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PHOTOELECTROCHEMICAL ANALYSIS OF TITANIUM DIOXIDE BY USING OXALIC ACID AS A SACRIFICIAL DONOR

Siti Nur Hidayah Jaafar[a], Lorna Jeffery Minggu[a]*, Khuzaimah Arifin[a], Mohammad Kassim[a,b], Wan Ramli Wan Daud[a,c]

[a]Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
[b]School of Chemical Sciences & Food Technology, Faculty of Science & Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
[c]Department of Chemical & Process Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

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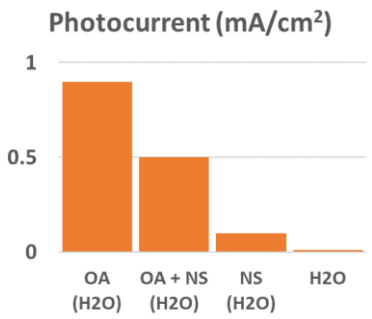
*Corresponding author
lorna_jm@ukm.edu.my

Graphical abstract



Saturation photocurrent at 0.5V
OA – Oxalic Acid
NS – Na_2SO_4

Abstract

Photoelectrochemical (PEC) water splitting is a very promising green method to produce solar fuel. Titanium dioxide (TiO_2) has been widely used as photocatalyst for this type of reaction. Improving the performance of TiO_2 for PEC water splitting has been ongoing and addition of sacrificial donor especially from waste is an attractive option to achieve this. Oxalic acid is one component in organic waste stream that can be used as sacrificial donor. The TiO_2 thin films has been fabricated by coating TiO_2 paste on Fluorine Tin oxide (FTO) glass surface. The morphology of the TiO_2 thin films were porous and rough with uniform particles size with crystallite size of about 20 nm and dominant anatase peak. The TiO_2 photoelectrode undergo PEC testing to measure its photolectroactivity by using oxalic acid as a sacrificial donor in two different type of electrolytes which are distilled water and sodium sulfate (NA_2SO_4) aqueous solution. The photocurrent produced without addition of oxalic acid is much lower than with the acid. The saturation photocurrent for aqueous NA_2SO_4 solution and water electrolyte is 0.1 mA/cm^2 and negligible respectively. While the photocurrent for addition of oxalic acid in NA_2SO_4 aqueous solution is 0.5 mA/cm^2 and the photocurrent for oxalic acid in water only is 0.9 mA/cm^2, which is almost double compared to in NA_2SO_4 and tenfold in water only. The highest photocurrent produced by TiO_2 photoelectrode is by addition of oxalic acid in aqueous (H_2O) electrolyte.

Keywords: Water splitting, photoelectrochemical cell, titanium dioxide, oxalic acid, donor

1.0 INTRODUCTION

The development of renewable and sustainable energy via conversion of solar energy have received a lot of attention especially by photoelectrochemical (PEC) water splitting to generate hydrogen gas as an energy carrier [1,2]. Metal oxide semiconductor materials were commonly used in PEC water splitting due to its potential to cleanly produce hydrogen gas from water with oxygen gas as its only byproduct using sunlight. When a semiconductor electrode is irradiated with photons energy (hv) equal to or larger than the semiconductor band gap the result is formation of electronic charge carriers, electrons in the conduction band and holes in the valence band as shown in equations below [3].

$$2hv + \text{Semiconductor} \rightarrow 2h^{\bullet} + 2e^{-} \qquad (1)$$

$$2h^{\bullet} + H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^{+} \qquad (2)$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad (3)$$

A lot of research have been done to study PEC reaction by using metal oxide semiconductor such as TiO_2, ZnO, and WO_3 [4]. TiO_2 is the most promising material used as photoanodes for its photochemical stability, low cost, non-toxic and great chemical and thermal properties [5, 6]. Besides that, the anatase crystalline phase of TiO_2 also have high phocatalytic activities and easily prepared in variety of range of shapes and sizes [7]. However, the efficiency of TiO_2 is influenced by several factors, such as [8, 9]:

(i) Light absorption properties: The wide band gap of TiO_2 (3.2eV) can only absorb UV light for hydrogen production which is only about 4% of solar radiation energy.
(ii) Rate of electron-hole pair recombination: Electrons in conduction band can recombine with the holes in valence band in the very fast rate and released energy.
(iii) Fast backwards reactions: Recombination of hydrogen and oxygen to produce water is easily occurred as process of water decomposition required energy.

Thus, continuous efforts have been made in order to get higher performance of TiO_2 for PEC water splitting. One of them is the addition of sacrificial electron donor to reduce recombination rate of electron-hole pairs and prevent reversible reaction of hydrogen and oxygen [10]. However, some sacrificial agents are expensive thus organic waste and water pollutants containing organic such as oxalic acid is more attractive to be used in PEC system. Recently, Tao *et al*. reported the DFT study of adsorption and oxidation of oxalic acid on the reactive anatase of TiO_2 [11]. Meanwhile, Sawsan *et al*. 2014 [12] carried out the study to improve the photogalvanic cell by using twin system of oxalic acid-rose bengal. Oxalic acid is also used in wastewater treatment study by PEC degradation of organic contaminants using TiO_2 as a catalyst [13]. Therefore, in this research, the focus is more into oxalic acid as a sacrificial electron donor in the electrolyte since it is a waste water pollutant from industries and also due to its strong reductive properties.

2.0 METHODOLOGY

2.1 Materials

Materials used were TiO_2 (P25 Degussa), Fluorine-doped Tin oxide coated conductive glass, FTO (Asahi Co), ethanol (Merck), acetone (Sigma Aldrich), sodium sulfate (Na_2SO_4, Sigma Aldrich) and Oxalic Acid (99%, Merck). The Na_2SO_4 aqueous solutions was prepared in the laboratory using double distilled water.

2.2 Preparation of TiO_2 Thin Films

FTO glass were cleaned in acetone and ethanol for five minutes respectively for each solvent through sonification. After cleaned, FTO glass was rinsed by using distilled water then allowed to dry in air at room temperature. Meanwhile, titanium oxide paste was prepared with 1 gram of TiO_2 nanoparticles powder mixed homogenously in 3 ml of double distilled water [14]. A Scotch tape at four sides was used as masking material on the conductive layer of FTO to restrict the thickness and area of the paste. A thin layer of TiO_2 paste was coated using glass plate on exposed FTO area via doctor blade technique [15]. It was then sintered in the furnace at 450°C for two hours with constant heating rate of 5 °C/min and then let cooled to room temperature.

2.3 Characterization

The morphology, particle size and thickness of the TiO_2 thin films were observed with scanning electron microscope, SEM (Zeiss AM10) from its surface and cross-sectional images. Next, the crystalline phase of TiO_2 were determined using X-ray diffraction measurement, XRD (Bruker D8 Advance diffractometer) with CuKa radiation while the crystals size can be determined by using Scherrer equation (Scherrer 1918):

$$D = \frac{K\lambda}{\beta \,\mathrm{kos}\, \theta} \qquad (4)$$

where K is the crystal shape factor (0.9), λ is the wavelength of x-ray (CuKa1 = 0.15406 nm), β is full width at half the maximum intensity (rad) and Θ is diffraction angle.

The light absorption of TiO_2 thin films were measured by UV-Vis spectrophotometer (PerkinElmer Lambda 35). Light absorption of thin films can be calculated using following equation:

$$T = e^{-ad} \qquad (5)$$

where T is normalised transmittance, a is the absorption coefficient, *d* is the thickness of the film (cm). Besides that, the optical absorption coefficient is corresponding to the energy band gap (E_g) determined by using the Tauc formula:

$$Ahv = B(hv - E_g)^n \qquad (6)$$

where A is absorption coefficient, B is a constant; E_g is optical band gap energy of the film and n is the exponent. For crystalline semiconductors, n is ½, 3/2, 2, and 3 when the transition is direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively.

2.4 Photoelectrochemical Measurement

For the photoelectrochemical analysis, TiO_2 photoelectrodes were prepared by assembling TiO_2 thin films on FTO glass with copper wire based on previous method [16]. The electrochemical cell set-up with an optical window was used for the photoelectrochemical analysis which included an Ametek Versastat 4 with 100 $mWcm^{-2}$ Xenon full arc lamp as light source, a platinum electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and a TiO_2 photoelectrode fabricated earlier as the working electrode. In this test, there are two types of electrolyte used which are double distilled water and 0.5M sodium sulfate (Na_2SO_4) aqueous solution. Then, oxalic acid with concentration of 0.002M was added to both electrolytes. All the solutions prepared were deaerated by purging with high purity nitrogen gas for 30 minutes before the test. For the analysis, the potential was set between -0.5V to 1.0 V at the scan rate of 0.05 V/s. All the measurements were performed under room temperature (25°C).

3.0 RESULTS AND DISCUSSION

3.1 Morphological Analysis

Figure 1 shows the morphology by scanning electron microscopic (SEM) image of the TiO_2 thin film. From the Figure 1(a), it shows that the surface of TiO_2 thin film is rough and porous with good uniformity. The particle size of TiO_2 is composed of small nanoparticles and almost homogenous in shape. The particles size of TiO_2 is about 40 nm which is slightly large due to agglomeration compared to the crytalite size obtained from XRD below [14,17,18]. Figure 1(b) show the cross-sectional image of TiO_2 thin film deposited onto the FTO glass. The single-layer TiO_2 film were approximately 7 µm thick where there is clear boundary between FTO and TiO_2 layers. Particle size of TiO_2 can enfluence the performance of solar cell where films with larger particles posses greater contact points at interface between particles and underlying substrate or at between sintered colloidal TiO_2 particles [17].

3.2 Crystalline Phase of Thin Film

Figure 2 shows the XRD pattern of TiO_2 nanoparticles contained crystallized phase with the presence of sharp and high intensity peaks. There are three different peaks observed which are anatase, rutile and SnO_2 after been calcined at 450°C for 2 hours. The major crystalline phase of TiO_2 are anatase and rutile where anatase have higher photoactivity while rutile generally does not give any photocatalytic reaction in aqueous medium [19]. Meanwhile, the presence of SnO_2 peak in the TiO_2 thin film is due to the FTO glass.

The anatase peaks are detected at 25.43°, 48.15° and 54.70° corresponding to the plane (101), (200) and (105) respectively which matched the standard XRD pattern file no. 03-065-5714. The rutile peak appears at 27.55° at plane (110) and has lower intensity than anatase as reported by previous study using TiO_2 P25 Degussa [20]. From the Scherrer equation (refer Eqn. 4) the crystal size of TiO_2 is about 20 nm which is similar to previous report [21]. The intensity of SnO_2 peak is reduced due to the overlaying TiO_2 thin film. However, there is no peak shift which means that TiO_2 thin film only formed on the surface of FTO without incorporation into the SnO_2 lattice [22].

3.3 Light Absorption and Band Gap

UV-Vis spectrum in Figure 3 shows that TiO_2 thin film absorbs light in ultra-violet (UV) range where the maximum absorption is at 375 nm wavelength which mean it is transparent to light more than 400 nm wavelength and did not absorb visible light. The band gap of TiO_2 thin film can be determined using Tauc formula (refer Eqn. 6) by plotting graph $(-\text{In}T)^{1/2}$ versus band gap (hv) as shown in Figure 3. In this work, the TiO_2 thin film has band gap of 3.50 eV which is close to values reported earlier [23, 14].

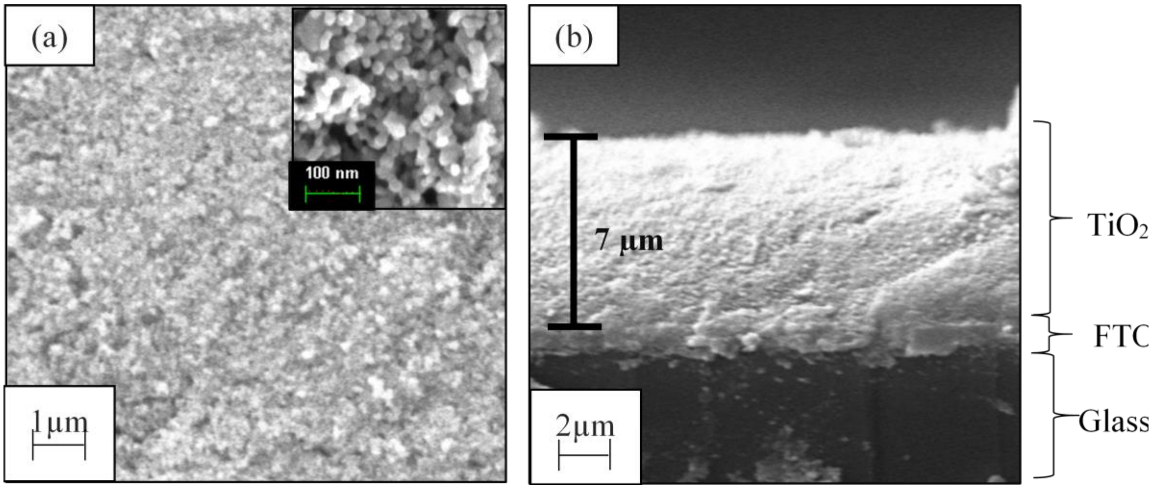


Figure 1. SEM images of the TiO_2 thin film (a) surface and (b) cross-sectional respectively. Inset image in (a) is 50kx magnification

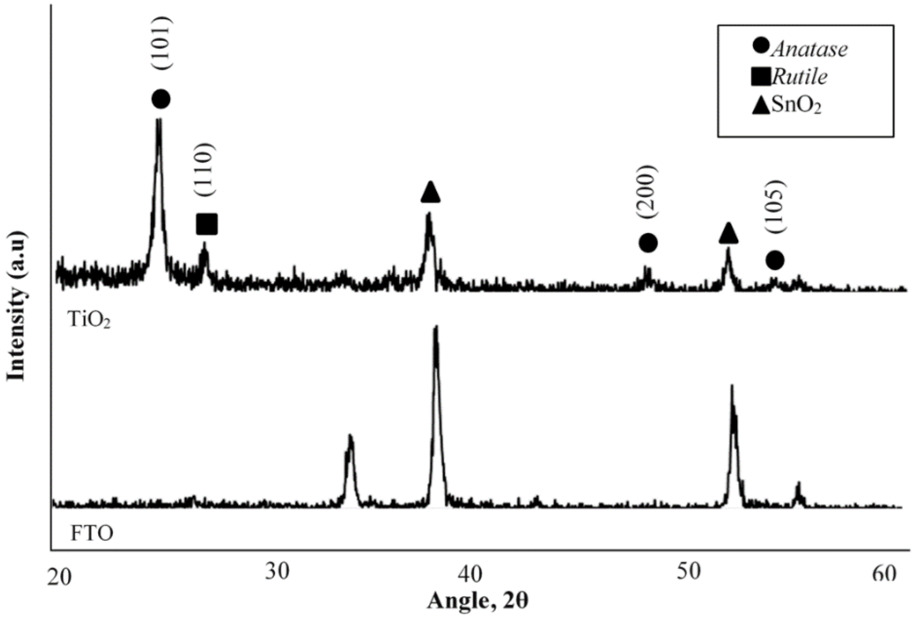


Figure 2 XRD diffraction pattern for TiO_2 thin film

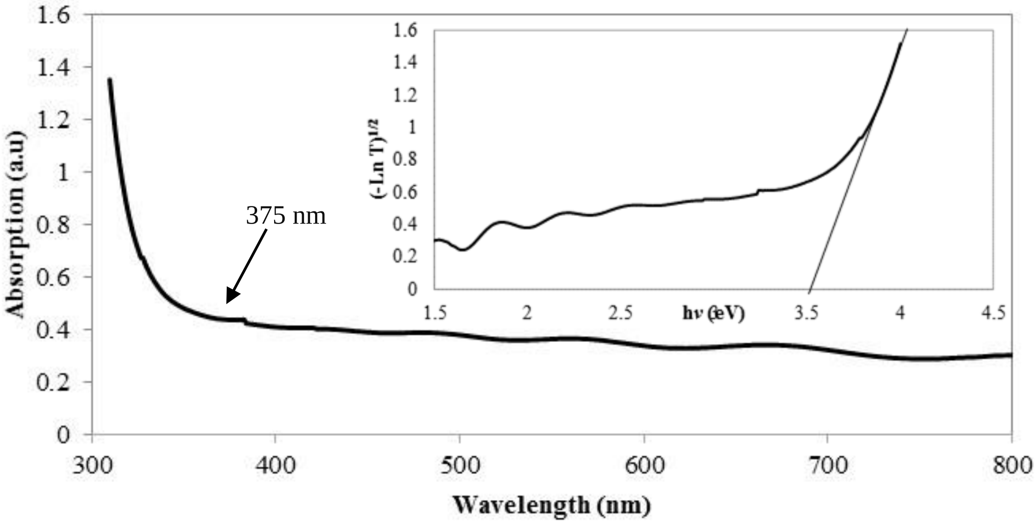


Figure 3 UV-Vis spectrum for TiO_2 thin film. Inset-determination of band gap for TiO_2 thin film

3.4 Photoelectrochemical Analysis

Photocurrent density was measured in two different electrolytes which are distilled water (H_2O) and 0.5M sodium sulfate (Na_2SO_4) aqueous solution with and without addition of 0.002M oxalic acid as sacrificial donor. The response of photocurrent density of TiO_2 photoelectrode were shown in Figure 4. The lowest photocurrent density is in the water electrolyte as expected which is 0.04 mA/cm^2. Whereas photocurrent in electrolyte with Na_2SO_4 only is second lowest at 0.15 mA/cm^2. Water is known as poor electrolyte due to its poor ionic conductivity thus presents a high Ohmic over potential. Conversely, electrolyte containing Na_2SO_4 possess low electrical resistance because of its high ionic concentrations and mobility thus increased the photocurrent [3].

The addition of oxalic acid into both water and Na_2SO_4 electrolytes have enhanced the photocurrent generation. However, addition of oxalic acid into water only gives higher photocurrent (0.93 mA/cm^2) compared to addition of oxalic acid into Na_2SO_4 solution (0.52 mA/cm^2). The photocurrent obtained by addition of oxalic acid in water electrolyte is close to the photocurrent reported by An *et al*. 2006 [24] for photoelectrocatalytic reactor degradation of oxalic acid. Inorganic anion such as SO_4^- compete for TiO_2 active site and can block the sites for oxalic acid degradation [25]. Hence oxalic acid in water only without Na_2SO_4 has higher photocurrent. Oxalic acid is an efficient electron donor to promote the reaction effectively during the degradation process.

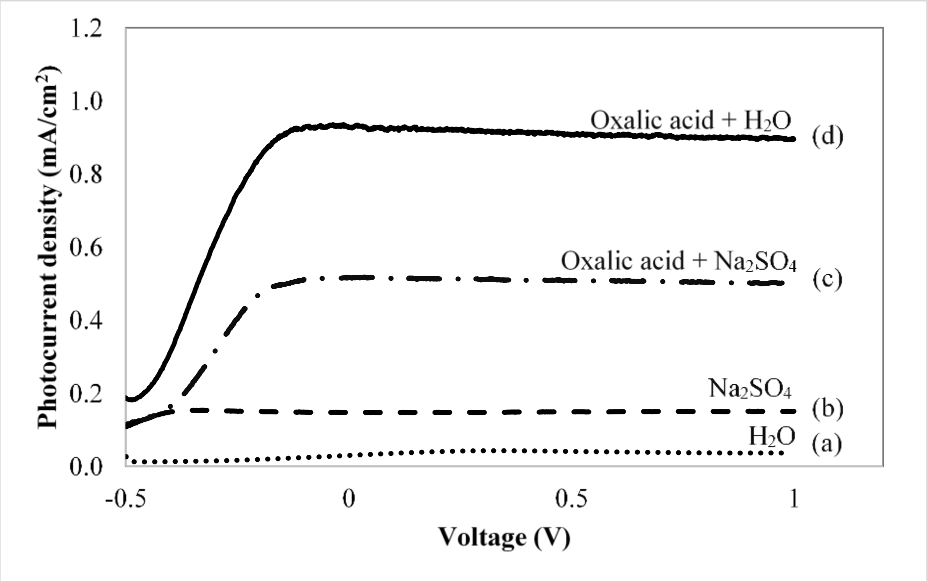


Figure 4 Photocurrent density of TiO_2 photoelectrodes with/without oxalic acid as a sacrificial donor in two different electrolytes; (a) & (d): distilled water and (b) & (c): 0.5M Na_2SO_4 aqueous solution

Oxalic acid can decompose photocatically on TiO_2 and has been reported in studies using suspended TiO_2 particles/colloid and immobilized TiO_2 particles without electrochemical cell. The reaction is started by the photoexcitation of electrons in TiO_2 particles, which formed the electron–hole pairs. Photogenerated holes are either captured by adsorbed OH^- ions/water and generating adsorbed OH radicals [26]. Other than that, it can also be filled by the electron donors from oxalic acid and surface hydroxyl groups on TiO_2. Oxalic acid can produce more than one species during photocatalytic degradation through oxidation as shown in the equations below [27]:

$$C_2H_2O_4+\frac{1}{2}O_2 \xrightarrow{hv,\ TiO_2} 2CO_2+H_2O$$

$$C_2HO_4^-+\frac{1}{2}O_2 \xrightarrow{hv,\ TiO_2} 2CO_2+OH^-$$

$$C_2O_4^-+\frac{1}{2}O_2+H_2O \xrightarrow{hv,\ TiO_2} 2CO_2+2OH^-$$

Furthermore, oxalic acid also is a bidentate ligand which forms a chelate on TiO_2 thin film, hence oxalic acid can be more strongly adsorbed on TiO_2 rather than SO_4^- ions. It is also a strong reductive electron donor, and can be irreversibly combined with photogenerated holes or the resulting hydroxyl radicals OH [10]. This indicates that under the same illumination with the same bias potential, more photoexcited electrons on the TiO_2 electrode transfer to the platinum cathode thus leaving more photogenerated holes involved in the oxidation reaction when using distilled water compared to Na_2SO_4 solution. Thus the photocurrent is improved by 10 folds with addition of oxalic acid in the electrolyte.

4.0 CONCLUSION

From this work, the fabrication of TiO_2 as photoelectrode in PEC system has been done and characterized through SEM, XRD and UV-Vis analyses. The particle size of TiO_2 thin film is about 40 nm and thickness is 7μm. The TiO_2 thin film exhibit a good degree of crystallinity with band gap of 3.5 eV. The addition of oxalic acid as sacrificial donor has increased the photocurrent produced in photoelectrochemical analysis. The photoelectrochemical degradation of oxalic acid in water electrolyte produced higher photocurrent compared to Na_2SO_4 electrolyte.

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