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Diphenylcarbazone and tartrazine as sensitizer metal complex dyes for dye sensitized solar cells

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Abstract: Dye sensitized solar cells (DSSCs) are photovoltaic devices that produce electricity from the photon energy of sunlight using dyes. Dyes used DSSCs should have a broad absorption spectrum at the UV-Vis region and should be strongly bound to the photoanode surface. Dyes are used in DSSCs can be classified into three types: metal complex dyes, metal-free organic dyes and natural dyes. For metal complex dyes, ruthenium is usually used as metal centers. While most Ru complex dyes have high efficiency, Ru is a rare metal. To decrease the cost of Ru complex dyes, transition metals are widely investigated. In this work, diphenylcarbazone and tartrazine with different metal complexes were synthesized and investigated for their suitability for DSSCs. UV-Vis was used for the characterization of dyes and linear sweep voltammetry and electrochemical impedance spectroscopy were used to investigate the performance of DSSCs.

Keywords: Dye sensitized solar cells, metal complex dyes, diphenyl carbazone, tartrazine

1. Introduction

Dye sensitized solar cells (DSSCs) are classified in 3. Generation solar cells that convert sunlight to electricity by the photovoltaic effect. After Gratzel published the first paper about DSSCs (Oregan and Gratzel 1991), dye sensitized solar cells have attracted scientists' attention because of their easy preparation and use of low-cost materials. However, DSSCs cannot compete with other solar cells by the aspect of light conversion efficiency (Sharma et al. 2017). Therefore, intensive research has been done on DSSCs.

DSSCs consist of four main parts: photoanode, dye, electrolyte and counter electrode (Jena et al. 2012). As photoanode, semiconductor metal oxide coated transparent conductive oxide substrates (FTO or ITO) are usually used. TiO_2, ZnO, SnO_2 are usually used as semiconductor metal oxide photoanode materials (Kumar et al. 2017). The main roles of photoanodes in DSSCs are collection of the excited electrons from the dye LUMO and carry forward to these electrons through an external circuit to counter electrode (Jung and Lee 2013). As electrolyte usually redox couple including organic solvents are used. In this regard, I^-/I_3^- is usually used as a liquid electrolyte (Wu et al. 2015). Electrolytes are collected electrons from the counter electrode and give an electron to the excited dye molecule to regenerate it simultaneously (Gong et al. 2017). Counter electrodes used in DSSCs are generally platinum coated FTO and collect electrons from the external circuit and regenerate redox couple in the electrolyte (Sugathan et al. 2015).

Dyes are one of the essential components of DSSCs because electron excitation/movement starts with dye molecules. Dyes used in DSSCs can be categorized as Metal complex dyes, metal-free organic dyes and natural dyes (Mishra et al. 2009). Although metal-free organic dyes have a high molar absorption coefficient and can be manipulated to change suitable molecular geometry or HOMO-LUMO energy levels, solar cells' efficiency using this type of dye is low. Natural dyes are cheap sensitizers obtained from plants, herbs, vegetables etc., but they have very poor stability (Richhariya et al. 2017). Metal complex dyes have high stability and broad light absorption at the UV-VIS region. However, rare and expensive ruthenium metal is used as metal center at metal complex dyes at dye sensitized solar cells.

Tartrazine (trisodium 1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-5-pyrazolone-3-carboxylate)) is a yellow-colored synthetic azo dye that is used for food or drinks coloring. Tartrazine has two sulfonic acid and one carboxylic acid group on its structure, so it can change molecular form with pH change (Saleh et al. 2016). Diphenylcarbazone (1-anilino-3-phenyliminourea) is a molecule from the carbazone family. Diphenylcarbazone is used as a chelating agent to determine the presence of metal ions because it can form metal complexes with intense colors (Deshmukh and Bokil 1956).

In this study, it was aimed to prepare tartrazine (TART) or diphenylcarbazone (DPC) metal complexes with cobalt and zinc metals to find a cheap alternative to Ru complexes. While Ru metal is rare and expensive, using cheap and easily accessible transition metal complexes as sensitizers might eliminate the low efficiency of DSSCs for low-cost technologies or applications. Therefore, these dyes were used as sensitizers at DSSCs and investigated how they affect the efficiency of DSSCs.

2. Materials and Method

All chemicals that were used in this study were purchased from Sigma Aldrich. $ZnCl_2$ and $CoCl_2.6H_2O$ were entirely dissolved with the proper amount in ethanol to prepare 0.3 mM Co^{2+} and Zn^{2+} solution. Same as metal solutions, tartrazine and diphenylcarbazone were dissolved in ethanol with the proper amount to prepare 0.3 mM ligand solutions. While vigorously stirring, 10 mL ligand solutions were added to 5 mL metal solutions dropwise to prevent precipitation. After adding process was completed, solutions were stirred for 10 min. Then, prepared metal complexes were put in the dark and observed to see whether precipitation occurred or not. Prepared metal complexes were named Co-TART, Zn-TART for tartrazine complexes and Co-DPC, Zn-DPC for diphenylcarbazone complexes.

Dye-Sensitized Solar Cells were prepared as in our previous study (Ünlü and Özacar 2020). TiO_2 photoanodes were immersed in prepared dye solutions for 24 h in the dark.

3. Results and Discussion

UV-VIS Spectroscopy was used to characterize prepared dyes and obtained spectra can be seen in Figure 1. For TART, Co-TART and Zn-TART, all spectra are nearly the same. Although there is a slight shift at n-π* transition band between 425-475 nm, there are no disappearing or new bands. That means there is some interaction between TART and Co or Zn, but complexation was not completely occurred. For DPC and its Co and Zn complexes, the situation is different than TART and TART complexes. Zn-DPC shows a new broad absorption band at nearly 525 nm, which means the formation of Zn-DPC complex was successful. Therefore, even though there is no new band for Co-DPC, the band seen at 290 nm for DPC disappeared. It also shows that the synthesis of Co-DPC was successful.

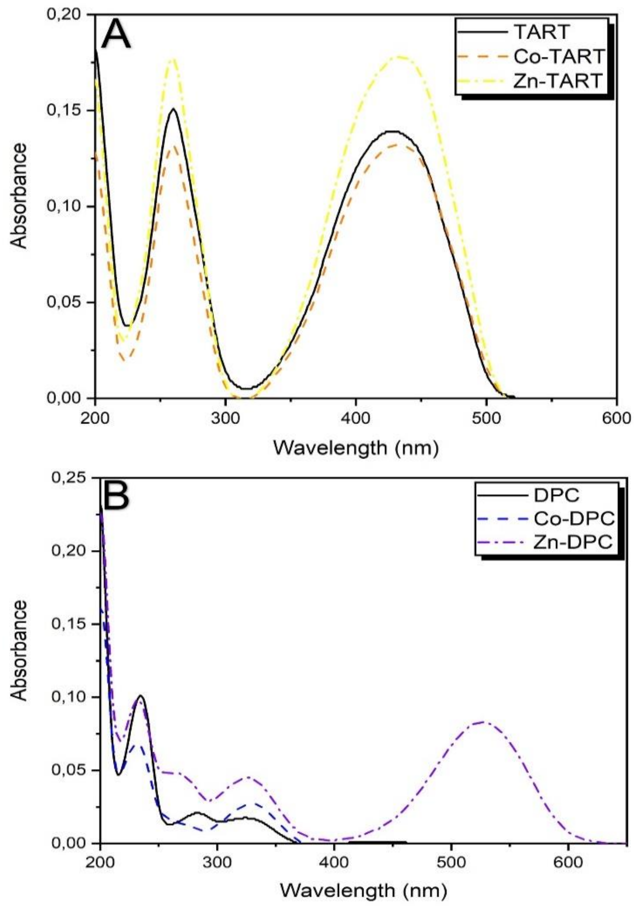

Fig. 1 UV-VIS spectra of A) TART, Co-TART, Zn-TART and B) DPC, Co-DPC, Zn-DPC

Linear sweep voltammetry was used to characterize DSSCs sensitized with TART, DPC and their metal complexes. FF and solar conversion efficiency (η) were calculated with the Equation 1 and Equation 2:

$$FF = \frac{Jmax*Vmax}{Jsc*Voc} \quad (1)$$

$$\eta = \frac{Jsc*Voc*FF}{Pin} \quad (2)$$

where Jsc is short current density, Voc is open-circuit voltage, Jmax and Vmax are maximum current density and maximum voltage and Pin is the power of the light source. The J-V curves of the prepared DSSCs can be seen in Figure 2. and electrochemical values and efficiencies of DSSCs can be seen in Table 1. DSSC that was sensitized with TART was showed the highest efficiency among all TART dyes. While TART and TART metal complexes have the same light absorption property, unreacted metal ions were caused to decrease at the efficiency. For DPC dyes, it can be seen that Zn-DPC has the highest efficiency and Co-DPC is following it. Zn-DPC has the highest efficiency because it can absorb light between 450-600 nm, so it can absorb more photons from sunlight to produce excited electrons. Co-DPC can absorb more light than bare DPC dye, but it does not have a broad light absorption like Zn-DPC dye. That's why its efficiency is lower than Zn-DPC.

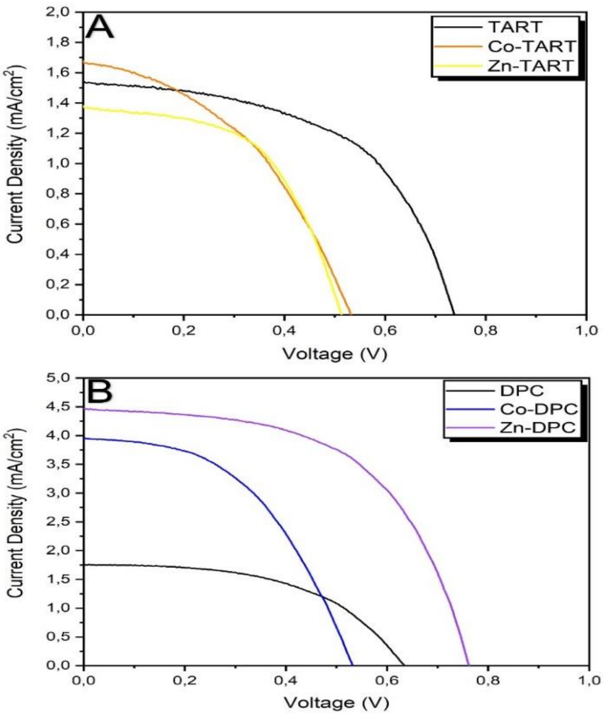

Fig. 2 J-V curves of DSSCs that were sensitized with A) TART, Co-TART, Zn-TART and B) DPC, Co-DPC, Zn-DPC

Table 1. Photoelectrochemical Values of Prepared DSSCs

Dye	Jsc (mA/cm^2)	Voc (V)	FF	η (%)
TART	1,54	0,74	0,54	0,61
Co-TART	1,68	0,53	0,43	0,38
Zn-TART	1,38	0,51	0,55	0,39
DPC	1,76	0,63	0,52	0,58
Co-DPC	3,96	0,53	0,48	1,01
Zn-DPC	4,47	0,76	0,56	1,91

Electrochemical Impedance Spectroscopy (EIS) was used to investigate solar cell characteristics such as resistance and electron lifetime. Nyquist and Bode plots of prepared DSSCs can be seen in Figure 3. For TART, Co-TART and Zn-TART sensitized solar cells, Zn-TART has the highest resistance among them all. This high resistance value can be explained with unreacted Zn^{2+} ions at the dye solution. While there are unreacted Co^{2+} ions for Co-TART dyes, it has the lowest resistance value than all TART dyes. However, Co-TART dye has the lowest electron lifetime value that can be seen at the Bode plot. That can explain the low efficiency that Co-TART sensitized DSSC has. For DPC dyes, all resistance and electron lifetime value are in good harmony with the efficiency of DSSCs. Both Co-DPC and Zn-DPC dyes have less resistance value than DPC and it can explain the high efficiency of these dyes.

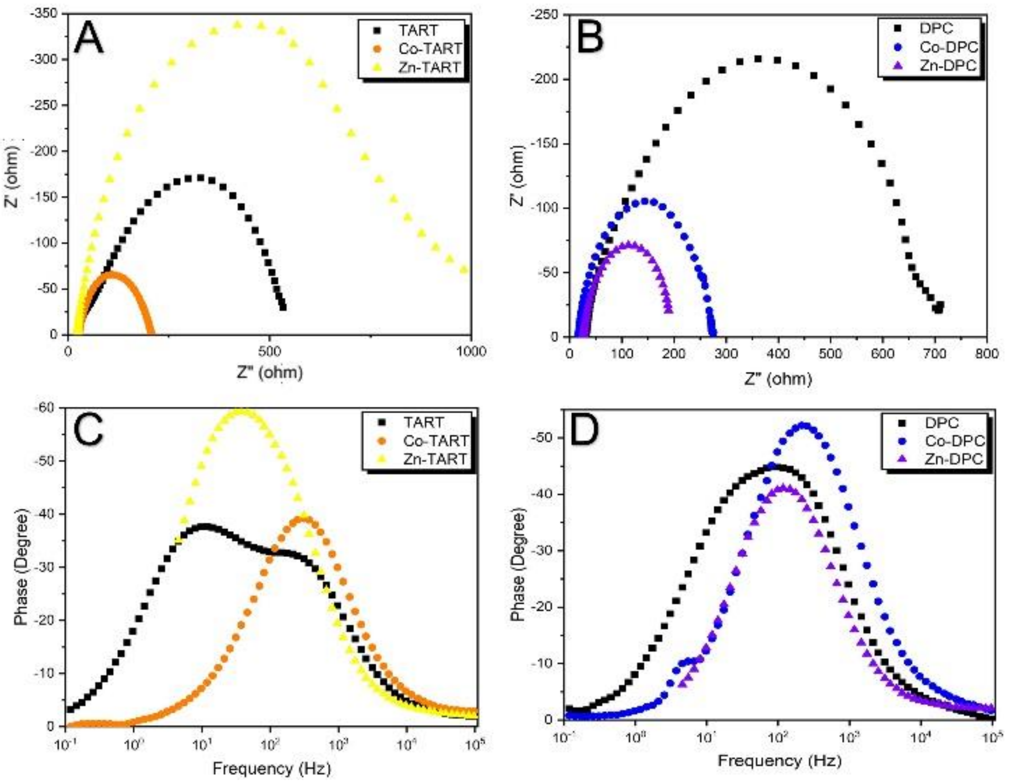

Fig. 3 Nyquist Plots for A) TART, Co-TART, Zn-TART and B) DPC, Co-DPC, Zn-DPC and Bode Plots for C) TART, Co-TART, Zn-TART and D) DPC, Co-DPC, Zn-DPC dyes

4. Conclusion

The new TART and DPC dyes and their metal complexes were developed and were used as a sensitizer in DSSCs. For TART dyes, complexations were a failure. However, we believed that Co or Zn complexes could be prepared by adjusting pH or using heat. Co and Zn complex with DPC were prepared successfully and showed high-efficiency value than DPC as expected. Finally, by mixing with TART and Zn-DPC to prepare cocktail dyes, we think that efficiency can be improved because of broadening the light absorption at the UV-VIS region.

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References

Deshmukh GS, Bokil I. 1956. Diphenylcarbazone as an Internal Indicator in Volumetric Analysis. III. Volumetric Determination of Thorium by Ammonium Molybdate. Bull Chem Soc Jpn. 29:449–450

Gong J, Sumathy K, Qiao Q, Zhou Z. 2017. Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends. Renew Sustain Energy Rev. 68:234–246

Jena A, Mohanty SP, Kumar P, Naduvath J, Lekha P, Das J, Narula HK, Mallick S, Bhargava P, Gondane V. 2012. Dye Sensitized Solar Cells: A Review. Trans Indian Ceram Soc. 71:1–16

Jung HS, Lee J. 2013. Dye Sensitized Solar Cells for Economically Viable Photovoltaic Systems. J Phys Chem Lett. 10:1682–1693

Kumar R, Umar A, Kumar G, Nalwa HS, Kumar A, Akhtar M.S. 2017. Zinc oxide nanostructure-based dye-sensitized solar cells. J Mater Sci. 52:4743–4795

Mishra A, Fischer MKR, Büuerle P. 2009. Metal-Free organic dyes for dye-Sensitized solar cells: From structure: Property relationships to design rules. Angew Chemie Int Ed. 48:2474–2499

Oregan B, Gratzel M. 1991. a Low-Cost, High-Efficiency Solar-Cell Based on Dye-Sensitized Colloidal TiO_2 Films. Nature. 353:737–740

Richhariya G, Kumar A, Tekasakul P, Gupta, B. 2017. Natural dyes for dye sensitized solar cell: A review. Renew Sustain Energy Rev. 69:705–718

Saleh M, Hashem E, Salahi N. 2016. Oxidation and Complexation-Based Spectrophotometric Methods for Sensitive Determination of Tartrazine E102 in Some Commercial Food Samples. Comput Chem. 04:51–64

Sharma S, Bulkesh S, Ghoshal SK, Mohan D. 2017. Dye sensitized solar cells: From genesis to recent drifts. Renew Sustain Energy Rev. 70:529–537

Sugathan V, John E, Sudhakar K. 2015. Recent improvements in dye sensitized solar cells : A review. Renew Sustain Energy Rev. 52:54–64

Ünlü B, Özacar M. 2020. Effect of Cu and Mn amounts doped to TiO_2 on the performance of DSSCs. Sol Energy. 196:448-456

Wu J, Lan Z, Lin J, Huang M, Huang Y, Fan L, Luo G. 2015. Electrolytes in dye-sensitized solar cells. Chem Rev 115:2136–2173