ISSN-1996-918X

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Pak. J. Anal. Environ. Chem. Vol. 24, No. 1 (2023) 86 – 93

http://doi.org/10.21743/pjaec/2023.06.08

Synthesis and Characterization of Photoanode by Immobilisation of Pyridyl Complexes on ITO for Photo-Conversion System

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Received 15 September 2022, Revised 15 May 2023, Accepted 20 May 2023

Abstract

Increasing developments on the application of copper complexes as dyes are due to their dual function in dye-sensitized solar cells (DSSCs) as redox mediators and dye sensitizers. The economical (abundance, low cost) and environmentally friendly properties of copper motivate researchers on the use of copper complexes for replacement of ruthenium-based dyes in solar cells. A novel [Cu(I)(2,9-dmp)(phen-dione)]PF_6 (A2) bearing polypyridyl ligands, 1,10-phenanthroline-5,6-dione (phen-dione), 2,9-dimethyl-1,10-phenanthroline (dmp) was prepared by metal complexation reaction. The photofunctionality of A2 as a promising photosensitizer in DSSCs was studied. Interestingly, A2 exhibited two absorption peaks, one is detected in the ultraviolet region due to π-π^* transition and the other is a metal-to-ligand charge transfer (MLCT) band at 405nm in the visible region. A2 was compared to the same complex with Cu(II) ion as the metal centre which only absorbed light in the ultraviolet region thereby implying limited use of Cu(II) complex in its light harvesting application. The photofunctionality of A2 was studied by employing it as an active material for photoelectric conversion by engaging it with ITO to create a photoanode. Upon light irradiation, an anodic current was observed. In conclusion, introduction of Cu(I), instead of Cu(II), in polypridyls ligands resulted in successful enhancement of photophysical properties of A2, making the photoanode of A2 suitable for light harvesting applications.

Keywords: Coordination chemistry, Photocurrent, Photoanode, Solar cells

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Introduction

Energy is an essential necessity for the survival of each living organisms. In the 21st century, population and economic growth and infrastructure development have caused a surge in energy consumption. Energy security is vital for countries to focus on sustainable development [1]. Renewable energy (RE) options are surging, wind and solar devices costs have plummeted, but global energy demands are continually rising. The use of RE sources such as solar in energy production is likely to be sustained because of their environmental benefits, like low emissions of carbon dioxide (CO_2) and no pollution to the surroundings [2]. However, few issues need to be resolved, such as high operational cost, lack of improvement of the device's efficiency as well as involvement of different types of chemicals which are harmful to the environment in the production of the dye-sensitized solar cells (DSSCs), although it was claimed that solar industries have no direct negative effects on surroundings. DSSC generally consist of electrodes, electrolyte and dyes. The electrodes can be any transparent conductive oxide (TCO) such as aluminium doped zinc oxide (ZnO:Al), indium tin oxide (ITO), fluorine-doped tin oxide (FTO) and many more [3]. A photoanode is usually made up of a TCO and light harvested dyes. For the dyes, it can be either organic, inorganic as well as natural dyes from leaves and fruits [4]. DSSCs offer cheaper production costs, facile fabrication procedures, flexible, lightweight, relatively high efficiency and low toxicity [5]. A DSSC is resembling the photosynthesis process that occurs at the chlorophyll inside the leaves. In DSSC, there are four main processes: light harvesting, electron injection, carrier transportation and current collection as shown in Fig. 1 [6].

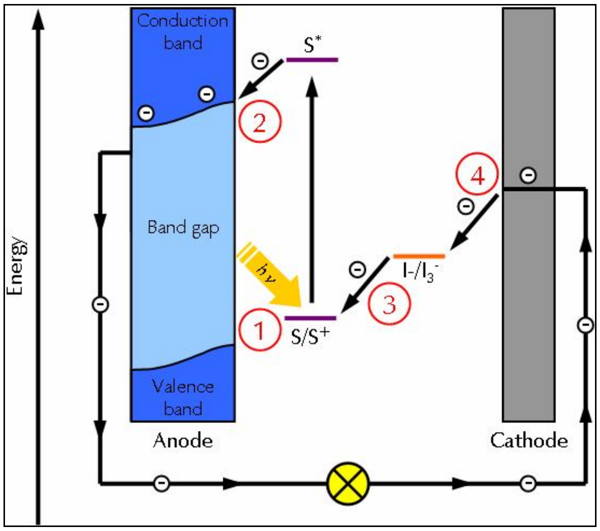

Figure. 1. **Schematic operation principle of DSSC. This figure is adapted from [6].**

As the light strike on the photoanode surface, the photons are absorbed by the dye sensitizers (S) and get excited to a higher energy state (S*), see equation 1.

$$S \xrightarrow{hv} S^* \qquad \text{Eq. 1}$$

As a result of the oxidation of an excited dye molecule, an electron is pushed into the semiconductor's conduction band (see equation 2) [3].

$$S^* \rightarrow S^+ + e^- \qquad \text{Eq. 2}$$

Through the external circuit, electrons flow to the counter electrode. The oxidised dye molecule (S^+) is regenerated by accepting electrons from the electrolyte's iodide.

$$S^+ + \frac{3}{2}I^- \rightarrow S + \frac{1}{2}I_3^- \qquad \text{Eq. 3}$$

When the external circuit completes the circuit, the electrolyte regenerates at the counter electrode.

$$\frac{1}{2}I_3^- + e^- \rightarrow \frac{3}{2}I^- \qquad \text{Eq. 4}$$

Generally, cell efficiency can be affected by the absorption of incident photons, the charge transfer process and the rate of conversion of the incident photon to electron-hole pairs.

Dyes are the crucial component to harvest light spectrum in a DSSC. Therefore, sensitizer must be economical, easily available, less toxic and biocompatible [7]. Good sensitizers should be stable enough to be used for a long period and absorb light in a wide range of light spectrum from visible light to the near infrared. Besides that, sensitizers must be able to anchor effectively on semiconductor oxide to facilitate the electron injection from the conduction band. The highly efficient dyes generally have more negative LUMO than the conduction band of the semiconductor and more positive HOMO than the electrolyte's redox potential [8].

Ruthenium(II) metal is one of the transition metals widely used as sensitizers in Gratzel's DSSCs. However, this precious metal is quite costly compared to Cu(I). Recently, lots of research groups are focusing on finding a replacement for Ru(II). Therefore, Cu(I) has become a prominent choice in the fabrication of sensitizer to replace Ru(II) since Copper is more abundant in nature than Ruthenium [9], displays vibration in the electromagnetic spectrum from visible light to the infrared region and has competitive price as compared to other eminent transition metals [10]. Moreover, Copper(I) complexes are labile, have high charge carrier mobility, and have favorable band energies relative to fuel-producing redox couples. In addition, Copper(I) complexes can swap the ligands rapidly [11], show luminescence due its electron configuration [12] and enhance the absorption of visible light by their unique localized surface plasmon resonance (LSPR) [13]. Therefore, Cu(I) complexes are prone to be engaged as a dye in DSSCs due to their similar characteristics with Ru(II) complexes [14]. The exciton diffusion length can be increased in a solar cell by the intrinsic long-lived triplet excited state of Cu(I) complexes. Moreover, the charge recombination rate also will reduce and subsequently increase the DSSC's performance [15]. The coordination of d-block elements with bidentate heterocyclic nitrogenous bases has been shown to form complexes with good photophysical and redox properties, making them ideal for light harvesting antennas in solar energy conversion systems [16]. In this research, Copper(I) coordination complexes with polypyridyl ligands which 1,10-phenanthroline-5,6-dione (PDON) and 2,9-dimethyl-1,10-phenanthroline (DMP) were engaged as dyes sensitizers. PDON has O-quinone and N-pyridine moiety as well as two carbonyl groups attached at positions 5 and 6. Aim of this study was to use the complexes as active materials in the fabrication of photoanode with interesting optical and electrical properties for a photo-conversion system [17].

Materials and Methods

Synthesis of Ligand 1,10-phenanthroline-5,6-dione (Phen-dione)

Ligand 1,10-phenanthroline-5,6-dione was prepared with a modification of reported method [18]. All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise stated. Upon synthesis, 3 mL of sulphuric acid (H_2SO_4) was cooled overnight in the freezer. The solution of concentrated H_2SO_4 (3 mL) was poured into a round bottom flask and immersed in the ice bath. After that, the 1,10-phenanthroline (1.0 g, 5.04 mmol) was added. The temperature of the solution was maintained between 0 - 5°C. Then potassium bromide (KBr) (0.6 g, 5.40 mmol) and concentrated HNO_3 (1.47 mL) were slowly added and stirred for 20 minutes at room temperature, followed by refluxing at 250°C for 1 hour. The solution was brought to room temperature and neutralized with 1% wt sodium carbonate (Na_2CO_3). The solution was filtered and then extracted three times with dichloromethane (CH_2Cl_2). Afterwards, the water residue was removed with anhydrous sodium sulphate (Na_2SO_4). After solvent removal, the organic phase was recovered and the yellow solid (51%) dried under vacuum.

Synthesis [Cu(I)(2,9-dmp)(phen-dione)]PF$_6$ (A2)

DMP (20.83 mg, 0.10 mmol) was dissolved in ethanol and bubbled with Argon gas. Then, tetrakis (acetonitrile) Cu(I) hexafluorophosphate (0.15 mmol, 55.91 mg) was dissolved in acetonitrile and poured into the dmp solution. After that, pdon (0.10 mmol, 21.02 mg) was dissolved in ethanol and added into the Cu(dmp) solution. The solution mixture was stirred at room temperature under inert conditions for 24 hours, and the resultant precipitate was filtered, washed with solvents, and dried under reduced pressure to yield a powdered solid (24%), A2. The complete metal complexation was measured by UV-Visible spectroscopy. The structure of A2 is shown in Fig. 2.

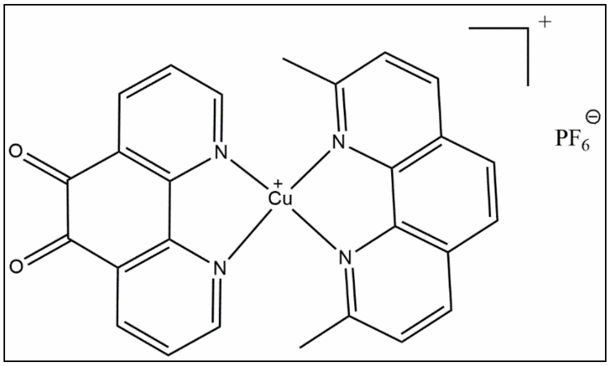

Figure. 2. **[Cu(I)(2,9-dmp)(phen-dione)]PF_6 (A2)**

Fabrication of Photoanode

The surface of ITO was cleaned by sonicating in acetone for 10 minutes, followed by sonication in a nonionic detergent solution (Alconox) for 60 minutes. Then, the ITO was sonicated for 10 minutes in deionized water and dried with cloth paper. As shown in Fig. 3, the dispersion of A2 in acetonitrile was casted on ITO using a dropper and the solvent was left to dry as a result A2 was mounted on the ITO surface. The topographic image of modified ITO with a dispersion of A2 (T2) displayed greenish colour on it, as shown in Fig. 3(b). The dye-coated photoanodes were dried in a vacuum desiccator.

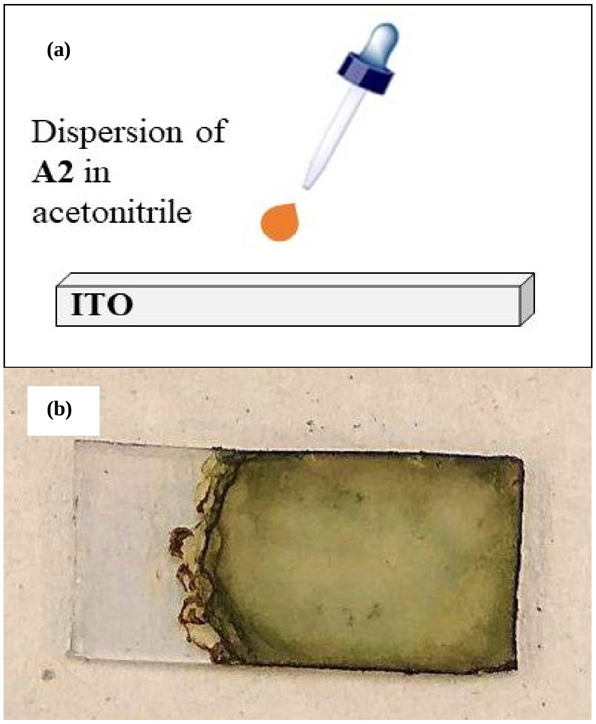

Figure. 3. **(a) Drop cast method (b) Modified ITO with dispersion of A2**

Results and Discussion

Photophysical Study

The absorption spectra of the A2 and T2 (film of A2 on ITO) were recorded using Cary 60 Agilent Technologies UV-Visible spectrophotometer. The steady state absorption spectra of the 0.4 mM A2 were recorded in acetonitrile solutions at room temperature in the range from 300 nm to 600 nm. As shown in Fig.4(a), A2 exhibited two absorption peaks. One peak was detected in the ultraviolet region and showed an intense ligand-based $\pi - \pi^*$ band (363 nm) and a broad metal-to-ligand (MLCT) peak in the visible region (451 nm). On the other hand, only the MLCT peak was detected in the T2 spectrum while the ligand-based $\pi - \pi^*$ band was disappeared, which might be due to the aggregation of A2. Both absorption spectra of A2 and T2 are identical and this confirmed the successful immobilisation of A2 as thin film onto the ITO surface. The ITO's surface modification with A2 was expected to happen due to the strongly physisorbed A2 onto the ITO surface [19]. These spectra were compared to the same complex with Cu(II) ion as the metal centre. The absorption spectrum of [Cu(II)(2,9-dmp)(phen-dione)Cl]Cl showed peaks at 227 nm and 274 nm which meant it only absorbed light in the ultraviolet region, thereby limiting its usage in light harvesting applications [20]. Thus, the engagement of Cu(I) ion as the metal centre successfully enhanced the light absorption range to the visible light region.

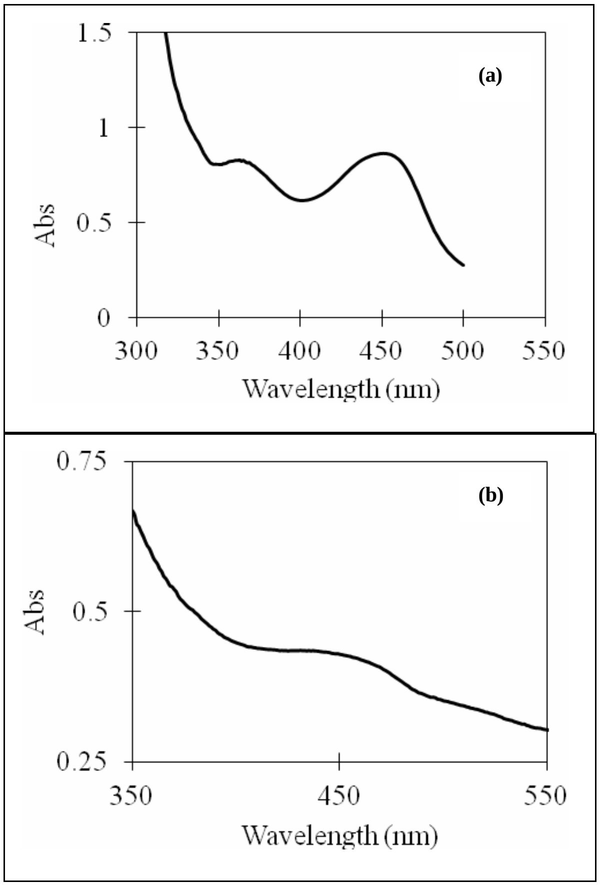

Figure. 4. **(a) Absorption spectra of A2 (b) Absorption spectra of T2**

Band Gap of the Modified ITO

Analysing energy gap values is one approach to identify a material's electrical properties. An energy gap is a region of energy in which the density of electron states is zero. The energy gap separates two allowed electronic energy states which are the valence and the conduction band. The Tauc plot approach is one of the most preferred methods for estimating energy gap, especially for amorphous materials because the calculations are precised and accurate for these materials. This method only requires UV-Vis absorbance spectrum data for the calculation of the energy gap. The optical band gap of ITO is 3.5-4.3 eV and has high transmission in the near infrared and visible regions of the electronic spectrum. If the band gap of the semiconductor is too wide, a significant amount of energy is required to excite one electron from the valence band to the conduction band. The band gap impacts both how much energy is required from the sun for conduction and how much energy is produced. [21]. By immobilising A2 onto the ITO, the band gap of this semiconductor can be tuneable to approximately 2.3 eV, as shown in Fig. 5, which is suitable for photo harvesting applications. Narrowing the ITO band gap is critical in the manufacturing of DSSCs because semiconductors with smaller band gaps can absorb a much greater range of the solar spectrum, increasing DSSC efficiency.

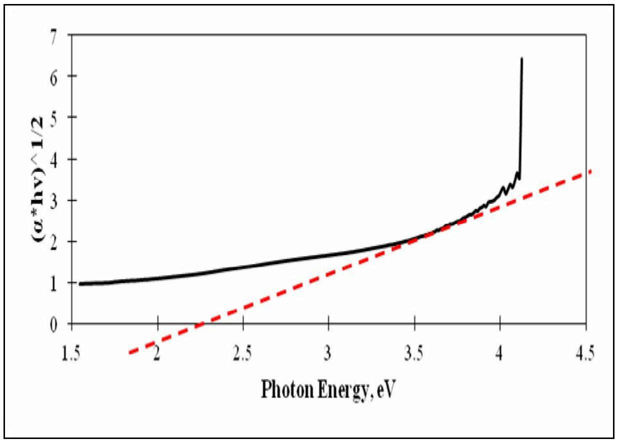

Figure. 5. **Schematic diagram of Tauc plot used to measure the optical bandgap of T2**

Film Morphology

FE-SEM images were recorded using Hitachi SU80200 with an acceleration voltage of 1.0 kV. Film images captured by SEM helped get a better understanding of the surface modification. As shown in Fig. 6, a smooth polymeric texture and continuous greenish film was observed upon drop casting A2 onto ITO. The polymeric texture represented the formation of thin film on the ITO, while a clean smooth surface on the bare ITO indicated nothing was deposited onto it. Comparison between these two domains indicated successful deposition of A2 on the ITO.

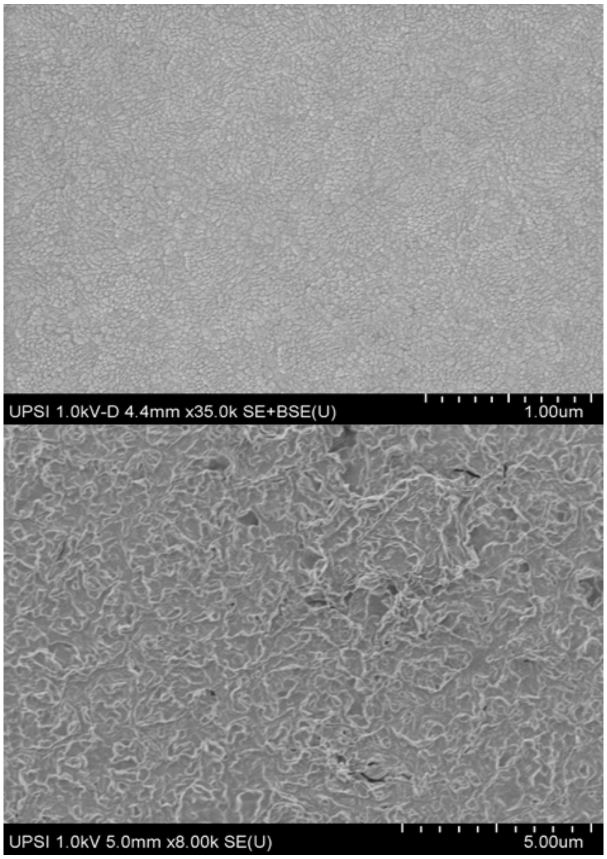

Figure. 6. **FE-SEM images with different magnification scales of (a) Bare ITO (b) T2 clearly shown the physical difference between bare ITO and modified ITO.**

Photoelectric Conversion

The photofunctionality of T2 was studied by employing it as an active material for photoelectric conversion by engaging it as the photoanode, while the Ag/AgCl with a 3 M NaCl filling solution acted as the reference electrode accompanied by platinum as the counter electrode. The measurement was conducted in an aqueous solution using a three-electrode PEC workstation, while a Xenon lamp was used to supply the simulated sunlight (100 mW cm^{-2}). The initial potential applied was -0.19 V and the current generated was -749 nA. As the result of visible light irradiation onto the photoanode, anodic current was observed, as shown in Fig. 7 where the photoresponse spans were at 400-550 nm. T2 was found suitable to be engaged in the photoconversion system when Cu(I) metal was used instead of Cu(II) metal. Kashanian et *al.*, reported the same coordination compound, but Cu(II) was the metal centre. That complex was engaged as DNA-based electrochemical biosensor, which exhibited UV absorbances at 260 and 280 nm [20]. Cu(I) complexes are tetrahedral in structure, whereas Cu(II) complexes are square planar. Therefore, Cu(I) complexes are prone to be utilised as a dye in DSSCs due to their similar characteristics with Ru(II) complexes [22]. In general, ligands with substituents at the position of 6, such as the phenanthroline family of ligands is more superior in stabilizing the Cu(I) state [23]. For this research, the coordination complexes between Cu(I) and 1,10-phenanthroline derivatives have been selected as suitable sensitizers for solar cells [24].

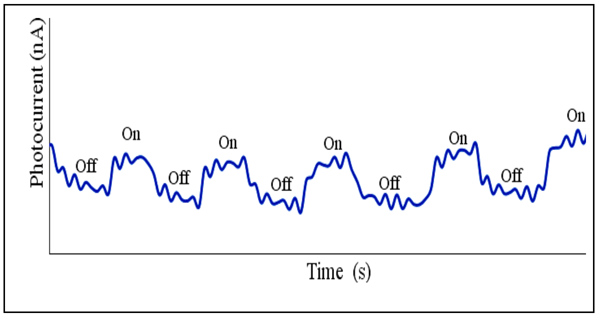

Figure. 7. **Chronoamperometric scans under chopped conditions for the photoanode**

Conclusion

Copper, as one of the cheapest and most abundant elements on the Earth, is an excellent choice for developing low-cost and efficient coordination complexes for application related to energy conversion and storage. These compounds have the potential to successfully replace high toxicity metals such as Co, Pt, Ir and Ru, which are not sustainable. This study found the heteroleptic copper complex visible-light absorption properties could be improved via engagement of copper(I) metal as metal centre. More development in copper coordination complexes is urgently needed to improve the performance of energy-relevant applications. Simple replacement of metal centre or ligands will enhance the absorption wavelength from UV range to visible range. Generally, Copper complexes do not perform well as dyes, and those that do perform well owe their success to their ligands rather than the complex as a whole.

It is possible to precisely modulate key properties such as colour and solubility by modifying the ligands. The colour of the light that is being produced is fine-tuned across the entire visible spectrum, from red to green to blue, by subtly altering the structure of the ligands and the electronic properties that correspond to them. In this research, the novel [Cu(I)(2,9-dmp)(phen-dione)]PF_6 **(A2)** was successfully synthesised upon facile metal coordination reaction. This coordination compound was immobilised onto ITO to fabricate a photoanode that potentially to be engaged in a DSSC. Immobilisation of **A2** directly narrower bandgap of ITO from ~3 eV to ~2eV. Narrowing the ITO's band gap really crucial in the fabrication of DSSCs since semiconductors with narrower band gaps can absorb a much greater portion of the solar spectrum, thereby increasing the efficiency of the DSSCs. In addition, besides engaging as dye in DSSCs, copper complexes and clusters have demonstrated their potential as an alternative to OLEDs made of noble metals. Thus, warrant further detailed studies to be conducted.

Acknowledgement

This research has been carried out under Fundamental Research Grant Scheme for Research Acculturation of Early Career Researchers-FRGS-RACER (code: 2019-0162-103-62)(RACER/1/2019/STG01/ UPSI//4) provided by Ministry of Higher Education (MOHE), Malaysia

Conflict of Interest

The authors declare no conflicts of interest.

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