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Interface engineering of cross-linkable ruthenium complex dye to chelate cations for enhancing the performance of solid-state dye sensitized solar cell

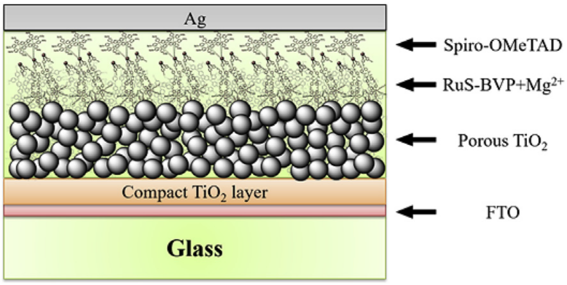
Hsin-Hsiang Huang, Wen-Fu Lo, Yen-Chen Shih, King-Fu Lin*

Department of Materials Science and Engineering, National Taiwan University, Taipei, 10617, Taiwan

HIGHLIGHTS

- The outward bipyridine groups of RuS-BVP dyes are capable of chelating cations.
- Chelated cations in the interface can increase the PCE of solid state DSSC.
- Chelated cations with higher charge density give rise to higher PCE.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study a cross-linkable ruthenium complex dye, Ru(2,2′-bipyridine-4,4′-bicarboxylic acid)(4,4′-bis((4-vinyl-benzyloxy)methyl)-2,2′-bipyridine)(NCS)$_2$ denoted as RuS, was applied to the solid-state dye-sensitized solar cell, by which the photovoltaic performance was superior to the traditional N3 dye. However, the power conversion efficiency (PCE) was only 1.48%, resulting from poor pole filling of the hole conductor, 2,2′,7,7′-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9′-spirobifluorene (spiro-OMeTAD). To modify the interface between RuS and spiro-OMeTAD, additional 4,4′-bis((4-vinylbenzyloxy)methyl)-2,2′- bipyridine (BVP) ligand was employed to crosslink with RuS. The cross-linked dye (denoted as RuS-BVP) on TiO$_2$ was more sustainable and the PCE rose to 2.12%. Besides, the outward bipyridine groups of RuS-BVP are capable of chelating cations. As lithium bis(trifluoromethane)sulfonimide was applied to modify the interface between RuS-BVP and spiro-OMeTAD, the PCE increased to 2.55% and the interfacial resistance for charge transfer under sunlight dramatically decreased. As divalent cation compounds such as magnesium, calcium and barium acetylacetonate were individually adsorbed onto the RuS-BVP, the cell with magnesium acetylacetonate has the highest PCE of 2.82%, highest open circuit voltage and lowest interfacial resistance. The results suggest that the cations with higher charge density have stronger Coulomb's force to couple between RuS-BVP and spiro-OMeTAD.

1. Introduction

It is well known that the performance of dye-sensitized solar cell (DSSC) has almost reached the commercialization stage [1–7]. However, some problems such as desorption of dyes from TiO$_2$ to

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* Corresponding author.
E-mail address: kflin@ntu.edu.tw (K.-F. Lin).

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liquid electrolyte [8], evaporation of liquid [9], precipitation of salts [10] et al. that limit its service life still remain. To avoid these disadvantages, many solid state electrolytes have been developed [11–16]. Especially, Grätzel et al. developed a solid-state DSSC (ssDSSC) with Ru(4,4′-dicarboxy-2,2′-bipyridine)$_2$(NCS)$_2$ (commonly known as N3 dye) and 2,2′,7,7′-tetrakis-(N,N-di-4-methoxy phenyl-amine)9,9′-spirobifluorene (commonly known as spiro-OMeTAD) as hole transport material (HTM) in 1998 [15]. Although the reported power conversion efficiency (PCE) was rather low, the open-circuit voltage (V_{OC}) compared to the traditional DSSC is substantially higher on account of high discrepancy of energy levels between the quasi-Fermi level of electrons in the TiO_2 and redox potential of spiro-OMeTAD [17].

In general, ssDSSC consists of transparent conducting oxide (TCO), condensed TiO_2 layer, mesoporous TiO_2 layer, sensitizing dye, hole transport layer and counter electrode. The condensed TiO_2 layer was introduced to prevent direct contact of HTM with the TCO [18]. While the electrons generated from the photoexcited dye molecules inject into the conduction band of TiO_2, the oxidized dyes can be recovered through the oxidation of HTM by which the holes were created in HTM layer and transported toward the counter electrode by hopping [19]. Therefore, HTM should be intimately contacted with the dyes on the mesoporous TiO_2. Poor pore filling of HTM would cause the inefficient charge transfer across the TiO_2/dye/HTM interface and reduce its photovoltaic performance. Several methods have been reported for improving the pore filling of HTM such as reducing the thickness of TiO_2 [20], choosing a proper HTM [21], thermal annealing of the cast HTM, reducing the capping layer of HTM [22] et al. However, few researchers have tried to modify the TiO_2/dye/HTM interface for better contact between HTM and dye.

In our previous studies, we have synthesized a cross-linkable ruthenium complex dye, Ru(2,2′-bipyridine-4,4′-bicarboxylic acid)(4,4′-bis((4-vinyl-benzyloxy)methyl)-2,2′-bipyridine)(NCS)$_2$ (denoted as RuS) containing two styryl groups for crosslinking (see Fig. 1) [23,24]. As RuS was cross-linked with glycerol propoxylate triacrylate on TiO_2, it is not only more sustainable (89% of dye retained on TiO_2 mesoporous surface after rinsing with 0.1 N NaOH), the power conversion efficiency (PCE) of resulting DSSC with liquid electrolyte also increased to 7.88%. Moreover, in time-course test, the PCE almost unchanged for a month [23]. Notably, ruthenium–diacetylide dye was also reported to remain stable for several weeks under ambient conditions [25].

In this work, to modify the TiO_2/dye/HTM interface for better contact between HTM and dye in the ssDSSC, we developed a novel sensitizing system with RuS crosslinking with 4,4′-bis((4-vinylbenzyloxy)methyl)-2,2′-bipyridine (BVP) ligand. The outward bipyridine groups of resulting RuS-BVP on mesoporous TiO_2 (see Fig. 1) are capable of chelating cations. The monovalent and divalent cation compounds were then individually adsorbed onto the RuS-BVP and employed as a coupling agent to bind the spiro-OMeTAD HTM. With the enhancement of pore filling and charge transfer efficiency, the photovoltaic performance of resulting ssDSSC is significantly improved.

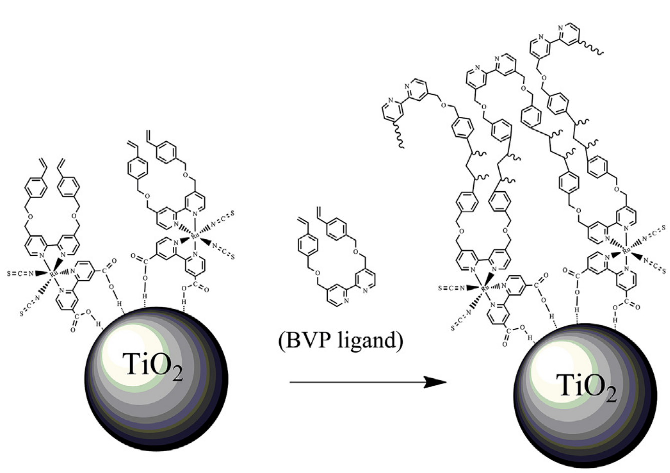

Fig. 1. Schematic illustration of RuS dyes being chemisorbed on mesoporous TiO_2 surface to crosslink with BVP ligands.

2. Experimental

2.1. Materials

All chemicals and solvent were obtained from Acros and Aldrich. N3 dye was the commercial product purchased from Solaronix S.A., Aubonne, Switzerland. RuS dye was synthesized by the typical one-pot synthetic method developed for heteroleptic polypyridyl ruthenium complexes. The detail synthesis procedure was given in the literature [23]. BVP ligand is the intermediate product to synthesize RuS and its ^{1}H NMR spectrum is provided in the supporting information (Fig. S1).

2.2. Fabrication of ssDSSCs

A ~100 nm thick compact TiO_2 as blocking layer was prepared by spin-coating the precursor, which consists of titanium isopropoxide (TTIP) in 1.818 mL absolute ethanol (1:10 vol ratio) and 20 μL of 12 M hydrogen chloride, at 3000 rpm for 45 s on cleaned fluorine-doped tin oxide-coated glass substrate (FTO glass, 15 Ω per square, Solaronix). The sample was then heated at 450 °C for 30 min. After cooling to room temperature, the sample was immersed in 0.02 M titanium tetrachloride aqueous solution at 70 °C for 30 min and then heated to 450 °C for 30 min to afford the compact TiO_2 layer. To prepare the mesoporous TiO_2 layer, a nanocrystalline TiO_2 paste was prepared first by following the reported method [26]. In general, 71.66 mL TTIP was added to 430 mL of 0.1 M nitric acid solution. After stirring for 30 min, the solution was heated to 85–90 °C and kept stirring for 8 h. The obtained slurry was filtered to remove the large agglomerates, which was then hydrothermally treated at 240 °C for 12 h in an autoclave. The obtained colloidal suspension was concentrated to a paste containing 13 wt% of TiO_2. Then, polyethylene glycol (MW = 20000) was added into the paste at 30 wt% to TiO_2 weight and stirred for several days. The paste was coated on the compact TiO_2 by doctor-blade technique and sintered by heating at 450 °C for 30 min to afford the mesoporous TiO_2 layer.

To prepare the photoelectrode, the sintered mesoporous TiO_2 was immersed in a mixed solution of acetonitrile (ACN) and *tert*-butanol (1: 1 by volume) containing 0.5 mM of RuS or N3 dye for 24 h, rinsed with acetone and dried. To crosslink RuS dye with BVP ligand, 5×10^{-3} M BVP solution in chlorobenzene (CB) containing 10% initiator of 2,2′-azobis(2-methylpropionitrile) (relative to BVP) was spin-coated on top of the RuS. The cross-linking reaction, which is schematically illustrated in Fig. 1, was immediately carried out by ultraviolet light exposure at 300 W/m^2 for 1 min and followed by heating at 80 °C for 30 min. The product was denoted as RuS-BVP. Furthermore, to adsorb various metal ions onto the RuS-BVP, 10^{-2} M lithium bis(trifluoromethane) sulfonimide (LiTFSI) and 2.5×10^{-3} M magnesium, calcium and barium acetylacetonate solutions all in ACN were individually applied on top of the RuS-BVP.

HTM solution was prepared by dissolving 200 mg spiro-OMeTAD in 1 mL CB, which was added with 9.7 μL 4-*tert*-