Energy harvesting of dye-sensitized solar cells assisted with Ti-mesh and phosphor materials

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Abstract. We used the Ti-meshes for both the photoanode and counter electrode of the dye-sensitized solar cells (DSSCs) to improve the flexibility and conductivity of electrodes. This mesh type electrode showed good transparency and high bendability when subjected to an external force. The overall efficiency of the best cells was approximately 5.3% under standard air mass 1.5 global (AM 1.5 G) solar condition. We also modified the TiO₂ nanoparticle based dye-sensitized solar cells (DSSCs) by depositing a layer of long-persistent phosphor SrAl₂O₄:Eu²⁺, Dy³⁺ on top of the TiO₂ nanoparticle layer to prepare working electrodes of DSSCs. SrAl₂O₄:Eu²⁺, Dy³⁺ red-shifted short UV wavelengths into the main absorption range of the dye commonly used in DSSCs. The SrAl₂O₄:Eu²⁺, Dy³⁺ layer also acted as a light-scattering layer to reduce the loss of visible light. An overall 13% improvement in the conversion efficiency of modified DSSCs was achieved due to the presence of the phosphor layer.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered to be one of the most promising photovoltaic conversion technologies [1]. DSSCs are made from low-cost materials and they can be significantly less expensive than conventional solid-state solar cells. These cells can also be designed as flexible sheets and be mechanically robust [2]. Recently, plenty of innovations of the DSSC structure were reported [3-6]. Although a conversion efficiency of those innovative DSSC was less than the best thin-film cells, its price/performance ratio (kWh/(m²·annum·dollar)) should be high enough to allow them to compete with traditional energy sources based electrical generation. DSSCs are still in their development stages, however, a higher efficiency gains are possible and more widespread studies have been carried out [2-13].

Considerable efforts have been devoted to the development of more efficient photoanode structures. In particular, 1-D TiO₂ nanotube (TNT) structures are attracting more interest from the solar cell community because of their superior charge transport speed, great diffusion length and small charge recombination rate [14,15]. The development of anodization method [16] makes it quite facile for the fabrication of uniform and highly ordered TNTs. On the other hand, this method requires the use of Ti foil which is not transparent and DSSCs based on anodic TNTs on Ti foil should be illuminated from the back side, leading to a decrease in light harvesting and hence low conversion efficiency. Also, the use of TCO glass as the counter electrode has restricted the efficiency to a low level (η ~ 1.47%).

For DSSCs, efficiency relies on the light harvesting to a great extent, and the dye plays a key role in converting light to electrical power. However, the most commonly used Ru(II)
dyes in current DSSCs have an optical band gap of about 1.8 eV and only absorb portions of the UV and visible spectrum[17,18]. Thus, in order to achieve higher light harvesting, new-type dyes have been under development. A possible way to avoid the loss of photon energy evolved is the utilization of a luminescence layer composed of up-conversion (UC) or down-conversion (DC) phosphor materials[19-21]. DC phosphors have the ability to transform higher energy photons into visible photons, whereas UC phosphors work in the opposite way.

In this study, we present a DSSC with high flexibility utilizing Ti-mesh as both electrodes. An anodization method at a relatively low temperature was carried out to fabricate TNTs on a Ti-mesh. The TNTs on the mesh substrate were oriented in all directions ranging from parallel to perpendicular to the incoming photons. Furthermore, the voids in a mesh substrate allow light to enter the cell from the photoanode side leading to possible front illumination. We also describe DSSCs assisted by long-persistent SrAl2O4:Eu2+, Dy3+ phosphor particles. Those have a wide UV-light absorption band and emit an output in the blue-green spectral regions, which matches the peak absorption region of the most commonly used dye N719. In addition, the micro-sized particles contribute to visible light scattering path length and hence, benefit light collection. Furthermore, the open-circuit voltage and the photocurrent of modified DSSCs were improved.

2. Experiments

For Ti-mesh based DSSC study, the meshes made from commercially pure titanium (99.5% purity) were purchased from Alfa Aesar. In this study, a 50-mesh wire cloth woven from 0.102 mm diameter wire with an open area of 64% was used. For an anodization, the mesh was fixed by contacting with a Cu plate as the anode and a graphite plate was used as the counter electrode. Anodization was performed at a constant potential of 60 V at 5 °C, and the growth time was varied from 4 h to 8 h. For phosphor particle based DSSC study, commercially-available P25 TiO2 powder (Aldrich, 99.5% purity) was used and the mean particle size was approximately 21 nm. The SrAl2O4:Eu2+, Dy3+ phosphor powder (99% purity, mean particle size: 5~10μm), purchased from Dalian Zhongbang Chemical Industry Co., Ltd., was mixed with 2 wt% ethyl cellulose in 100ml ethanol. The resulting phosphor colloid was deposited on the FTO/TiO2 electrode twice by a repeated doctor blade coating and was treated post-thermally at 500 °C for 0.5 h. The counter electrode was fabricated by dip-coating a FTO glass substrate with a H2PtCl6 (Sigma-Aldrich, 37.5% Pt basis) solution (2-mg Pt in 1-ml ethanol), followed by calcining at 400 °C for 0.5 h.

The morphology of the samples was examined by scanning electron microscopy (SEM, Hitachi-S4700). The current-voltage curves of cells were measured under a simulated AM 1.5 G illumination with a light intensity of 100 mW cm−2 (300 W, model 91160B, Oriel) with the aid of a computer-controlled potentiostat (CHI-660B, CH Instruments). The active area of the cell was 0.25 cm2. The incident photon to current conversion efficiencies (IPCEs) were measured as a function of the wavelength from 300 to 800 nm using a solar cell spectral response measurement system (PV Measurements, Inc. QEX7).

3. Results and Discussion

The SEM images of the anodic TNTs on the Ti-mesh substrates are shown in Figure 1. After anodization, the mesh remains sufficient void regions. The TNTs grew perpendicularly to the
surface of the titanium wire and covered the entire wire uniformly. The lengths of the TNTs increased with increasing growth time and were 6.1, 9.3, and 11.4 μm after 4, 6, and 8 h anodization, respectively. The inner diameter of the TNTs retained a constant value of approximately 100 nm over various growth times. With increasing TNT length, cleavage was observed at the top part, which was derived from the curvature of the round-shaped titanium wire. The divergently grown TNTs tended to bundle through van der Waals attraction and capillary forces during drying [22]. When assembling a DSSC, the TNTs might be peeled off partially by an external bending force.

Figure 1. Low-magnification SEM images from top view (a) and cross-section (b) of TNTs on Ti-mesh substrate. Top view SEM image of the anodic TNTs (c). Cross-section SEM images of TNTs anodized for 4 (d), 6 (e) and 8 h (f) [23].

The dye-sensitized TNTs with different lengths grown on mesh substrates were sandwiched with the same sized Pt coated mesh to fabricate DSSCs. Figure 2 and Table 1 present the photocurrent-voltage characteristics of the cells and the key factors, respectively. The cells had a constant open circuit voltage around 0.73 V whereas the short circuit current showed an uptrend when the TNTs became longer. The photocurrent increased from 11.74 to 17.48 mA/cm² and the efficiency was improved. This might be contributed by the elevated dye loading in a thicker TNT layer. The cell using 11.5 μm long TNTs yielded the highest conversion efficiency of 5.3% among the cells tested. A properly thick layer could preserve the intact TNT layer around the Ti wires during operation. For comparison the efficiency of a DSSC assembled using TNTs grown on Ti-foil as a photoanode and Pt-coated ITO glass as a counter electrode was measured together with the mesh type DSSCs. Although the foil type cell has a TNT layer with a longer length, the efficiency was much lower, due to the low photocurrent. Therefore, the mesh type electrodes developed in the present study could effectively improve the performance of DSSCs. However, the fill factor of the mesh type cell
was lower than the typical value of other DSSCs based on TNTs. This phenomenon might be explained by the long diffusion path through the electrolyte for the redox species to reduce the e-* emitted dye molecules [22].

![I-V curves of DSSCs utilizing the TNTs with different length on mesh or foil substrates][1]

**Figure 2.** I-V curves of DSSCs utilizing the TNTs with different length on mesh or foil substrates [23].

| NT Length(μm) | η (%) | V<sub>oc</sub> (V) | J<sub>sc</sub> (mA/cm²) | FF (%) |
|---------------|-------|-------------------|------------------------|--------|
| 11.5          | 5.30  | 0.73              | 17.48                  | 42.1   |
| 9.3           | 4.92  | 0.73              | 15.21                  | 44.3   |
| 6.1           | 3.67  | 0.74              | 11.74                  | 42.2   |
| 15 (on foil)  | 2.24  | 0.72              | 5.29                   | 39.0   |

Table 1. Performances data of the DSSCs based on TNTs/Ti-mesh or TNT/Ti-foils structure [23].

The enhanced performance of the mesh type DSSCs was attributed to three prominent advantages. First, the photoanode is front-illuminable in the cell, which preserves light harvest from absorption by the counter electrode and electrolyte. In addition, the cell can absorb light from the surroundings at various angles compared to conventional DSSCs based on planar electrodes as both electrodes are the mesh type and the titanium wires of the meshes possesses a circular shape. An efficiency of about 3.15% is obtained by illuminating the back side of the DSSC using 11.5 μm long TNTs. Second, the titanium wires fully covered with TNTs showed a higher surface area than that of TNTs on an equivalent sized foil substrate. Third, after the absorption of solar energy, electrons emitted from the dye molecules should be transported through the TiO<sub>2</sub> layer to the anode substrate and finally to the external circuit.

The standard redox couple used for dye regeneration, iodide/triiodide (I⁻/I₃), has unmatched performance but typically requires a catalyst during DSSC operation [27]. Although the titanium mesh manifests a good conductivity, it does not meet the demand of

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[1]: http://example.com/image.png
assisting the redox reaction between the $\Gamma/\Gamma_3^-$ group. In the present study, a 10 nm thick Pt layer was coated on the Ti-mesh for the counter electrode and a Pt coating can improve the redox reaction rate.

For phosphor particle based DSSC study, the working electrode was prepared in multi-layers. Figures 3(a)–(d) show SEM images of the TiO$_2$ layer coated FTO glass and the FTO/TiO$_2$/phosphor electrode. The TiO$_2$ film contained no aggregates of P25 particles, which were dispersed homogeneously, and formed a porous structure throughout (Figure 3(b)). The thickness of the TiO$_2$ film was uniform at ~12 $\mu$m, as determined by cross-sectional SEM (Figure 3(a)). The phosphor layer had a large degree of roughness due to the nonuniform micro-size of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ particles with a mean thickness of approximately 23.4 $\mu$m, as shown in Figures 3(c) and 3(d). The particle size and thickness of TiO$_2$ SL was approximately 450 nm and 2.1 $\mu$m, respectively. The composition of the multi-layer film was confirmed by XRD (data are not shown) and all peaks marked with solid squares were derived from the SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphor. The XRD pattern of the TiO$_2$-coated FTO revealed clear anatase crystallization of the TiO$_2$ layer.

**Figure 3.** Cross-section and surface SEM images of FTO/TiO$_2$ (a), (b) and SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ FTO/TiO$_2$/phosphor electrode (c), (d) [24].

SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ can be excited by natural sunlight, and its phosphorescence is derived from a transition from the 5d level to the 4f level of Eu$^{2+}$. S2 Regarding the mechanism for protracted afterglow, the co-doped Dy$^{3+}$ ions are believed to act as hole trap levels, which play an important role in this process[25]. Under UV illumination, the excitation transitions of Eu$^{2+}$ 4f$^7$ → 4f$^6$5d$^1$ occur immediately, generating a large number of electrons and holes in the vicinity of the valence band (VB). The holes migrate through the valence band and are captured by Dy$^{3+}$ ions located at a suitable depth to form Dy$^{4+}$ ions [JPCC]. The return to the ground state of Eu$^{2+}$ with light emission is triggered by the thermo-activated promotion of an electron from the valence band to the first unoccupied levels of Dy$^{4+}$, followed by the transition of trapped holes to a photo-generated Eu$^{7+}$ cation. This process causes the long afterglow of the phosphors.
Figure 4 shows the photovoltaic performances of the phosphor-assisted DSSCs, scattering layer-inserted DSSCs and pure-TiO₂-based DSSC, and Table 2 lists the key parameters. When the phosphor material was inserted into the DSSCs, the open-circuit voltage ($V_{OC}$) increased to approximately 0.8 V from 0.72 V, which is typical for pure-TiO₂ devices. On the other hand, the short-circuit current density ($J_{SC}$) increased only when the phosphor material was placed at a proper position in terms of the FTO/TiO₂/phosphor multi-layer structure. The photocurrent of DSSCs with the FTO/phosphor/TiO₂ electrode decreased to 6.14 mA/cm². This might be due to mismatch between the electronic band structure of the phosphor and that of the FTO substrate and dyes, so that the electrons cannot be collected effectively and are transported by the phosphor. The presence of a phosphor layer between FTO and TiO₂ also
increases the length of the electron-transporting path, which would raise the electron/I$_3^-$ recombination rate. The cell with the different layer structure: i.e., FTO/TiO$_2$/TiO$_2$ SL electrode showed an obvious increase in photocurrent compared to the pure TiO$_2$ based DSSC due to the insertion of a scattering layer. Nevertheless, it was still slightly lower than the photocurrent of the FTO/TiO$_2$/phosphor type DSSCs. The total conversion efficiency of the FTO/TiO$_2$/TiO$_2$ SL-based DSSCs was much lower than that of the FTO/TiO$_2$/phosphor-based DSSCs due to the lower open-circuit voltage. In the device performance, the DSSCs with the multi-layer structure in the order of the FTO/TiO$_2$/phosphor were found to produce the highest current density of 12.84 mA/cm$^2$, resulting in the highest conversion efficiency of 6.85%.

The increase in current could be explained by promoted light harvesting. As shown in Figure 5, the IPCE of the phosphor-assisted DSSC are higher in both the UV and visible regions, whereas it was only improved in the visible region in the case of TiO$_2$ SL-inserted DSSC. An apparent decrease in IPCE in the range from 350 to 400 nm could be observed for the pure-TiO$_2$ based DSSC and TiO$_2$ SL-inserted DSSC, and this drop did not appear for the phosphor-assisted DSSCs. The SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphor could absorb near UV-photons, giving rise to characteristic visible green emission, which is a unique property that the TiO$_2$ scattering layer does not possess. Green light was emitted from the excited dye N719 and yielded excess electrons. In this way, solar energy was converted to electric energy more effectively than by the DSSC without phosphors, resulting in an increase in quantum efficiency. In the visible light range, the improved IPCE of both the phosphor-assisted DSSC and TiO$_2$ SL-inserted DSSC could be explained by the presence of a large-size particle layer on top of the TiO$_2$ layer, prolonging the optical-path length due to light scattering. Consequently, an increase in IPCE in the full light range could be achieved by adding a phosphor layer on top of the TiO$_2$ conducting layer.

Figure 5. IPCE spectra of pure-TiO$_2$ DSSC (black squares), TiO$_2$ SL inserted DSSC (pink triangles) and phosphor assisted DSSC (orange circles) [24].
4. Conclusion

The cell based on a 11.5 μm long TNTs/Ti-mesh structure exhibited the best performance of 5.3%. The mesh type DSSCs has several unique advantages such as availability of front-illumination, high surface area, and low sheet resistance. The influence of the Pt layer on the impedance was also studied. A FTO/TiO₂/phosphor multi-layered photoelectrode was also fabricated for DSSCs by depositing a layer of a long-persistent phosphor, SrAl₂O₄:Eu²⁺, Dy³⁺, on a porous TiO₂ film. The conversion efficiency of the phosphor-assisted DSSCs was improved to 6.85%, which is more than 13% higher than that of pure-TiO₂-based DSSCs.

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