Band-engineering of TiO₂ as a wide-band gap semiconductor using organic chromophore dyes

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Abstract. Bond-engineering as applied to semiconductor materials refers to the manipulation of the energy bands in order to control charge transfer processes in a device. When the device in question is a photoelectrochemical cell, the charges affected by drift become the focus of the study. The ideal band gap of semiconductors for enhancement of photocatalyst activity can be lowered to match with visible light absorption and the location of conduction Band (CB) should be raised to meet the reducing capacity. Otherwise, by the addition of the chromofor organic dyes, the wide-band gab can be influences by interacation resulting between TiO₂ surface and the dyes. We have done the impruvisation wide-band gap of TiO₂ by the addition of organic chromophore dye, and the addition of transition metal dopand. The TiO₂ morphology influence the light absorption as well as the surface modification. The organic chromophore dye was syntesized by formation complexes compound of Co(PAR)(SiPA)(PAR) = 4-(2-piridyldiazoresorcino), SiPA = Silyl propil amine). The result showed that the chromophore groups adsorbed onto TiO₂ surface can increase the visible light absorption of wide-band gab semiconductor. Initial absorption of a chromophore will affect light penetration into the material surfaces. The use of photonic material as a solar cell shows this phenomenon clearly from the IPCE (incident photon to current conversion efficiency) measurement data. Organic chromophore dyes of Co(PAR)(SiPA) exhibited the long wavelength absorption character compared to the N719 dye (from Dyestol).

1. Introduction
Bond-engineering as applied to semiconductor materials refers to the manipulation of the energy bands in order to control charge transfer processes in a device. When the device in question is a photocatalyst, the charges affected by drift become the focus of the study. Band-engineering is conceptually tied to defect engineering, where defect engineering aims to address issues affecting properties in the photocatalyst such as point defects, charge transfer and doping [1,2,3] General strategies are passiving co-doping to improve the photocatalys activity of semiconductors [2,4,5].

TiO₂ has several good properties, such as nontoxic, relatively inexpensive, physical and chemical stability, and high photocatalytic activity [6]. Because of these excellent properties, TiO₂ has attracted extensive attentions during decades as an extremely promising photocatalyst for environmental
applications. However, TiO$_2$ has a wide band gap, which limits the application of visible light [6]. Therefore, the effective utilization of visible light is one of the important subjects for TiO$_2$ as a photocatalyst as well as a photoelectrochemical solar cell. Controlled band gap engineering is immensely important to enhanced visible light absorption.

The ideal band gap of semiconductors for enhancement of photocatalyst activity can be lowered to match with visible light absorption and the location of conduction Band (CB) should be raised to meet the reducing capacity. Otherwise, by the addition of the chromophore organic dyes, the wide-band gap can be influences by interacation resulting between TiO$_2$ surface and the dyes. The ideal band gap for any visible light driven photocatalyst is around 2.0 eV for effective utilization of solar spectrum. The investigation of suitable semiconductor as the photocatalyst for splitting water into hydrogen using solar energy is one of the noble missions on materials science study [7-8]. In water splitting photocatalyst technology, the conduction band minimum (CBM) has to be higher (more negative) than the hydrogen reduction potential, while the valence band maximum (VBM) has to be lower (more positive) than the water oxidation potential ($H_2/O_2$) [8].

Over the past two decades, dye-sensitized solar cells (DSSCs) have become a viable and relatively cheap alternative to conventional crystalline silicon-based systems. At the heart of a DSSC is a wide band gap semiconductor, typically a TiO$_2$ nanoparticle network, sensitized with a visible light absorbing chromophore. Ru(II)-polypyridines are often utilized as chromophores due to their chemical stability, long-lived metal-to-ligand charge transfer (MLCT) excited states, tunable redox potentials, and near perfect quantum efficiency of interfacial electron transfer (IET) into TiO$_2$. More recently, coordination compounds based on first row transition metals, such as Fe(II)-polypyridines and Co(II)-polypiridyl, gained some attention as potential sensitizers in DSSCs due to their low cost and abundance [9,10]. Iron(II) and Co(II) was identified many years ago as a promising substitute for ruthenium. In our study, they also have good light-absorption properties, with intense metal to ligand charge transfer (MLCT) band in visible region. While such complexes can in principle sensitize TiO$_2$, they do so very inefficiently since their photoactive MLCT states undergo intersystem crossing (ISC) into low-lying metal-centered states on a sub picosecond time scale [11]. Enormous efforts have been devoted to extend the light absorption range of TiO$_2$ from UV to visible light, such as surface modifications using chromophore dye [10]. In general, a molecule chromophore is coordinated to the surface of a wide band gap semiconductor, most commonly TiO$_2$. A long lived charge separation is established when the semiconductor conduction band accepts an electron from the photoexcited chromophore [6]. Molecular level factors were reported affecting the efficiency of organic chromophores for p-Type Dye Sensitized Solar Cells [12].

2. Experimental

Materials used in this research are titanium tetra isopropoxide, glass conductive indium tin oxide (ITO) (resistivity: 10 $\Omega$ / cm2, Asahi Glass), triton X-100, acetylacetone (acac), CoCl$_2$, FeCl$_2$, methanol, 37% hydrochloric acid, and sodium hydroxide from Merck, aminopropiltrimetosisilan (APTS) and 4- (2-piridilazoresorsinol) (PAR) from Aldrich. These materials were used directly without further purification or pretreatment particular.

2.1 Measurement electronics spectrum of 4-(2-piridilazo) resorcinol (PAR) in various pH

Measurement electronics spectrum of 4-(2-piridilazo) resorcinol (PAR) (10-3 M) was conducted at various pH condition, i.e. pH of 1, 3, 5, 6, 7, 9 and 13 in methanol. The solutions of PAR 10-3 M, in various pH were prepared by additin a certain amount of HCl solution as well as NaOH solution in order to gain the certain pH of PAR solution i.e. pH 1, 3, 5, 6, 7, 9 dan 13. Each electronic spectrum of PAR solution then were measured in the range of 200 - 800 nm using Shimadzu UV 1799 Pharma-Spec.
2.2 Formation and electronic spectrum measurement of aminopropiltrimetoksilin (APTS), CoII-SiPA, CoII-PAR, dan SiPA-CoII-PAR
The development wide-band gap of TiO2 by the addition of organic chromophore dye, and the addition of transition metal dopand. The organic chromophore dye was synthesized by complexes compound formation of Co(PAR)(SiPA) (PAR=4-(2-piridylazo)resorcinol), SiPA=Silyl propil amine). Electronic spectrum measurements of CoII-SiPA, and SiPA-CoII-PAR, was done by dissolving of CoII, and CoII-PAR with methanol into a concentration of 10-4 M (APTS at a concentration of 0.08% v/v). Each solution was measured UV-Vis absorption spectrum at a wavelength of 200-800 nm using Shimadzu UV 1799 Pharma-Spec.

2.3 Syenthesis of mesoporous TiO2
2.993 g of Pluronic P123 was dissolved in 14 gr isopropanol (iPr) (~ 15 ml) (A solution); while we also prepared solution of 3 g TTIP + 0.53 gr acetylaceton (acac) + 4 iPr + 2.5 ml of HCl 5M (B solution) (molar ratio: TTIP / P123 / acac / HCl / iPr = 1.00: 0, 05: 0.53: 1.25: 12.00: 30.00). The A solution was added to B solution drop wise then stirred until homogeneous for 3 hours to obtained yellow-orange sol solutions. The solution was then allowed to stand at room temperature for 7 days. The gel obtained is heated up to temperatures of 120°C for 24 hours to obtain a xerogel. After the sample allowed to stand at a temperature of ± 30°C, TiO2 xerogel was annealed at a temperature of 400°C for 2 hours with a speed temperature a 20°C/ min. Annnealing processing of TiO2 mesoporous preparation was conducting using Furnace Carbolite CWF 1300.

2.4 Preparation of thin layer of TiO2
Preparation of thin layer of TiO2 was done by 1 mg TiO2 was added to 1 drop of acac and 6 drops of triton X-100 and pounded until a paste TiO2 forms. Through the Doctor Blading technique, TiO2 paste then was coated on an ITO glass plate (1 cm x 1 cm in size). The thickness of the layer was made equal to the thickness of adhesive tape (~ 20 μm) that was used as a barrier edge. The thin layer TiO2 then was dried in air at room temperature, and at a temperature of 400°C for 90 minutes.

2.5 Modification of wide band gap TiO2 surface structure via chromophore additn
Sensitization of TiO2 structure was done in order to arrange sensitizer complexes in situ. TiO2 thin layer was prepared on a conductive glass of indium tin oxide (ITO) through slit casting. TiO2 thin layer was dipped to a solution of 5% v/v APTS in methanol for 120 minutes for binding APTS (as an anchoring ligand) to the TiO2 surface. After the adsorption process done completelly, the thin layer was washed with methanol and acetone, and dried at 120°C for 1 hour. CoII ions (or FeII ions) is then fastened to the anchoring ligand by means immersing thin film of modified-TiO2 (TiO2-SiPA) into the solution of 10-3 M metal ions for 120 minutes. After the immersion, the thin-layer samples were washed again with methanol, and dried at room temperature for ± 30 minutes. The last stage, the thin layer samples was dipped into secondary chromosphere of PAR (10-3 M) for 24 hours.

Electronic properties of TiO2 and modified TiO2 were done by UV Vis specular-reflectant spectroscopy (Shimadzu UV 1799 Pharma-Spec). TiO2 thin layer and modified TiO2 (TiO2-SiPA) was characterized by X-Ray Diffraction (Shimadzu XRD-6000) on 2θ = 20-60° using CuKα radiation (λ= 1.5406 Å). X-Ray diffractogram was used for determination the type of TiO2 crystal and compared the crystal deviations before and after surface modification treatment. Silylpropilamine group attact to TiO2 was determined by FTIR spectrophotocopy (Shimadzu 8201 PC). Thin-layer micro-scale morphology was observed with Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDX) equipped (Joel JSM 6360LA). By means of SEM-EDX obtained thin-layer thickness, the metals of sensitizer content have been determined. Induced Photon to current efficiency (IPCE) of those modified TiO2 thin layer were also calculated and compared with N719 dye modified TiO2. IPCE spectras were measured by build DSSCs using Oriel QE/IPCE measurement, Newport Corporation.
3. Result and Discussion

3.1. Electronic properties of 4- (2-piridilazo resorcinol) (PAR) as chromophore dye

UV-Vis absorption spectra of 4- (2-piridilazo resorcinol) (PAR) in methanol at various pH were determined using UV-Vis spectrophotometer in the wavelength range 300-600 nm (Figure 1). PAR as a ligand chromophore is expected to have four main species on the state of protonation and deprotonation is $H_3 PAR^+$, $H_2 PAR$, $HPAR^-$, and $PAR^2-$, as studied by Ghasemi et al. [13]. In circumstances very acidic (pH = 1), the state of the protonated $H_3 PAR^+$ dominate the species present. The spectra are very wide of the species $H_3 PAR^+$ likely caused by agglomeration of species $H_3 PAR^+$ through hydrogen bridges. With the increasing of the pH system, $H_2 PAR$ species was increasing $HPAR^-$ replace apart of $H_3 PAR^+$ species. Electronic transition of protonated species showed no separation of the electronic transition from $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$, but the electronic transition of deprotonated species, $HPAR^-$ and $PAR^2-$ occured at relatively high pH showed a separations of $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions (Figure 1). The $\sigma \rightarrow \pi^*$ electronic transitions have a higher energy than $\pi \rightarrow \pi^*$ electronic transition (Figure 1).

![Figure 1](image)

**Figure 1.** Electronic spectrum of 4-(2-piridilazoresorsinol) (PAR) at various pH conditions (a) pH = 1 (2) pH = 3 (c) pH = 5 (d) pH = 6 (e) pH = 7 (f) pH = 9 dan (g) pH = 13

PAR ligands have acidity constant, $pK_{a1} = 12.08 \pm 0.05$, $pK_{a2} = 5.48 \pm 0.09$ and $0.19 \pm pK_{a3} = 2.98$. The $K_{a1}$, $K_{a2}$ $K_{a3}$ value were governed by protonation and deprotonation equilibrium reaction of PAR. In a highly acidic condition, the dominant PAR species are $H_3 PAR^+$, under acidic conditions (pH = 3-5) as $H_2 PAR$ and at neutral and weakly alkaline (pH = 6-9) as $HPAR^-$ and $PAR^2-$ (Figure 2).
Figure 2. Mayor species of 4-(2-piridilazo)resorcinol (PAR) (a) H$_3$PAR as bidentat chromophore (b) H$_2$PAR as bi- and tri-dentat chromophore (c) HPAR as a tridentat chromophore (d) PAR$^{-2}$ as a tridentat chromophore.

Figure 3. Electronic spectra of (a) Co$^{II}$ ions (b) SiPA-Co$^{II}$ complexes (c) SiPA-Co$^{II}$-PAR complexes. The solutions were dissolved in methanol.

Study of complex formation of Co$^{II}$-PAR describe with the electronic spectrum of Co$^{II}$ ions, SiPA-Co$^{II}$ complexes and SiPA-Co$^{III}$-PAR complexes (Figure 3). Analog with relevant pyridyl complexes compounds Rul'(NCS)$_3$ (L' = 4,4'-COOH-2,2'-bipyridine), RuL$_2$ (NCS)$_2$ (L = 4,4 ', 4'- COOH -2,2 ': 6', 2 '' -terpyridine), [Ru (bpy)$_3$]$^{2+}$ (bpy = bipyridine), electronic spectrum of SiPA-Co$^{II}$-PAR show transition electronics of intra ligand $\pi \rightarrow \pi^*$ in the UV region, the electronic transition metal to ligand charge transfer (MLCT), and d$\rightarrow$d electronic transitions in the visible region [14-16]. In this circumstance, the electronic spectrum of SiPA-Co$^{II}$-PAR (Fig. 3) show electronic transitions in the visible region ($\lambda_{max} = 505$ nm) which are transitions that generated by electronic transitions of both intra ligand $\pi \rightarrow \pi^*$PAR and $^{1}$MLCT (eg $\rightarrow \delta^*$) overlapping (superimposed) with d$\rightarrow$d transitions. The electronic spectrum of SiPA-Co$^{III}$-PAR shows a very strong MLCT transitions in the visible region. Based on these results, the SiPA-Co$^{II}$-PAR complexes can be used as a photosensitizer of wide band gap inorganic oxides such as TiO$_2$ and ZnO. While PAR as chromophore ligand show a very strong absorption character in visible region. PAR ligand complexes (molar absorptivity $= 3.27 \times 10^4$ M) will be able to produce a colored complexes with highly molar absorptivity.
3.2. Photosensitization process of wide band TiO2 semiconductor

In the case of photosensitizing process, the formation of complex compounds sensitzers in situ by dissolve of APTS, metal ions (CoII and FeII) and PAR as starting point of sensitization process by direct methods through the creation of SiPA-CoII-PAR sensitizer complexes in situ on the TiO2 surface. APTS first attached to the TiO2 surface, forming a bound TiO2-SiPA. CoII ion then was bounded to the surface of TiO2-SiPA generated TiO2-SiPA-CoII; furthermore PAR will bind with TiO2-SiPA-CoII complexes resulted the TiO2-SiPA-CoII-PAR coordination.

Whereas, in other cases, sensitization of TiO2 thin layer on indium tin oxide (ITO) as a substrate through the formation of sensitizer complexes in situ is probable to permit through the reactions as shown in equation 1-3.

\[
\text{ITO/TiO}_2(1) + (\text{MeO})_3-\text{Si-CH}_2\text{CH}_2\text{CH}_2-\text{NH}_2 \rightarrow \text{ITO/TiO}_2=\text{Si-CH}_2\text{CH}_2\text{CH}_2-\text{NH}_2 \quad (1)
\]

\[
\text{ITO/TiO}_2=\text{Si-CH}_2\text{CH}_2\text{CH}_2-\text{NH}_2 + \text{M(II)} \rightarrow \text{ITO/TiO}_2=\text{Si-CH}_2\text{CH}_2\text{CH}_2-\text{NH}_2-\text{M}^{\text{II}} \quad (2)
\]

\[
\text{ITO/TiO}_2=\text{Si-CH}_2\text{CH}_2\text{CH}_2-\text{NH}_2-\text{M}^{\text{II}} + \text{PAR} \rightarrow \text{ITO/TiO}_2=\text{Si-CH}_2\text{CH}_2\text{CH}_2-\text{NH}_2-\text{M}^{\text{II}}-\text{PAR} \quad (3)
\]

**Figure 4.** UV-Vis absorption spectra of (a) TiO2 (b) TiO2/SiPA (c) TiO2/SiPA-CoII-PAR dan (d) TiO2/SiPA-FeII-PAR

The electronic absorption spectra in Figure 4a represents an electronic transition of TiO2 (\(\lambda_{\text{max}}=349\) nm, \(\lambda_g=405\) nm). APTS has not characteristic absorption in the visible region, so that there are not absorption shift to the visible region of TiO2 modified APTS (TiO2-SiPA) (\(\lambda_{\text{max}}=400\) nm) (Figure 4b), while the TiO2-SiPA-CoII-PAR showed the of absorption character in the visible region (\(\lambda_{\text{max}}=500\) nm) (Figure 4c.) as \(\pi\rightarrow\pi^*\) electronic transitions. This is attribute of PAR group transitions and metal-to-ligand charge transfer (1MLCT, eg \(\pi\rightarrow\sigma^*\)) transitions overlapping (superimposed) with d\(\rightarrow\)d transitions from SiPA-CoII-PAR complexes (Figure 4c). The addition of SiPA-FeII-PAR as sensitizer complexes as a comparation study in this case also show new absorption character of sensizied TiO2. The electronic transition at \(\lambda_{\text{max}}=490\) nm is the electronic transitions MLCT whereas electronic transition at 720 nm is a d\(\rightarrow\)d electronic transition of the sensitizer complexes (Figure 4d).
The addition of APTS for surface modification of TiO$_2$ does not alter the crystal structure due to isomorphic substitution or transformation phase. However, analysis result of FTIR spectras show the APTS intake to the TiO$_2$ surfaces (Figure 5).

![FTIR spectra of TiO$_2$ and modified TiO$_2$ at various APTS concentration formed TiO$_2$-SiPA](image)

**Figure 5.** FTIR spectra of TiO$_2$ and modified TiO$_2$ at various APTS concentration formed TiO$_2$-SiPA

![X-Ray difractogram of (a) ITO/TiO$_2$ thin film (b) ITO/TiO$_2$-SiPA. TiO$_2$ was synthesized with molar ratio of TTIP/P123/acac/HCl/H$_2$O/iPr = 1,00:0,051:0,53:1,25: 12,00:30,00, annealed at 400°C at a speed of 5°C/min for 2 hour. A = anatase, R = rutile, (B) = TiO2 (B)](image)

**Figure 6.** X-Ray difractogram of (a) ITO/TiO$_2$ thin film (b) ITO/TiO$_2$-SiPA. TiO$_2$ was synthesized with molar ratio of TTIP/P123/acac/HCl/H$_2$O/iPr = 1,00:0,051:0,53:1,25: 12,00:30,00, annealed at 400°C at a speed of 5°C/min for 2 hour. A = anatase, R = rutile, (B) = TiO2 (B)
Wide-band gap semiconductor of TiO$_2$ show clearly the influence of chromophore dye incorporated in the TiO$_2$ surface. The results of calculations using EDX data show the presence of Co in the range of 0.08% (w/w) in ITO/TiO$_2$/SIPA-Co$^{II}$-PAR have been capable to generate the spectrum shift in the visible region. The related ITO/TiO$_2$/SIPA-Co$^{II}$-PAR thin film have morphology and thickness as shown in Figure 7. The measurement of induced photon to current efficiency of ITO/TiO$_2$/SIPA-Co$^{II}$-PAR in DSSC’s shows good performance of photon to current conversion, which were depended on the wavelength absorbed by those cell (Figure 7). Chromophore group on PAR capable to absorb highly visible light. If we compare those complexes with N719 (di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)ruthenium(II), the intensively light absorption is fall on the different areas. The optimum conditions of SiPA-Co$^{II}$-PAR light absorption are in the 600-750 nm regions.

Figure 7. Micrograph SEM cross section of (a) ITO/TiO$_2$, (b) ITO/TiO$_2$-SIPA-Co$^{II}$-PAR. ITO/TiO$_2$ was annealed at 400°C for 2 hours.

![Figure 7](image)

Figure 8. Normalized IPCE spectra of (a) m-TiO$_2$/SiPA-Co-PAR (b) P25-TiO$_2$/SiPA-Co-PAR. (c) m-TiO$_2$/N719

4. Conclusion
Photosensitizing TiO$_2$ with the piridilazoresorcinolcobalt(II) and piridilazoressorcinoliron(II) complexes formation in situ can improve the visible light response significantly. Improved responsiveness TiO$_2$ to visible light was caused by the presence of photosensitizer indicated by the appearance of the absorption spectra of sensitiser complexes of SIPA-Co$^{II}$-PAR and SIPA-Fe$^{II}$-PAR in the visible region. TiO$_2$ without sensitization only have an electronic transition energy of 3.55 eV
($\lambda_{\text{max}} = 349$ nm) related to the $E_g$ value of 3.25 eV, while TiO$_2$ sensitized by the SIPA-TiO$_2$-Co$^{II}$-PAR corresponded to an electronic transition energy in the visible region of 2.75 eV ($\lambda_{\text{max}} = 505$ nm) and by SIPA-Fe$^{II}$-PAR have electronic transitions energy in the visible region of 2.58 eV ($\lambda_{\text{max}} = 505$ nm) and 1.72 eV ($\lambda_{\text{max}} = 720$ nm), respectively. Generally, chromophore type attached to the TiO$_2$ surface is specifically influence the transition energy character of sensitized TiO$_2$. The IPCE (incident photon to current conversion efficiency) properties of the sensitized TiO$_2$ exhibited the long wavelength absorption character compared to the N719 dye.

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