

## Dye-Sensitized Solar Cells Based on In Situ Sensitized of N-doped TiO<sub>2</sub>

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**Abstract.** Dye-sensitized solar cells (DSSCs) are being a potential technology for application in solar energy and photovoltaic processes. Light harvesting and photocurrent generation are highly dependent on the nanostructured semiconductor film and the mode of dye adsorption. The TiO<sub>2</sub> with mesoporous structure, which synthesized through sol gel method, was used as semiconductor material. The ruthenium polypyridine complex that contain carboxylic anchoring group was used as dye sensitizer. The dye adsorption process has been performed *in situ* solid state, stepwise, and directly on the surface of the TiO<sub>2</sub> film. FTIR spectrophotometer, Scanning Electron Microscopy and X-Ray Photoelectron Spectroscopy are used to study the surface interactions of Ru complex with TiO<sub>2</sub> surface. The high wavenumber region (3000~4000 cm<sup>-1</sup>) of dye adsorbed TiO<sub>2</sub> is analyzed by FTIR spectra to investigate the role of surface Ti-OH to the anchoring mode. The result showed that the coordination of Ru-complex on TiO<sub>2</sub> film occurs mainly by the contribution of unidentate (i.e., ester-like linkage) and partially by bidentate linkage. The absorption spectrum, IPCE and I-V curve were used to study the efficiency of *in situ* adsorption process in DSSCs, providing fill factor (*ff*) 54 % IPCE and overall DSSCs (*η*) efficiency 3.4%.

**Keywords:** Dye-sensitized solar cells, dye sensitizer, solid state synthesis

### 1. Introduction

The use of sensitized semiconductor film for the direct conversion of sunlight into electricity is an attractive alternative in photovoltaic technology. The first photovoltaic cell based on sensitized TiO<sub>2</sub>, called dye-sensitized solar cell (DSSC), was invented by Gratzel et al. [1-3]. This cell used Ru(II) complex – which involving the anchor ligand 4,4'-dicarboxy-2,2'-bipyridine – to sensitize TiO<sub>2</sub> [4-6] and provided a light-to-electricity conversion efficiency around 11%, a level that is not easily obtained since the concept firstly noticed in early 1970 [7,8].

A critical component of such a photosensitized device is the sensitizer or dye, because it determines the efficiency of electron injection into TiO<sub>2</sub> and thus the efficiency of the device [9]. Sensitizer or dyes are typically deeply colored materials that absorb light in the visible and ultraviolet region of the spectrum [10]. Many different compounds have been investigated for semiconductor sensitization, which is transition metal complexes especially ruthenium polypyridine complex, have been the most optimum sensitizer so far [11].

Ruthenium polypyridine complexes are usually prepared independent from TiO<sub>2</sub> by a series synthetic steps involving both organic and inorganic chemical methodology. These preparations involve the actual synthesis, followed by purification or isolation of the product, an also followed by identification or characterization of this product [12,13]. Purification and characterization may occur at each and every steps of the traditional synthetic method. The prepared sensitizer is then applied to the surface of TiO<sub>2</sub> to provide the sensitized semiconductor. Several processes that needed to synthesize the complexes caused complexity and highly cost of the sensitizer. Therefore, a faster and more efficient method to synthesize ruthenium polypyridine complex which serve as sensitizer for TiO<sub>2</sub> is being an interest research to be investigated.

The *in situ* solid state synthesis method which provides a general method for the stepwise synthesis of transition metal complexes directly on the surface of TiO<sub>2</sub> semiconductor could be a much simpler and more efficient technique to sensitize TiO<sub>2</sub>. In particular, by preparing the sensitizer on the surface of TiO<sub>2</sub>, the lengthy and tedious independent preparation and final absorption of the sensitizer onto TiO<sub>2</sub> is avoided. The

*in situ* synthesis method also does not require purification at any stage and unwanted side products or reagents not anchored to TiO<sub>2</sub> are merely washed away with solvent after each preparative step.

In this article, we report an *in situ* solid state ruthenium complexes formation onto titania film to enhance its photoactivity. The complex formation and resulting sensitized TiO<sub>2</sub> material were characterized using FTIR spectrophotometer, UV/Vis diffuse reflectance spectrophotometer, XRD, SEM and XPS. The solar cell performances including the overall conversion efficiency ( $\eta$ ), fill factor ( $FF$ ), open-circuit voltage ( $V_{OC}$ ) and short-circuit current ( $I_{SC}$ ) were evaluated from the  $I-V$  curves measured.

## 2. Experimental

### 2.1. Materials

Tetra Iso-propoxide, Ti(OPr)<sub>4</sub>, 97% and acetylacetone were purchased from Aldrich. Dodecylamine 98 % and TritonX-100 were purchased from Fluka. Ethanol absolute, CH<sub>3</sub>COOH, KSCN and RuCl<sub>2</sub> were obtained from Merck. Di-tetrabutylammonium cis-di(isothio-cyanato)bis (2,2'-bipyridyl-4,4'-dicarboxylato) Ru(II) (N719 dye), 2,2'-bipyridyl-4,4'-dicarboxylate (dcbppy) ligand and TEC 15 electrode glass plate are commercial products of Dyesol. All materials were used as received.

### 2.2. Method

TiO<sub>2</sub> powders were synthesized by a procedure that we developed, as described in our previous paper [14]. The TiO<sub>2</sub> paste was prepared using small amount of aquadest, TritonX-100 and acetylacetone. The paste then coated on 0.25 cm<sup>2</sup> area of 2 cm<sup>2</sup> electrode glass plate to provide working electrode thin film. *In situ* solid state process were done with two method: first method, the TiO<sub>2</sub> film was dipped into 1.5 x 10<sup>-4</sup> M solution of RuCl<sub>3</sub> in 30:70 (v/v) acetonitrile:ethanole continued by immersed in 3 x 10<sup>-4</sup> M solution of dcbpy and 3 x 3 x 10<sup>-4</sup> M solution of KNCS. Second method, TiO<sub>2</sub> film was dipped into 3 x 10<sup>-4</sup> M solution of dcbppy in 30:70 (v/v) ecetonitrile:ethanol continued by dipping it into 1.5 x 10<sup>-4</sup> solution of Ru(SCN)<sub>2</sub>. After the solid state process, both working electrode washed with ethanol then air dried at room temperature. The commercial complex of N719 was used to sensitize (*ex situ* method) the thin film as standard.

The cells were assembled by placing the Pt-counter electrode (CE) over the active area of TiO<sub>2</sub> working electrode. The electrolyte was introduced through drilled hole on CE by capillary action, the hole was then sealed.

## 3. Result and Discussion

The mesoporous titania has been fabricated through templated sol gel method using dodecylamine surfactant for pore generating structure. The self assembly micelle structure of dodecylamine facilitated porous titania formation. It provided an eco-environmentally route on nanocrystalline mesoporous titania synthesis. The TiO<sub>2</sub> thin film were produced from the resulting mesoporous TiO<sub>2</sub> which calcined at temperature of 400°C before the solid state synthesis of rutenium complex process. In this research, rutenium complex was constructed from RuCl<sub>2</sub> as ruthenium source, 2,2'-bipyridyl-4,4'-dicarboxylate (dcbppy) as anchoring ligand, and KNCS as <sup>-</sup>NCS source (secondary ligan). The *in situ* complex solution of rutenium absorption spectra was compared to absorption spectra of N719 solution (Figure 1) indicated that there is similar trend on electronic transition of both complex solution.

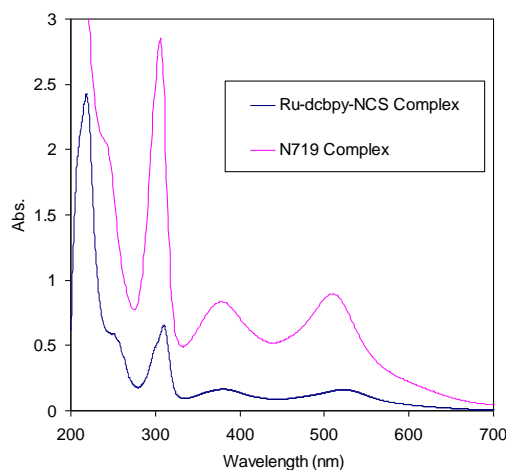


Figure 1 Absorption Spectrum of Ru(II) and N719 complexes

The efficiency of the charge injection process of DSSCs system is highly dependent on bonding structure of the dye molecules adsorbed on the semiconductor. In addition, the electron transfer is strongly influenced by electrostatic and chemical interactions between  $\text{TiO}_2$  surface and the adsorbed dye molecules. The *in situ* complex solution used in this work has two bipyridyl ligands with two carboxyl groups at the 4 and 4' position of the bipyridyl groups. It has been known that the carboxyl groups can coordinate in different two ways to  $\text{TiO}_2$  surface by physical adsorption via hydrogen bonding or via chemical bond formation with a unidentate (or ester-like) linkage, a bidentate (or chelating) linkage, or a bridging linkage.

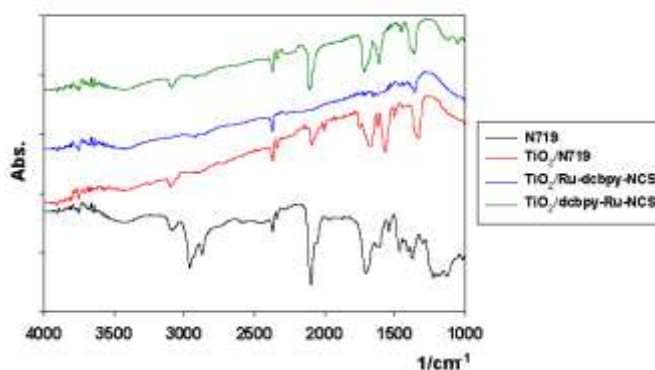


Figure 2 FTIR spectrum of sensitized  $\text{TiO}_2$

In this work, the interfacial binding between the dye molecules and  $\text{TiO}_2$  surface of the *in situ* solid state synthesis methods was investigated by FTIR spectra of sensitized thin film comparing to the signal of N719 powder and N719 sensitized  $\text{TiO}_2$  (Figure 2). The first solid state synthesis method has lead  $\text{TiO}_2$  surface to bind Ru(II) complex metal center, continued by coordinating the first ligand (dcbpy) and secondary ligand (NCS). FTIR spectra of first method solid state synthesis showed there is only small weak vibrational peak at  $1370\text{ cm}^{-1}$  which contributed by bidentate coordination. It is indicated that ruthenium metal center hind the coordination between  $\text{TiO}_2$  surface and carboxylic group of dcbpy. The second solid state synthesis method provide better interaction between  $\text{TiO}_2$  surface, showed strong absorptions at  $1720\text{ cm}^{-1}$ , indicating the C=O stretch mode of the protonated carboxylic acid (i.e., ester-like linkage). The FTIR spectra also showed two vibrational peaks at  $1370\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$  which is related to bidentate coordination. The vibrational spectra (Figure 3) of N719-sensitized  $\text{TiO}_2$  showed that the coordination of N719 on  $\text{TiO}_2$  films occurs mainly by the contribution of unidentate (i.e., ester-like linkage) and partially by bidentate linkage. Absorption at  $2105\text{ cm}^{-1}$  of N719 powder is attributed to the SCN stretch model of N-bonded SCN ligand. When the dye anchored on  $\text{TiO}_2$  film, the IR spectra have absorptions at  $1370\text{ cm}^{-1}$ ,  $1610\text{ cm}^{-1}$  and  $1720\text{ cm}^{-1}$ . The IR spectra located at  $1370\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$  is consistent with the bidentate coordination. It was different to the result reported by Leon et al. [16] which addressed that coordination of the adsorption of Ru-bpy dyes on  $\text{TiO}_2$  films occurs via bidentate or bridging linkage. Also, Finnie et al. [17] reported from the chemical bonding structure of Ru(II) dye molecule is a bidentate chelate or bridging coordination to nanocrystalline  $\text{TiO}_2$  surface via two carboxylate groups per dye molecule.

The transition electronic of ruthenium complexes sensitized  $\text{TiO}_2$  were studied using Diffuse Reflectance Spectroscopy as showed in Figure 3, it is indicated that second solid state method more reasonable to synthesis Ru(II) complex on  $\text{TiO}_2$  surface through anchoring carboxylate group of dcbpy ligand.

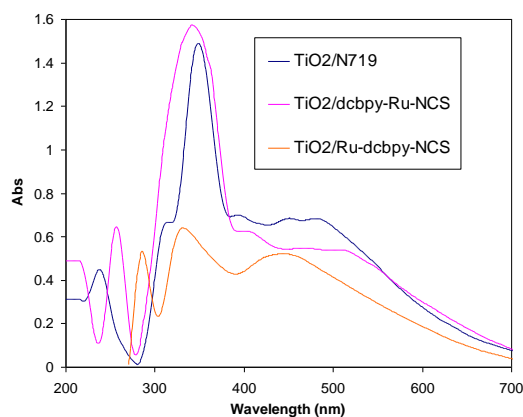


Figure 3 XRD pattern and  $\text{N}_2$  adsorption desorption isotherm

The binding energy spectra N 1s two different method of solid state synthesis Ru(II) complex on TiO<sub>2</sub> surface, which analyzed by X Ray Photoelectron Spectroscopy showed in Figure 4. The different binding energy was found in N1s, O1s, Ti 2p and Ru 3d spectra. There is no interaction between ruthenium-nitrogen and titanium-nitrogen in the spectra of first method, but appeared in the second method spectra. It is consistent with the FTIR spectra; if the ruthenium metal center is bind first to the TiO<sub>2</sub> surface it will prevent the interaction between TiO<sub>2</sub> surface and the ligand. The ruthenium complex, which analogue to N719 complex, was probably difficult to form with first solid synthesis method since TiO<sub>2</sub> surface could also play a role as a ligand.

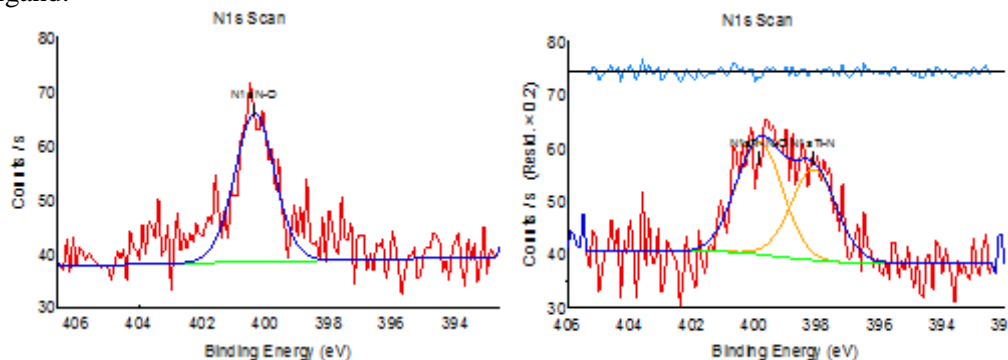


Figure 4 Binding energy spectra N 1s of first (left) and second (right) solid state synthesis

The Incident Photon to Current Efficiency (IPCE) of both solid state synthesis methods and N719-sensitized TiO<sub>2</sub> were showed in Figure 4, which is indicated that the second method was resulted a higher IPCE value than the first method. Figure 4 also indicated that the N719-sensitized TiO<sub>2</sub> provide highest IPCE than the *in situ* method. It could be happened because *in situ* sensitization more difficult to obtain ordered dye anchoring.

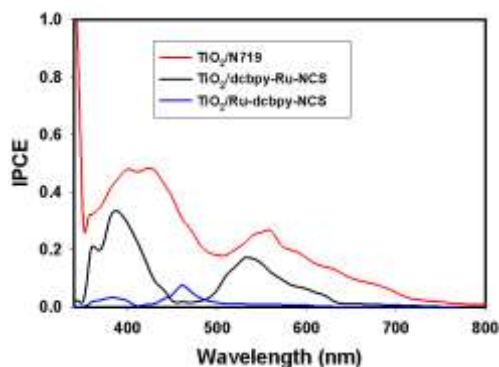


Figure 5 IPCE spectra of DSSC based on different semiconductor sensitization method

Tabel 2 DSSC performa of different sensitization method

DSSC system	I <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	I <sub>pp</sub> (mA/cm <sup>2</sup> )	V <sub>pp</sub> (V)	FF	η (%)
TiO <sub>2</sub> /N719	8.86	0.62	6.94	0.42	0.54	4.9
TiO <sub>2</sub> /dcbpy-Ru-NCS	6.96	0.49	3.29	0.37	0.52	3.4
TiO <sub>2</sub> /Ru-dcbpy-NCS	2.94	0.35	2.23	0.24	0.47	0.8

The performance properties of the DSSCs are summarized in Table 2. It is showed that second solid state synthesis method of Ru(II) complex of TiO<sub>2</sub> film provide a high solar cell efficiency, a little bit lower than DSSC based on N719-sensitized TiO<sub>2</sub>. That means the solid state *in situ* sensitization method could be develop as a simpler and cheaper method as sensitization method on DSSC technology. The lower IPCE spectra of first solid state method lead to a low efficiency of its DSSC system.

#### 4. Conclusion

The solid state synthesis of ruthenium complex on TiO<sub>2</sub> surface through anchoring ligand that consist carboxylic group is successfully developed to result dye-sensitized TiO<sub>2</sub> as fotoanode electrode in DSSC

system. It provide a comparable solar cell efficiency with indirect sensitization method, so the *in situ* solid state synthesis method could be an alternative method to a more complex sensitization technology based DSSC.

## 5. Acknowledgements

Financial support from Indonesian Government granted by the Directorate General of Higher Education through HIBAH STRANAS Project contract no. 03/H34.21/KTR.STRANAS/ DP2M.II/2010 is gratefully acknowledged.

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