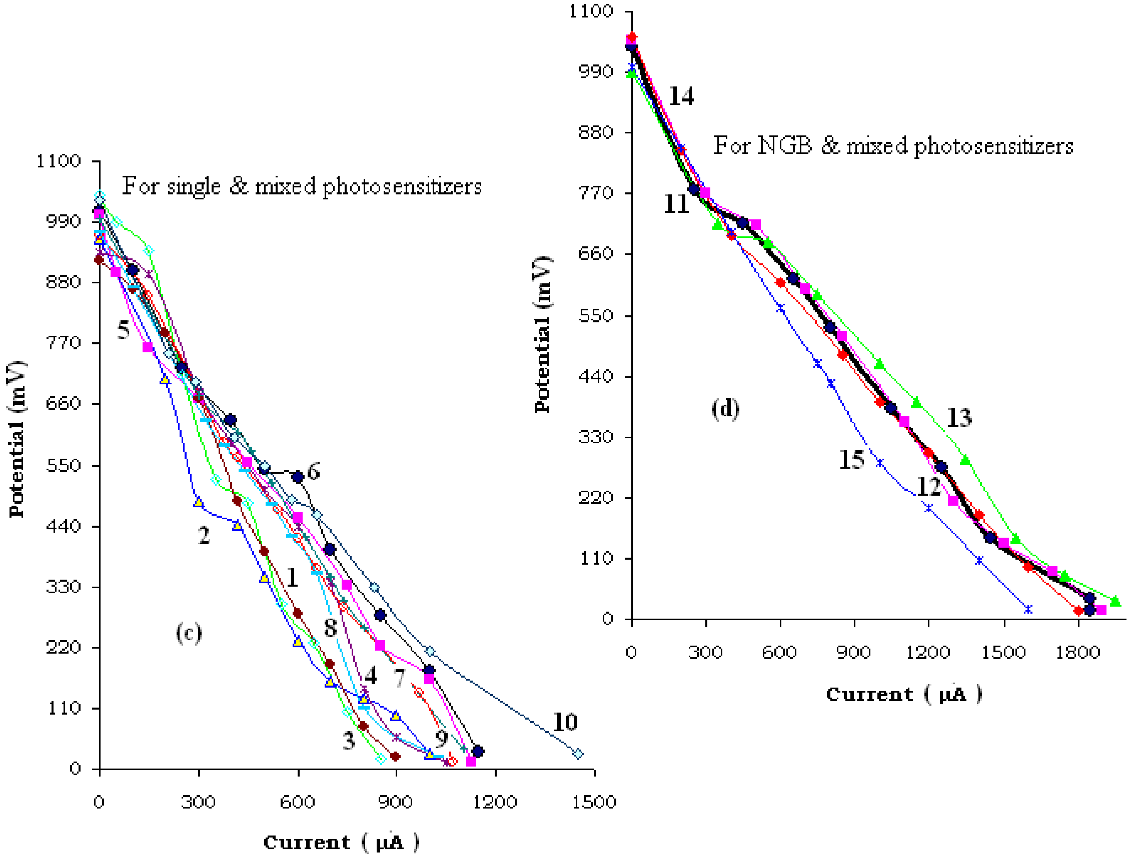


Fig. S3(c,d)Variation of potential with current(i- V characteristic of the cell), 1.NGB (714 nm),2.FCF(622 nm),3.BCB(622 nm),4.SPE(435 nm & 680 nm),5.RHD(543nm),6.SUD(476nm),7.NGB,FCF,8.NGB,FCF,SPE,9.NGB,FCF,RHD, 10.NGB,FCF,BCB,SPE,RHD,SUD,11.NGB,12.NGB,FCF,BCB,13.NGB,FCF,BCB,SPE,14.NGB,FCF,BCB,SPE,RHD,15. NGB,FCF,BCB,SPE,RHD,SUD.

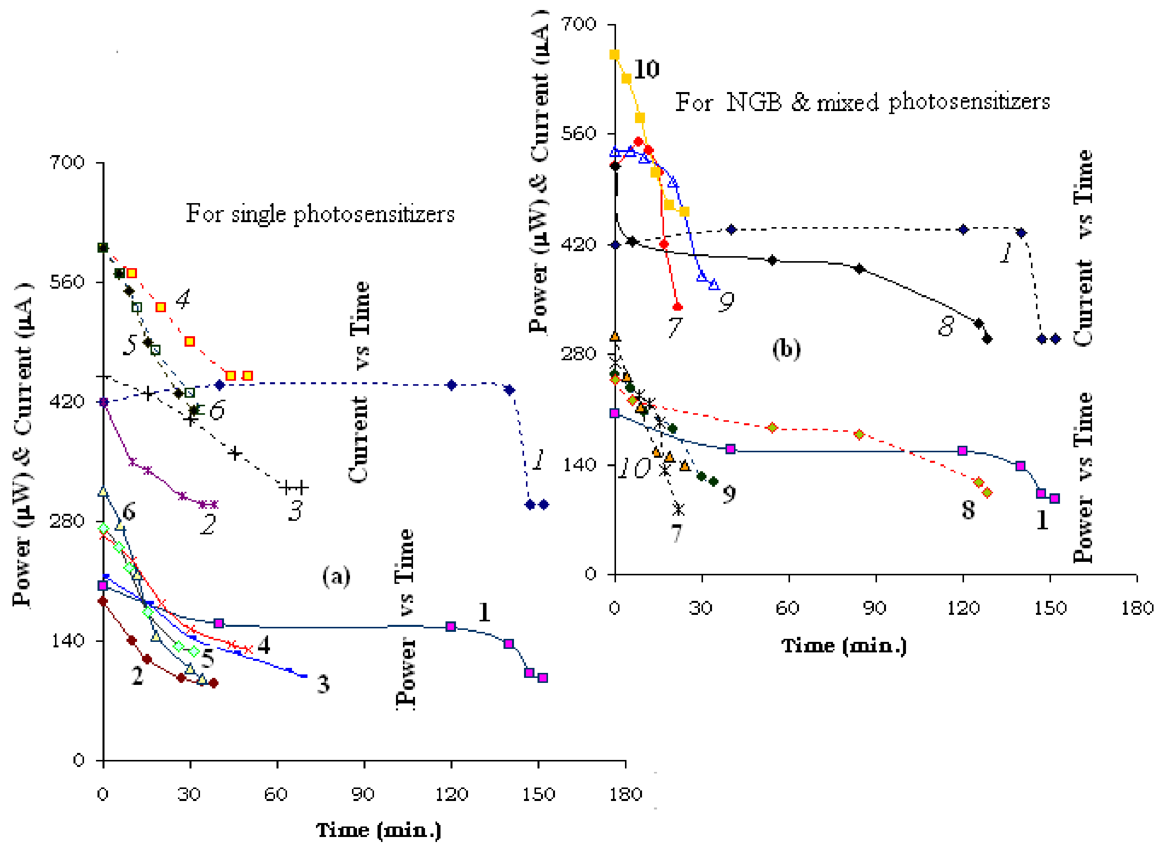


Fig.S4(a,b). Study of cell performance (i)Power vs Time(1-10,bold& unitalic),(ii) CurrentvsTime(110,unbold&italic).1.NGB(714nm),2.FCF(622nm),3.BCB(622nm),4.S PE(435nm&680nm),5.RHD(543nm),6.SUD(476nm),7.NGB,FCF,8.NGB,FCF,SPE,9. NGB,FCF,RHD,10.NGB,FCF,BCB,SPE,RHD,SUD.

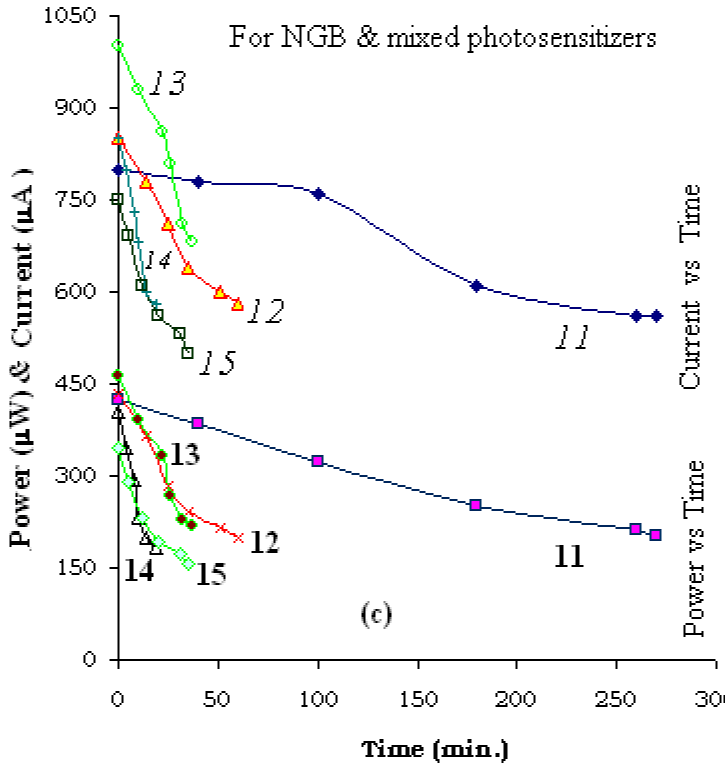


Fig.S4(c).Study of cell performance (i) Power vs Time (11-15, bold& unitalic), (ii) CurrentvsTime(11-15,unbold&italic). 11.NGB,12.NGB,FCF,BCB,13.NGB,FCF,BCB,SPE,14.NGB,FCF,BCB,SPE,RHD,15. NGB,FCF,BCB,SPE,RHD,SUD.

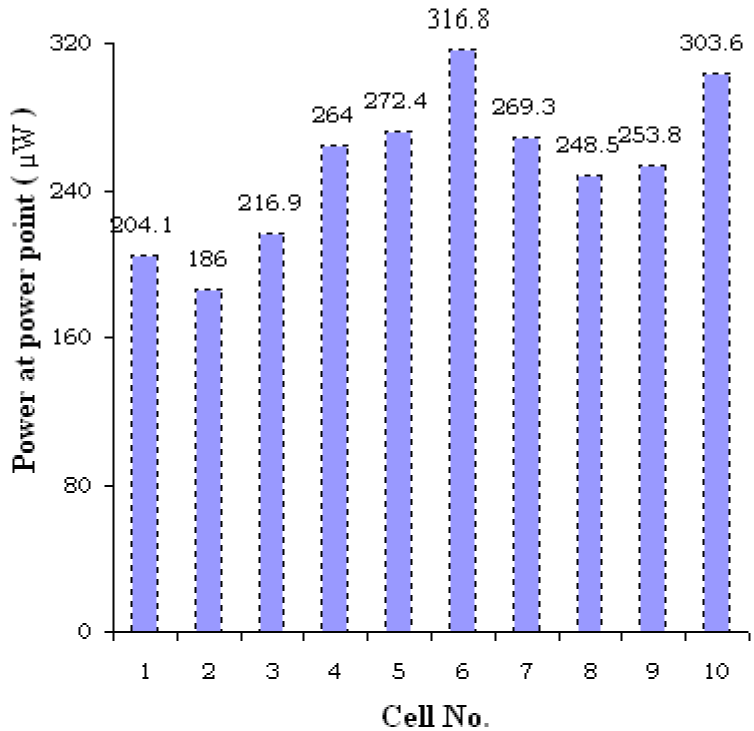


Fig. S5*(a). Power at power point for various cells.*

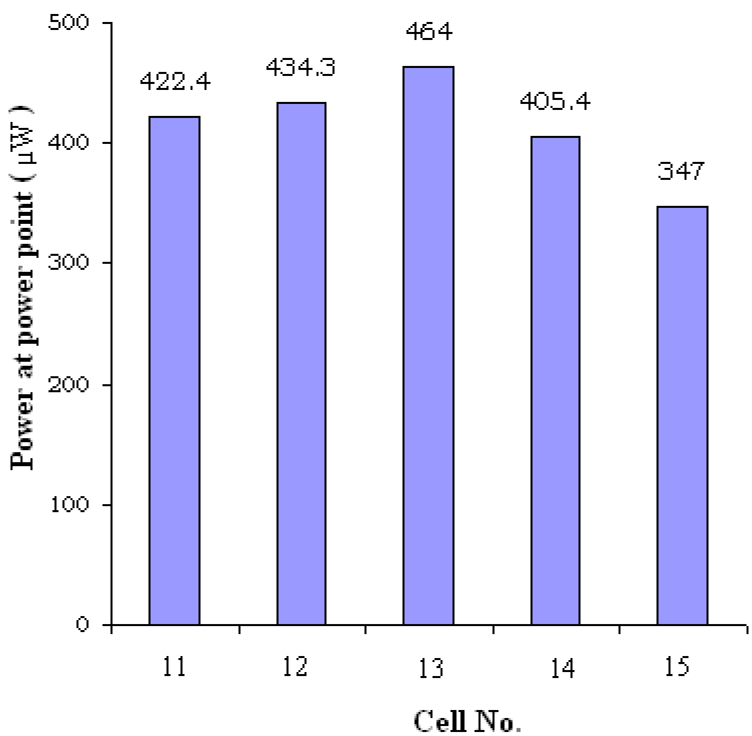


Fig. S5*.(b). Power at power point for various cells.*

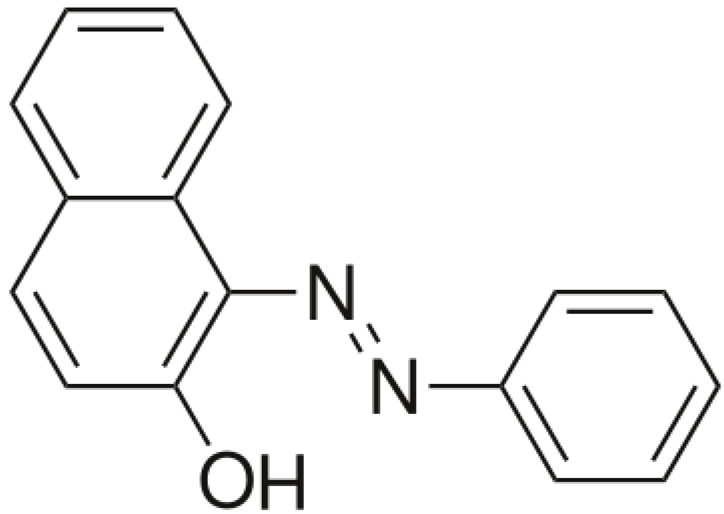


Fig.S6(a)Structure of Sudan-I

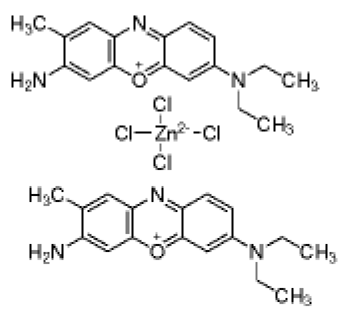


Fig. S6(b)Structure of Brilliant Cresyl Blue (M.W. 385.96).

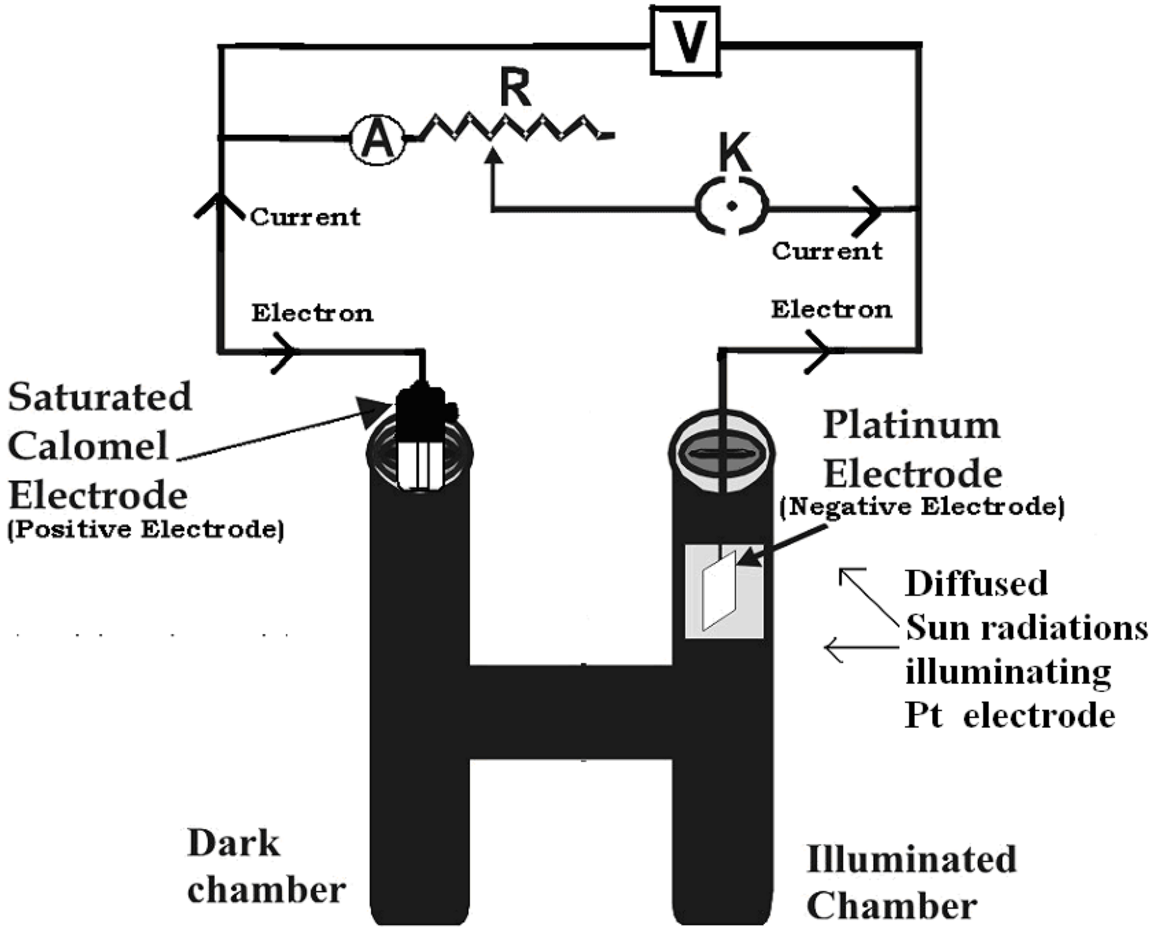


Fig. S7: Photogalvanic cell set–up. A, Micro-ammeter; K, Key; R, Resistance;; V, Digital pH meter.