Developing dye sensitized solar cells with polymer electrolytes

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Abstract. We have fabricated dye sensitized solar cells and improved their efficiency. The working electrodes were made of Al-doped and Cu-doped TiO$_2$ nanotubes by anodization process. We also prepared 2 polymers: the poly acrylonitrile-co-styrene and polyethylene oxide to compare efficiency of these polymer electrolytes. X-ray diffraction (XRD) was used to study the microstructure of the titania nanotubes, scanning electron microscopy (SEM) was used to study structural morphology, and UV-visible spectroscopy optical property was employed to determine the optical property. The effect of Al-doping and Cu-doping on the efficiency of the solar cells was investigated. The conversion efficiencies of poly (acrylonitrile-co-styrene), Poly(ethylene oxide), Al-doped TiO$_2$ and Cu-doped TiO$_2$ were 0.184, 0.121, 0.008 and 0.169 respectively for irradiation of 800 W/m$^2$.

1. Introduction

The energy is important for all human activities. Fossil fuels are formed by natural processes. Fossil fuels contain with high percentages of carbon in forms of petroleum, coal, and natural gas. The use of fossil fuel not only depletes world natural resources but also generate carbon emission. The carbon emission is one the biggest environmental problems leading to global warming, which causes of increasing the average temperature of Earth's atmosphere. Moreover, several environmental problems in the world face today including climate change, air pollution, oil spills, acid rain, global warming and greenhouse [1-2]. Because of the burning of fossil fuels produces carbon dioxides and heat-trapping gases that are the main cause of increasing global atmospheric temperatures. Scientists try to find new alternative energy to reduce using energy from fossil fuels. They have been developed new technology for producing energy to decrease the using of power squint as petroleum, coal and nuclear power. There are the alternative energy including wind energy, hydrogen fuels, biomass and solar cells.

Solar energy was used as alternative energy through Photovoltaics (PVs) cells. The energy which is produced from this method is the most abundant renewable, clean energy and provides a good solution for the electrical current which lack of sufficient long-term energy supplies [3]. O’Regan and Grätzel discovered dye-sensitized solar cells (DSSCs) in 1991. Dye-sensitized solar cells (DSSCs) have received extensive attention because of their low cost and relatively high efficiency [4-5]. Dye sensitized solar cells (DSSCs) which were based on the photo-injection of electrons from dye molecules into an inorganic semiconductor and holes transport by a redox mediator were studied by redox couple in an organic solvent as a liquid electrolyte [6-7]. However, such DSSCs suffer from
leakage and volatilization of the organic solvent, which greatly limits the long-term performance of liquid electrolyte-based DSSCs. Therefore, numerous materials, such as (solid-state electrolyte) and quasi solid-state electrolyte(polymer gel electrolyte)[8-9] have been used to replace liquid electrolytes.

There are alternative materials for solving leakage problems in mater including solid-state or quasi-solid-state electrolytes [10]. They offer high electrolyte stability and the additional opportunity to incorporate ordered nanostructures to tailor light propagation in DSSCs. This work achieve light-harvesting enhancement, as mentioned above. Therefore, we synthesize Al-doped and Cu-doped titania nanotubes as working electrodes and reports the efficiency of quasi-solid-state polymer gel electrolytes and presents the polymer electrolytes for DSSCs by comparing 2 polymers: the poly acrylonitrile-co-styrene and polyethylene oxide.

2. Experimental procedures

2.1. Synthesis of Al/ titania nanotubes (TiO₂NTs)

Titanium (Ti) sheets with 0.25 mm thick 99.7% purity were cleaned by sonication in ethanol and deionized water. Then Ti sheets were drying in air. NTs were fabricated by anodization in a self-designed equipment consisting of a two-electrode configuration with Ti sheet as the working electrode and a piece of highly pure platinum as the counter electrode. The distance between the anode and cathode was 1 cm. Anodization was performed at 50 V for 1 h in 100 ml glycerol solution containing 0.3 wt% NH₄F deionized water (2 Vol%) and Al (1M). The obtained TiO₂ nanotube arrays were annealed at 450 1C for 2 h.

2.2. Preparation of gel electrolytes

The liquid electrolyte polymer was prepared by mixing the amount of ethylene carbonate (EC) propylene carbonate (PC) and Y- butyrolactone ( Y- BL ) ratio 3:2:1,M/M/M dissolved by mixture Potassium iodide 0.5 M (KI) with iodine 0.05M (I₂) then dissolved in the electrolyte polymer. The dissolved Poly (acrylonitrile-co-styrene) and Poly(ethylene oxide), 17 wt% in acetone 50 ml then mixing in electrolyte. Finally mixing 4-tert-butylpyridine (TBP) was homogeneously stirred at 75-80 °C temperature. The gel electrolyte polymer was obtained.

2.3. Instrumentation and measurements

2.3.1 The characterization of TiO₂ nanotubes

The crystalline morphology TiO₂ nanotubes were studied by Scanning Electron Microscopy (SEM). The data were analyzed by program X’ Pert High Score. X-ray diffraction (XRD) patterns of TiO₂ nanotubes were analyzed to determine phase composition and crystal structures. The absorption measurement of the poly (acrylonitrile-co-styrene) and Poly(ethylene oxide), 17 wt% in acetone 50 ml then mixing in electrolyte. Finally mixing 4-tert-butylpyridine (TBP) was homogeneously stirred at 75-80 °C temperature. The gel electrolyte polymer was obtained.

2.3.2 Measurement efficiency

The photovoltaic measurement of DSSCs was measured using a the J-V character curves under sun light of 800 W/m² and overall areas of 0.25 cm². The photoelectrochemical performances fill factor (FF) and overall energy conversion efficiency (η), were calculated by the following equations [11-13].

\[ FF = \frac{V_{\text{max}}}{V_{\text{oc}}} \frac{J_{\text{max}}}{J_{\text{sc}}} \]

(1)

\[ \eta(\%) = \frac{V_{\text{max}}}{P_{\text{in}}} \frac{J_{\text{max}}}{J_{\text{sc}}} \times 100 = \frac{V_{\text{oc}}}{P_{\text{in}}} \times J_{\text{sc}} \times FF \times 100 \]

(2)

where \( J_{\text{sc}} \) is the short-circuit current density (mA/cm²), \( V_{\text{oc}} \) the open-circuit voltage (V), \( P_{\text{in}} \) is the incident light power, \( J_{\text{max}} \) (mA/cm²) and \( V_{\text{max}} \) (V) are the current density and voltage in the J–V curves, respectively, at the point of maximum power output.
3. Results and discussion

The TiO$_2$ nanotubes are firstly synthesized via anodization of pure Titanium metals. Figure 1 shows X-ray diffraction of the TiO$_2$ nanotubes. Electrochemically synthesized by anodization process before and after annealing sample the absolute-intensity X-ray diffraction patterns can be seen in Figure 1. The phase of the nanotubes is anatase when their thermal treatment at 450°C for 2 hours. All of the peaks are anatase, suggesting that the films were crystallized well after annealing. SEM images shown in Fig.2 indicate that the titania nanotubes has tubular structure in nanoscale.

![Figure 1. XRD patterns of the prepared TiO$_2$ nanotubes: (a) pure Titanium, (b) TiO$_2$ nanotubes, (c) Al doped TiO$_2$, (d) Cu doped TiO$_2$.](image1)

![Figure 2. SEM images: (a) pure Ti, (b) TiO$_2$ nanotubes, (c) Al doped TiO$_2$, (d) Cu doped TiO$_2$.](image2)

From Figure 1, it is shown that the treated TiO$_2$ is the structural film containing the anatase TiO$_2$ as the most. From the graph, it can be seen that the TiO$_2$ synthesis with anodization process by 1.0 M Al-doping does not cause any anatase structure. The phase is only Ti phase, as compared to the 1.0 M Cu-doped phases. The phase of Cu-doped TiO$_2$ is anatase phase. Anodization process under too much Al-doping could not make any anatase structure and lowly efficiency [14].

In studying, the structure of TiO$_2$ nanotubes by (SEM), figure 2 can be seen in TiO$_2$ synthesis with undoped and 1.0 M Al-doped, 1.0 M Cu-doped TiO$_2$ nanotubes. Figure 2 shows that the 1.0 M Al-doping does not produce TiO$_2$ nanotubes, which corresponds to the phase structure study with XRD. But TiO$_2$ synthesized with 1.0 M Cu-doping have produced TiO$_2$ nanotubes.

![Figure 3. UV–vis absorption spectra of the prepared poly (acrylonitrile-co-styrene) and Poly(ethylene oxide).](image3)

![Figure 4. J–V measurements of (a) Poly(ethylene oxide), (b) poly (acrylonitrile-co-styrene), (c) Al doped TiO$_2$, (d) Cu doped TiO$_2$ on photointensity of 800 W/m$^2$.](image4)
The results of the study of electrolyte properties by light in the range of 200-1000 nm with UV-visible machine show that the electrolyte polymers absorb light at 367 nm. The picture shows that the absorbance of Poly(ethylene oxide) is better than Poly(acrylonitrile-co-styrene) in the range of 350-375 nm, as shown in Figure 3. But the absorbance of Poly(ethylene oxide) is better than Poly(acrylonitrile-co-styrene) in the range of 375-600 nm.

Table 1 The photovoltaic parameters of DSSCs.

| Samples                     | \( J_{sc} \) (mA/cm\(^2\)) | \( V_{oc} \) (V) | \( J_{max} \) (mA/cm\(^2\)) | \( V_{max} \) (V) | FF  | \( \eta \) (%) |
|-----------------------------|-----------------------------|------------------|------------------------------|------------------|-----|---------------|
| Poly (acrylonitrile-co-styrene) | 0.209                       | 0.378            | 0.271                        | 0.544            | 1.866 | 0.184         |
| Poly(ethylene oxide)        | 0.181                       | 0.348            | 0.214                        | 0.454            | 1.542 | 0.121         |
| Al doped TiO\(_2\)         | 0.011                       | 0.546            | 0.011                        | 0.690            | 1.117 | 0.008         |
| Cu doped TiO\(_2\)         | 0.155                       | 0.618            | 0.176                        | 0.770            | 1.415 | 0.169         |

The results of the solar energy conversion test as shown in Fig. 5 and table 1 indicate that the efficiency of converting solar energy into electricity filled poly (acrylonitrile-co-styrene) is found to be more efficient than gel electrolysis filled Poly(ethylene oxide). That because the iodine used is KI and I\(_2\), which results Poly(ethylene oxide) in lowly efficiency [15].

4. Conclusion

We have made DSSCs using TiO\(_2\) nanotubes as working electrodes. The TiO\(_2\) nanotubes working electrodes were synthesised by anodization method. The efficiencies for solar conversion of DSSCs by using poly (acrylonitrile-co-styrene), Poly(ethylene oxide), Al-doped TiO\(_2\) and Cu-doped TiO\(_2\) were 0.184, 0.121, 0.008 and 0.169 respectively. The result shows that it is difficult to prepare 1.0 M Al-doped TiO\(_2\) nanotubes by anodization process. Thus, Al-doped TiO\(_2\) nanotubes may be prepared only small amount of Al doping.

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References

[1] Grätzel M 2005 Inor. Chem. 44 6841
[2] Petit J R, Jouzel J, Raynaud D, and et al. M 1999 Nat. 399 429
[3] Sahay A, Sethi V.K and Tiwari A.C, 2013 Int. J. Mech, Civ, Automobile Prod. Eng, 3 2249
[4] Zhao B, Li S, Che M and Zhu L 2016 Int. J. Electrochem. Sci. 11 6514
[5] Yu J, Fan J, and Bei C, 2011 J. Power Sources 196 7891
[6] Diamant Y, Chappel S, Chen S.G, Melamed O, Zaban A, 2004 Coord. Chem. Rev. 248 1271
[7] Brian A. G, Chen S.G, and Ferrere S, 2003 J. Phys. Chem. B 107 3019
[8] Matsumoto M, Miyazaki H, et al. 1996 Solid State Ionics 89 263
[9] Zhang S, Dong G.Y, Lin B, Qu J, Yuan N.Y,and Ding J.N, 2015 J. Power Sources 277 52
[10] Wantawee S, saentaweesuk S, Pukird S, saipn T abd Tipparach U 2010 Adv. mater Res 93 194
[11] Grätzel M,2000 Prog. Photovolt. Res. Appl. 8 171
[12] Wu J, Lana Z, Wang D, et al. T 2006 J. Photochem. Photobiol., A 181 333
[13] Li P.J, Wu J.H, Huang M.L, Hao S.C, Lan Z, Li Q and Kang S 2007, Electrochim. Acta 53 903
[14] Lia R, Zhaoa Y, Houa R, Rena X, Yuana S, et al. 2016 J. Photochem. Photobiol., A 319 62
[15] Shen X, Xu W, Xu J, Liang G, Yang H and Yao M 2008 Solid State Ionics 179 2027