Enhanced Photovoltaic Performance by Surface Modification of TiO₂ Nanorods with Aminopropyltrimethoxysilane (APTMS)

G Fadillah¹, S Wahyuningsih¹, A H Ramelan²
¹Inorganic Material Research Group, Mathematic and Natural Sciences Faculty, Sebelas Maret University, Indonesia
²Electronic Materials and Energy, Mathematic and Natural Sciences Faculty, Sebelas Maret University, Indonesia
E-mail: sayekti@mipa.uns.ac.id

Abstract. Modification of TiO₂ nanorods through the addition of aminopropyltrimethoxysilane (APTMS) for enhancement of efficiency of solar cells has been studied. Synthesis of TiO₂ nanorods was conducted through two major stages of mechanochemical and hydrothermal refluxing at a temperature of 120 °C for 24 hours on various concentration of NaOH. Material characterizations were performed by X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) and Transmission Electron Microscope (TEM). Mechanochemical treatment by ball milling showed that the TiO₂ phase changed from anatase into brookite and it decreased of TiO₂ crystals size. Morphology transformation of TiO₂ to form TiO₂ nanorods was showed by rod-shaped from TEM micrographs which are characteristic of the nanorods. FTIR spectra confirmed that amine group of aminopropyltrimethoxysilane (APTMS) were successfully grafted onto the TiO₂ nanorods surface. Sensitization of TiO₂ used Ruthenium complexes N3 (N3=cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium (II)) were able to increase the uptake of TiO₂ material to the visible region due to the absorption of visible light by N3 complex -APTMS. Sensitized TiO₂ nanorods were prepared for Dye Sensitized Solar Cell (DSSCs) photoanode. The maximum results of the DSSCs (Dye Sensitized Solar Cell) performance was showed that TiO₂ material modified by 10 % (v/v) APTMS capable increase efficiency of DSSCs.

1. Introduction
TiO₂ material has been widely used than the other inorganic oxide semiconductor because of its stability owned so it can be used up to several cycles. When TiO₂ particle size is reduced to the nanoscale, photovoltaic activity increases as a result of the expansion of light band-gap for quantum size and due to the enhancement of the effective surface area [1]. However, the consequences of the size of nanoscale electrodes is slow electrons movement because of its through a connection between nano particles randomly distributed [2].

In recent years, several studies reported that promising potential of change TiO₂ three-dimensional (3-D) into one-dimensional (1-D) such as nanorods, nanotubes and nanowires have received considerable attention due to their unique properties and novel applications [3, 4]. One of the most important and unique properties of TiO₂ 1-D is that the transfer of electron and holes in semiconducting materials is mainly governed by the quantum confinement phenomenon and transport characteristics related to photons and photons are largely affected by the size and geometrical building of the materials [2, 5]. Besides that, modification of nanostructure TiO₂ into 1-D is able to provide increase surface area of TiO₂ [1]. However, the major problem of application TiO₂ nanorods in
photovoltaics is dye adsorption onto TiO₂ nanorods. Dye adsorption onto TiO₂ is highly challenging due to the lack of chemical bonding between semiconductor TiO₂ and dye [6]. On the other hand, grafting active functional groups onto particle surface can increase the possibility of chemical bonds formation between TiO₂ and dye. Chen and Yakovlev (2010) [7] investigated the adsorption and interaction of organosilanes on TiO₂ nanoparticles and confirmed the bonding of functional groups on particle surface was realized through Si-O-Ti bonds.

In this study, the types of silane coupling agent aminopropyltrimethoxysilane (APTMS) was applied as a particle surface modifier for grafting functional groups onto surface of TiO₂ nanorods. Modification of semiconductor TiO₂ is efforts to increase the effectiveness of photovoltaic semiconductor with the aim of preventing the recombination of electrons (hereinafter abbreviated as e⁻) and holes (hereinafter abbreviated h⁺) to increase the conversion Incident Photon to Current Efficiency (% IPCE). In order to understand the effect of surface modifications on the TiO₂ nanorods photovoltaics activity was investigated.

2. Experimental

2.1. Materials

TiO₂ powder was provided from commercial TiO₂. Aminopropyltrimethoxysilane (APTMS) was purchased from ABCR, Germany. Sodium hydroxide (NaOH) and ethanol was provide by Merck. The material was used as received without any pretreatment.

2.2. Synthesis of TiO₂ nanorods

The ratio of ball :TiO₂ = 20:1 was inserted into a planetary ball milling at the rotation speed of 1000 rpm for 4 hours. 3 g of TiO₂ from the milling process was then added to aqueous NaOH solutions at various concentration of 8, 10 and 12 M. The mixture was then refluxed for 24 hours at a temperature of 120 °C. The mixture was neutralized with 0.1 M HCl until reach pH 7. The mixture was filtered and dried at a temperature of 60 °C for 12 hours and calcined at 400 °C for 2 hours.

2.3. Surface modification of TiO₂ nanorods

0.5 g of TiO₂ nanopowder, was dispersed in 2 ml ethanol to obtain a pasta. Then, the pasta was coated on FTO (Flourine doped Tin Oxide) glass with slip casting method. Then, the silane coupling agents of APTMS with different concentrations (5, 10 and 15%) were added in the thin layer of TiO₂ and allowed for 1 minute. After that, the thin layer of TiO₂ was washed with ethanol and water for at least 2 cycles to remove excessive silanes. The modified particles as thin film FTO/TiO₂-APTMS were dried in an oven at 40 oC for 30 minutes

2.4. Photovoltaics characteristic performance

Thin layer of FTO/TiO₂- APTMS was soaked in a dye solution of N3 Ruthenium complexes (3 x 10⁻⁴ M) for 24 hours. Whereas, a counter electrode was prepared by addition of carbon powder onto FTO glass. Both electrodes were sealed and given a distance to place electrolyte solution. After the electrolyte was inserted, the photoanoda cell was tested by a IV Keithley 2602A measurement by cell illumination cell by a halogen lamp (1000 W/m²).

3. Result and Discussion

3.1. Synthesis of TiO₂ nanorods

A material TiO₂ nanorod has been synthesized from TiO₂ nanoparticle that has been treated ball milling with the rotation speed of 1000 rpm for 4 hours. Figure 1 shows the results of XRD pattern of TiO₂ before and after ball milled treatment. Transformation of the X-ray diffraction pattern (Fig. 1) shows the revolution in anatase phase TiO₂ into brookite phase TiO₂. This mechanochemical technique of TiO₂ preparation has also been carried out by Dutta et al (2002) [8] and Rezaee et al (2011) [9]. Dutta et al (2002) have reported the phase transformation of TiO₂ crystals that can occur through mechanochemical ball milling treatment [8]. Those processes were influenced by the rotational speed and agitation time.
Figure 1. X-ray diffraction pattern of TiO$_2$ (a) before ball milled process (b) after ball milled process

We used ball milled TiO$_2$ to prepare TiO$_2$ NRs. Synthesis of TiO$_2$ NRs has been done by hydrothermal refluxing method at a temperature of 120$^\circ$C using a strong base of NaOH on various concentration of 8, 10, and 12 M for 24 hours. The hydrothermal process can be divided into four stages, e.g 1) the synthesis of nano-TiO$_2$ in an alkaline solution, 2) alkaline hydrolysis through bond disconnection Ti-O-Ti, 3) re-polymerisation by condensation process 4) crystallization growth through annealing process. If TiO$_2$ is reacted with a strong base it will hydrolyse, this is splitting the polymer chains of TiO$_2$ (depolymerization) by the presence of OH$^-$ groups. Depolymerization occurs because the strength of OH$^-$ ions that can break the Ti-O-Ti in the polymer. A result of subsequent alkaline hydrolysis was neutralized by the addition of HCl. At pH 7, it will obtain the most optimal condensation process. Condensation processes are H$_2$O releasing at the two ends of the polymer chain due to polymerization process. The condensation material result was heated at a temperature of 400 $^\circ$C to obtain TiO$_2$ nanorods. TiO$_2$ after calcination at 400 $^\circ$C were characterized using XRD shown in Figure 2. NaOH that used to synthesize TiO$_2$ nanorods influence the TiO$_2$ structure. XRD pattern of TiO$_2$ nanorods (Figure 2) shows that anatase TiO$_2$ phase is as most abundance. Rutile phase TiO$_2$ was increasing when the NaOH was added about 12 M. These results are related to the synthesis results reported by Tsai and Teng (2006) that the nano TiO$_2$ powder can be synthesized from a mixture of rutile and anatase phase at various concentration of NaOH [10].

Physicochemical treatment of TiO$_2$ influence both phase and size of TiO$_2$ crystal. Calculation using Scherrer equation resulted that the ball milled TiO$_2$ composed by anatase TiO$_2$ 54.07 nm in crystal size, and brokite TiO$_2$ 41.19 nm in crystal size. While after hydrothermal refluxing process, the crystal size of TiO$_2$ decrease into 7.65 nm. Gribb and Banfield (1997) have described that tendencious anatase phase transform to more stable phase of rutile if the crystal size extent to about 30 nm [11]. But the brokite phase was rare occur because of lower stability properties. Brokite phase in most case will develop at annealed in a range temperature of 200 - 500 $^\circ$C [12]. TiO$_2$ annealed at a higher than 500 $^\circ$C shows the lower anatase as well as brokite content, finally no found both of them at annealed result at more higher than 800 $^\circ$C [13].
Representative transmission electron microscopy (TEM) images of treated TiO$_2$ under NaOH solution are provided in Figure 3. An overview of the nanorods at low magnification in Figure 3c shows that the sample almost exclusively contains nanorods with an average length of 80 nm and diameters of 50 nm. But in the lower NaOH concentrations (Figure 3a and Figure 3b) 1D nanorods not appear.

Figure 3. TEM micrographs of the TiO$_2$ treated using NaOH solution of (a) 8 M, (b) 10 M, dan (c) 12 M.

TiO$_2$ preparation results using NaOH 10 M, showed flaking 3D structure, then has formed TiO$_2$ 2D structure (Figure 3b). We further discovered 1D structure of TiO$_2$ in preparation results using NaOH 12 M. Structural transformation of the ball milled TiO$_2$ to 1D TiO$_2$ nanorods was characterized from pore size distribution data. 1D TiO$_2$ nanorods have an average surface area 79 m$^2$/g, but ball milled TiO$_2$ only have it about 7.56 m$^2$/g. It was concluded that structural transformation to 1D nanorods capable increase surface area. Increasing of surface area will be increase dye adsorption onto TiO$_2$ surface. It will gain good performa for dye sensitized TiO$_2$ photoanode.

3.2. Modified of TiO$_2$ nanorods
The modification process of APTMS on the TiO$_2$ nanorods surface is illustrated in Figure 4(2). Different concentrations of silane coupling agents to TiO$_2$ have a significant influence on FTIR spectra. As can be seen in Figure 4, the transmission FTIR spectra of TiO$_2$, TiO$_2$-APTMS 5%, TiO$_2$-APTMS 10%, and TiO$_2$-APTMS 15% were shown. From spectra of TiO$_2$-APTMS the peaks below 700 cm$^{-1}$, which were assigned to Ti-O and Ti-O-Ti bonding of titania were ignored in this case because of their over saturated absorption [7]. The stretching vibration of absorbed water as well as surface hydroxyl groups (OH) which presented in the TiO$_2$ were confirmed by the broad absorption band between 3400 and 3200 cm$^{-1}$ and the low intensity peak at 1640 cm$^{-1}$ [7]. After surface
modification by APTMS, as presented in spectra of TiO$_2$-APTMS 5 %, TiO$_2$-APTMS 10 %, and TiO$_2$-APTMS 15 %, the asymmetrical and symmetrical stretching vibration of the C-H bond in methylene group were observed at 2928 and 2870 cm$^{-1}$ [14]. Furthermore, the peak corresponding to Si-O-Si bond was observed at around 1040 cm$^{-1}$ indicating the condensation reaction between silanol groups. The N-H bending vibration of primary amines (-NH$_2$) was observed as a broad band in the region 1605–1560 cm$^{-1}$, and another low intensity peak on the shoulder of titania peak at 1140 cm$^{-1}$ was assigned to the C-N bond. The appearance of these bands demonstrated that amine functional groups in organosilane were grafted onto the modified surface.

![FTIR spectra](image)

**Figure 4.** (1) FTIR spectra for (a) TiO$_2$ (b) TiO$_2$-APTMS 5 % (c) TiO$_2$-APTMS 10 % (d) TiO$_2$-APTMS 15% ; (2) Illustration of surface modification TiO$_2$ by APTMS

3.3. **Photoelectrochemical solar cells perform of modified TiO$_2$ NRs**

Modification of surface TiO$_2$ nanorods with APTMS was able to increase adsorption N3 complexes. APTMS has a amine group with a lone pair electrons which is caused the chemical bond between TiO$_2$ and N3 complexes more easy. Amount of the dyes was higher adsorbing onto modified TiO$_2$ compared with it onto unmodified TiO$_2$ NRs.

Figure 5 shows the current density-voltage curves of the dye sensitized solar cells based on the TiO$_2$ nanorods without modification and TiO$_2$ with modification on various concentration of APTMS (5,10 and 15 % (v/v)) composites. The values of short-circuit current density (J$_{sc}$), open-circuit voltage (V$_{oc}$) and overall power conversion efficiency (η) are summarized in Table 1.

**Table 1.** Performance of dye sensitized solar cell using unmodified and modified TiO$_2$ NRs thin film photoanodes

| Sample           | V$_{oc}$ (Volt) | I$_{sc}$ (mA) | P$_{max}$ (mW) | Efficiency, η (%) |
|------------------|-----------------|---------------|----------------|--------------------|
| TiO$_2$          | 0,000009        | 0,00004       | 0,0046         | 0,0023             |
| TiO$_2$-APTMS 5 %| 0,199           | 0,016         | 0,750          | 0,370              |
| TiO$_2$-APTMS 10 %| 0,400           | 0,015         | 2,260          | 1,130              |
| TiO$_2$-APTMS 15 %| 0,555           | 0,005         | 0,960          | 0,480              |
Figure 5. Current density-voltage curves of the dye sensitized solar cells based on the TiO$_2$ nanorods with modification of APTMS 10%.

Overall, photovoltaic performance test was showed that modification of TiO$_2$ nanorods can increase efficiency of solar cell. However, modification of APTMS on concentration 15% doesn’t provide optimum efficiency. Modification of high concentration was likely to occur polymerization from APTMS, which the polymerization will increase the resistivity of material [15]. Polymerization was triggered by bond formation at the end of the chain, it is causing hole recombination and the efficiency will be lower [16].

4. Conclusion
In this study, the effect of surface modification TiO$_2$ nanorods with silane coupling agent (APTMS) was investigated. The characterization using TEM and FTIR confirmed that surface modification has been successfully grafted onto TiO$_2$ surface through Ti-O-Si chemical bonds. By the modification of APTMS 10% (v/v) on the surface TiO$_2$ nanorods have been capable improved cell performance which was efficiency of 1.13%.

References
[1] Karimi L, Mirjalili M, Yazdanshenas M E and Nazari A 2010 Photochem. Photobiol. 86 1030 – 1037
[2] Mohamed A L R and Rohani S 2011 Energy and Envirotmental Science 4 1065
[3] Pan Z W, Dai Z R and Wang Z L 2001 Science 291 1947 – 1949
[4] Patzke G R, Krumeich F and Nesper R 2002 Oxidic Nanotubes and Nanorods-Anisotropic Modules For a Future Nanotechnology (Switzerland : Angew Chem. Int.)
[5] Wang Y Q, Hu G Q, Duan X F, Sun H L and Xue Q K 2002 Chemical Physics Letters. 365 427 – 431
[6] Sojka-Ledakowicz J, Lewartowska J, Kudzin M, Leonowicz M, Jesionowski T, Siwinska-Stefanska K and Krystaftkiewicz A 2009 J. Mater. Sci. 44 3852 - 3860
[7] Chen Q and Yakovlev N L 2010 Appl. Surf. Sci. 257 1395 – 1400
[8] Dutta H, Sahu P, Pardhan S K and De M 2002 Material Chemistry and Physics 77 153 - 164
[9] Rezaee M, Khoie S M M and Liu K H 2011 Cryst Eng Comm 13 5055 – 5061
[10] Tsai C C and Teng H 2006 Chem. Mater 18 367 – 373
[11] Bakardjieva S, Stengl V, Szatmary L, Subrt J, Lukac J, Murafa N, Niznansky D, Cizek K, Jirkovsky J and Petrova N 2006 J. Mater. Chem 16 1709 - 1716
[12] Wahyuningsih S , Fadilah G, Hidayat R and Ramelan AH 2016 Procedia Chemistry 19 632-637
[13] Ukaji E, Furusawa T, Sato M and Suzuki N 2007 Appl. Surf. Sci. 254 563 – 569
[14] Ogasawara T, Yoshino A, Okabayashi H and O’Connor C J 2001 Colloids and Surfaces A: Physicochem. Eng. Aspects 180 317 - 322
[15] Zhao J, Milanova M and Marijn M C G 2012 Colloids and Surfaces A: Physicochem. Eng. Aspects. 413 273 - 279