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Synthesis of a carboxylic acid-based ruthenium sensitizer and its applicability towards Dye-Sensitized Solar Cells

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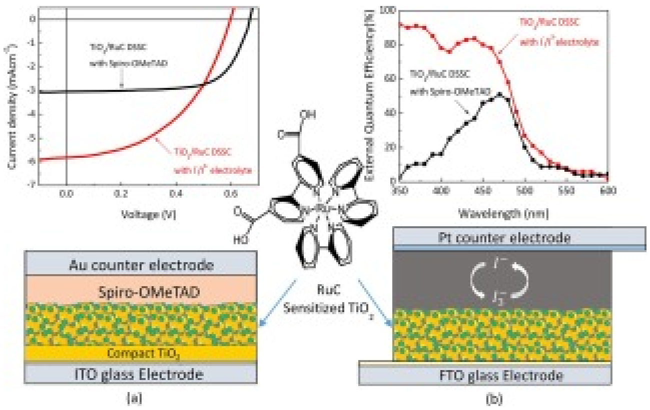
Abstract

This work reports the synthesis of ruthenium based $Ru(bpy)_2(dcbpy)(ClO_4)_2$[(bpy)2,2′-bipyridine;dcbpy=4,4′-dicarboxy-2,2′-bipyridine] (RuC) dye and its application in solid and liquid state Dye-Sensitized Solar Cells (DSSCs). Synthesis resulted with high-pure orange coloured dye with a high yield percentage of 45%. The dye was characterized *via* Nuclear Magnetic Resonance (NMR) spectroscopy, Mass spectroscopy, Cyclic Voltammetry (CV) and UV–vis spectroscopy. The calculated bandgap (E_g) of 2.38 eV from absorbance spectra of pure RuC in ethanol solution showed best proximity with the data obtained from CV measurements. The RuC showed strong absorption in near UV region with the highest molar extinction coefficient (MEC) of 14,746 $M^{-1}cm^{-1}$ at 463 nm. Plateau of over 80% of External Quantum Efficiency (EQE) spectra reveals the efficient carrier generation of RuC in near UV region. Carboxylic acid groups of RuC provide the potential for enhanced electron transfer from TiO_2 surface, and an increased electron density at the interface leads to higher current density. The RuC sensitized solid and liquid state DSSCs exhibited a short circuit current density (J_{SC}) over 3.04 mA/cm^2 and 5.82 mA/cm^2, and power conversion efficiency (PCE) of 1.2% and 1.8% respectively under simulated Air Mass 1.5 irradiation (100 $mWcm^{-2}$).

Graphical abstract



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Introduction

The Dye-Sensitized Solar Cells (DSSCs) have emerged as a promising economical photovoltaic device due to its flexibility, light weight, ease of fabrication, transparency, high power conversion efficiencies in diffuse light conditions, facile synthesis, eco-friendly nature etc. (Omar et al., 2020). The concept of DSSC was first introduced by Tennakone et al in 1988 [3], and O'Regen and Grätzel reported an efficiency of 7.1% in 1991 (Lee et al., 2017, O'Regan and Grätzel, 1991). Since then hundreds of studies are carried out to enhance the performance of DSSCs, and the reported record efficiency is around 14% [2]. To make DSSC a competitive PV technology in the market, a variety of issues that challenges DSSCs had to be sorted out. Research community has been focusing on improving their stability, durability, efficiency and reducing the cost of production (Mariotti et al., 2020). The major drawback with DSSC is the use of liquid electrolytes, which cause temperature stability issues. Electrolyte is crucial in DSSC for the inner charge carrier transportation between electrodes and continuous regeneration of the dye during the DSSC operation (Wu et al., 2015). Further, the interface between the electrolyte and electrodes significantly influences charge transport across the fabricated solar cell. Therefore, the choice of electrolyte is a focused issue, and intensive research has been carried out on liquid state, quasi-solid state, and solid-state electrolytes for DSSCs. (Chen et al., 2011, Dissanayake et al., 2021, Karakuş et al., 2020, Lee and Ho, 2018, Mehmood et al., 2017). The solid electrolyte based DSSCs have shown to have good mechanical stability and simpler fabrication techniques compared to liquid electrolyte based DSSCs (Zhang et al., 2018).

Titanium dioxide is a widely used material in both solid and liquid state solar cells as well as in various applications, such as solar energy utilization for hydrogen production through water splitting (Mahoney et al., 2015, Shanmugaratnam et al., 2019), environmental remediation applications (Senthilnanthan et al., 2010), and electrochromic applications(Abate et al., 2014, Dissanayake et al., 2019, Mahoney et al., 2015a, Maleki et al., 2021, Rasalingam et al., 2015a, Ravirajan et al., 2012). Among the Titanium dioxide polymorphs, the anatase TiO_2 is widely used in photovoltaic applications due to its higher activity with good chemical stability, and can be prepared in different forms and sizes with highly ordered porosity and crystallinity (Deiana et al., 2016, Deiana et al., 2013, Patrocinio et al., 2015). Further, several dyes had been used as a sensitizer in Titanium dioxide-based photovoltaics. The combined use of organic small molecules and inorganic semiconductor materials facilitate energy level tuning via varying the chemical structure (Fournier et al., 2018). Particularly the metal complexes such as ruthenium (Ru(II)) (Aguirre-Araque et al., 2020, Chang et al., 2012, Swarnalatha et al., 2016), containing organic ligands functionalized with carboxylic substituents as anchoring groups to the TiO_2 have intensively been investigated for DSSC application because of their broad absorption spectra and favorable photovoltaic properties (Baktash et al., 2016, Gorduk and Altindal, 2019, Sodeyama et al., 2012, Song et al., 2009, Tsaturyan et al., 2018, Veronese et al., 2019). It was found that the surface binding on TiO_2 metal oxide and the performance of fabricated solar cells were strongly influenced by both the chemical structure and the number of anchoring groups (Abdellah et al., 2019, Abdellah and El-Shafei, 2020, Park et al., 2006). In this regard, the carboxylic acid (–COOH) is an effective anchoring group compared to other anchoring groups like phosphonate and acetylacenonate in order to bind well with the TiO_2 which results these dyes having good adsorption on the TiO_2 surface (Braumüller et al., 2016, El Bitar Nehme et al., 2019, Giribabu et al., 2011, Neuthe et al., 2014, Park et al., 2006). In this case, the interaction between the dye and TiO_2 metal oxide is improved by involves either rapid proton shuttling between a carboxylic acid and the surface oxygen, or proton sharing due to quantum delocalization (Tabacchi et al., 2019). Furthermore, a crucial light absorption in the visible region is observed from the solar spectrum, due to the high charge transfer by metal complex (Pirashanthan et al., 2020). A broad absorption spectrum, suitable excited and ground state energy levels, relatively long excited-state lifetime and good electrochemical stability of Ru complexes resulted in the best photovoltaic performance in DSSCs (Oh et al., 2018). In addition, ruthenium is the most suitable element with a good band edge position, thus most of the dyes used in the recent era for photovoltaic devices are ruthenium based. For example, N719, N3 and Z907 dyes are the commercially available dyes for DSSC applications; the major difference between these dyes is the placement of ruthenium (Ru) in their organic structure (Chang et al., 2012, Khan et al., 2017, Sugathan et al., 2015, Wu et al., 2017). Since, these commercial products are comparatively expensive, in this work a novel ruthenium based $Ru(bpy)_2(dcbpy)(ClO_4)_2$[(bpy)2,2′-bipyridine;dcbpy=4,4′-dicarboxy-2,2′-bipyridine](RuC) dye was synthesized with a better anchoring group (–COOH) and RuC is used as a sensitizer to enhance the performance of solid and liquid state DSSCs.

The better compatibility of the energy levels of lowest unoccupied molecular orbital (LUMO) of the sensitizers and the band edge of the semiconductor metal oxide are important key factors to influence the electron injection of ruthenium sensitizers based solar cells (Aguirre-Araque et al., 2020, Louazri et al., 2016, Veronese et al., 2019). Carboxylic acid groups of RuC provide an enhanced electron transfer from the TiO_2 surface and thus increase electron density at the interface that leads to higher current density. Here we report the synthesis and characterization of a novel, cost effective ruthenium based $Ru(bpy)_2(dcbpy)(ClO_4)_2$[(bpy)2,2′-bipyridine;dcbpy=4,4′-dicarboxy-2,2′-bipyridine] (RuC) dye and its applicability towards solid-state and liquid-state DSSCs. Notably, few research articles can be found on synthesized Ru based dyes for DSSC application, however these lack detailed analysis of the dye and its characterization. This paper provides new insight in to cost effective synthesized ruthenium based dye for DSSC application.

Section snippets

Synthesis of RuC

All reagents, lithium perchlorate ($LiClO_4$), 2,2′-Bipyridine-4,4′-dicarboxylic acid (dcbpy), *cis*-Bis(2,2′-bipyridine)dichlororuthenium(II) hydrate($Ru(bpy)_2Cl_2$), Methanol (CH_3OH) were used without further purification. Deionized (DI) water was used as diluent. Appropriate amounts of *cis*-Bis(2,2′-bipyridine)dichlororuthenium(II) hydrate($Ru(bpy)_2Cl_2$) (0.5 g, 1.0 mmol), 2,2′-bipyridine-4,4′-dicarboxylic acid (dcbpy) (0.3 g, 1.2 mmol) and sodium bicarbonate (0.3 g, 3.6 mmol) were mixed in basic media …

Synthesis of RuC

A crystalline solid with a yield percentage of 45% was attained with high purity, and the melting point of the as-prepared crystals was found to be $> 300^\circ C$. The chemical structure and optical photograph of synthesized RuC dye are shown in Fig. 2.

Fig. 3**(a)** illustrates the absorbance and emission spectra of 0.05 mM solution (in ethanol) of RuC dye recorded using the UV–Visible spectrometer. The absorption spectra showed strong absorption in the near UV region with a sharp decay tailing around…

Conclusions

In this study, a carboxylic acid-based ruthenium RuC dye was synthesized and its applicability towards Dye-Sensitized Solar Cells was verified by fabricating solid Spiro-OMeTAD electrolyte and liquid I^-/I^3 electrolyte based solar cells. The novel crystalline solid RuC dye that was synthesized had high purity and a yield percentage of 45%. Formation of $Ru(bpy)_2(dcbpy)(ClO_4)_2$[(bpy)2,2′-bipyridine;dcbpy=4,4′-dicarboxy-2,2′-bipyridine] (RuC) was confirmed with Mass spectroscopy and NMR analysis.…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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