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Dye-Sensitized Solar Cells with Anatase TiO$_2$ Nanorods Prepared by Hydrothermal Method

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The hydrothermal method provides an effective reaction environment for the synthesis of nanocrystalline materials with high purity and well-controlled crystallinity. In this work, we started with various sizes of commercial TiO$_2$ powders and used the hydrothermal method to prepare TiO$_2$ thin films. We found that the synthesized TiO$_2$ nanorods were thin and long when smaller TiO$_2$ particles were used, while larger TiO$_2$ particles produced thicker and shorter nanorods. We also found that TiO$_2$ films prepared by TiO$_2$ nanorods exhibited larger surface roughness than those prepared by the commercial TiO$_2$ particles. It was found that a pure anatase phase of TiO$_2$ nanorods can be obtained from the hydrothermal method. The dye-sensitized solar cells fabricated with TiO$_2$ nanorods exhibited a higher solar efficiency than those fabricated with commercial TiO$_2$ nanoparticles directly. Further, triple-layer structures of TiO$_2$ thin films with different particle sizes were investigated to improve the solar efficiency.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention as possible candidates for low cost, high stability, and high efficient solar cells [1, 2]. There are many innovations in this emerging technology such as new dyes which are absorbed at a wider range of wavelengths and the introduction of nanostructure titanium oxides (TiO$_2$) to increase the surface area [3–5]. The DSSCs with the nanostructure titanium oxide/Porphyrins dye thin films on transparent conducting oxide- (TCO-) coated glass can achieve a solar efficiency as high as 13% [6]. The major improvements of the research are made not only by introducing highly absorbing dyes as light harvesters, but also by using the nanostructure layer to improve the absorption and collection efficiency. In principle, fast electron transport and slow recombination will be needed to obtain a high solar conversion efficiency. For conventional DSSC, the mesoporous film consisted of nanocrystalline TiO$_2$ particles, enjoying the advantages of a large surface for greater dye adsorption and facilitating electrolyte diffusion within their pores [7–12]. The hydrothermal method provides an effective reaction environment for the synthesis of nanocrystalline TiO$_2$ with high purity and well-controlled crystallinity [13–15]. Therefore, we use the hydrothermal method to prepare TiO$_2$ thin films in this work. The Taguchi method [16–20] is used to find the optimal parameters for the formation of high-quality TiO$_2$ films. The Taguchi method [16] is a process optimization technique that investigates how multiparameters affect the performance of a process. It can minimize the variation in a process through robust design of experiments. The Taguchi method uses orthogonal arrays [17] to organize the parameters affecting the performance characteristic and the levels at which they should be varied. It allows for the determination of factors mostly affecting a process performance characteristic with a minimum amount of experimentation. Generally, it employs a generic signal-to-noise (S/N) ratio to quantify the variation. These S/N ratios are used as measures of the effect of noise factors on performance characteristics. There are several S/N ratio types of characteristics: larger is better, nominal is best, smaller is better, and so forth [16, 18].

In addition, it is known that the strong back-scattering light due to the large particles near the conducting glass results in a light loss. To reduce light loss due to this strong back-scattering light, multiple-layer structure of TiO$_2$ with
Table 1: Level of process parameters.

| Symbol | Factor level | 1  | 2  | 3  |
|--------|--------------|----|----|----|
| A      | NaOH concentration (M) | 10 | 8  | 12 |
| B      | TiO₂ particle size (nm) | 14 | 21 | 100|
| C      | Autoclave temperature (°C) | 180 | 200 | 230|
| D      | Annealing temperature (°C) | 450 | 500 | 550|

Different particle sizes have been proposed in the past [21–27]. Here, triple TiO₂ layer structure with small particle sizes is at the bottom, medium sizes in the middle, and large particle sizes on top which are also investigated to improve the solar performance of DSSCs.

2. Experiments

The 2 cm × 1.5 cm fluorine-doped SnO₂− (FTO−) coated glass electrodes (sheet resistance 8 Ω/cm) were cleaned by acetone, isopropanol, and deionized water sequentially. In the hydrothermal procedure, 3 g TiO₂ powders were placed into a Teflon lined autoclave of 100 mL capacity. The autoclave was filled with 8 M, 10 M, or 12 M NaOH aqueous solution and sealed into a stainless steel tank and maintained at 180°C for 24 hrs. It was cooled down naturally to room temperature. The obtained sodium titanate was put into 200 mL of 1 N HCl aqueous solution at pH = 2 and stirred for 24 h. This HCl treatment was repeated many times in order to exchange Na⁺ ions completely by H⁺ ions leading to the formation of hydrogen titanate nanorods. Then these hydrogen titanate nanorods were washed with distilled water until the pH reached 7 and filtered to obtain the precipitated hydrogen titanate nanorods. These nanorods were dehydrated and recrystallized into the anatase TiO₂ nanorods. Table 1 shows the factors and three levels used in our experiment according to the Taguchi method [16-20]. If three levels were assigned to each of these factors, then conventional method would require 3⁴ or 81 experiments to find the optimal condition. Using the Taguchi method, we can reduce the number of experiments to nine. The orthogonal array of L₉ type [17] is used and shown in Table 2. This design requires nine experiments with four parameters at three levels of each. The interactions of these four parameters were neglected. TiO₂ solutions are prepared by mixing 3 g of TiO₂ powders, 1 mL of titanium tetraisopropoxide (TTIP), 0.5 g of Polyethylene glycol (PEG), and 0.5 mL of triton X-100 in 50 mL of isopropanol (IPA). The mixture was then grinded and stirred by zirconia ball for 8 hours. It is known that the addition of TTIP in the solution can reduce the surface crack and the PEG can make a porous thin film after annealing. The TiO₂ thin films were formed by spin-coating TiO₂ solutions on FTO-coated glass and annealed at 500°C for one hour. The coated TiO₂ photo-electrodes were then immersed for 24 hrs in a hydrous ethanol solution containing 3 × 10⁻⁵ M N719 dye. The liquid electrolyte consisted of 1 M lithium iodide (LiI), 0.1 M Iodine (I₂), 0.5 M 4-tert-butyl pyridine (TBP), and 0.6 M 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) in acetonitrile. The cathode electrode was made of FTO-coated glass, which was further coated with H₂PtCl₆ precursor and annealed at 450°C for 30 min. The cell was fabricated by applying a surlyn spacer, which is a hot-melting film with a thickness of 60 μm, between two electrodes. Two FTO-coated glasses were made with the surlyn heated at 100°C. The electrolyte was injected into the space between the electrodes by capillary action. Finally, these two FTO-coated glasses were sealed completely. The active area of cells is 1 cm². The photocurrent-voltage (I−V) characteristic curves were measured using Keithley 2420 under AM1.5G illumination.

3. Results and Discussions

Nine different hydrothermal experiments were performed using the design parameter combinations shown in Table 2. Three specimens were fabricated for each of the parameter combinations. The factor effects on the solar efficiency and S/N ratio for each experiment are listed in Table 3. The higher solar efficiency is the indication of better performance. Therefore, the larger-is-better criterion was selected for the solar efficiency to obtain the optimal solar performance. The following S/N ratios for the larger-is-better case can be calculated [16, 18]:

\[
(S/N)_{LB} = -10 \log \sum_{i=1}^{n} \frac{1}{n} \left( \frac{y_i}{y_{LB}} \right)^2,
\]

where \((S/N)_{LB}\) stands for the larger-is-better signal-to-noise ratio, \(y_i\) is the individually measured solar efficiency, and \(n\) is the number of solar cell samples measured. Figure 1 shows the factor effects on the S/N ratio. The larger slope means that the factor has a stronger effect on solar efficiency. It indicates that NaOH concentration (factor A) has a stronger effect on solar efficiency. The annealing temperature (factor D) is the next most significant factor. The objective is to maximize the S/N ratio. This implies that one can obtain high solar efficiency by using the factor with higher S/N ratio. It is clear from Figure 1 that the highest S/N ratio values in each factor are...
Table 2: Taguchi L9 orthogonal array.

| Order | A NaOH concentration (M) | B TiO₂ particle size (nm) | C Autoclave temperature (°C) | D Annealing temperature (°C) |
|-------|--------------------------|---------------------------|-----------------------------|-----------------------------|
| 1     | 10 M                     | 14 nm                     | 180° C                      | 450° C                      |
| 2     | 10 M                     | 21 nm                     | 200° C                      | 500° C                      |
| 3     | 10 M                     | 100 nm                    | 230° C                      | 550° C                      |
| 4     | 8 M                      | 14 nm                     | 200° C                      | 550° C                      |
| 5     | 8 M                      | 21 nm                     | 230° C                      | 450° C                      |
| 6     | 8 M                      | 100 nm                    | 180° C                      | 500° C                      |
| 7     | 12 M                     | 14 nm                     | 230° C                      | 500° C                      |
| 8     | 12 M                     | 21 nm                     | 180° C                      | 550° C                      |
| 9     | 12 M                     | 100 nm                    | 200° C                      | 450° C                      |

Table 3: The factor effects on the solar efficiency and S/N ratio.

| Factor | Efficiency (%) | S/N ratio |
|--------|----------------|-----------|
| A NaOH concentration (M) | B TiO₂ particle size (nm) | C Autoclave temperature (°C) | D Annealing temperature (°C) |
| 1      | 1              | 1         | 1                           | 2.31                         | 7.27       |
| 1      | 2              | 2         | 2                           | 1.80                         | 5.11       |
| 1      | 3              | 3         | 3                           | 1.57                         | 3.92       |
| 2      | 1              | 2         | 3                           | 1.27                         | 2.08       |
| 2      | 2              | 3         | 1                           | 2.06                         | 6.28       |
| 2      | 3              | 1         | 2                           | 1.32                         | 2.41       |
| 3      | 1              | 3         | 2                           | 1.11                         | 0.91       |
| 3      | 2              | 1         | 3                           | 1.23                         | 1.80       |
| 3      | 3              | 2         | 1                           | 1.27                         | 2.08       |

5.43, 4.39, 3.82, and 5.21, which correspond to the factor A₁, B₂, C₁, and D₁, respectively. Therefore, the best parameters of hydrothermal methods are (A₁) NaOH concentration of 10 M, (B₂) commercial TiO₂ particle size of 21 nm, (C₁) the temperature of 180°C, and (D₁) the annealing temperature of 450°C. Thus, these best parameters were used to prepare our TiO₂ nanorods.

Figures 2(a) and 2(b) show the surface morphology of TiO₂ films prepared by commercial TiO₂ particles and TiO₂ nanorods which we prepared using hydrothermal methods, respectively. Clearly, a particle-like surface in the film is prepared using commercial particles versus a nanorod-shape surface in the film prepared by our TiO₂ nanorods. From atomic force microscopy (AFM) measurement, it is observed that the mean roughness (~63 nm) of the TiO₂ thin films prepared by the TiO₂ nanorods is larger than that (~41.5 nm) prepared by the commercial TiO₂ particles. The large surface roughness in TiO₂ nanorods is beneficial for dye adsorption. In addition, a very pure anatase structure of TiO₂ nanorods is obtained by the hydrothermal method, as shown in Figure 3. There are no characteristic peaks of other impurity phases such as sodium titanium oxide or rutile TiO₂, except pure anatase TiO₂ nanorods. This pure anatase structure of TiO₂ is extremely important to achieve high performance for electrons transport and dye adsorption in TiO₂-based dye-sensitized solar cells [28, 29]. Figure 4 compares the J-V characteristics of dye-sensitized solar cell prepared with hydrothermally grown TiO₂ nanorods and the DSSC prepared with commercial TiO₂ particles. The dye-sensitized solar cells prepared with the hydrothermally grown TiO₂ nanorods clearly exhibit higher solar efficiency than that prepared with the commercial TiO₂ particles. This is due to the fact that TiO₂ nanorods have large surface area and pure anatase structure, which can absorb more dye and thereby better photoresponse.

It is also noted that the size of TiO₂ nanorods synthesized by hydrothermal method depends on the initial TiO₂ particle size. The nanorods are thin and long when small-size TiO₂ particles (size ~14 nm) are used; however the nanorods become thick and short when large-size TiO₂ particles, are used (size ~100 nm), as shown in Figures 5(a) and 5(b). One can control the shape of TiO₂ nanorods by suitably choosing the initial TiO₂ particle sizes used in the hydrothermal process. Next we will examine the effect of TiO₂ thin film thickness on the solar efficiency of the fabricated DSSCs. In Figure 6, the cross-section scanning electron microscopy (SEM) images of different thickness of TiO₂ thin films are shown. We can see that a nanorod-like morphology is observed when 21 nm TiO₂ powder is used in the hydrothermal reaction. The optical absorption and
Figure 2: Surface morphology of TiO$_2$ thin films prepared by (a) commercial particles and (b) hydrothermal method.

Figure 3: XRD spectra of TiO$_2$ thin films prepared by hydrothermal method (red color) and commercial particle (blue color).

Figure 4: The $I-V$ curve of dye-sensitized solar cells with the TiO$_2$ prepared by hydrothermal method and commercial particle.
The $I-V$ characteristic curve of dye-sensitized solar cells with different TiO$_2$ thicknesses are shown in Figures 7(a) and 7(b), respectively. The optical absorption initially increases with increasing TiO$_2$ thickness and reaches a maximum at 12 $\mu$m. For further increase in the TiO$_2$ film thickness, the light absorption begins to drop. The same behavior is observed in the photocurrent, as shown in Figure 7(b). The solar performance parameters of DSSCs with different TiO$_2$ thicknesses are listed in Table 4. The efficiencies of DSSCs with the TiO$_2$ thicknesses of 3.5, 5, 9.5, 12, and 15 $\mu$m are 2.12, 2.44, 2.63, 2.85, and 2.67%, respectively. The DSSC with the TiO$_2$ thicknesses of 12 $\mu$m exhibits the highest efficiency. It is known that dye in the film will build up with increasing TiO$_2$ thickness and hence increase the photocurrent. However, thicker TiO$_2$ layers will result in a decrease in the transmittance of light through these TiO$_2$ layers and thus reduce the incident light absorbed by the dyes. In addition, the charge recombination between electrons from the excited dye to the conduction band of TiO$_2$ and the $I^3$ ions in the electrolyte will become more difficult in thicker TiO$_2$ layers. Thus, there exists an optimal TiO$_2$ thickness to achieve higher solar efficiency for each particle size. In this work, the optimal TiO$_2$ thickness is 12 $\mu$m for particle size of 14 nm used in the hydrothermal reaction.

It is known that large-size TiO$_2$ particles have the advantage of strong light scattering ability, while small size TiO$_2$ particles have the advantages of large contact area and low contact resistance [18–24]. In order to take the advantages of both the strong light scattering and the large contact area/low contact resistance, we constructed a triple-layer TiO$_2$ DSSC DSSC.
Table 4: Solar performance parameters of DSSCs with different TiO$_2$ thicknesses.

| Working area: 1 cm$^2$ | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | Fill factor | Efficiency (%) |
|------------------------|--------------|----------------------|-------------|----------------|
| 3.5 um                 | 0.79         | 3.63                 | 0.62        | 2.12           |
| 5 um                   | 0.76         | 4.73                 | 0.62        | 2.44           |
| 9.5 um                 | 0.77         | 5.25                 | 0.64        | 2.63           |
| 12 um                  | 0.76         | 5.89                 | 0.63        | 2.85           |
| 15 um                  | 0.76         | 5.58                 | 0.62        | 2.67           |

Figure 7: (a) Light absorption and (b) $I$-$V$ curve of dye-sensitized solar cells with different TiO$_2$ thicknesses.

Table 5: Solar performance parameters of DSSCs with different particle sizes on the top in triple TiO$_2$ layers.

| Particle size (nm) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | Fill factor | Efficiency (%) |
|-------------------|--------------|----------------------|-------------|----------------|
| 50/hy21/9/FTO     | 0.67         | 8.85                 | 0.61        | 3.62           |
| 100/hy21/9/FTO    | 0.75         | 12.02                | 0.62        | 5.68           |
| 200/hy21/9/FTO    | 0.76         | 14.32                | 0.61        | 6.54           |

The efficiencies of DSSCs with the scattering layer prepared by 50, 100, and 200 nm particles are 3.62, 5.68, and 6.54%, respectively. The TiO$_2$ layers with larger particle sizes on the top layer exhibit higher solar efficiency than that with smaller particle sizes due to the strong back-scattering effect. It is known that smaller particles of TiO$_2$ layers have large surface area and adsorb more dyes. Hence, it has low contact resistance and high photocurrent. The strong back-scattering light due to large particle size will also increase the reabsorption in the small particle size of TiO$_2$ layer. This smaller particle size on the bottom is beneficial to recapture the scattering light from the top scattering layer. The larger particle sizes of TiO$_2$ layers on the top can enhance the back-scattering light effectively and result in higher photocurrent. Thus, the combination of larger particle sizes of TiO$_2$ on the top and smaller particle sizes of TiO$_2$ at the bottom will be better for achieving higher solar efficiency.

4. Conclusions

The dye-sensitized solar cells with the TiO$_2$ prepared by the hydrothermal method have demonstrated good solar performance. A high surface roughness and pure anatase structure are achieved by this method. The dye-sensitized solar cells with the TiO$_2$ nanorods exhibit higher solar efficiency than that with the commercial TiO$_2$ particles. The optimal TiO$_2$ thickness depends on the nanorod sizes of...
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