Cobalt complex dye as a novel sensitizer in dye sensitized solar cells

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Abstract

In this study, cobalt metal complex has been introduced as a novel class of sensitizer for more mechanistic consideration of the photovoltaic conversion efficiency (PCE) of dye sensitized solar cells. UV–vis spectroscopy of dye illustrates maximum absorption at wavelengths of dye in 498 and 650 nm. TiO2 was used as the photoanode of the cell whose x-ray diffraction spectrum indicates that its crystal phase is anatase (101). Surface morphology of photoanode was also investigated by scanning electron microscopy (SEM) and obviously showed ∼25 nm TiO2 nanoparticles. The cyclic voltammetry (CV) investigation of Pt-coated fluorine doped tin oxide (FTO) as the counter electrode of the cell indicates redox process on this electrode. Photovoltaic measurements of cobalt complex sensitized solar cell show that the short-circuit current density (Jsc), open-circuit voltage (Voc), fill factor (FF%) and photovoltaic conversion efficiency (PCE%) are 48.80 μA.cm−2, 0.7 V, 44% and 0.09% at the air mass 1.5 (100 mW.cm−2) irradiation condition, respectively. The high light harvesting efficiency (LHE) (∼61%) and high molar absorption coefficient of the cobalt complex dye (12,500 M−1.cm−1) were other optical advantages of the cobalt complex sensitized solar cell. The results indicate the quantum yield of electron injection (ϕing) which depends on dye structure as a parameter influences the Jsc. The pyridine rings conformation in donor part of the cobalt complex dye plays a significant role in ϕing and subsequently PCE. These findings open a new insight about mechanistic aspects of dye sensitized solar cells efficiency.

1. Introduction

The finite sources of nonrenewable energies assure scientists to think about developing new methods and devices for producing the clean and immortal sources of energy. The solar energy is one of the cheapest and cleanest energy sources that attracts a lot of attentions of solar scientists. Therefore, easy production process and high PCE are the main goals achieved in competition with fossil fuels in energy supplying [4]. For this purpose, dye sensitized solar cells have been introduced as one of the highly potent candidates for increasing the PCE of solar cells, while the exact understanding of PCE has been the most challenging parameter controlled by many factors [5–7]. Although dye sensitized solar cells are cheaper than silicon solar cells, they have not reached their maximum theoretical efficiency yet [8]. A major study in dye sensitized solar cells field is facile fabrication of the transparent semiconductor electrodes and the effects of sensitizer’s structure on the photovoltaic device efficiency [9–12]. Recently, several types of sensitizer have been developed and the effect of their structures were evaluated on PCE [13–15]. Results show the close relationship between PCE, the structure of ligands of dye and maximum absorption wavelength [16]. Inorganic dyes and organic dyes have recently been used as sensitizer in dye sensitized solar cells [17]. Ru-complexes such as Z910 (PCE = ~10.2%), Z709 (PCE = ~6%) and N719
(PCE = ∼9.18%)-bases solar cells have the highest efficiency in dye sensitized solar cells [18–20]. Bipyridine ligand-based copper complexes are also reported to have high efficiency sensitizer properties but their efficiency still is not acceptable for commercialization [21]. In recent years, many efforts have been done for understanding the parameters that play role in efficiency of dye sensitized solar cells. Among many effective parameters, recent reports concentrated on quantum efficiency of electron injection (φ_{ing}) as dye structure related factor on PCE of cells. From the mechanistic point of view, this parameter which principally could be related to the dye structure can open a new horizon about designing the appropriate dye for efficient dye sensitized solar cells [22–24]. In this context, bipyridine organic compounds have been introduced as very expensive and efficient dyes for dye sensitized solar cells. But, the mechanistic aspects of this fact about how these dyes can obtain high PCE for dye sensitized solar cells still remained under debates for many years [25, 26]. As the main goal of this work, we tried to disclose this fact that how the cobalt complex of 2, 3, 4, 5-tetra-(4-pyridyl) thiophen ligand with nitrate anchoring groups can act as sensitizer with appropriate absorption wavelength and good photovoltaic parameters. The high LHE, fast η_{reg} and acceptable η_{coll} for the cobalt complex sensitized solar cell were obtained. We understand that the low φ_{ing} efficiency of the cobalt complex sensitized solar cell which directly depends on the cobalt complex molecular structure can extremely decrease the short-circuit current. The pyridine rings configuration in donor part of dye not only influences the electron transfer from donor to acceptor, but also can remarkably adjust the φ_{ing} efficiency and subsequently changes of PCE. Our finding opens a new insight about mechanistic overview of the φ_{ing} efficiency of the dye sensitized solar cell that had not been obtained before. The schematic structure of the prepared solar cell using cobalt complex dye and the molecular structure of dye is depicted in figure 1.

2. Experimental sections

2.1. Materials

In this work, the following materials were used:

- TiO₂ P25 (80% anatase, 20% rutile crystal phase, 25 nm in average diameter, Degussa Co.), α-terpineol (90% Sigma Co.), ethyl cellulose (46080 and 46070 grade, Sigma Co.), ethanol (99.9%, Merck Co.), iodine (99.9%, Merck Co.), sodium iodide (99.9%, Merck Co.), acetonitrile (99.8% Sigma Co.), 4-tert-butylypyridine (TBP)(98% Sigma Co.), hexachloroplatinic acid hexahydrate (∼40% Pt, Merck Co.), fluorine doped tin oxide (FTO)(conductive glass 10 × 10 cm sheet resistance 7 Ω cm⁻², Solaronix Co.), surlyn polymer sheet (60 μm in thickness, Solaronix Co.), hydrochloric acid (37%, Merck Co.), acetone (≥ 99.8% Merck Co.), TiCl₄ (≥ 97.0% Merck Co.), 2, 3, 4, 5-tetra-(4-pyridyl) thiophen (≥ 98% Sigma Co.), cobalt(II) nitrate hexahydrate (98% Sigma Co.), sodium perchlorate (≥ 98.0% Sigma Co.).
2.2. Synthesis of 2, 3, 4, 5-tetra (4-pyridyl) thiophenindinitratocobalt (II) complex
In order to synthesize the dye, 100 mL of 2, 3, 4, 5-tetra (4-pyridyl) thiophen ethanol solution (0.2 mM) was sonicated in ultrasonic setup for 10 min then was added to ethanol solution of the cobalt (II) nitrate hexahydrate (0.2 mM) dropwise and was vigorously stirred at 60 °C for three hours. During the reaction, the temperature was kept constant at 60 °C. Then, 2, 3, 4, 5-tetra (4-pyridyl) thiophen dinitrato cobalt (II) complex purple participate was formed. The solution was cooled at room temperature and the precipitate was separated using centrifugation for 20 min Then, the precipitate was recrystallized in pure ethanol for several times to remove unreacted ions and molecules. Finally, the precipitate was dried in oven at 50 °C for two hours.

2.3. Cell fabrication
A dye sensitized TiO2 nanocrystalline solar cell was assembled in sandwich type solar cell structure [27]. FTO sheets (1.5 × 1.5 cm) were washed in acetone, hydrochloric acid (0.1 M) and pure ethanol then the sheets were treated at 60 °C for 40 min in aqueous solution of TiCl4 (40 mM). After that, TiO2 films were deposited layer by layer on the treated FTO using the doctor blade method [28] until a smooth, uniform, transparent layer with thickness of 10.86 μm was obtained after sintering at 500 °C for 30 min The effective area of deposited TiO2 in cell structure was 0.25 cm² (0.5 cm × 0.5 cm). The cobalt complex dye was deposited on the TiO2 using dip coating method. According to this instruction, the prepared TiO2 layers were immersed in 0.04 mM ethanolic solution of dye at room temperature for 24 h. The cell was completed using Pt counter electrodes fabricated by using Pt paste deposition on the FTO sheets by the doctor blade method and sintering at 500 °C for 30 min In order to seal the cell, the hot-melt surlyn polymer film was applied at 110 °C. Then, the electrolyte was prepared using the mixture of 0.05 M Li2, 0.4 M LiI and 0.2 M TBT in acetonitrile and injected into the sealed cell by using the double-hole injection method. Then, the cell was left for more than 45 min at room temperature to stabilize. After that the cell was tested under AM 1.5 irradiation condition [29].

2.4. Characterization
In order to evaluate the photoanode surface morphology and the thickness, the SEM instrument (VEGA-TESCAN inst.) was applied and for UV–vis spectroscopy studies, the mini spectrometer (mini 1240 Shimadzu Co.) was used. In UV–vis spectroscopy, the Beer–Lambert equation was used to calculate the molar absorption coefficient of dye. This equation can be written as:

\[ A = \varepsilon bc \]  

(1)

Where the A, ε, b and c represent the absorbance, molar absorption coefficient (M⁻¹·cm⁻¹), length of the vessel and dye concentration respectively. In order to study the electrochemical properties of the Pt counter electrodes the CV instrument (Sama 100., Iran) was applied and the photovoltaic considerations were tested by using the solar simulator I1000 (Sharif Solar Co., Iran) under 100 mW.cm⁻² AM 1.5 standard output irradiation condition. The I-V and I-t plots were obtained using the potentiostat (EmStat2, PalmSens BV, Netherlands) which controlled by its software under the AM1.5 irradiation condition that was prepared by solar simulator in linear sweep mode. The PCE of the cell was calculated by using equation that can be written as:

\[ PCE(\%) = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{in}} \times 100\% \]  

(2)

Where the PCE, Jsc, Voc, FF and Pin represent the photovoltaic conversion efficiency, short-circuit current, open-circuit voltage, fill factor and input light power, respectively. The x-ray diffraction of the photoanode was characterized using Philips x-ray diffractometer PW1800-CuKα radiation (LFF tube, 40 kV, 50 mA) with 2θ ranging from 20° to 70°. Drying process of the synthetic dye was done using adjustable oven (Memmert Co.). Diffused reflectance spectroscopy (Shimadzu Co. Japan) (DRS) and cyclic voltammetry (Sama 500 Co. Iran) (CV) instruments were applied to measure band gap (Eg) and oxidation potential (Eox) of dye according to equations (3)–(5) that can be written as:

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

(3)

Where the α, hν, A and Eg represent the absorption coefficient, incident light frequency, proportionality constant and band gap respectively [30]. Additionally, using CV method the HOMO and LUMO of dye can be measured by equations (4) and (5) [31]:

\[ HOMO \ (eV) = E_{OX} - E_{FC/FC^+} + 4.8 \]  

(4)

\[ LUMO \ (eV) = E_{HOMO} - E_g \]  

(5)

Where the HOMO, Eox, EFC/F+ and LUMO represent highest occupied molecular orbitals, oxidation potential of dye, standard ferrocene/ferrocenium (Fc/Fc⁺) redox couple and lowest unoccupied molecular orbitals respectively. It should be noted that CV measurement was carried out using Pt work and counter electrodes, 0.5 M sodium perchlorate and scan rate of 0.05 V s⁻¹ in acetonitrile medium.
3. Results and discussions

3.1. UV–vis spectroscopy

The UV–vis results of dye and TiO₂ demonstrate that the maximum absorption of light occurs in wavelengths \( \lambda_{\text{max}} \) of 498 nm and 650 nm for dye and sensitization enhances the cell photoanode light absorption in comparison to the bare TiO₂ (figure 2). The \( \lambda_{\text{max}} \) in 498 and 650 nm can relate to the charge transfer from ligand to metal and \( \pi-\pi^* \) transition in donor part of dye. The molar absorption coefficient at 498 nm and 650 nm were 12,500 and 62,500 M \(^{-1}\) cm \(^{-1}\) that show the great amount of absorption and subsequently their potential of application in the solar cell field \([28]\). The LHE which represents the fraction of the absorbed light by dye can be measured using equation (6):

\[
LHE = (1 - R)(1 - 10^{-A})
\]  

(6)

Where the \( R \) and \( A \) represent the reflectance and absorbance. The LHE at 498 nm and 650 nm has been measured \( \sim \) 61% and \( \sim \) 40%, respectively which can be acceptable for the cobalt complex sensitized solar cell.

3.2. XRD analysis

X-ray diffraction pattern of photoanode after sintering process at 500 °C shows that the TiO₂ has stable crystallinity which is suitable for the solar cell applications. The results show the major crystal phase of TiO₂ is anatase \([29, 32]\) (figure 3). According to XRD pattern, the TiO₂ shows 8 sharp peaks that were related to the \((101), (004), (200), (211), (002), (301), (215)\) and \((212)\) planes which were appeared in 24.88, 37.84, 47.92, 53.68, 62.32, 68.56, 74.8 and 79.6 degree respectively (JCPDS card no. 89–5009).

![Figure 2. UV–vis spectrum of cobalt complex dye in ethanol solvent (black) and TiO₂ photoanode (red).](image)

![Figure 3. XRD pattern of TiO₂ photoanode of solar cell after sintering process at 500 °C.](image)
3.3. Morphological studies

Top-view SEM image of the photoanode surface showed that the diameter of TiO₂ nanoparticles are ∼25 nm which do not have any cracking after sintering process and the surface of the photoanode was completely smooth (figure 4). The organic materials decomposition kinetics during the sintering process can influence the quality of the photoanode surfaces and make some cracks. The mentioned cracks can cause more recombination. As shown in figure 4, the surface of the photoanode is free of the crack that makes it suitable for the dye sensitized solar cells applications and significant dye deposition.

Cross-SEM image shows the thickness of TiO₂ on FTO substrate. According to figure 5, the thickness of TiO₂ layer is 10.86 μm which is suitable for photoanode optimum structure [32–34]. The uniform and smooth structure of the photoanode refers to the fact that the doctor blade deposition method can be used for solar cells application as a significant technique.

3.4. Electrochemical studies

The electrochemical measurements of FTO and Pt-coated FTO were evaluated at a scan rate of 0.05 V S⁻¹. For Pt-coated FTO, 0.5 M sodium Iodide and 0.05 M Iodine were used as the electrolyte. In addition, 0.05 M sodium
perchlorate was used as the supporting electrolyte and acetonitrile was used as the solvent. The results indicate that the Pt-coated FTO has two redox peaks in 0.75 V and 0.25 V. Therefore, this counter electrode with great stability and electrochemical properties can be used in dye sensitized solar cells [35–37] (figure 6). Moreover, DRS (figure 7) and CV (figure 8) measurements of dye showed the highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) energy and $E_g$ for cobalt complex dye are equal to $\sim 6.85$, $\sim 4.52$ and 2.3 eV respectively. The results showed that HOMO, LUMO and $E_g$ of dye are thermodynamically appropriate to convert photons to electrons.

### 3.5. Photovoltaic studies

The photovoltaic measurements illustrate that 2, 3, 4, 5-tetra (4-pyridyl) thiophendinitratocobalt (II) dye is suitable for electron injection from excited state of dye to the conduction band of TiO$_2$. This dye can be attached to the TiO$_2$ nanocrystals using two nitrate anchor groups. The 2, 3, 4, 5-tetra (4-pyridyl) thiophendinitratocobalt (II) dye can be loaded on the TiO$_2$ nanocrystals and convert the visible light to the electricity. As shown in table 1, under AM 1.5 irradiation condition, $J_{SC}$, $V_{OC}$, FF (%) and PCE (%) are 48.80 $\mu A\cdot cm^{-2}$, 0.7 V, 44% and 0.09% respectively (figure 9). According to figure 10, maximum short circuit current was reduced by 11.5% in in operating condition. The I-t diagram illustrates the $J_{SC}$ fluctuation under the on and off condition ($\Delta J_{SC}$). In the on-condition the low reduction in $J_{SC}$ can be related to the efficient electrolyte diffusion in to the TiO$_2$ nanoparticles networks. Moreover, the $\eta_{reg}$ represents the significant regeneration process of the dye $^+$ to dye during the interaction with I$^-$ ions of electrolyte according to the acceptable $\Delta J_{SC}$ of the cell (11.5%). Additionally, the stable $J_{SC}$ can demonstrate the high kinetics of the hole transfer from the dye to the electrolyte. After five seconds the stable $J_{SC}$ was obtained that refers to the suitable and unlimited process of the electrolyte diffusion into the photoanode nanoparticles networks. The V-t diagram shows that the voltage reduction occurs in off-condition of cell after approximately after five seconds that can
The joining that represents the dye ability in electron injection from LUMO of dye to the CB of TiO2 can be affected by cobalt complex dye structure. For the cobalt complex sensitized solar cell, we estimate that this parameter plays a key role in low JSC of the cell.

**Figure 8.** CV diagram of cobalt complex dye that was carried out in acetonitrile medium using Pt work and counter electrodes in presence 0.5 M sodium perchlorate and scan rate of 0.05 V s⁻¹.

**Table 1.** The cobalt complex-based dye sensitized solar cells photovoltaic parameters.

| (%)LHE | (%)PEC | (%FF) | V_OC (V) | J_SC (μA cm⁻²) | ε (M⁻¹ cm⁻¹) | λ_max in EtOH (nm) |
|--------|--------|-------|---------|----------------|-------------|-------------------|
| 40.61  | 0.99   | 44    | 0.7     | 48.80          | 62,500, 12,500 | 650, 498          |

**Figure 9.** J-V diagram of cell under AM 1.5 irradiation (100 mW.cm⁻²) condition.

**Figure 10.** The plots of current transients measured at AM 1.5 irradiation (100 mW.cm⁻²) under on and off condition.

represent the low recombination in operating condition (figure 11). The ϕ_{inj}, that represents the dye ability in electron injection from LUMO of dye to the CB of TiO2 can be affected by cobalt complex dye structure. For the cobalt complex sensitized solar cell, we estimate that this parameter plays a key role in low J_SC of the cell.
shown in figure 12, structure of the donor part depends on the pyridine rings conformations. We can imagine two main conformations for the donor part of the cobalt complex dye. Under the condition that the pyridine rings make right angle with thiophen ring, the weak hyperconjugation interrupts the efficient electron transfer from the donor to the acceptor part at excited state which can subsequently influence the quantum yield of the electron injection. We understand that the low \( \varphi_{\text{ing}} \) efficiency of the cobalt complex sensitized solar cell which directly depends on the cobalt complex molecular structure can extremely decrease the short-circuit current. The pyridine rings configuration in donor part of dye not only influences the electron transfer from donor to acceptor, but also can remarkably adjust the \( \varphi_{\text{ing}} \) efficiency and subsequently changes of PCE. Therefore, the cobalt complex dye structure opens a new insight for designing new dyes with high \( \varphi_{\text{ing}} \) that isn’t achievable from the reported dyes.
4. Conclusion
In this work, a cobalt complex dye was introduced as sensitizer for dye sensitized solar cell. Results demonstrated that the maximum absorption of light occurs in 498 and 650 nm for dye. The photovoltaic measurements of cell showed the $J_{SC}$, $V_{OC}$, FF and PCE 48.80 $\mu$A.cm$^{-2}$, 0.7 V, 44% and 0.09% under the AM 1.5 irradiation condition respectively. This sensitizer with high stability of the $J_{SC}$ and low recombination can be as a highly potent sensitizer. High LHE ($\sim$61%), and high molar absorption coefficient of the cobalt complex dye (12,500 $M^{-1}.cm^{-1}$) were other optical advantages of cobalt complex dye. The results indicated that the $\varphi_{img}$ as a parameter that depends on the dye structure influences the $J_{SC}$. The pyridine rings conformation in the donor part of the cobalt complex dye plays a significant role in $\varphi_{img}$ and subsequently the PCE. This finding opens a new insight about the mechanistic aspects of the dye sensitized solar cells efficiency. Therefore, we propose this structure for designing a new class of dyes for the dye sensitized solar cells.

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