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Research article

IMPROVED PERFORMANCE OF DYE SENSITIZED SOLAR CELL USING CARBON AND ZINC CO-DOPED SEMICONDUCTOR

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ABSTRACT

Dye sensitized solar cells (DSSCs) has been fabricated by co-doping of TiO_2 with Zn (metal) and C (non-metal). Zn and C co-doped TiO_2 semiconductor was prepared by sol-gel method and deposited on FTO glass, which was sensitized with Rhodamine-B.This cell consists of a carbon as a counter electrode andiodide ion/triodide ion redox couple as an electrolyte solution between the electrodes. The experimental results show V_{OC}=129.8mV, i_{SC}=0.052mA,i_{pp}=0.0315mAand V_{pp}= 55.2 mV with fill factor (FF)=0.25. Power conversion efficiency of the cell was 0.004%.**Copyright © IJRETR, all rights reserved. USA**

Key words: Dye sensitized solar cell, Metal, Non–metal, Co-doped semiconductor.

INTRODUCTION

The entire globe is facing a major problem of energy crisis and it is likely to increase in future as other conventional energy resources will be exhausted due to their exploitation in coming few decades. In this context, solar energy is an important source of renewable energy. Solar energy technology suffers from two major issues, the cost of manufacture and the rate of electrical energy conversion efficiency. To overcome these issues, many solar devices were developed like photovoltaic cells, photogalvanic cells, photo-electrochemical cells, dye sensitized solar cells, etc.

A dye sensitized solar cell is a low cost solar cell belonging to the group of thin film solar cells.First version of the DSSC known as the Gratzelcell was invented byO'Regan and Gratzel[1].It is based on a semiconductor placed between a photo-sensitized anode and an electrolyte.Manynanocrystallinesemiconductors such as a TiO_2[2],ZnO [3]and SnO_2 have been used as a photoanode materials. Quintana et al.[4] reported that TiO_2 based solar cell has highly efficient than ZnO based solar cells. Doping by metals and non-metals shows improvement in the activity of semiconductor materials. Doped semiconductor shows strong red shift in their absorption into the visible region as compared toundoped semiconductors [5]Gu et al. [6]observedthat metal doping improved the open-circuit voltage due to the upward shift of the Fermi level but defect oxygen generated retardation inthe negative shift of the Fermi level.Doping of TiO_2 semiconductor with metal and nonmetalelements such as Fe doped Zndoped, and F doped TiO_2attempted by Wen et al. [7] Wang et al. [8] and Yang et al. [9] respectively.Liu et al.[10] reported thatthe doping byV,Nb,Ta (VB group) increase the doping density by the shifting of the flat band potential positively and show highest photovoltaic efficiency (8.33%).

Researcher have investigated co-doping of various ions on TiO_2 such as N, S[11] andZn+Mg co-doped TiO_2 [12]. 9.07% power conversion efficiency was observed for Zn + Mg co-doped TiO_2 compared with the undoped TiO_2 based cell.In the present work, Zn + C-TiO_2 were synthesized by sol-gel method. The DSSC was fabricated with this co-doped $TiO_2$and the effect of different parameters on the performance of cell was observed like dye concentration, electrolyte concentration, light intensity and exposed surface area of semiconductors.

EXPERIMENTAL

Preparation of nanocrystalline pure and Zn + C co-doped TiO_2

Both pure and co-doped Zn+C-TiO_2 were synthesized by sol-gel method. 2mL of titanium tetraisopropoxide was mixed with 10mL of 2-propanol in a beaker. A solution of 10 g of $Zn(CH_3COOH)_2$ and 10 g fructose was prepared in 100 mL distilled water, separately. Both these solutions were mixed with continuous stirring. Precipitates of Zn + C-$Ti(OH)_4$ was obtained. This mixture was transferred to the oven for drying at 60-110ºC up to dryness. After cooling down to room temperature, it was calcined in a furnace at 400ºC for 3 hours. Then again, it was brought to room temperature and the obtained powder of Zn-C-TiO_2 was grounded in a mortar with pestle to from fine crystals. The same procedure was followed to prepare undoped TiO_2 with the difference,thenno dopant was added (zinc acetate and fructose) in this case.

IR spectroscopy was used to know the presence of particular functional group. Zn-C-Ti-OHshows peak at 3429 cm^{-1}due to O-H stretching which is contributed by water contents[13]. A peak around2339 cm^{-1} may be due to absorption of atmospheric CO_2[14]. Absorption peaks around 1626, 1386 and 1118 cm^{-1} correspond to Zn-OH bending mode, Zn-C-OH in-plane bending and Zn-C-OH out-of-plane bending, respectively[15]. Two sharp peaks were obtained at 702 and 517 cm^{-1}.These peaks may be attributed to presence of Zn-O.[16]. Another peak at about 422 cm^{-1} may be assigned to the stretching vibrations of Ti–O–Ti.[17].

Fabrication of the cell

The photoanode was prepared with Zn -C-TiO_2 paste in acetic acid with few drops of dishwashing liquid as a surfactant. This paste was coated on the FTO glasses (2.2 mm thickness, 7-9 ohmscm^2,L 25mm x W 25 mm, Shilpa Enterprises, Nagpur, India) by doctor blade method and left for a few minutes to let it dry. Then the glass was heated on a hotplate at 450ºC for 45 min. A solution of Rhodamine B (1.0 x 10^{-3} M) dye in ethanol was used for the sensitization of this working electrode. The working electrode was immersed in the dye solution for 15 min. and then rinsed with ethanol to remove extra dye. A graphite coated counter electrode was clipped on to the top of the working electrode. 0.43 M iodine and 0.5 M potassium iodide was dissolved in 10 mL of ethylene glycol. This I^-/ I_3^- redox shuttle was used as liquid electrolyte.

Photovoltaic performance of the DSSC

Variation of potential with time

The effect of variation of potential with time on the electrical output of the cell was observed, and results are reported in Table 1.

The cell was placed in dark and the potential was measured. Then, the cell was exposed to light (40mWcm^{-2}). A change in potential was observed with the time of illumination. The potential was measured with digital multimeter (Mastech-M830bZ). The cell was charged for 70 min. to attain a constant potential. Then the irradiation was cut off. It was observed that the potential starts increasing with time, but it never reached its initial value indicating that the reaction is reversible but not completely.

Table 1. Variation of potential with time

Time (min.)	Potential (mV)	Time (min.)	Potential (mV)
0	223.0	75	38.5
5	182.9	80	36.2
10	180.5	85	34.4
15	180.4	90	30.2
20	170.8	95	29.4
25	174.5	100	27.3
30	169.7	105	26.0
35	165.8	110	25.5
40	161.2	115	22.3
45	156.2	120	20.2
50	154.8	125	19.9
55	152.0	130	19.8
60	151.0	135	19.5
65	150.2	140	19.5

70 (Light off)	70.5		

[Rhodamine B] = 1.0 x 10^{-3} M; [I_2]= 0.43 M; [KI] = 0.5 M; Exposed surface area = 1.0 x 1.0 cm^2; Light intensity =40$mWcm^{-2}$

Variation of current with time

The effect of variation of current with time on the electrical output of the cell was observed, and results are reported in Table 2.

The current was measured with a digital multimeter (Mastech-M830bZ).The photocurrent of cell rapidly increases on illumination and after a few minutes, it reaches to its maximum. This current is represented as i_{max}. When illumination time was further increased, the current starts decreasing gradually, and it reaches at equilibrium value. This value is represented as i_{eq}.

Table 2. Variation of current with time

Time (min.)	Photocurrent (µA)	Time (min.)	Photocurrent (µA)
0	0.0	75	20.4
5	0.1	80	19.3
10	2.5	85	15.0
15	51.6(i_{max})	90	14.7
20	49.4	95	14.6
25	47.6	100	13.5
30	47.2	105	13.2
35	45.6	110	13.0
40	43.0	115	10.3
45	40.2	120	10.3
50	38.7	125	10.1
55	38.5	130	10.1
60	38.2	135	10.0
65	37.2	140	10.0 (i_{eq})
70 (Light off)	37.0		

[Rhodamine B] = 1.0 x 10^{-3} M; [I_2] = 0.43 M; [KI] = 0.5 M; Exposed surface area = 1.0 x 1.0 cm^2; Light intensity = 40$mWcm^{-2}$

Effect of dye concentration

The dependence of the photo potential and the photocurrent on the dye concentration was observed by taking different concentration of Rhodamine-B (1.6 x 10^{-3} M –0.3 x 10^{-3}M), and the results are reported in Table 3.

It was observed that the electrical output of the cell increased on increasing the concentration of Rhodamine B. It may be explained on the basis that as the concentration of dye was increased, the number of sensitizer molecules also increased, and accordingly, the electrical output of cell was relatively higher.A reverese trend was observed on increasing the concentration of dye further. It may be due to the fact that dye starts acting as an internal filter for the incident light and does not permit desired light intensity to reach semiconducting photoanode.

Table 3. Effect of dye concentration

Dye × 10^3 (M)	Potential (mA)	Current (μA)
1.6	105.9	15.8
1.3	121.0	35.4
1.0	129.8	52.0
0.6	94.0	12.6
0.3	78.7	10.4

Exposed surface area = 1.0 x 1.0 cm^2; [I_2] = 0.43M; [KI] = 0.5M; Light intensity = 40.0 $mWcm^{-2}$

Effect of electrolyte concentration

The effect of concentration of the component of liquid electrolyte (I_2 and KI) on the electrical power of the cell was observed, and the results are reported in the Tables4 and 5. To know the individual effect of I_2 and KI, the concentration of one component was kept constant varying the other. It was observed that as the concentration of iodine was increased, the potential and current decreased, while potentialdecreased on increasing concentration of potassium iodide, and current increased. The optimum conditions were obtained for I_2 and KI were 0.43 M and 0.50 M, respectively.

Table 4. Effect of iodine concentration

(I_2) M	Potential (mA)	Current (μA)
0.39	31.5	4.5
0.43	129.8	52.0
0.47	104.0	15.1
0.51	59.5	9.8
0.55	13.5	8.9

[Rhodamine B] =1.0 x 10^{-3} M; KI = 0.50 M; Exposed surface area = 1.0 x 1.0 cm^2; Light intensity=40.0$mWcm^{-2}$

Table 5. Effect of KI Concentration

KI (M)	Potential (mA)	Current (µA)
0.44	69.7	2.5
0.46	95.0	7.9
0.48	98.1	12.4
0.50	129.8	52.0
0.51	29.55	17.0

[Rhodamine B] = 1.0 x 10^{-3} M;[I_2] = 0.43 M; Exposed surface area = 1.0 x 1.0 cm^2; Light intensity=40.0mWcm^{-2}

Effect of exposed surface area of semiconductor

The surface area of semiconductor affects the performance of cell and therefore, its effect was observed. The results are reported in Table 6.

It was observed that both, potential and current increase with increasing surface area of semiconductor. It may be due to more exposed area of electrode.

Table 6. Effect of exposed surface area

Area (cm^2)	Potential (mA)	Current (µA)
1.6 x 1.6	66.90	28.0
1.3 x 1.3	105.9	26.2
1.0 x 1.0	129.8	52.0
0.6 x 0.6	84.7	11.8

[Rhodamine-B] = 1.0 x 10^{-3} M; [I_2]= 0.43 M; [KI] = 0.50M;Light intensity =40.0mWcm^{-2}

Effect of light intensity

Light intensity may also affect the electrical parameters of DSSC and therefore, light intensity was changed from 40.0 to 66.0 mWcm^{-2} to observe the effect of light intensity on electrical output of the cell. The results are reported in Table 7.It shows an increasing trend with increasing light intensity because an increase in light intensity increases the photons per unit area. Higher light intensities were avoided as an adverse effect was observed with higher intensities.

Table 7. Effect of light intensity

Light Intensity(mWcm^2)	Potential (mA)	Current (µA)
40.0	129.8	52.0
50.0	71.9	21.6
60.0	29.2	18.4
66.0	12.1	14.5

[Rhodamine-B] = 1.0 x 10^{-3} M; [I_2]= 0.43 M;[KI] = 0.50 M; Exposed surface area = 1.0 x 1.0 cm^2

i-V Characteristics of the cell

The open circuit voltage (V_{oc}) (keeping the circuit open) and short circuit current (i_{sc}) (keeping the circuit closed) of the cell were measured with a digital multimeter. The values of photocurrent and photopotential were observed with the help of a carbon pot (log 470 k) connected in the circuit by applying an external load. The variation of potential with respect to current is presented in Table 8 and graphically in Figure 1.

Table 8.i-V Characteristics

Potential (mV)	Photocurrent (µA)	Fill Factor
129.8	0.0	0.25
126.1	0.5	
125.0	2.2	
121.0	5.0	
112.5	8.1	
104.0	10.2	
87.2	12.6	
75.0	13.4	
68.2	17.0	
65.0	19.2	
55.2	31.5	
30.1	36.5	
11.5	43.4	
8.9	50.1	
0.5	51.7	
0.0	52.0	

Rhodamine B = 1.0 x 10^{-3} M; [I_2]= 0.43 ;[KI] = 0.50 M; Exposed surface area = 1.0 x 1.0 cm^2; Light intensity = 40.0mWcm^{-2}

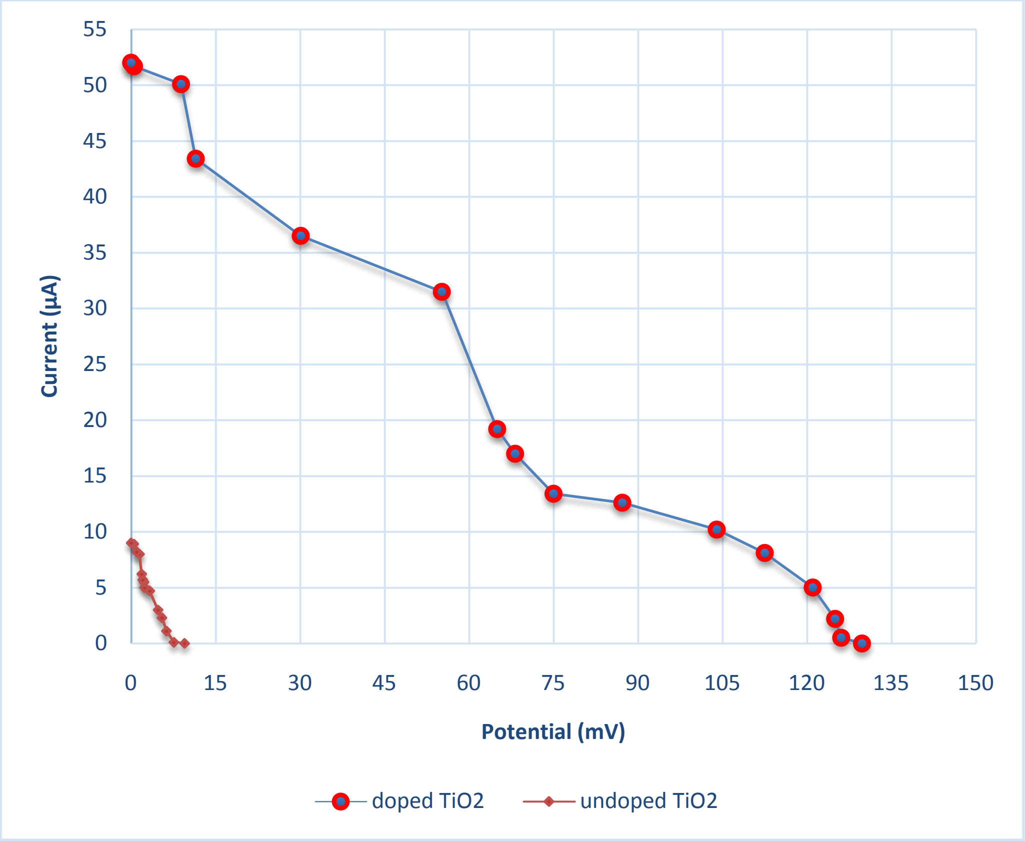

Figure 1.i-V characteristics

Values of V_{oc}, i_{sc},voltage at power point (V_{pp}) and current at power point (i_{pp}) were determined with this curve. The maximum voltage for open circuit (V_{oc}) was 129.8 mV and the maximum current for short circuit (i_{sc}) conditions was 0.052 mA. 55.2 mV voltage (V_{pp}) and 0.0315 mA current (i_{pp}) were obtained at power point. Using these values, the fill factor (FF) was calculated from Equation (1) and it was observed as 0.25 in the cell.

$$\text{Fill Factor (FF)} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \quad \text{….. (1)}$$

Cell efficiency

The conversion efficiency of the cell is the ratio of electrical output at power point and the power of incident radiations (P_{in}). The solar energy-to-electricity conversion efficiency (η) was determined by the equation (2),

$$\eta = \frac{FF \times i_{sc} \times V_{oc}}{P_{in}} \times 100\% \quad \text{…..(2)}$$

The cell showed (0.004) over all power conversion efficiency. Comparative electrical parameters, fill factor, and conversion efficiency of DSSC with undoped and co-doped TiO_2 are given in Table 9.

Table 9. Camparative results with pure and Zn –C co-doped TiO_2 in DSSC

Sample	i_{pp} **(mA)**	V_{pp} **(mV)**	i_{sc} **(mA)**	V_{oc} **(mV)**	***FF***	$\eta x 10^2$(%)
Pure TiO_2	0.0047	3.3	0.008	9.5	0.20	0.0042
Zn-C- TiO_2	0.0315	55.2	0.052	129.8	0.25	0.4

Performance of cell

The performance of cell was measured by applying the external load necessary to have current and potential at power point, after removing the source of illumination. It is defined as the time taken in decreasing half of its maximum power. It was observed that the electrical output does not reach zero even after 60 min. The cell worked for 10 minutes even in the dark.

Conclusions

In the present investigation, it was observed that doping of titania by metal (Zn) and non-metal (C) has increased the photocatalytic activity of semiconductor in visible light. The performance of cell was improved, as compared to pure TiO_2. The cell fabricated with co-doped titaniawas 95 time more efficient thenusing pure titania.

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