

Efficiency Enhancement of Dye Sensitized Solar Cells by Nickle Ion Chelation on Dye Extracted From *Amherstia Nobilis* Flowers

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1.ABSTRACT

This study employed natural dye extracted from the pink flower of the *Amherstia nobilis* (Pride of Burma) chelated with Ni²⁺ ions as the sensitizer for Dye-Sensitized Solar Cells (DSSC). Using a light source with an intensity of 100mW/cm², the solar cells were tested first for bare dye and then for Ni²⁺ ion chelated dye as the sensitizers. Bare dye used solar cells had a short circuit current density (J_{sc}) of 2.811mA, while its open circuit voltage (V_{oc}) was 511 mV. The fill factor of the cell was 0.601% and its efficiency was 0.865%. The UV visible absorption spectrum showed an absorption peak at 527 nm. The cyclic voltammogram was used to find the oxidation reduction potential of the dyes and then to determine the energy level of Lowest Unoccupied Molecular Orbital (LUMO) which is roughly -0.2 V versus the Ag/AgCl reference electrode for the bare dye. DSSC with Ni²⁺ ion chelated dye resulted a short circuit current density (J_{sc}) of 5.676mA, while its open circuit voltage (V_{oc}) was 458.3mV. The fill factor of the cell was 0.533% with an efficiency of 1.438%. The UV visible absorption spectrum showed that the absorption peak has blue shifted to 540 nm. The redox potential of the dye also shifted to more negative value of, -0.5 V versus the Ag/AgCl reference electrode which, helped to determine the LUMO level by the cyclic voltammogram. It is evident that Ni²⁺ ion chelation with dye extracted from *Amherstia nobilis* flowers enhance the efficiency of dye sensitized solar cell by elevating the LUMO level to a higher energy as well as increasing the energy gap between HOMO and LUMO levels which can be determine by Tauc's plot using the UV visible absorption data.

Keywords: DSSC, TiO₂, Solar cell, Doctor-blade, IPCE, I-V Characteristics

2.INTRODUCTION

The human dependence on fossil fuels for energy has significant drawbacks, primarily due to the environmental pollution caused by the release of greenhouse gases and harmful particles, leading to adverse health effects and climate change. Despite being naturally occurring; fossil fuels are finite and do not replenish at a rate compatible with consumption. To address the energy crisis and mitigate environmental impact, there is a pressing need to shift towards eco-friendly and cost-effective green energy sources. Solar energy emerges as a highly promising alternative, harnessing the abundant energy reaching the Earth's surface at a rate of 700 megawatts per minute [6]. Solar cells play a pivotal role in converting solar energy into electricity, offering substantial advantages. Particularly noteworthy are cost-effective and highly efficient solar cells utilizing photo-sensitizers. In 1991, Michael Gratzel and his team pioneered a breakthrough by introducing efficient solar cells using dyes as photo-sensitizers [6]. Known as Dye Sensitized Solar Cells (DSSC), they represent the third generation of solar cells and can be produced using both synthetic and natural dyes. While synthetic dyes typically

exhibit higher efficiency, they come at a higher cost. On the other hand, natural dyes, sourced from readily available materials like plant leaves, fruits, bark, seeds, and flowers, offer a more affordable option. Although synthetic dyes are more efficient, ongoing research is steadily improving the efficiency of DSSC with natural dyes, making them a sustainable choice for solar energy conversion.

Anthocyanins, found in various shades of blue, red, and purple, are natural pigments prevalent in flowers, fruits, and tubers. Among these, cyanidin, delphinidin, pelargonidin, peonidin, petunidin, and malvidin are the most commonly occurring anthocyanins in plants [2]. Notably, the *Amherstia nobilis* (Pride of Burma) flower exhibits a unique reddish-orange petal color, with cyanidin 3-O-glucoside identified as the primary pigment in this floral species [5]. It's noteworthy that cyanidin 3-O-glucoside is more commonly found in fruits rather than in flowers [4] [5] [1] [3]. Therefore, the occurrence of cyanidin 3-O-glucoside in the flowers of *Amherstia nobilis* is a rare phenomenon. Then the Dye extracted from the petals of the *Amherstia nobilis* flower is a good sensitizer for DSSC with higher efficiency. [7] In this research study, attempt has been made to enhance the efficiency of DSSC by complexing the pigment extracted from *Amherstia nobilis* flower petals with Ni²⁺ ions

3. METHODOLOGY

3.1 Natural dye extraction

Amherstia nobilis (Pride of Burma) flower petals (20 g) were cut into small pieces, and 50 ml of ethanol was added and the mixture was allowed to stand at room temperature within a covered beaker for 24 hours, resulting the colour of the flower petals to fade. The final step involved the filtration and collection of the extracted, rose-coloured dye, which was then carefully stored in a sample bottle covered with aluminum foil. This sealed bottle found its place in a refrigerator at 4°C, awaiting future use.

3.2 Ni²⁺ ion complexzation with dye extraction

Nickle chloride was used to prepare 0.2M Ni²⁺ ion solution with distilled water. Ion solution was added drop wise to 2ml of natural dye of *Amherstia nobilis* until the colour of the dye change to dark red.

3.3 Preparation of dye-coated TiO₂ film

Glass plates of Fluorine-doped Tin Oxide (FTO), cut into 2 cm × 1 cm pieces, underwent a thorough cleaning process. The glasses were initially placed in a small beaker filled halfway with distilled water. Following a few drops of washing liquid, and the mixture was sonicated for 10 minutes using an ultrasonic bath. After sonication, the water was discarded, and the glass plates were re-rinsed with distilled water containing a few drops of concentrated H₂SO₄. The FTO glasses were then washed with distilled water and subjected to boiling in isopropyl alcohol at 80 °C. Following this treatment, the FTO glasses were removed from the beaker, dried with gentle heat, and the conducting side was identified using a conductivity meter.

To prepare the TiO₂ paste, a combination of 0.25 grams of TiO₂ nano powder (20 nm), 0.1 ml of 0.1M HNO₃, a drop of Triton x-100, and a drop of PEG 400 was utilized. After grinding in a mortar with a pestle, resulting TiO₂ paste was applied onto the conductive surface of FTO glass plates using the doctor blade method. The film underwent sintering for 45 minutes at 450°C in a furnace. Following the sintering process, the TiO₂ film was allowed to cool down to room temperature. In the final step, the TiO₂ films coated on FTO glass were immersed in dye extract of *Amherstia nobilis* flowers and the dye chelated with Ni ions for 6 hours within covered test tubes.

3.4 Fabrication of the cell

For the preparation of the electrolyte in dye-sensitized solar cells, 0.127 grams of Iodine (I₂) and 0.83 grams of potassium iodide (KI) were dissolved in 10 ml of acetonitrile and ethylene carbonate, maintaining volume ratio of 8:2, in a volumetric flask. The solution underwent stirring for a duration of 5 hours to ensure the complete dissolution of all solid particles.

In assembling the DSSC, the dye-coated TiO₂ film served as the anode, while the Pt-sputtered glass plate functioned as the counter electrode. These components were positioned side by side and securely fastened together using crocodile clips. Subsequently, the electrolyte was carefully introduced into the capillary gap between the two plates.

3.5 Cyclic voltammetry

Using Ag/AgCl as reference electrode, Platinum electrodes as anode and cathode Cyclic voltammetry was measured with 50ml of dye solution. To obtain the cyclic voltamogram for Ni²⁺ ion chelated dye solution, the same procedure was followed.

3.6 Dye and Solar Cell Characterization

To determine the absorption spectra of the natural dye, a UV-visible spectrometer was used and with the help of a computerised PK-I-V 100 I-V Analyzer, the photovoltaic measurements of the dye-sensitive solar cell were measured under a light source of 100mW/cm² intensity. Metrohm Autolab PGSTAT204 was used to take the cyclic voltammetric measurements. Incident Photon Current Conversion Efficiency (IPCE) was measured by using computerized VK-IPCE-10.

4. RESULTS AND DISCUSSION

Anthocyanins and flavonols are present in the *Amherst nobilis* flower which is an endemic species to Myanmar [5]. Figure 1 shows the chemical structures of those anthocyanins and flavanols where, R₁, R₂ and R₃ groups represent different chemical constituents. The pigments, cyanidin 3-O-glucoside (R₁ = glucosyl, R₂ = OH), 3-O-xyloside (R₁ = Xylose, R₂ = OH) and (peonidin 3O glucoside (R₁ = glucosyl, R₂ = OMe) were recognized as anthocyanins. Flavanols, on the other hand, were identified as isorhamnetin 3-O-glucoside (R₁ = glucosyl, R₂ = OMe, R₃ = H), 7- O-glucoside (R₁ = H, R₂ = OMe, R₃ = glucosyl), 3,7-di-O-glucosiden (R₁ = R₃ = glucosyl, R₂=OMe), 3-O-rutinoside (R₁= rutinosyl, R₂=OH, R₃=H), quercetin 3-O-rutinoside (R₁=rutinosyl, R₂ = OH, R₃=H), kaempferol 3-O-rutinoside (R₁=rutinosyl, R₂=R₃=H), Pelargonidin 3-O-pentoside (R₁=glucosyl R₂=R₃=H). Also, an anthocyanin pelargonidin 3-O-pentoside (R₁=glucosyl, R₂=R₃=H) has been reported from *Amherstia nobilis* flower.



Fig 1 Chemical structures of (a) anthocyanins and (b) flavanols found in the flowers of *Amherstia nobilis* with different R₁, R₂ and R₃ groups referred above.

The chelation of the Ni²⁺ ion with anthocyanin molecule is depicted in figure 2. Most possibly Ni²⁺ ion can chelate with anthocyanin molecule with the elimination of a water molecule. There is also possibility of Ni²⁺ ion chelation with flavanol by eliminating an alcohol (R-OH).

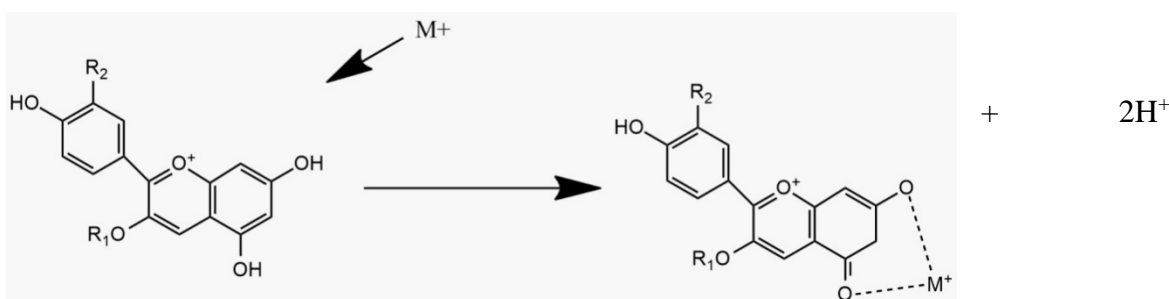


Figure 2 suggested mechanism for Ni²⁺ ion chelation with anthocyanin

4.1 UV-Visible Absorption Spectra

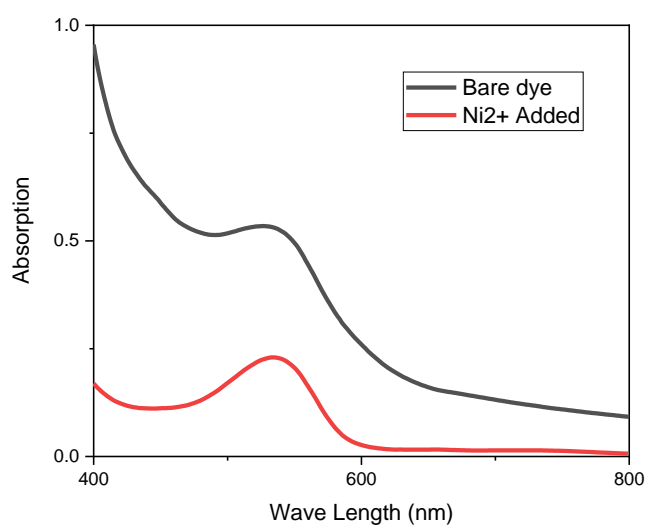


Figure 3: UV-Vis absorption spectra of bare dye and Ni²⁺ ion chelated dye extracts of *Amherstia nobilis* flowers in Ethanol

Figure 3 shows the UV-Vis absorption spectra of bare dye and Ni²⁺ ion chelated dye extracted from *Amherstia nobilis* flower. The absorption measurement used a wavelength range of 400 nm to 800 nm. Specific peaks at 527 nm and 540 nm in the absorption spectra could be observed for the bare dye and Ni²⁺ ion chelated dye respectively.

The absorption spectra of dyes exhibit energy absorption in visible region. The energy band gap of the dyes is determined by the Tauc's equation:

$$(\alpha h\nu)^2 = A (h\nu - E_g)$$

Where α is the absorption coefficient, which indicates the absorption ability for a certain wavelength of the dye, h is the Planck's constant, E_g is the band gap, A is the energy independent constant and its value is considered as 1 for general condition, ν is the incident photon frequency, $h\nu$ is the energy of the incident photon. The energy band gap (E_g) can be determined by extrapolating the linear region of the plot $(\alpha h\nu)^2$ versus $h\nu$. The energy band gaps of the bare dye and dye chelated with Ni²⁺ ions are estimated as 2.08eV and 2.16eV respectively. Figure 4 shows the Tauc's plots for bare and Ni²⁺ ion chelated dye extracts of *Amherstia nobilis* flowers.

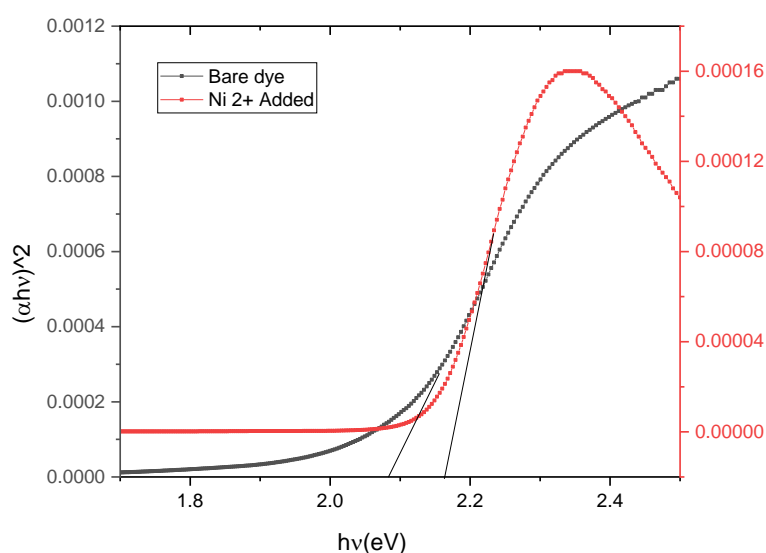


Figure 4: Tauc's plots for bare and Ni²⁺ ion chelated dye extracts of *Amherstia nobilis* flowers

4.2 Cyclic voltamograms

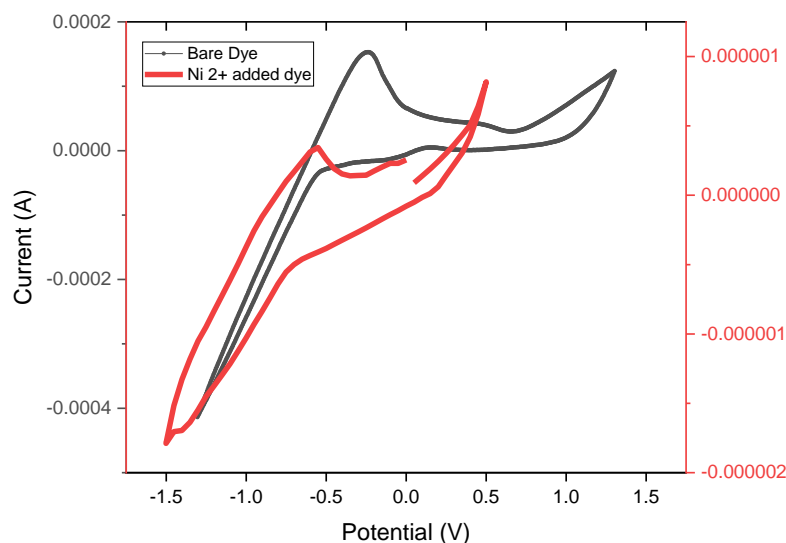


Figure 5 Cyclic Volta monogram of bare dye and Ni^{2+} ion chelated dye from *Amherstia nobilis* flower

The cyclic voltammogram can be used to measure the pigment's oxidation and reduction potential. The oxidizing potential is roughly -0.2V for the bare dye solution and -0.5V for the Ni^{2+} ion chelated dye solution, versus the Ag/AgCl reference electrode. There is not any sharp reducing peaks appeared for both the dyes but slight curvature could be observed in the lower segment of the cyclic voltamograms close to the oxidizing potentials. The oxidation reduction potential of the dye corresponds to the energy of the Lowest Unoccupied Molecular Orbital (LUMO), when calculated reference to the vacuum scale is at -4.497eV and -4.197eV for bare dye and dye chelated with Ni^{2+} ions respectively.

The energy band positions of bare dye from *Amherstia nobilis* flower and same dye after chelation with Ni^{2+} ions are shown in figure 6. It is evident that with the chelation of Ni^{2+} ions, the LUMO level of the dye shifts to a higher energy level. Also, the band gap energy calculated from the Tauc's plot is also higher. Due to these reasons, it can be expected that the cell performance will be enhanced.

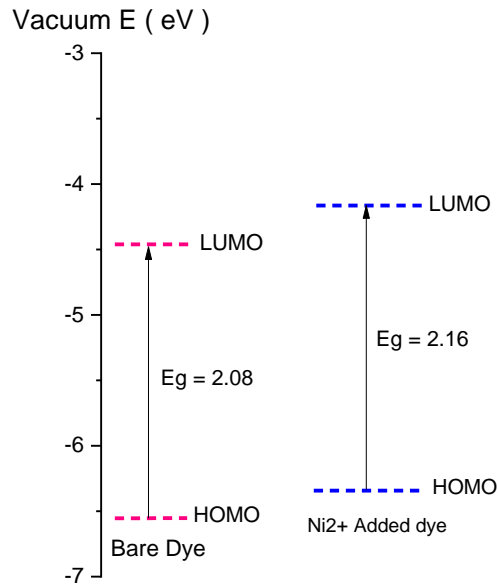


Figure 6: Band structure of dye extracted from *Amherstia nobilis* flower, same dye chelated with Ni^{2+} ions and the band positions of TiO_2 with respect to the vacuum level.

4.3 J-V characteristics

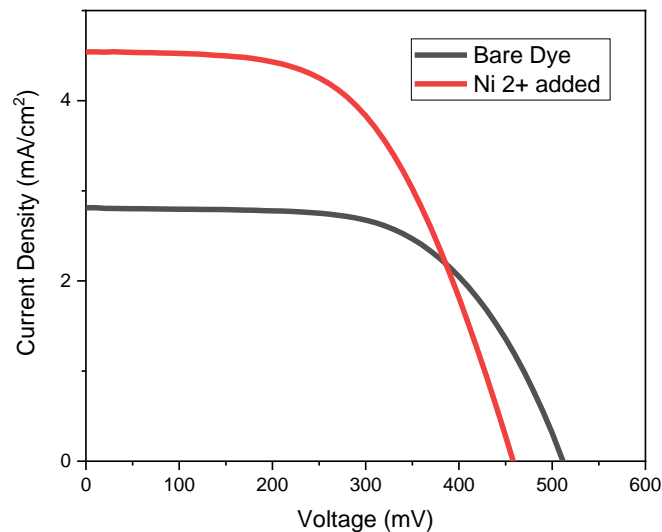


Figure 7: JV Characteristic curve of - Dye-sensitized solar cell sensitized with *Amherstia nobilis* flower dye and Ni^{2+} ion chelated dye sensitized solar cell (DSSC) under the Light source of 100 mW/cm^2

As shown in Figure 7, photovoltaic measurements of the dye-sensitized solar cells were conducted in the presence of a light source with an intensity of 100 mW/cm². The *Amherstia nobilis* flower dye-sensitized solar cell has a fill factor of 0.601 and Jsc of 2.811 mA, Voc of 511.6 mV, and efficiency of 0.865%. The measured photovoltaic parameters of Ni²⁺ chelated dye-sensitized solar cell was comparably higher than bare dye with a fill factor of 0.553, current density of 5.676 mAcm⁻², photovoltage of 458.3mV and efficiency of 1.438%. This enhancement is resulted from the shift in the LUMO level to a higher energy position that take place with the Ni²⁺ ion chelation which boost the fast charge injection from the dye to the conduction band of TiO₂.

4.4 IPCE characteristics of the DSSC

Figure 8 shows the incident photon to current efficiency (IPCE) spectra of bare dye and dye chelated with Ni²⁺ ions. The action spectrum of the dye-sensitized solar cell with Ni²⁺ added falls between 500 and 700 nm, which is in consistent with the absorption spectra of the dye. Comparably it is having a higher photo current conversion efficiency with respect to the DSSC with bare dye.

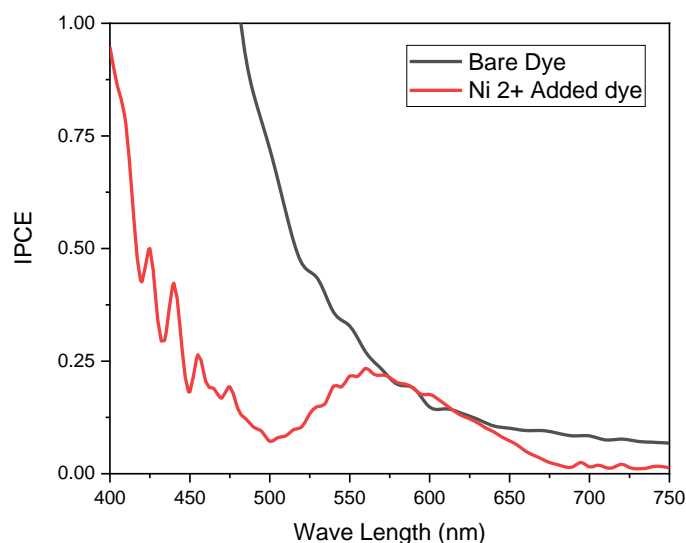


Figure 8 IPCE Observation for Ni²⁺ Added dye Sensitized solar cell

5. CONCLUSION

The *Amherstia nobilis* flower, often known as the Pride of Burma, was used to extract a natural dye for DSSC sensitization. In the UV–Vis spectra between 400–800 nm wavelength range, an absorption peak could be seen at 527 nm for the dye. Using this dye as the sensitizer DSSCs had an efficiency of 0.865%, an open circuit voltage of 511.6 mV and a short circuit current density of 2.811 mA. The fill factor of the cell was approximately 0.601. When the oxidation and reduction potential of the dye is measured with cyclic voltammetry it is -0.2V. After adding Ni²⁺ ions to the bare dye, the colour of dye was changed and in the 400–800 nm wavelength

range of UV–vis spectra, an absorption peak could be observed at 540 nm. When fabricating the dye sensitized Solar cell using Ni²⁺ ion chelated dye solution, the cell produced a short circuit current density of 5.676 mAcm⁻² and an open circuit voltage of 458.3 mV with an efficiency of 1.438%. The fill factor of the cell was around 0.553. The approximate oxidation and reduction potential is -0.5V. Thus, it can be concluded that the efficiency of dye sensitized solar cell has been enhanced by chelating Ni²⁺ ions to dye extracted from *Amherstia nobilis* flower due to elevation of the LUMO of the dye towards more energetically favorable position.

6. REFERENCES

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