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# Production and Performance of Dye Sensitive Solar Cells Using $Co^{+2}$ Doped Photo-Anodes

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***Abstract –*** In order to increase the use of solar energy, which is one of the renewable energy sources, it is to produce high-efficiency, low-cost and environmentally friendly dye-sensitive solar cells from solar cells provided by photovoltaic technology that generates electricity from solar energy. Therefore, there is a need to develop new materials and modified designs to produce solar cells at lower cost. One way to increase the efficiency of dye-sensitized solar cells (DSCC) is by doping at the anode. At the same time, graphene paste was used instead of Pt cathode to reduce the cost. In this study, pure and Cobalt ($Co^{+2}$) added $TiO_2$ pastes were prepared to produce DSCC. Photovoltaic performances were determined by comparing pure and doped batteries with each other. For this purpose, pure and $Co^{+2}$ added $TiO_2$ pastes were first prepared. The resulting pastes were applied to FTO glasses with the doctor-blade method. Then, DSCCs were produced by sandwiching pure and $Co^{+2}$ doped $TiO_2$ photoanodes sensitized with N-719 dye with graphene-coated FTO thin films. The performance of the produced DSCCs was determined by Current Density (J) - Voltage (V) analysis. There was a certain increase in FF and Jsc values with doping. However, the results showed that the efficiency value of $Co^{+2}$ doped batteries is 370% above the value of batteries using pure $TiO_2$ photo-anodes.

*Keywords – Dye-Sensitized Solar Cell, $Co^{+2}$, Photo Anode, Graphene, $Tio_2$*

## I. INTRODUCTION

Energy, which has become a symbol of political power for countries, has also become a criterion showing the level of development of nations. Both the abundance of the energy source and the parameters such as the capacity of the energy source, its economic status, its compatibility with the environment, and its sustainability should be taken into consideration. [1] Considering the rapid depletion of fossil fuels, which is one of the energy sources, and the damage they cause to the environment, the scientific world has directed the world to different energy sources. [2] Among renewable and clean energies such as wind, hydroelectric, and bioenergy, solar energy is definitely the main energy source preferred in terms of energy efficiency due to its advantages such as being a more general and common source, not having a transportation problem, and being able to be directly converted into electrical energy. ([3]-[5]) Photovoltaic technology, which is used to obtain electricity from solar energy, is considered as clean and sustainable energy sources. The basic working principle of photovoltaic devices; It is the movement of charge between two materials with different conductivity properties. [6] When light falls on the solar cells, electrical voltage occurs at their ends. Photovoltaic technology, on the other hand, is used to describe equipment that produces electricity directly from light and converts solar energy into usable energy. Solar cells are structures that produce electrical energy as a result of photovoltaic features. Solar cells can be produced using very different materials and materials, and they are divided into different groups according to

the way they are made and the materials used in their structures. Recently, it is aimed to both reduce the costs and increase the efficiency of photovoltaic systems. In order for solar cell designs to take their place in industrial applications, it is necessary to develop features such as low-cost production, light panel production, availability of battery raw materials, flexibility, taking sunlight from different angles, and returning the cost in a short time. [2] Dye-sensitized solar cells (DSCC) are photonic devices that directly convert light into electricity, working with the idea of photo-electro-chemistry, proposed as an alternative to silicon-based solar cells. Although DSCC has low efficiency compared to other solar cells, its advantage over other solar cells is that dye molecules can be obtained cheaply, produced in a shorter time, easily purified and therefore produced at low cost. Black dyes as photoactive dyes in dye-sensitized solar cells, ruthenium dyes called N719 and N3 are the most efficient dyes due to their superior light absorption, durability, and most importantly, metallic bonding properties that allow photo-excited charges to be injected into $TiO_2$. Since the adsorption of dye molecules and the transport of electrons play a major role in the DSCC yield, the most important part is the photo anode section. [7] The nano-sized materials used in dye-sensitized solar cells, photoanodes and counter-electrodes are of great importance. Therefore, DSCC will absorb more of the light from the sun by using a semiconductor consisting of carefully structured materials with a large inner surface area. [8] Dhonde et al. (2017), pure, 0.1%, 0.3% and 0.5 mol% Cu additives to $TiO_2$ were synthesized by the sol gel method. Pt coated cathode is used on FTO in photocathode. It has been observed that there is a 26% increase in efficiency compared to pure $TiO_2$ with 0.3 mol% Cu doped battery efficiency with 8.65%. Dhonde et al. In their studies in 2018, Cu and Nitrogen were added to the anode part together, and the highest efficiency was again 11.70% in 3 mol% Cu/N. The improvement in photovoltaic performance of dye-sensitized solar cells combined with Cu/N-doped $TiO_2$ is attributed to the stabilized structure, higher surface area, improved visible light absorption, improved charge transfer and delayed charge carrier recombination. [9] Chahid et al. (2018) examined the effect of $TiO_2$ Cu additive in their studies and a thin film doctor blade method was applied on FTO at the photo anode. Commercial N3 dye was used as a dye, and plantin thin film was used at the cathode. The efficiency of pure, 1% Cu and 10% Cu doped solar cells were 0.94%, 2.87%, and 0.12%, respectively. It is seen that the highest efficiency is in the 1% Cu doped dye-sensitized solar cell. One of the potential solutions to increase the photocatalytic efficiency of $TiO_2$ in the visible region is to shift its optical absorption from the UV region to the visible light region so that more photons are absorbed. It is widely accepted that the efficiency of photocatalytic reactions of $TiO_2$ can be significantly increased by doping through modification of the band gap energy structures. Doping $TiO_2$ with various metals is known to reduce electron recombination, increase electrical conductivity, and increase the absorption of light and electron transport. Doping $TiO_2$ with transition metals is an effective way to increase photocatalytic efficiency.

In this study, the effect of $Co^{+2}$ doping on DSCC performance by producing pure and 0.5% M $Co^{+2}$ doped DSCC at the photo anode was investigated.

## Materials and Method

FTO (Fluorine doped tin oxide coated glass slide, L × W × thickness 25 mm × 25 mm × 2.2 mm, surface resistivity ~7 Ω/sq), Ethanol ($C_2H_5OH$, 99.9%), Titanium(IV) isopropoxide, Degusa P25, Sulfuric acid ($H_2SO_4$ %99), Sodium Nitrate ($NaNO_3$ %99), Potassium Permanganate ($KMnO_4$, %99), sodiumdodecylsulfate ($CH_3(CH_2)_{11}OSO_3Na$, %99), PVP (($C_6H_9NO$)n ), N719 Dye, $Co(NO_3)_2 \cdot 6H_2O$, graphite powder (C, %99) and Hydrogen peroxide ($H_2O_2$) were purchased from Sigma-Aldrich.

### A. *Preparation of Pure and $Co^{+2}$ Added $TiO_2$ Pastes and Application on FTO*

In order to prepare the $TiO_2$ paste, firstly, 3.8 ml of ethanol was poured into a small beaker, 0.16 ml of titanium (IV) tetraisopropoxide was added and mixed with a magnetic stirrer for 30 minutes. After the first process was finished, 1gr of nanocrystalline (P25) titanium dioxide ($TiO_2$) was added to the mixture and mixed for 10 more minutes with a magnetic stirrer to obtain a titanium dioxide paste. After the 0.5% M $Co^{+2}$ added $TiO_2$ cake was prepared in the same way, the FTO coated glasses were cleaned in an ultrasonic cleaner, washed with ethanol and left to dry. Pure and 0.5% M $Co^{+2}$ added pastes were applied to the surface of the conductive glass (FTO) using the doctor-blade method. Then,

the prepared sample was heat treated in the ash oven at 450 °C for 1 hour for the calcination process. [10]

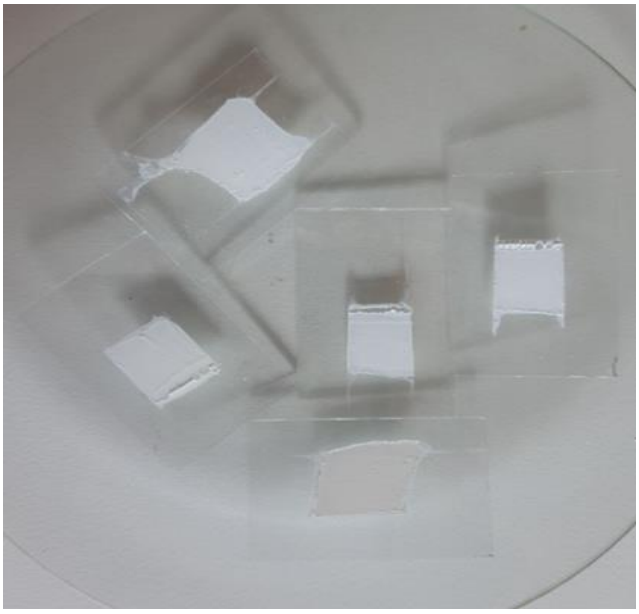

Fig. 1 Conductive glasses (FTO) coated with titanium dioxide ($TiO_2$) by the Doctor-blade method

### B. *Preparation of Graphene Paste and Application on FTO*

Graphene Oxide was synthesized by the Hummers Method. 0.44 g of prepared graphene and 1% by weight of sodium dodecylsulfate (SDS) were added to 20 ml of distilled water and ultrasonically dispersed for 1 hour. The graphene paste was magnetically stirred vigorously for 1 hour. For the graphene-PVP thin film, 1% wt of PVP was added to prevent graphene aggregation in the paste and mixed for an additional 1 hour. Graphene-PVP paste was dried at 50 °C until it reached the desired consistency. FTO was cleaned with ultrasound assistance. The synthesized graphene oxide was applied to the FTO conductive glasses with the Doctor-Blade technique.

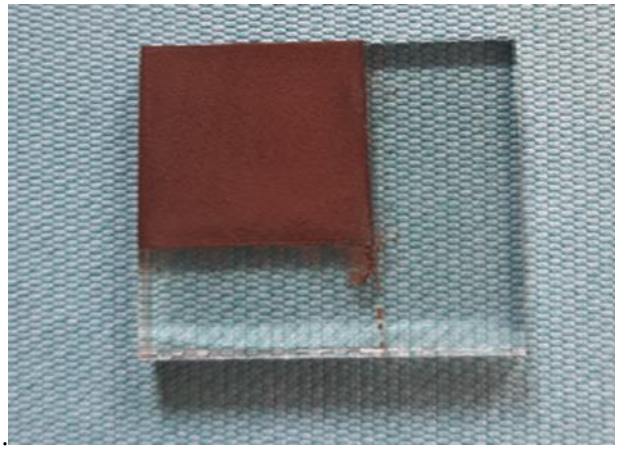

Fig. 2 Digital image of Graphene Oxide/FTO Doctor-Blade application

### C. *Preparation of Dye Sensitive Solar Cell*

0.01 g of N719 dye was prepared by mixing in 25 ml of ethanol for 1 hour. The prepared photo-anodes were kept in the dye for 24 hours. The image of dye adsorbed photoanodes is shown in Figure 3. While preparing the liquid electrolyte solution, in 3-methoxypropionitrile solvent; It was prepared by dissolving 0.6 M 1-butyl-3-methylimidazoium iodide, 0.01 M iodine, 0.1 M 4-tert-butylpyridine and 0.1 M lithium iodide hydrate by stirring in a magnetic stirrer for 2 hours.

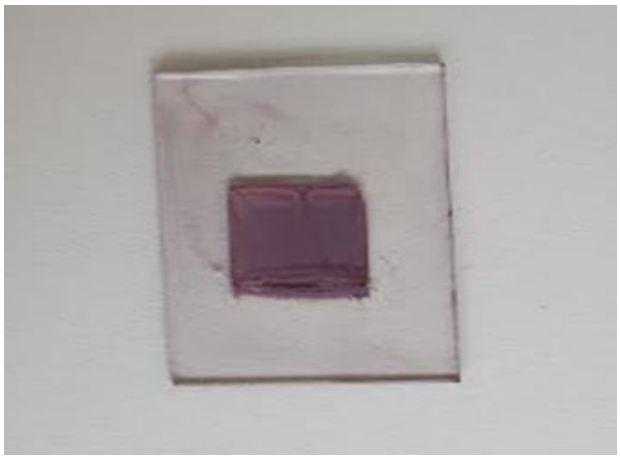

Fig. 3 Working electrode obtained by keeping it in a dye solution prepared with N719 dye

Photo anodes and Graphene/FTO counter electrode prepared with pure $TiO_2$ paste and 0.5 M $Co^{+2}$ doped $TiO_2$ were brought together in a sandwich geometry with their conductive surfaces facing each other. Then, iodide/triiodide ($I^-/I_3^-$) redox couple (electrolyte) was dropped between the two electrodes and waited for a while for the electrolyte to spread well on the active layer. The electrodes of

the two electrodes were adhered to each other using epoxy glue and made ready for measurement, leaving 1 cm of the electrodes outside for later measurement and characterization processes.

## II. RESULTS

*Current-Voltage Measurements*

The designed DSCC current-voltage characteristics were made using a computer-controlled semiconductor characterization device (Keithley 4200-SCS), a 1.5 AM (100 mW/cm$^2$) filter solar simulator with Xenon lamp, and data processing software prepared with LabView. The open-circuit voltage ($V_{OC}$), short-circuit current ($I_{SC}$), short-circuit current density ($J_{SC}$), max power (Pmax), filling factor (FF) and power conversion efficiency (Ƞ (%)) of the solar cell cells designed in these measurements. parameters have been obtained.

$$P = V \times I \quad (1)$$

$$FF = \frac{V_{MAX} I_{MAX}}{V_{OC} I_{SC}} = \frac{P_{MAX}}{V_{OC} I_{SC}} \quad (2)$$

$$\eta = \frac{I_{SC} \times V_{OC} \times FF}{P_{In}} \times \%100 \quad (3)$$

Max power 1. Equation, fill factor 2. Equation and power conversion efficiency is calculated according to Equation 3.

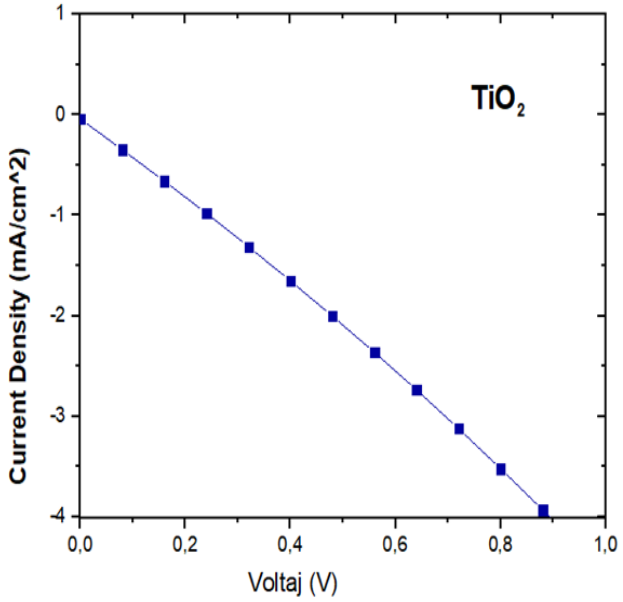


Fig. 4 Current density-voltage characteristic plot of pure $TiO_2$ prepared DSCC

The current density-voltage characteristic graph of DSCC prepared with pure $TiO_2$ is shown in Fig. 4.

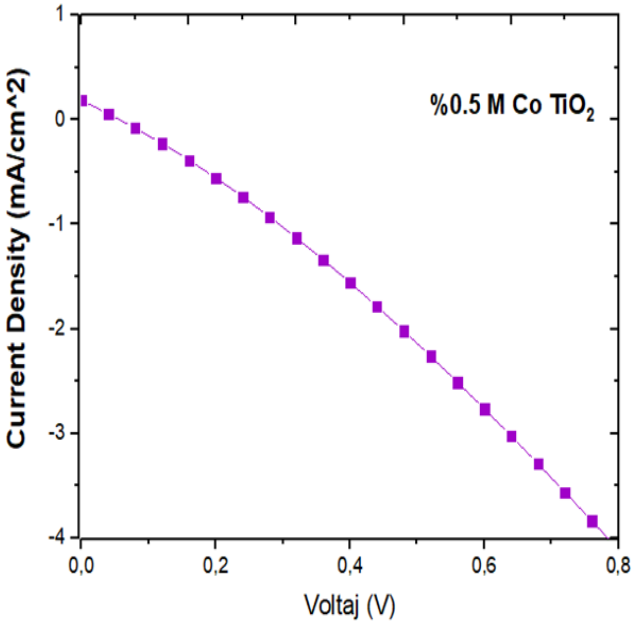


Fig. 5 Current density-voltage characteristic plot of 0.5% M $Co^{+2}$ doped DSCC

In Fig. 5, the current density-voltage characteristic graph of 0.5% M $Co^{+2}$ doped DSCC is shown.

Table 1. Photovoltaic parameters of produced DSCCs

| **Solar Cell** | **$V_{OC}$ (V)** | **$I_{SC}$ (mA)** | **$J_{SC}$ (mA /cm$^2$)** | **$P_{max}$ (W)** | **FF** | **Ƞ (%)** |
|---|---|---|---|---|---|---|
| **$TiO_2$** | 0,97 | 0,120 | 0,058 | 2,21x10$^{-5}$ | 0,19 | 0.01 |
| **% 0.5 M $Co^{+2}$ $TiO_2$** | 0,84 | 0.481 | 0.20 | 1,06x10$^{-4}$ | 0,26 | 0,047 |

## III. DISCUSSION

Components such as maximum current density (Jmax), open circuit voltage (Voc), short current circuit density (Jsc), factor filling (FF) and charging (η) of the produced dye-sensitized solar cells were calculated using J-V curves. Pure and 0.5% (M) $Co^{+2}$ doped $TiO_2$ photo-anodes were compared in line with the results obtained from the J-V analysis. A power conversion efficiency of 0.01% was obtained from 0.5% (M) Co-doped $TiO_2$ photo-anode, while the power conversion efficiency was

calculated as 0.047% in pure $TiO_2$ photo-anode. As expected, there is an increase in yield with doping. It is thought that the increase in yield value with doping is mainly due to the change in Jsc. The efficiency obtained in solar cells prepared with non-additive and Co-doped N719 was not at the desired level.

Jeba Beula et al. (2019) in their study, Co-doped 0,025%, 0.05%, 0.075% and 0.1%M $TiO_2$ nanoparticle thin film on the photo anode was synthesized by the sol gel method by spin coating technique, with reduced graphene oxide to the ITO substrate and P2P-Ru dye as a dye. used. The highest yield was 4.25% with 0.1 M Co added. Compared to pure $TiO_2$ thin film, an increase of 65% was achieved. [11] In the measurements taken from the undoped and Co-doped solar cells, Voc was at the expected levels in the two solar cells, which were especially designed, and the JSC and FF values were very low contrary to the expectations, so it was determined that this situation directly affected the efficiency of the cells. When the previous studies were examined, it was observed that low yield of DSCC was a very common problem. DSCC power conversion efficiency is dependent on many parameters. Pt is used as the cathode material in many studies with high efficiency. Since Pt is an expensive material, we aim to reduce the cost of the solar cell produced, so it has a negative impact on battery performance. Another reason for the low efficiency of the DSCCs designed in this study is the low FF value, which greatly affects the power conversion efficiency. FF is the interface junction between the paint surface and the electrolyte. This semiconductor liquid junction can create large non-linear resistance in the current path. There are several possible causes for low FF and all are related to the series resistance inside the cell. [10]

Compared to the DSCC prepared without additives, an increase in $J_{SC}$, FF, Pmax and power conversion efficiency of the 0.5% M $Co^{+2}$ doped battery was observed. It can be said that the increase in $J_{SC}$ value increases the electron lifetime in photo-anodes with $Co^{+2}$ doping. In all these results, the power conversion efficiency of DSCC produced with Co-doped $TiO_2$ photo-anodes was obtained as 0.047%. This value is approximately 370% above the yield value of pure DSCC. As a result, it was determined that there was a positive improvement in the parameters of DSCC with doping.

## IV. CONCLUSION

In dye-sensitized solar cells, the photoanode semiconductor determines the photocurrent density because it is an important component because it plays an active role in determining not only the movement of photoinduced electrons towards the charge, but also the adsorbing of dye molecules. Semiconductor photo anode plays an important role in determining the working process of dye-sensitized solar cells. The wide bandgap of $TiO_2$ limits its use for visible light as the number of excited dyes cannot inject electrons into the conduction band of $TiO_2$ due to insufficient electron injection driving force. Doping $TiO_2$ is an effective way to overcome this problem and improve the performance of dye-sensitized solar cells. However, $Co^{+2}$ doping can provide better balance for the Fermi energy level, helping to maximize FF, $P_{MAX}$ and Jsc, resulting in improved performance of dye-sensitized solar cells. In addition, one of the biggest advantages of adding metal ions at appropriate concentrations is that it carries the light absorption spectrum of the semiconductor from the ultraviolet region to the visible region (>400 nm) in a wide range. Therefore, it is important to produce modified $TiO_2$ working electrode materials by co-doping for dye-sensitized solar cells. [12]

Since the dye molecules are bonded to Ti atoms, the displacement Ti with another cation also affects the dye adsorption because of the different bonding strengths between the dye and the additive, or because the dopant induces oxygen vacancies. Doping generally inhibits the growth rate of $TiO_2$ nanoparticles, resulting in smaller particles. This is more beneficial as it will result in a larger surface area per volume of $TiO_2$. The increased surface area accommodates more dye, resulting in higher light absorption and current densities. The main advantage of high light absorption is that thinner films can be used in photovoltaic devices resulting in reduced recombination benefiting both $J_{SC}$ (short circuit current density) and FF (fill factor). [13]

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