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SYNTHESIS, CHARACTERIZATION AND PHOTOVOLTAIC PROPERTIES OF Ni SCHIFF BASE COMPLEX WITH THE LIGAND OF -4,4'-METHYLENE BIS (2,6-diethyl) ANILINE-3,5-DI-TERT-BUTYLSALICYLALDIMINE

D. KILINC[a], O. SAHIN[b], S. HOROZ[c*]
[a]*Siirt University, Faculty of Art&Sciences, Department of Chemistry, Siirt, 56100, TURKEY*
[b]*Siirt University, Faculty of Engineering and Architecture, Department of Chemical Engineering, Siirt, 56100, TURKEY*
[c]*Siirt University, Faculty of Engineering and Architecture, Department of Electrical and Electronic Engineering, Siirt, 56100, TURKEY*

In the present study, we have synthesized Ni schiff base complex with the ligand of -4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine at room temperature in aqeous solution. The structural, morphological and optical properties of complex were investigated by XRD, FTIR, SEM, and UV-Vis spectroscopy,respectively. The obtained results show that the complex can be used as a sensitizer in dye-sensitized solar cells (DSSCs). The photovoltaic properties of Ni schiff base complex used as dye sensitizer was studied for the first time. A DSSC was fabricated using Ni schiff base complex with the ligand as the dye sensitizers on nanoporous TiO_2 thin film and the photovoltaic parameters of the cells were determined. Our study suggests that Ni schiff-base complex can be used as a suitable sensitizer in applications of DSSCs.

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*Keywords:*Characterization**,** dye-sensitized solar cells, Ni schiff base complex, synthesis,

1. Introduction

In parallel with the increasing human population, demand for energy is increasing. But the energy provided by fossil fuels does not meet this demand. Owing to this situation, scientists have searched for alternative energy sources that would not have a negative impact on the environment [1-3]. The dye-sensitized solar cell (DSSC) used to strengthen solar energy is one of the alternative energy sources that do not produce pollutants [4-5].

The basic components of DSSC can be listed as semiconductor glass, electrolyte solution, electrode comparators and dye sensitizers [6-7]. Many effort has been made to synthesize both organic and inorganic dyes and to examine their application [8].

Dye sensitizers that enhance solar cell performance by capturing photons from sunlight have an important role in DSSCs [9-10]. In the last few years, Ru-polypyridyl complex with intense panchromatic behavior and highmetal-to-ligand charge transfer(MLCT) has been used as a dye sensitizer and highly efficient DSSCs have been achieved [11]. However, these complexes are difficult to synthesize and costly, so more convenient complexes are needed.

Thus, as an alternative to Ru complex, Fe (II) [12], Os (II) [13], Cu (I/II) [14], Co (II) [15] and Re (I) [16] metal complexes have been used in DSSCs as dye sensitizers. The efficiency of the dye used as sensitizer depends on the electron injection from an excited state of the dye used to the conduction band of the semiconductor. Environmentally friendly TiO_2 is a nano-sized semiconductor material that is widely used in DSSCs because of its high photocatalytic activity, stable chemical and high adsorption properties [17-18].

In present study, nickel (Ni) schiff base complex with 4,4'-methylene bis(2,6-diethyl)aniline-3,5-di-tert-butilsalisilaldimine as ligand was synthesized. The photovoltaic properties of Ni schiff base complex used as dye sensitizer were studied for the first time.

*Corresponding author: sabithoroz@siirt.edu.tr

Furthermore, the synthesized Ni base complex was investigated in terms of structural, morphological and optical properties, respectively.

2. Experimental Details

The method followed by Kilic et al. [19] was used to synthesize 3,5-di-tert-butylsalicylaldimine-4,4'-methylene bis (2,6-diethyl) aniline ligand. In a typical ligand synthesis process, a certain amount of 4,4'-methylene bis (2,6-diethyl) aniline (2 mmol) and 3,5-di-tert-butylsalicylaldimine (1 mmol) were dissolved in a flask containing 30 mL of ethanol. The formic acid (a few drops) used as catalyst was then added to the solution. After stirring at a certain temperature for 5-6 hours, the mixture was cooled to room temperature. The resulting crystals were removed from slovent under vacuum using a filter paper. Then, the samples were recrystallized using methanol. The structure of the obtained ligand is shown in Fig 1.

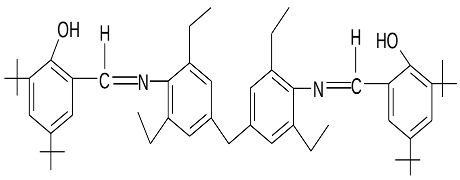

Fig. 1. The structure of the obtained ligand.

To synthesize Ni schiff base complex with the ligand of -4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine, an aqueous solution of Ni compounds in the absolute ethanol salt, was added to a solution of the ligand of methyl-bis (2,6-diethyl) aniline-3,5-di-tert-butylalycylaldimine. The resulting mixture was stirred at the particular temperature for approximately 1 hour. The solution was cooled to room temperature after the volume was reduced to 15 to 20 ml. The mixing process was stopped to allow the compound to be precipitated. The precipitate was removed from the solvent by means of filter paper and then washed several times with methanol. Finally, the obtained product was crystallized with methanol and chloroform. Figure 2 indicates structure of Ni schiff base complex with the ligand of 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand.

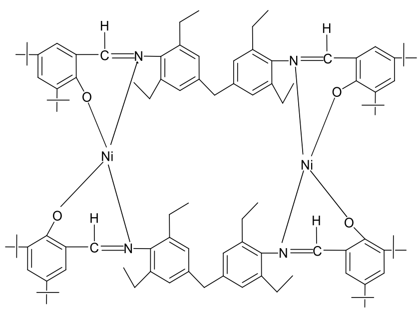

Fig. 2. Structure of Ni schiff base complex with the ligand of -4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand.

3. Characterizations

X-ray diffraction (XRD) on a Rigaku X-ray diffractometer with Cu Kα (λ=154,059 pm) radiation and scanning electron microscope (SEM) (JEOL JSM 5800) were used to analyze structural and morphological properties of Ni schiff base complex with the ligand of 4,4'-

methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine. UV–Vis spectra of samplewas obtained with a Perkin-Elmer Lambda 2. Current density (J) versus voltage (V) measurement was performed by using PCE-S20 with a monochromatic light source consisting of a 150-W Xe lamp and a monochromator. For J–V measurement, fluorine doped tin oxide (FTO, 13Ω sq^{-2}) conductive glass substrates were used as the photo electrodes. The TiO_2paste was coated on the FTO substrates using the doctor blade method, then sintered at 450°C for 45 min. A suspension of Ni schiff base complex with the ligand of 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine was dropped on the FTO substrates coated with TiO_2 paste. The substrates were dried with N_2 gas and secured against Cu_2S counter electrodes containing polysulfide electrolytes.

4. Results and Discussions

X-ray diffraction (XRD) measurement

The structural properties of Ni schiff-base complex with4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand were investigated by XRD measurement. Figure 3 reveals the XRD patterns of the synthesized complex.

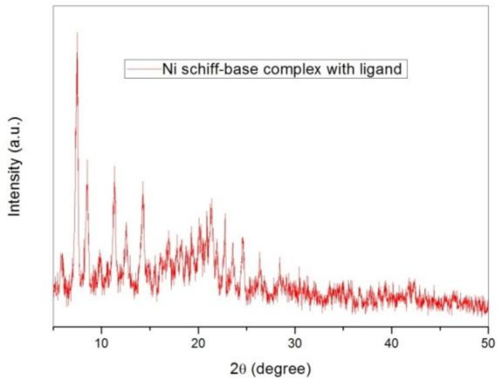

Fig. 3. Diffraction patterns of Ni schiff-base complex with 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand

The well-defined patterns obtained show that the synthesized example is in the crystalline phase. This result is in agreement with the data reported by Joseyphus et al. Owing to its natural crystalline structure, which is possessed by the Ni metallic compound,a crystalline appearance of the Ni metal schiff base complex is observed.The average grain size of the complex synthesized using the Scherre's equation (Equation 1) shown in the study published by Cullity [20] was calculated.

$$d = {}^{0,9\lambda}/_{(\beta cos\theta)} \quad (1)$$

where d is the average size of the synthesizedNi schiff-base complex, λ is the wavelength of X-ray, β is the broadening measured as the full width at half maximum (FWHM) in radians, and θ is Bragg's diffraction angle.The d-value for the Ni schiff-base complex was found as 40 nm. This value is an indication that the synthesized complex is in nanoscale.

Scanning Electron Microscopy (SEM) Measurement

The morphological properties of Ni schiff-base complex containing 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand were investigated by SEM measurement.Figure 4 demonstrates the SEM image of Ni schiff-base complex containing 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand.

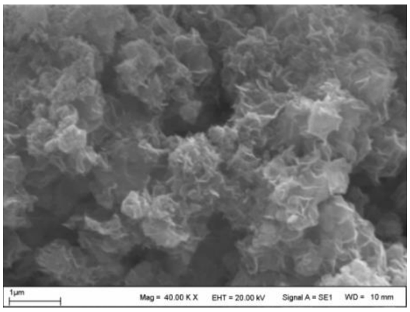

Fig. 4. SEM image of Diffraction patterns of Ni schiff-base complex with 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand.

The obtained SEM image indicates that the Ni schiff base complex has a platelet-like structure.Although the particle size of the synthesized complex was determined to be several microns in diameter, particles smaller than 100 nm in size were also observed. Moreover, the average particles size obtained from XRD reveals that the synhtesized complexwas agglomerated that it has polycrystalline with nanosized grains.

Fourier-Transform Infrared (FT-IR) Measurement

The FT-IR measurement was performed to investigate whether the reaction occurred during the synthesis.The FT-IR spectra obtained for4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand and Ni schiff-base complex with ligand are indicated in Figure 5a and 5b, respectively.

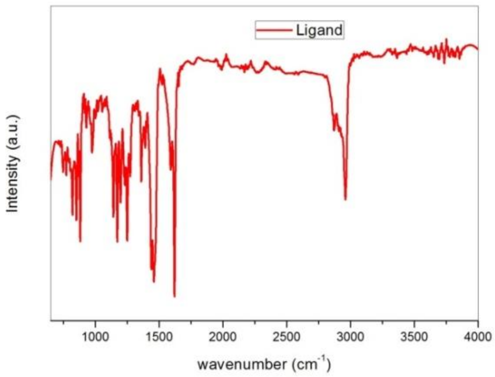

Figure 5a FT-IR spectra for 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand.

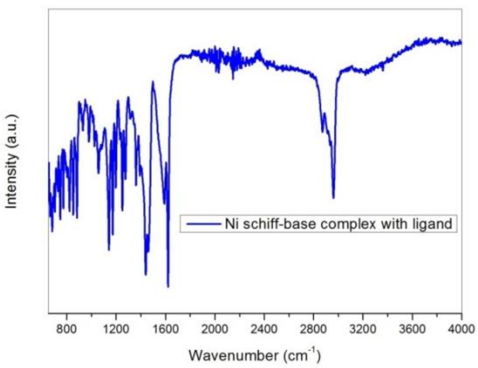

Fig. 5b. FT-IR spectrum of Ni schiff-base complex with 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand.

In the FT-IR spectrum of the ligand, peaks observed between 2745-2976 cm^{-1} are due to -CH_3 asymmetric vibrations whereas peaks detected between 1689-1748 cm^{-1} originate from –O=C vibrations.In a study by Tas et al. [21], it was reported that the peaks detected between 1602-1619 cm^{-1} belong to the azomethine group.A shift in the peaks of these groups was observed in the FT-IR spectrum of the Ni schiff base complex. This can be explained by the fact that the nitrogen atoms of the azomethine groups are coordinated with Ni.In Figure 5b, the bands detected between 3440-3500 and 723-730 cm^{-1} are due to water molecules.The peak observed at 1734 cm^{-1} corresponds to the C = O streching vibration mode.For the Ni schiff-base complex, the peaks observed at approximately 1000 and 1200 cm^{-1} represent C-O stretching vibrations.The peak detected at 1250 cm^{-1} can be correlated with C-O-C symmetric stretching mode.

Optical Absorption Measurement

Optical absorption measurements were carried out in range of 400 and 1000 nm to determine the geometry of synthesized Ni schiff-base complex containing 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand. The recorded electron spectra of the complex is indicated in Fig. 6.

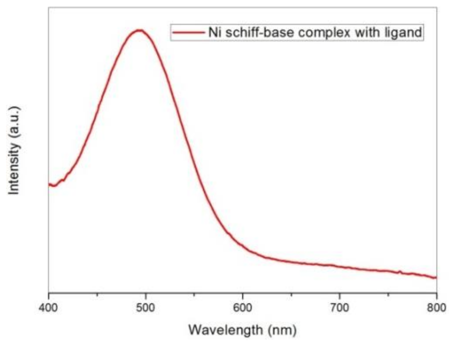

Fig. 6 UV-Vis spectra of Ni schiff-base complex containing 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand

As can be seen from Fig. 6, a broad absorption band at 494 nmwas observed for Ni schiff-base complex.This transition corresponds to $^3A_{2g}$(F)-$^3T_{1g}$ (F). This reveals that the synthesized Ni complex has an octohedral geometry and D_h symmetry [22-23].

Current density (J)- Voltage (V) Measurement

The efficiency of a solar cell structure is defined as the ratio of the output power density to the input power density in a J-V measurement.If the power density of incoming light is defined as P_{in}, the efficiency (η) of a solar cell is calculated using the equation given in Equation 2.

$$\eta = \frac{P_m}{P_{in}} = \frac{J_{SC}V_{OC}FF}{P_{in}} \quad (2)$$

The fill factor (shown in Equation 3) indicated by FF is obtained by dividing the maximum output density ($P_{m)}$ by the value obtained by multiplying the short circuit current ($J_{sc)}$ by the open circuit voltage (V_{OC}).

$$FF = \frac{P_m}{J_{SC}V_{OC}} = \frac{J_{mp}V_{mp}}{J_{SC}V_{OC}} \quad (3)$$

Where J_{mp} and V_{mp} represent the current and voltage, respectively, corresponding to the maximum power point.Once the necessary equations and parameters were defined, the photovoltaic properties of synthesized Ni schiff-base complex containing 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand using the J-V curve demonstrated in Figure 7 were examined and parameters such as short circuit current density, open circuit voltage, fill factor, and power conversion efficiency were determined for this complex.The numerical values of these parameters are given in Table 1. As clearly shown in Table 1, the synthesized Ni schiff-basecomplex can be used as a suitable sensitizer in DSSCs.

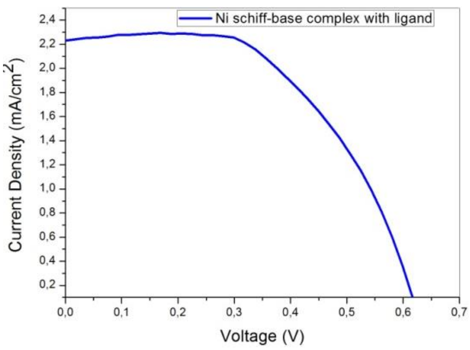

Fig. 7 J-V curve of Ni schiff-base complex containing 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine ligand.

Table 1 Value of V_{OC}, J_{SC}, FF, and η% for Ni schiff-base complex attached on the TiO_2 paste.

V_{OC} (V)	J_{SC} (mA/cm^2)	FF	η%
0.61	2.23	0.52	0.71

5. Conclusions

In the present study, Ni schiff base complex with ligand of 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine was synthesized at room temperature in aqeous solution. The photovoltaic properties of Ni schiff base complex used as dye sensitizer was studied for the first time. The power conversion efficiency (η) of Ni schiff base complex based solar cell was calculated as 1% using photovoltaic parameters determined from the J-V curve. Furthermore, the synthesized Ni base complex ligand of 4,4'-methylene bis (2,6-diethyl) aniline-3,5-di-tert-butylsalicylaldimine was investigated in terms of structural, morphological and optical properties, respectively.

Consequently, Ni schiff-base complex can be used as a suitable sensitizer in applications of DSSCs.

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