iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 6 **Issue:** III **Month of publication:** March 2018

DOI: http://doi.org/10.22214/ijraset.2018.3228

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 6.887
Volume 6 Issue III, March 2018- Available at www.ijraset.com

Photochemical Study of Photosensitizer by Photogalvanic Cell for Solar Energy Conversion and Storage

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Abstract: ***The Photovoltages and Photocurrents in photogalvanic cell containing Phloxine B as a photosensitizer with Xylose as reductant for the enhancement of the conversion efficiency and storage capacity of photogalvanic cell for its commercial viability. The observed value of the photogeneration of photopotential was 910.0mV and photocurrent was 260.0 μA. The observed power at power point was 126.16μW and the conversion efficiency was 1.21 %. The fill factor 0.533 was observed experimentally at the power of the cell. The photo galvanic cell that developed can work for 120 min in dark. The storage capacity of the cell is 54%. The effect of different parameters on electrical output of the cell was observed. A mechanism has also been proposed for the generation of the photocurrent and photopotential in photogalvanic cell.***
Keywords: ***Phloxine B, Storage capacity, Xylose and Conversion efficiency***

I. INTRODUCTION

Solar energy is accepted as a key resource for the future of the word. Energy is the soul of life. The utilization of solar energy could cover a significant part of the energy demand in the countries. Solar energy is one of the best renewable energy sources with least negative impacts on the environment. The photogalvanic effect was first discovered in 1925 by rideal and Williams[1].but systematically investigated by rabino witch[2]. The performance of dye sensitized solar cells based on nano crystals TiO_2 films prepared with mixed template method by Gratzel and Regan. Optimum efficiency of photogalvanic cell for solar energy conversion has been studied by Albery and Archer. In beginning, the researchers emphasized on coated pt electrode with Fe^{+2} as reducing agent, later on the researcher started using non coated pt electrode with saturated calomel electrode; synthetic dye as photosensitizer [3] –[14]. Some researcher have studied on how to enhance the performance and optimum efficiency of dye sensitized solar cell for solar energy conversion. Ameta et al.[15] reported use of toluidine blue nitroloacetic acid (TB-NTA) system in photo galvanic cell for solar energy conversion. They also reported the use of micelles in photogalvanic cell for solar energy conversion and storage in Azur Glucose system,. Gangotri et al studied the photo galvanic effect in mixed reductants system for solar energy conversion and storage. Photo galvanic cells containing reductants, surfactants and photosensitizers were reported by Meena et al. [16]-[19]. This paper focuses on the e photochemical study of photo galvanic cell for enhancing their efficiency. Which is containing Phloxine B, Xylose system

II. MATERIALS AND METHODS

A. Materials Used

Phloxine B as photo sensitizer, M/100 Xylose as reductant, 0.5M Oxalic acid used for standardization of NaOH, 1M NaOH has been used as alkaline medium.

B. Method

Phloxine B (MERCK), Xylose (MERCK) and NaOH (MERCK) were used in the present work. The stock solutions of all chemicals were prepared by direct weighing, in doubly distilled water and were kept in colored container to protect them from light. The system was systematically set for photogalvanic studies, which consists of electrochemically treated platinum as electrode and saturated calomel electrodes as a reference electrode. Water filter was used to cut-off IR radiations. The photopotential was obtained as the difference between the initial potential of the system in dark and the equilibrium potential attained by the system under constant illumination. First of the potential measured in dark and the change in potential on illumination was measured as a function of time. Solutions of dye, reductant, and sodium hydroxide were taken in an H-type glass tube. A platinum electrode (1.0 x 1.0 cm^2)

was immersed into one arm of H tube and a saturated calomel electrode (SCE) was kept in the other. The whole system was first placed in dark till a stable potential was obtained and then, the arm containing the SCE was kept in the dark and the platinum electrode was exposed to a tungsten lamp. A digital pH meter (Systronics Model-111) and a microammeter (osawa) were used to measure the potential and current generated by the system, respectively. The effect of variation of different parameters has also been observed.

III. RESULT AND DISCUSSION

A. Mechanism of Current Generation

The photo current in photo galvanic cell generated by electron exchange among dye, reductant and electrode can be represented as follows.

(A) In illuminated chamber

$$Dye \xrightarrow{h\nu} Dye^{*}(S) \xrightarrow{ISC} Dye^{*}(T)$$

$$Dye^{*}(T) + R \longrightarrow Dye^{-} (\text{Semi or leuco}) + R^{+}$$

$$Dye^{-} \longrightarrow Dye + e^{-}(\text{at pt electrode})$$

(B)In Dark Chamber

$$Dye + e^{-} \longrightarrow Dye^{--} (\text{Semi or leuco})$$

$$Dye^{-} + R^{+} \longrightarrow Dye + R^{+}$$

Here Dye*,Dye^{-},R and R^{+} are the excited state of photosensitizer, its semi or leuco form, reductant and oxidized form of reductant respectively. (S), (T), and ISC are excited singlet state, excited triplet state of dye and inter system crossing respectively

B. Effect of Variation of Dye (Phloxine B) Concentration On the Cell:

It is founed that when concentration of dye increased, the photopotential and photocurrent were increased with it. A maximum was obtained for a particular value of Phloxine B concentrations, above which a decrease in the electrical output of the cell was obtained. The reason of the change in electrical output is that lower concentration of photosensitizer resulted into a fall in electrical output because fewer photosensitizer (Phloxine B) molecules are available for the excitation and consecutive donation of the electrons to the platinum electrode where as the higher concentration of photosensitizer (Phloxine B) again resulted into a decrease into electrical out puts the intensity of light reaching the dye molecules near the electrode decrease due to absorption of the major portion of the light by dye molecules present in the path.

Table I

EFFECT OF PHOTO SENSITIZER (PHELOXINE B) QUANTITY ON CELL PARAMETERS[b]

[Pheloxine B] × 10^{-5} M	Photo potential V_{OC} (mV)	Photo current I_{SC} (µA)	Power at power point (µW)	Fill factor	Conversion efficiency (%)
3.66	688	190	66.66	0.510	0.64
4.00	790	220	89.68	0.516	0.86
4.33	910	260	126.16	0.533	1.21
4.66	820	230	98.82	0.52	0.95
5.00	690	195	68.62	0.510	0.66

At [Xylose] = 6.60 × 10^{-4}M , pH = 12.86 , Tem = 303 K , Light intensity = 10.4 mW cm^{-2}, electrode area = 1 cm^{2}, Diffusion length = 5.3 cm

C. Effect of Variation of pH

The effect of variation in pH on photoelectric parameters of cell is observed and found that the cell containing Phloxine B, Xylose to be quite sensitive to the pH of the solution. It is observed that there is an increase in the photoelectric parameters of this cell with the pH value (In the alkaline range). At pH 12.86 a maxima is obtained. On further increase in pH, there is a decrease in photoelectric parameters. It is observed that the pH for the optimum condition has a relation with pKa of the reductant and the desired pH is higher than in pKa value (pH>pKa). The reason of the change in electrical output is that the availability of the reductant in its anionic form, which is a better donor form.

TABLE II.
EFFECT OF VARIATION OF pH[C]

pH	Photo potential V_{OC} (mV)	Photo current I_{SC} (µA)	Power at power point (µW)	Fill factor	Conversion efficiency (%)
12.77	810	190	78.95	0.513	0.76
12.81	870	235	107.33	0.525	1.03
12.86	910	260	126.16	0.533	1.21
12.91	865	230	103.65	0.521	0.99
12.95	820	195	81.70	0.511	0.78

[C] At [Pheloxine B] = 4.33×10^{-5}M, [Xylose] = 6.60×10^{-4}M , Tem = 303 K , Light intensity = 10.4 mW cm^{-2}, electrode area = 1 cm^2, Diffusion length = 5.3 cm

D. Effect of Variation of Xylose *Concentration*

Effect of variation of reductant concentration is that the photopotential and photocurrent were found to increase with the increase in concentration of the reductant Xylose, till it reaches a maximum. On further increase in concentration of Xylose, a decrease in the electrical output of the cell was observed. The reason of the change in electrical output is that the lower concentration of reducing agent resulted into a fall in electrical output because fewer reducing agent molecules are available for electron donation photosensitizer (Phloxine B) molecule where as the higher concentration of reducing agent again resulted into a decrease in electrical output, because the large number of reducing agent molecules hinders the dye molecules from reaching the electrode in the desired time limit..

TABLE III
. EFFECT OF VARIATION OF XYLOSE CONCENTRATION[D]

[Xylose]$\times 10^{-4}$ M	Photo potential V_{OC} (mV)	Photo current I_{SC} (µA)	Power at power point (µW)	Fill factor	Conversion efficiency (%)
6.46	700	200	71.54	0.511	0.68
6.53	860	235	104.88	0.519	1.00
6.60	910	260	126.16	0.533	1.21
6.66	850	230	101.85	0.521	0.98
7.33	680	190	66.66	0.516	0.64

[D]At [Pheloxine B] = 4.33×10^{-5}M, pH = 12.86 , Tem = 303 K , Light intensity = 10.4 mW cm^{-2}, electrode area = 1 cm^2, Diffusion length = 5.3 cm

E. Effect Of Light Intensity On The Cell

Table IV, shows rate of change in photoeletric parameter with respect to light intensity. The light intensity is measured in terms of $mWcm^{-2}$ with the help of solarimeter (CEL Model SM 111). It is found that the photocurrent show linear increasing fashion with light intensity whereas the photopotential show an increment in a irregular fashion.

TABLE IV.

EFFECT OF VARIATION OF LIGHT INTENSITY ON THE SYSTEM[E]

Light intensity ($mW\ cm^{-2}$)	Photo potential V_{OC} (mV)	Photo current I_{SC} (µA)	Power at power point (µW)	Fill factor	Conversion efficiency (%)
3.1	720	170	35.7	0.292	1.19
5.2	800	210	62.40	0.371	1.20
10.4	910	260	126.16	0.533	1.21
15.6	930	276	133.47	0.520	0.85
26.0	940	288	140.50	0.519	0.54

[E] At [Pheloxine B] = 4.33×10^{-5}M, [Xylose] = 6.60×10^{-4}M , pH = 12.86 , Tem = 303 K , electrode area = 1 cm^2, Diffusion length = 5.3 cm

F. The Effect of Variation of pt Electrode Area

Electrode area. Under the observed effect of electrode area, the conversion efficiency and storage capacity are found highest for electrode area 1×1 cm^2. The batter cell performance is found for small electrodes (TABLE V) owing to relatively less hindrance to diffusion of ions.

TABLE V

THE EFFECT OF VARIATION OF pt ELECTRODE AREA[F]

Electrode area (cm^2)	Photo potential V_{OC} (mV)	Photo current I_{SC} (µA)	Power at power point (µW)	Fill factor	Conversion efficiency (%)
0.64	740	230	79.87	0.469	1.20
0.81	830	240	101.88	0.511	1.20
1.00	910	260	126.16	0.533	1.21
1.21	923	248	119.94	0.524	0.95

[F] At [Pheloxine B] = 4.33×10^{-5}M, [Xylose] = 6.60×10^{-4}M , pH = 12.86 , Tem = 303 K , Light intensity = 10.4 mW cm^{-2}, Diffusion length = 5.3 cm

G. Effect of Variation of Diffusion Length

The effect of variation of diffusion length (D_L) i.e. Distance between both electrodes, on cell parameters has been studied having all factors common except diffusion length. It is observed that with an increase in diffusion length, photopotential shows decrease and photocurrent shows increase.(TABLE- VI)

The photopotential decrease with diffusion length, the reason is that concentration gradient disturbs the photosensitizer layer on pt electrode. As D_L increase the current increase as conductivity of dye increase due to increase volume of solution between electrodes.

TABLE VI
EFFECT OF VARIATION OF DIFFUSION LENGTH[G]

Diffusion length (cm)	Photo potential V_{OC} (mV)	Photo current I_{SC} (µA)	Power at power point (µW)	Fill factor	Conversion efficiency (%)
4.5	920	255	124.57	0.531	1.19
5.3	910	260	126.16	0.533	1.21
6.3	895	270	125.66	0.520	1.20
6.8	890	275	125.80	0.514	1.20

[G] At [Pheloxine B] = 4.33×10^{-5}M, [Xylose] = 6.60×10^{-4}M , pH = 12.86 , Tem = 303 K , Light intensity = 10.4 mW cm^{-2}, electrode area = 1 cm^2

H. Variation of Photopotential with Time During Charging of Cell

The photopotential of each photogalvanic cell increase regularly and reach to a highest value (V_{max}) which then decrease and become quite constant after some time (V_{OC}). The variation of photopotential with time of photogalvanic cell consisting 0.13 ml of M/100 dye, 1.98 ml of M/100 Xylose, 2.8 ml of 1 M NaOH and 25.09 ml of doubly distilled water(to make volume of solution 30 ml) are shown in table VII.

TABLE VII
VARIATION OF PHOTOPOTENTIAL WITH TIME DURING CHARGING OF CELL[A]

Time (min)	00	10	20	30	40	50	60	70	80	90	100	110
Potential (mV)	245 (V_{Dark})	252	264	277	298	320	343	367	402	470	650	640
Time (min)	120	130	140	150	160	170	180	190	200	210	220	230
Potential (mV)	710	770	815	845	869	887	902	915	919	923 (V_{MAX})	910 (V_{OC})	910

[A] At [Pheloxine B] = 4.33×10^{-5}M, [Xylose] = 6.60×10^{-4}M , pH = 12.86 , Tem = 303 K , Light intensity = 10.4 mW cm^{-2}, electrode area = 1 cm^2, Diffusion length = 5.3 cm

I. i-V Characteristic of the Cell

The short circuit current (isc) and open circuit voltage (Voc) of the photogalvanic cells are measured with the help of a multimeter (keeping the closed) and with a digital pH meter (keeping the other circuit open), respectively. The current and potential values in between these two extreme values are recorded with the help of a carbon pot (log 470 K) connected in the circuit of Multimeter, through which an external load is applied. A point in i-V curve, called power point (pp) was determined where the product of current and potential was maximum and fill factor was calculated by using the following formula.

Fill factor (FF) = $V_{PP} \times i_{PP} \ / \ V_{OC} \times i_{SC}$

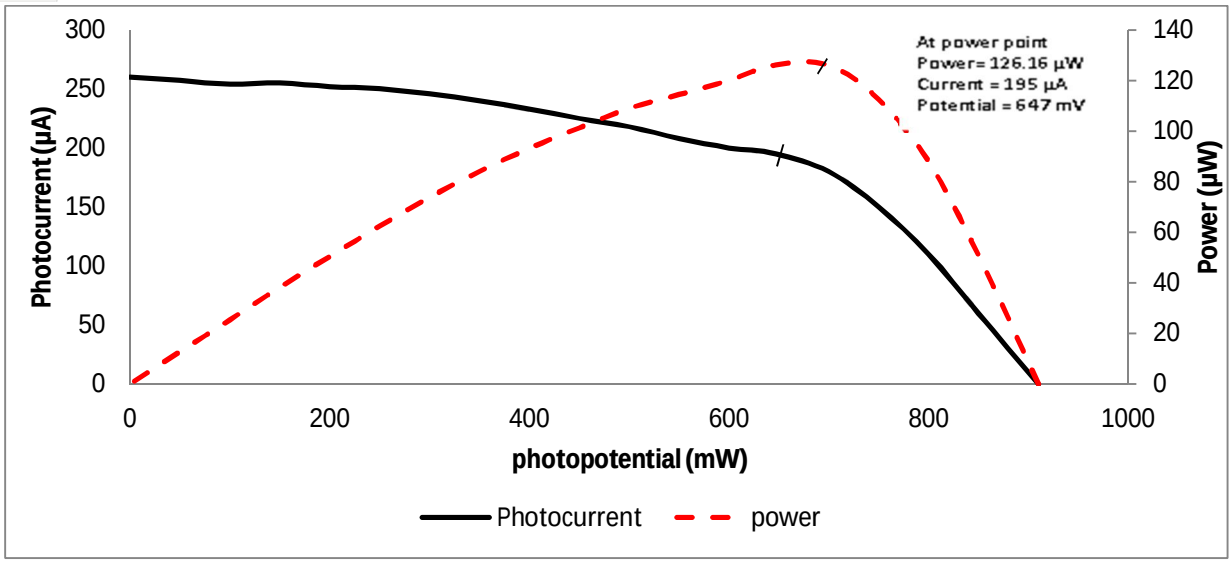

Fig 1. i-V Characteristic of the cell[a]

[a] At [Pheloxine B] = 4.33 × 10^{-5}M, [Xylose] = 6.60 × 10^{-4}M , pH = 12.86 , Tem = 303 K , Light intensity = 10.4 mW cm^{-2}, electrode area = 1 cm^2, Diffusion length = 5.3 cm

J. Storage Capacity and Conversion Efficiency of the Cell

The storage capacity (performance) of the photogalvanic cell is observed by applying an external load (necessary to have current at power point) after terminating the illumination as soon as the potential reaches a constant value. The storage capacity is determined in terms of $t_{1/2}$, i.e., the time required in the fall of the output (power) to its half at power point in dark. It is observed that the cell can be used in dark for 120 minutes on irradiation for 220 minutes. So the observed storage capacity of the cell is 54%.The conversion of the efficiency of the cell is determined as 1.21 % with the help of photocurrent and photopotential values at the power point and the incident power of radiations by using the formula

Conversion efficiency = $V_{pp} \times i_{pp} \times 100$ / Electrode Area(1 cm^2)×10.4 $mWcm^{-2}$

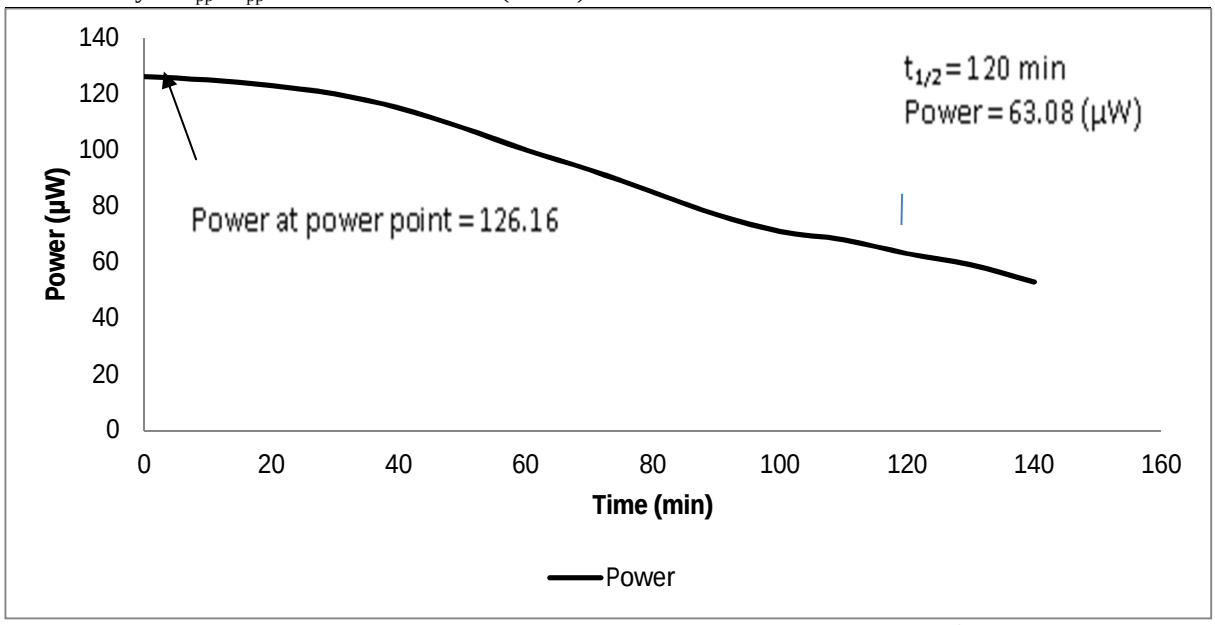

Fig 2. Storage Capacity and Conversion Efficiency of the Cell[a]

[a] At [Pheloxine B] = 4.33 × 10^{-5}M, [Xylose] = 6.60 × 10^{-4}M , pH = 12.86 , Tem = 303 K , Light intensity = 10.4 mW cm^{-2}, electrode area = 1 cm^2, Diffusion length = 5.3 cm.

IV. CONCLUSION

Conclusively the reductant (Xylose) and dye (Phloxine B) can be used successfully in a photogalvanic cell. The conversion efficiency and storage capacity of the cell is 1.21% and 120 minutes respectively, on irradiation for 220 minutes developed photogalvanic cell. It has been observed that the reductant has not only enhanced the electrical parameters (i.e. photopotential, photocurrent and power) but also enhanced the conversion efficiency and storagecapacity of photogalvanic cell. The efforts are also successful because of the photogalvanic cells showed good prospects of becoming commercially viable.

V. ACKNOWLEDGEMENT

The author is thankful to university Grant s Commission (UGC), Bhopal for providing Teacher Research Fellowship (latter no. 25-11/(12) 16-17 (TRF/CRO) date 30.03.2017, commissionerate college education rajasthan jaipur to give permission (latter no. F 1 (115) estt./DCE/12/349 date 30.05.2017) to join the research work for PhD. and also thankful to department of chemistry, J.N.V. University Jodhpur.

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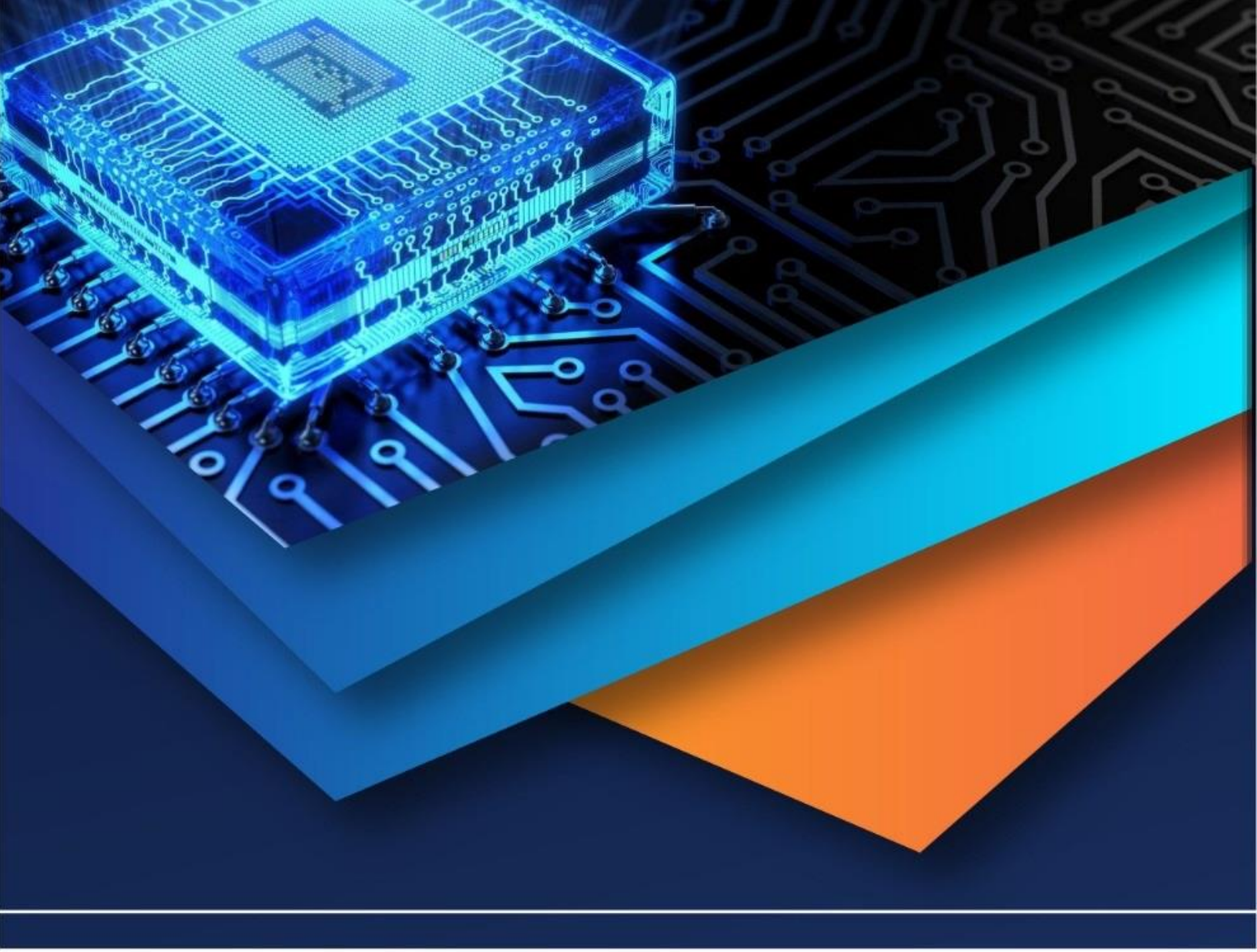

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