Enhancing the efficiency of dye-sensitized solar cells by hydrothermal post-treatment in acidic environment

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Abstract. Dye-sensitized solar cell (DSSC) have been extensively studied due to its low production cost and simple production process. In this research, DSSC with improved performance is acquired by modification of TiO$_2$ layer through hydrothermal post-treatment with different hydrochloric acid (HCl) concentrations to obtain various particles and pore sizes. Qualitative and quantitative characterizations of the TiO$_2$ film were conducted using thickness measurement, scanning electron microscope (SEM), and X-ray diffraction (XRD), while the solar cell performances were characterized using current-voltage (I-V) measurement under 0.5 Sun. When hydrothermally treated with 1 mol/L HCl at 180 °C for 3 h, the DSSC showed the most optimum photo-electricity conversion performance of 3.60%, which improved the efficiency of the non-treated DSSC by a factor of 1.2. As the HCl concentration increased, the treated TiO$_2$ film became thinner with smaller particle size and denser structure. It was suspected that the modification in the TiO$_2$ film morphology has led to better light absorption, which consequently resulted in the improvement of DSSC performance.

1. Introduction

Since its first invention by Grätzel and coworkers in 1991, power conversion efficiency of DSSC up to 12% has been reported, using co-sensitizer of carboxy-anchor organic dye of LEG4 as the collaborative sensitizer to the silyl-anchor dye of ADEKA-1[1]. Typically, DSSC is a sandwich structure of photo anode with dye-sensitizer adsorbed on its surface, iodine based redox-coupled electrolyte and a counter electrode. The entire assembly is embedded between two conducting glass supports.

The photo anode is a key component of DSSCs that plays important roles in dye loading, electron injection, transportation and collection, and thus has significant influence on the photocurrent, photo voltage and the power conversion efficiency [2]. The photo anode materials should meet several conditions: first, the semiconductor bandgap must match with the dye energy level to ensure an effective injection of the photo-generated electrons from the dyes to the semiconductor; second, it must have a high surface area to adsorb more dye molecules, so that more photon from the solar energy can be harvested; third, the porosity of the film must be high enough to ensure infiltration of electrolyte into the interior of the film and form a good contact between them; fourth, the electron
mobility of the semiconductor should be high enough to transport the injected electrons quickly to the outer circuit.

Among numerous material candidates for photo anode, titanium dioxide (TiO₂) is a typical material used as the photoelectrode in DSSC. TiO₂ has wide band gap (~3.2 eV), high energy level at that match with the energy level of Ru-based dye, and good chemical stability [3]. Nanoparticle and microporous TiO₂ are expected to have high surface area for better dye particles adsorption [4]. However, smaller pore size may lead to poor electrolyte infiltration [5]. It is also reported that high porosity of TiO₂ may lead to complex electron transport pathways, hence decreasing the electron transport rate [4, 6].

Many techniques have been developed to synthesize suitable porous TiO₂ structure for obtaining better efficiency in DSSC. Various particle sizes, pore size distributions and crystallinity can be achieved by different TiO₂ growing technique or structure modification. Hydrothermal process has been widely used to produce nanostructured TiO₂. Hydrothermal treatment could improve the crystallinity of a powder at relatively low temperature [7]. Hydrothermal can also be used as post treatment to modify TiO₂ structure after fabrication. Water vapor exposure in the post-hydrothermal treatment can successfully enhance the nano-crystallinity of TiO₂ produced from sol-gel method [8]. Hydrothermally prepared TiO₂ films that were treated by hydrochloric acid (HCl) via hydrothermal method was reported to reform the nanostructure of TiO₂ and improve the efficiency of DSSC by 18% from the initial non-treated condition [9]. It has been demonstrated that the electron recombination between conduction band and I² in the electrolyte was reduced and electron injection efficiency was increased when the nano-porous TiO₂ film was modified with 0.1 M hydrochloric acid compared to other acid [10]. Nevertheless, effect of hydrothermal post-treatment in acidic environment for commercial TiO₂ paste with anatase phase has never been discussed. In this research, different hydrochloric acid (HCl) concentrations were used in hydrothermal post-treatment to obtain various particles and pore sizes of TiO₂.

2. Experiment

2.1. TiO₂ photoelectrode preparation
Precut (2 × 2 cm²) fluorine-doped tin oxide (FTO) coated glass TEC™ 15 (15 Ω/sq, Dyesol) were used as substrate. The FTO glasses were cleaned with Teepol, water, and ethanol by ultrasonic cleaning, respectively. The cleaned FTO glasses were immersed in 40 mmol L⁻¹ TiCl₄ solution at 70 °C for 30 min followed by sintering process at 450 °C for 15 min. TiO₂ films were prepared by screen printing of the TiO₂ commercial paste (DSL 18 NR-AO opaque titanium paste, Dyesol) onto the pre-treatment FTO glass in size of 0.5 × 0.5 cm² and 8 µm thickness. After drying, the films were sintered at 500 °C for 45 min.

The prepared TiO₂ photoelectrodes were placed against the inside wall of teflon-liner hydrothermal chamber with the TiO₂ film facing down. The electrodes were immersed in different concentrations of hydrochloric acid, 0.5 mol L⁻¹, 1 mol L⁻¹, 2 mol L⁻¹, and 4 mol L⁻¹. The chamber was put in an electric oven for 3 hours at 180 °C. The samples were taken out when the temperature down to ± 25 °C, dried in the ambient air, and subsequently sintered at 500 °C for 45 min.

2.2. DSSC fabrication
The post-treatment TiO₂ electrodes were put into dye solution of Z-907 (cis-Bis(isothiocyanato)(2,2’-bipyridyl-4,4’-dicarboxylato)(4,4’-di-nonyl-2’-bipyridyl) ruthenium(II), Dyesol) dissolving in ethanol, and kept for 24 hours at room temperature. The films were further rinsed with ethanol and dried in the air. Counter electrodes were prepared using DC magnetron sputtering on pre-cut 2x2 cm² of FTO coated glass TEC™ 15 (15 Ω/sq, Dyesol). The DSSC was fabricated by sandwiching the working and counter electrodes. Thermoplastic Surlyn (50 µm thickness, Dyesol) was used as spacer between the electrodes. The I/I⁺ based liquid electrolyte (Dyesol, EL-HSE) was added into the gap between the electrodes by an injector.
2.3. Characterizations

Film thickness was measured with digital thickness measurer Mitutoyo, Model ID-C112B. The field emission scanning electron microscopy (FE-SEM) was performed on a STEM JEOL JB-4610F using 15 kV beam to characterize the morphology, size and the structure of TiO$_2$. The phase purity and crystallite structure of TiO$_2$ samples were characterized by X-ray diffraction (XRD) on Rigaku, RINT 2200 VK/PC diffractometer and radiation of copper Kα ($\lambda=1.54056$ Å), 40 kV 30 mA. The crystallite sizes of TiO$_2$ nanoparticles were estimated using Scherrer’s equation [11]:

$$L = \frac{0.9}{B \cos \theta}$$

where $L$ is the average crystallite size, $\lambda$ is the X-ray wavelength, $B$ is the full-width at half maximum (FWHM) in radians and $\theta$ is the Bragg’s angle. The photocurrent-voltage (I-V) characteristics were measured with National instrumet I-V measurement system under simulated AM 1.5 illumination with constant light intensity of 500 W/m$^2$ provided by a solar light simulator (Oriel, Model: 91192). The size of the active area of the cells used for this measurement was 0.25 cm$^2$.

3. Results and discussion

3.1. Morphology analysis of TiO$_2$ film

The thickness of TiO$_2$ film as the result of hydrothermal treatment were 5.0±1.1 µm for sample with 0.5 M HCl treatment, 3.7±0.9 µm for 1 M HCl, 1.9±0.6 µm for 2 M HCl, and 1.1±0.3 µm for 4 M HCl, while sample without hydrothermal post treatment had thickness of 5.0±1.1 µm. The thickness of the film decreased when the HCl concentration increased. TiO$_2$ is known as chemically stable, even in acidic environment [12]. However, hydrothermal treatment in high pressure and temperature had caused TiO$_2$ particles to dissolve in HCl solution and reduced the thickness of the film. Higher concentration of HCl had a greater effect in dissolution of TiO$_2$ particles, which resulted in TiO$_2$ film that was treated with 4 M HCl having the lowest thickness.

The acidic environment also induced some changes in the film morphology. The transformation of the TiO$_2$ films morphology as the result of hydrothermal post-treatment was observed in SEM images in figure 1. With the increase in the HCl molar concentration, the particles started to agglomerate and stick to each other so the film become denser with smaller gap between the particles. However, the particle size was smaller and distributed evenly when the acid concentration increased. The particle size was 38.9±9.6 nm for the control sample and it was reduced for hydrothermal treated sample, i.e. 35.0±6.7 nm, 34.9±6.6 µm, 75.9±23.9 µm, and 34.0±5.1 µm for 0.5 M, 1 M, 2 M, and 4 M samples, respectively.

Figure 1. SEM images showing the surface morphology of (a) control sample and samples with hydrothermal post-treatment in HCl with a concentration of (b) 0.5 M, (c) 1 M, (d) 2 M, (e) 4 M.
Better photovoltaic performance is normally obtained for anatase TiO$_2$ compared to the rutile structure as the result of higher dye adsorption and faster electron transport rate [13]. XRD analysis was carried out to study the crystallinity of the TiO$_2$ film (figure 2). The diffraction peaks of the TiO$_2$ nanoparticles on FTO glass matched with the anatase phase (ICSD 98-015-4604), while the other peaks come from tin oxide glass substrate match with ICSD 98-009-1517 for SnO$_2$. No other phases of TiO$_2$ were observed, suggesting that the hydrothermal post-treatment have no effect on the phase of TiO$_2$ crystal.

![Figure 2. XRD patterns of TiO$_2$ films sample.](image)

Hydrothermal post-treatment in acidic environment also caused the increase in the grain size of TiO$_2$. The estimated crystallite diameter from observed XRD pattern (figure 2) were 283.32 Å, 286.62 Å, 292.67 Å, 334.07 Å, and 341.66 Å for control, 0.5 M, 1 M, 2 M, and 4 M samples, respectively. Bigger crystallite size was observed when the HCl concentration was increased. The growth of grain size for synthesizing TiO$_2$ using hydrothermal method in acidic environment had also been reported [11]. Even though the particle size was smaller at higher acid concentrations, the crystallite size was increased. TiO$_2$ typically has a great chemical stability. However, when hydrothermally treated with high pressure and temperature, it was possible for TiO$_2$ particles to be slightly dissolved and reformed with bigger crystallite structure [14]. The acidic condition may also induce the grinding of the particles surface, hence the diameter of TiO$_2$ particles became smaller. The changes in the morphology of the TiO$_2$ film, i.e. thickness, particle size and crystal size, consequently affected the amount of dye adsorbed on the surface of TiO$_2$ particles. From visual observation (as shown in figure 3), it was clear that the 4 M sample showed the brightest red colour, while the other samples had dark red colour. The dark red colour of TiO$_2$ film indicated that the dye is adsorbed well by the film.
Figure 3. Photograph showing the TiO$_2$ photoelectrodes after the sensitizing process (from left to right: control, 0.5 M, 1 M, 2 M, and 4 M).

3.2. Performance analysis of DSSC

Hydrothermal post-treatment has caused the transformation in the TiO$_2$ film morphology, which subsequently affect the DSSC performance. The performance of DSSC can be described with several parameters, such as efficiency, fill factor, and short circuit current. Current-voltage characteristics of DSSC with different photoelectrodes is shown by figure 4. Highest efficiency, short circuit current density ($J_{sc}$) and open circuit voltage ($V_{oc}$) were exhibited by 1 M sample (table 1). The efficiency of 1 M sample was 3.30%, which was 1.2 times higher than the sample without treatment. Furthermore, the lowest resistance value also shown by 1 M sample. Low value of series resistance indicated high conductivity of electron in the DSSC system, which contributed to higher current [15].

![J-V Curve of the DSSC with different photoelectrodes.](image)

Figure 4. J-V Curve of the DSSC with different photoelectrodes.

| Table 1. Photovoltaic characteristics of the DSSC with different photoelectrodes. |
|------------------|------------------|------------------|---------------|-----|
|                 | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (Volt) | $R_s$ (ohm) | Efficiency (%) | FF |
| Control         | 3.32             | 0.66            | 175.15       | 2.67           | 0.61 |
| 0.5 M           | 3.30             | 0.67            | 188.20       | 2.75           | 0.62 |
| 1 M             | 3.91             | 0.68            | 166.68       | 3.30           | 0.62 |
| 2 M             | 1.67             | 0.66            | 497.24       | 1.34           | 0.58 |
| 4 M             | 1.26             | 0.66            | 726.87       | 0.88           | 0.50 |

The DSSC performance was affected by key structural properties of the film, such as thickness, phase composition, particle size and porosity [3]. Film thickness served as electron pathways. Film
with higher thickness would have longer electron pathways, and thus had higher possibility for electron recombination. Fewer defects and smaller particle size are known to inhibit the recombination of electrons and holes [16]. Materials with higher crystallite size tend to have fewer defects and thus decreasing the recombination rate, which led to greater current flow. Smaller particle size attributed to larger surface area, permitting a greater amount of dye molecules to be adsorbed to the film surface [2]. However, further reduction of film thickness could decrease the available surface of TiO$_2$ particles for adsorbing dye molecules. Although 4 M sample has the smallest particle size, and biggest crystallite size, the efficiency was the lowest due to its thickness.

The pores of the dye-coated TiO$_2$ film are filled with electrolyte for regeneration of the dye through reduction-oxidation process and transport of positive charges through the cell. The pore size influences the electrolyte infiltration and dye adsorption. It is more difficult for electrolyte to permeate into the film with smaller pore size. Smaller particles tend to have smaller gaps between them which cause poor pore-penetration. This will lead to low electron transport from electrolyte to the TiO$_2$ film.

After being hydrothermally treated, the film thickness was reduced and the particle was smaller and had better interconnection; thus, more electron can be transferred from dye to external load through TiO$_2$ film as photoelectrode. Smaller chance of electron recombination was also expected at 1 M sample, therefore leading to higher current density.

4. Conclusion

TiO$_2$ film treated with hydrothermal post-treatment in hydrochloric acid solution become thinner with denser structure and the particle is distributed evenly as the HCl molar concentration increased. The particle size of treated TiO$_2$ decreases and the crystallite size increase in the higher concentration of HCl compared to TiO$_2$ without treatment. Hydrothermal post-treatment with 1 mol/L HCl produces the optimum TiO$_2$ film, with thickness of 3.7 µm, average particle size of 34.9 nm and crystallite size of 292.7 Å, which resulted in efficiency of 3.3% and $J_{sc}$ of 3.9 A/cm$^2$. The efficiency increases 1.2 times compared to TiO$_2$ film without treatment.

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