Incorporation of Nickel with Azo Dye and its Applications in Dye-Sensitized Solar Cells

Eman H. Sahap*, Fatima A. A. Sajad, Hutham M. Y. Al-Labban

Faculty of Science, Department of Chemistry, University of Kufa, Kufa, Iraq

Received: 22nd February, 2022; Revised: 20th April, 2022; Accepted: 10th May, 2022; Available Online: 25th June, 2022

ABSTRACT
Titanium dioxide (TiO$_2$) was prepared at 180°C for 4 hours by using an unpretentious hydrothermal method. TiO$_2$ was inspected by using field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), x-ray diffraction spectroscopy, and UV-visible spectroscopy. This work expresses the construction of dye-sensitized solar cells (DSSCs) from TiO$_2$ thin films with complex Ni-azo dye and azo ligand. The spectroscopic studies (Fourier-transform infrared spectroscopy (FTIR), UV-vis, and Proton Nuclear Magnetic Resonance ($^1$H-NMR)) are used to identify the azo ligand and its complex Ni (II) to synthesize the DSSC. Current-Voltage (I-V) characteristics show that the DSSCs is the highest change efficiency for TiO$_2$/Ni-azo dye than TiO$_2$/azo dye, about 2.30% and 1.88%, respectively, under 100 mW/cm$^2$ standard visible light.

Keywords: Dye-sensitized, Efficiency, Ni-azo dye, Solar cells (DSSCs).


Source of support: Nil.

Conflict of interest: None

INTRODUCTION
Since the 1990s, a third-generation solar cell (DSSCs) has garnered a lot of interest and been respected as a substitute for fossil fuel energy. To reduce the cost, we preferred solar cells to conventional silicon-based cells (Obaid et al., 2020). The solar cells are characterized by flexibility in the shape, smooth access to dye resources, and great achievement DSSC Transformation of sunlight into electrical energy Symmetry the photocomposition operation Through the use of artificial or natural dye as light harvest tincture (Kwak et al., 2021). Photo sensor in the solar cell absorbs photons and urges on the excitement of electrons to the broadband gap semiconductor, dyes, and electrolyte (Jabbar & Latif, 2021). The Ruthenium complex is one of the most efficient light-harvesting sensitizers mentioned in DSSCs because of the great risks of these materials being sensitive to ruthenium (Huan, 2020). These are complicated procedures In terms of increased cost, environmentally unsafe, and carcinogenic (Chan et al., 2019). Thermal stability, strong absorption in the visible region, and intrinsic advantages of a good photo for organic dye such as azo benzene have prominent chromospheres. Azo benzene is a reactive essential for functional group diversion and connection such as alkoxy and vinyl chain with amended optical properties during the initial photo excitation (Yesodha et al., 2004). The mechanism of a traditional damp type DSSC containing redox couples in the electrolyte is shown in Figure 1 by Murakoshi et al. (1989). The photo anode, made of a nonporous dye-sensitized and n-type semiconductor, receives electrons from the photo-excited dye sensitizer, thereby oxidizing to S+. The neutral dye sensitizer (S) can be renewed by the oxidation reaction (RO) of the redox species dissolved in the electrolyte, which is usually I$_3$/-I-. The mediator R will then be renovated by reduction at the cathode (OR) by the outer circuit the electrons circulated through it (Jang et al. 2020).

Heterocyclic azo dyes compounds and their complexes are used in the manufacture of dyes and electromagnetic materials, and in the printing process, in addition to nonlinear optical elements (Witwit et al., 2019). Considered the imidazole azo

![Figure 1: Operation mechanism of the dye-sensitized electrochemical solar cell (Murakoshi et al., 1989).]

*Author for Correspondence: emanh.hamza@uokufa.edu.iq
Incorporation of Nickel with Azo Dye and its Applications in Dye-Sensitized Solar Cells

and its derivatives are assigned as heterocyclic compounds, and it has lots of uses in various fields. And it is used in chemical and biological applications such as Appreciation for many metal ions (Chhetri et al., 2021). Complex agents, dyeing materials, antidepressants, tubercular ant agents, and models for biological systems. Hence, Metal complexes chelates of azo dyes are considered a higher important component in dyeing the wool; nylon and silks lead to higher fastness for washing and light (Pielesz et al. 2000). In the current study, 2-[(4-acetophenone)azo]-4,5-diphenyl imidazole (4-ACPI) and its complex with Ni(II) are synthesized. The photoelectric properties of a nickel complex (II) as a sensor have been studied for the first time. The Mentioned compound’s structural, morphological, and optical properties were also identified.

MATERIALS AND METHODS

The materials for this research are from Merck company and have been used without Re-purify. The conductive glass slides are coated ITO- (Indium- tin oxide) (surface resistivity 16Ω/sq, thickness 2.3 mm) obtained from China and were used as substrates for preparing TiO₂ thin films electrode and a carbon cathode electrode.

Preparation of Ligand

Preparation of the First Compound 5,4-diphenylimidazole 75 mL of ice acetic acid was added to a mixture of (2.1 g, 0.01 mole) of benzyl and (0.28 g, 0.002 mole) of hexamethylene tetramine and (5.75 g, 0.175 mole) of ammonium acetate., then the mixture was stepped up for 1 hour using a reflecting condenser. Then the solution was transferred to a beaker capacity (1 L) and after cooling it was diluted by adding (200 mL) of distilled water, and then the ammonium hydroxide solution was added drop by drop to neutralize the solution and obtain A white precipitate, the precipitate was filtered and washed after the sedimentation process was completed and washed with distilled water several times to get rid of the excess base residues and salts. It was air-dried, recrystallized with ethanol, and then left to air dry (Al-Labban, 2017).

Preparation 2-[(4- acetophenone)azo]-4,5-diphenyle imidazole (4-ACPI)

The Shibata method was adopted to prepare the ligand of 2-[ (4- acetophenone) azo]-4,5-diphenyl imidazole, including 4-amino acetophenone and the nitrogen pairs coupled with the imidazole derivative in an alcoholic base environment (Li et al., 2014). Using the mixture from (10ml distal water; 2 mL conc. HCl) to melt (0.675g; 0.005mole) from 4-amino acetophenone, Cool the mixture to (0-5) °C and add to it (0.69 g, 0.01 mole) of sodium nitrite dissolved in (10 ml) of distilled water drop by drop with constant stirring and note that the temperature does not rise above 5°C The diazonium salt solution was dropped on a basic alcoholic solution of (4,5-diphenyl imidazole 1.1 g; 0.005 moles) with cooling under 5°C; a Reddish orange color was observed; this colored solution was saved for 24 hours. Then the pH value of the solution is corrected to 7 with dilute HCl solution Deposits are observed, allowed to settle, and then dried in the air. The following diagram shows the course of the reaction to prepare the azo compound (Adam et al. 2019).

Synthesis of Ni (II) complex

(0.0336 g; 0.0001 mole) of (4-ACPI) dissolved in (10 mL) of alcohol was appended slowly with stirring to the (0.0118 g; 0.000005 mol) of NiCl₂·6H₂O that dissolved in (5 mL) of DW after cooling the reaction mixture, it was filtered and washed several times with DW water and allowed to settle and then dried in the air (Fu et al., 2020) (Figure 2).

Preparation of the Working Electrodes

First, TiO₂ is prepared by adding 8 mL of isopropanol dropwise to 2 mL of 5.27 M titanium tetrachloride with constant stirring to obtain TTIP (Titanium Tetra Iso Propoxide) Ti(OCH₃)₄. A 1.0 mL from (TTIP) is added to 5.8M of HCl. To 70 mL Teflon-lined stainless-steel autoclave, the prepared mixture is transferred and fixed inside the oven at a temperature of 180 °C for 4 hours. The autoclave is left to cool at room temperature after completing the preparation. A white precipitate is obtained, and the product is washed with deionized water (DW) and ethanol three times using a centrifuge at 500 rpm and dried at 80°C for 30 minutes. The product is annealed at 450 °C for 3 hours to enhance crystallinity (Cinti et al., 2019). The ITO glass slides are well cleaned using isopropanol for 5 minutes, followed by acetone for another 5 minutes.

Finally, all cleaned substrates are washed using DIW and dried with hot air. To apply the TiO₂ paste, ensure the...
Incorporation of Nickel with Azo Dye and its Applications in Dye-Sensitized Solar Cells

Preparation of Counter Electrode
A counter electrode was developed from a thin carbon layer on an ITO plate. A carbon black electrode was easily made by moving the substrate (conductive side of ITO) above the flame of a candle, as shown in Figure 3. The substrate became black after some time, and then it was cooled; a few drops of ethanol were added to the dried surface for diffusion across the carbon layer and the substrate was further dried (Aftabuzzaman et al., 2020).

Device Fabrication of DSSC
The solar cell consists of seven layers arranged by placing a double-sided adhesive tape over the outer area of the adsorbed dye on the ITO glass with TiO2 film surface. The photoanode and cathode were fabricated into a sandwich-type cell. Iodine/iodide electrolyte solution was injected into the cell to ensure that the electrolyte did not spill outside the mask.

RESULTS AND DISCUSSION
The 1H-NMR Spectrum of the Ligand
1H-NMR spectrum δ(ppm) (Figure 4) of compounds [A] showed the following characteristic signals (DMSO-d6 as a solvent): δ(C-H) Aromatic rings at δ(7.26-8.18)ppm that could be attributed to the aromatic protons for three phenyl rings, δ (s-CO–CH3) at δ (2.65) ppm and δ (–NH imidazole rings) at δ (13.65) ppm.

IR Spectra
The wave numbers of some characteristic bands in the IR spectra of ligand, The stretching vibration of (N-H) groups at (3419 cm⁻¹) back to the imidazole ring. When compared with the metal complex band, no significant change was observed (The ν(N═N) stretching vibration appears at (1440 cm⁻¹) of the imidazole ring, which was showed a medium band at 1448 cm⁻¹ when complexion. This group has observed changes in the size and strength of the metal complexes spectra, which proves their involvement in the coordination process (Kataoka et al., 2020).

UV-Visible spectroscopy
Electronic spectra of the ligand showed three major absorption bands in alcohol within the range of 200–800 nm. The first at 442 nm is related to n-π* transitions, and bands at 210 nm are due to π–π* transitions for imidazole molecule, while the third band is due to ( π- π*) transition for benzene ring paired with imidazole ring throw (N=N) group. When comparing the color
and absorption positions between ligand and its complexes, we observed a clear difference in color and shifting in absorption position (\(\lambda_{\text{max}}\)) toward higher wavelengths (Nienhaus & Nienhaus, 2005). This may be referred to coordination and complex formation between ligands and these ions as shown in Figures 7 and 8.

The important parameter to determine the DSSC efficiency is the optical properties of the dye adsorption on the TiO\(_2\) surface. The dye molecules collected light and produced excitation of electrons (Hossain et al., 2018); therefore, the Ni complex (NiL\(_2\)Cl\(_2\)) dye has been higher \(\lambda_{\text{max}}\) than ligand (C\(_{23}\)H\(_{18}\)N\(_4\)O) that were carried out Ni complex the best efficiency of DSSC.

**X-Ray Diffraction**

The x-ray diffraction pattern of the synthesized tetragonal anatase TiO\(_2\) nanoparticles agrees with the JCPDS card no.

![Figure 5: The FT-IR spectrum of the (4-ACPI).](image)

![Figure 6: FTIR spectrum of the Ni(II) complex](image)

![Figure 7: UV-Visible spectra for the Ni complex](image)

![Figure 8: UV-Visible spectra for the ligand](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(N=\overline{N}))</th>
<th>(v(C=\overline{N})) imidazole</th>
<th>(v(C=O))</th>
<th>(v(C-H)_{Ar})</th>
<th>(v(C-H)_{aliph})</th>
<th>(v(N-H))</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{23})H(</em>{18})N(_4)O</td>
<td>1440w</td>
<td>1598s</td>
<td>1678s</td>
<td></td>
<td></td>
<td></td>
<td>(C_{23})H(_{18})N(_4)O</td>
</tr>
<tr>
<td>NiL(_2)Cl(_2)</td>
<td>1448m</td>
<td>1600s</td>
<td>1680s</td>
<td>3061m</td>
<td>3062m</td>
<td>3992s</td>
<td>[NiL(_2)Cl(_2)]</td>
</tr>
</tbody>
</table>
Incorporation of Nickel with Azo Dye and its Applications in Dye-Sensitized Solar Cells

21-1272 is shown in Figure 9. The 2θ peaks at 25.27° and 47.01° endorse its anatase structure (Bui et al., 2019). The X-ray intensity of the sample indicates that the shaped nanoparticles are crystalline, and expansion diffraction peaks refer to small crystallite. The absence of false diffraction refers to the purity of the sample.

**The Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscopy (TEM) Analysis**

The FESEM image of TiO$_2$ nanoparticles prepared using the hydrothermal method (Kumar et al., 2019) is shown in figure 10. The particle size is ranged from 25 nm to 35 nm with a spherical shape. The TEM gives the particles shapes of NC-TiO$_2$ seem as nano plates with very thin Nanochips and a size ranging from 15 to 60 nm, as shown in Figure 11.

**The I-V Characteristics of DSSC.**

I-V characteristics of DSSC showed in Figure 12. The following equations determined the general efficiency ($\eta$) (Buene et al., 2019).

$$\text{FF} = \frac{V_m J_m}{V_{oc} J_{sc}}$$

$$\%\eta = \left(\frac{V_{oc} J_{sc} \text{FF}}{P_{in} \text{cm}^2 A}\right) \times 100$$

Where $P_{in}$ is the power incident light on the solar cell, $J_m$ is short-circuited current density at zero voltage, $V_{oc}$ is the open-circuit voltage at zero current density, $J_m$ is the maximum current density, $V_{oc}$ is maximums voltage, and FF is the fill factor. All the results are abridged in Table 2. It is clearly shown that the DSSC efficiency of NC-TiO$_2$ with Ni complex azo dye is greater than the DSSC efficiency of NC-TiO$_2$ with azo dye.

The DSSCs is fabricated using TiO$_2$ nanoparticles as a photoanode electrode with Ni complex (NiL$_2$Cl$_2$) dye and azo dye (C$_{23}$H$_{18}$N$_4$O) as absorber media. Figure 12 shows the I-V characteristics of DSSCs prepared based on TiO$_2$/Ni azo dye and TiO$_2$/azo dye. However, TiO$_2$/ Ni azo dye has shown $V_{oc}$ of 0.69V and $I_{sc}$ of 8.0mA to give conversion efficiency ($\eta$) of 2.30%, while TiO$_2$/azo dye DSSCs have shown $V_{oc}$ of 0.65V and $I_{sc}$ of 7.15mA to give $\eta$ of 1.88% (Table 3). The results reveal that the efficiency of DSSC is fabricated based on NC-TiO$_2$ with Ni azo dye is higher than those fabricated
Incorporation of Nickel with Azo Dye and its Applications in Dye-Sensitized Solar Cells

3. The complex of NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dye was synthesized at (0 – 5) °C. The photovoltaic properties of NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dyes used as sensitizer dyes were studied for the first time. The conversion power efficiency of NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dyes-based solar cell was calculated as 2.30% and 1.88%, respectively. Using photovoltaic parameter determined from I-V curve, the synthesized NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dye was investigated in terms of structural, morphological, and optical properties, respectively. Consequently, NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dyes can be used as a suitable sensitizer in the application of DSSCs.

CONCLUSION

The complex of NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dye was synthesized at (0 – 5) °C. The photovoltaic properties of NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dyes used as sensitizer dyes was studied for the first time. The conversion power efficiency of NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dyes-based solar cell was calculated as 2.30% and 1.88%, respectively. Using photovoltaic parameter determined from I-V curve, the synthesized NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dye was investigated in terms of structural, morphological, and optical properties, respectively. Consequently, NiL\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{23}H\textsubscript{18}N\textsubscript{4}O azo dyes can be used as a suitable sensitizer in the application of DSSCs.

REFERENCE


4. Huan H, Jile H, Tang Y, Li X, Yi Z, Gao X, Chen X, Chen J, Wu P. Fabrication of ZnO@ Ag@ Ag3PO4 ternary heterojunction: superhydrophilic properties, antireflection and photocatalytic properties. Micromachines 2020; 11(3):309.


