Effect of Doping a Rare-Earth Oxide on the Photovoltaic Parameters of Dye-Sensitized Solar Cells

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Abstract

Yb$_2$O$_3$-doped TiO$_2$ were prepared using mechanochemical process to obtain Dye Sensitized Solar Cells (DSSCs) photoanodes. The parameters of DSSC devices were calculated. The study showed that the addition of Yb$_2$O$_3$ improved the open-circuit voltage via a p-type effect, whereas, a negative effect on the generated photocurrent was observed. This reduction in photocurrent was attributed to increasing crystal defects as a result of increasing the concentration of Yb$_2$O$_3$ dopants.

Keywords: Dye Sensitized Solar Cells, Yb$_2$O$_3$, P-type

1 Introduction

Earth receives 120 000 TW of solar power, whereas, the global energy consumption is only 15 TW. Therefore, solar energy hold great considerable potential for addressing the world’s growing energy need (Gratzel et al., 2012). An enormous effort has been devoted to Dye Sensitized Solar Cells (DSSCs) due to its low cost production, environmentally friendly components and relatively high conversion efficiency (Heimer et al., 2000, Yang et al., 2008). Typically, DSSC consists of a working electrode, iodine based redox-couple electrolyte and a counter electrode coated with a platinum layer (O’regan and Graetzel, 1991, Grätzel, 2001, Mansa et al., 2013).

The semiconductor (working) electrode is a crucial component of DSSCs as it mainly controls its performance. So, many studies focus on doping TiO$_2$ photoanode of DSSC to improve the efficiency of DSSCs (Wang et al., 2012). For the metal-doped TiO$_2$ nanomaterials, Lü and coworker (2010) reported that DSSC based on the Nb-doped TiO$_2$ photoelectrode showed an improved short-circuit current density. This improvement was related to the ability of charge transfer and to an increase in electron concentration due to Nb-doping. Also, the doping of TiO$_2$ with low valent metallic element was investigated (Wang, et al., 2012). Whereas, Sb-doped TiO$_2$ showed an improvement of the performance of DSSC due enhancement of the short-circuit current density. For N-doping, TiO$_2$ photoelectrode confirmed higher photoelectric performance than that of pure TiO$_2$ photoelectrode (Qin et al., 2013).

Doping of TiO$_2$ with multielements (B, C, N and F) enhanced the efficiency of DSSCs, as reported by Im et al. (2012). This enhancement was attributed to a reduction in the recombination of electrons (in the conduction band of TiO$_2$) with the dye and/or electrolyte. Furthermore, Yang et al. (2012) reported that the photocurrent conversion efficiency of N3-sensitized N-doped and F-doped TiO$_2$ electrodes was about 17.1% higher than that of a pure TiO$_2$ electrode. Also, bisemiconductors of TiO$_2$ and Fe$_2$O$_3$ were used as photoelectrodes of DSSC devices (Im et al., 2011). The use of these bisemiconductors caused an increase in the efficiency and was attributed to a cocktail effect of the two conduction bands.

Rare-earth-doped compounds have been the subject of extensive research, as well. Hafez et al. (2011) reported that Lanthanide (Ln$^{3+}$)-doped TiO$_2$ enhanced the efficiency of DSSCs. In the current work, we have investigated the influence doping titanium(IV) oxide photoanodes with...
2 Experimental Part

2.1 Materials

Chemicals and materials including titanium dioxide (BHD, 98.0%), distilled water, acetyl acetone (Elnaser pharmaceutical chemical, 98.0%), triton X-100 (El- gounhouriya), terpanol (Alpha Chemie, 95.5%), ethylene glycol (SDFCL), iodine resublimed (Elnaser pharmaceutical chemical), potassium iodide (Elnaser pharmaceutical chemical, 99.5%), N719 dye (Dyesol) and FTO (fluorine doped SnO$_2$ coated glasses (Dyesol, 15Ω/sq.m) were used.

2.2 Materials Preparation

a) Preparation of TiO$_2$ Paste: We added 1.5 ml of distilled water to 1 gm of titanium dioxide nanoparticles. Then, 0.1 ml of triton X-100, 0.1 ml of acetyl acetone and a drop of terpanol was added to the mixture. The final solution was held under continuous stirring for 24 h.

b) Preparation of Yb$_2$O$_3$–Doped TiO$_2$ Paste: Yb$_2$O$_3$–doped TiO$_2$ was prepared via a method similar to non-doped TiO$_2$ preparation process described above. However, the only difference was adding Yb$_2$O$_3$ powder (ground for 1h) with different concentrations \([Yb_2O_3]_{x}-(TiO_2)_{1-x}\) where x= 2%, and 6%) to TiO$_2$ powder during the initial stage of the preparation process.

c) Preparation of Film Electrodes and Assembly of the DSSCs: The paste was spread on the conductive side of the substrate using a doctor-blade technique. The film was sintered at 450 °C for 30 min. After cooling down to room temperature, the substrate was soaked in an ethanol solution of N-719 for 24 h to absorb the dye adequately. The DSSC was assembled by injecting the electrolyte (50 ml of ethylene glycol, 0.635 gm of I$_2$, 4.15 gm of KI in acetonitrile) into the aperture between the TiO$_2$ electrode (anode electrode) and the platinum-coated counter electrode. The two electrodes were clipped together by an adhesive tape (parafilm) to prevent the electrolyte solution from leaking.

3 Measurements and Characterization

The photocurrent density-voltage (J–V) measurement was tested using a source meter (Keithley Instruments, Inc.), digit multimeter-counter (Model–1087- APLAB), homemade device holder and solar simulator irradiation with Xe (55 W) Lamp. The tested solar cells were masked to a working area of about 0.2 cm$^2$.

4 Results and Discussion

The photocurrent density-voltage (J–V) curves of DSSCs with \((Yb_2O_3)_x-(TiO_2)_{1-x}\) photoanodes with different concentrations of Yb$_2$O$_3$ (x= 0%, 2% and 6%) under simulated solar irradiation are were in Figure 1. As seen, the lowest value of open-circuit voltage (V$_{oc}$) corresponds to the DSSC of the undoped photoelectrode (V$_{oc}$=0.453 V for x= 0.0). Moreover, V$_{oc}$ increases with increasing of the concentration of Yb$_2$O$_3$ (V$_{oc}$=0.462 V for x= 0.02%) and had the largest value (V$_{oc}$=0.475 V) for the highest concentration (x= 6%). Therefore, we conclude that the V$_{oc}$ increased gradually with the increase of doping and this effect can mainly be ascribed to the p-type effect. According to published reports (Gratzel, M., 2009, Hagfeldt et al., 2010), V$_{oc}$ has been determined by the difference between the quasi-Fermi level of photoanode and the redox potential of electrolyte. Consequently, when Yb$^{3+}$ ions substitutes Ti$^{4+}$ ions, a p-type doping effect occurs as the quasi-Fermi level will be shifted upward and hence V$_{oc}$ will increase (Ko et al., 2005). Also, it was noted from J-V curves that the short-circuit photocurrent density (J$_{sc}$) had the largest value for undoped DSSC (x= 0.0) and decreased by increasing the doping percent of Yb$_2$O$_3$. The reason of this behavior could be attributed to the fact that Yb$_2$O$_3$ impurities produce more crystal defects and those defects can capture photoinduced electrons, hence the photocurrent decreases (Ko et al., 2005, Murakoshi et al, 1995).

![Figure 1: The photocurrent density-voltage (J–V) curves of DSSCs with different Yb$_2$O$_3$ concentrations.](image-url)
The maximum power and doping concentration relation was shown in Figure 2. As shown, the maximum power decreased by increasing the doping concentration and this referred to the large decrease in photocurrent by increasing of x.

The photovoltaic parameters were calculated and indicated in Table 1. The fill factor (FF) is a measure of ideality of a solar cell. The fill factor was calculated using the equation:

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

where $V_{\text{max}}$ and $J_{\text{max}}$ are the voltage and current at the point of maximum output power in J-V curves. The values of fill factors for DSSCs with different concentration of the dopant were calculated and indicated in Table 1. It was noted that FF decreases by increasing the concentration of dopant as the series resistance ($R_s$) increases. This means that to the value of contact resistance and transfer resistance in the semiconductor material (TiO$_2$) increased which corresponded to the lower value of produced photocurrent. Accordingly, the efficiency of the cell also decreases with doping, as shown in Table 1. The overall light-to-electrical energy conversion efficiency ($\eta$) of DSSC was calculated according to the following equation:

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{V_{\text{oc}}J_{\text{sc}}FF}{P_{\text{in}}}$$

where $P_{\text{max}}$ is the generating maximum power and $P_{\text{in}}$ is the input power of the incident light on the active area of the cell.

### Table 1: The photovoltaic parameters of DSSC devices with different concentrations of Yb$_2$O$_3$ powder, x.

<table>
<thead>
<tr>
<th>x (wt%)</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$J_{\text{sc}}$ (mA/cm$^2$)</th>
<th>$V_{\text{mp}}$ (V)</th>
<th>$J_{\text{mp}}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.453</td>
<td>7.83</td>
<td>0.359</td>
<td>3.607</td>
<td>0.375</td>
<td>4.600</td>
</tr>
<tr>
<td>2</td>
<td>0.462</td>
<td>2.789</td>
<td>0.300</td>
<td>2.257</td>
<td>0.325</td>
<td>1.360</td>
</tr>
<tr>
<td>6</td>
<td>0.475</td>
<td>1.871</td>
<td>0.300</td>
<td>1.28</td>
<td>0.432</td>
<td>0.76</td>
</tr>
</tbody>
</table>

### Conclusion

In summary, Yb$_2$O$_3$ was introduced into TiO$_2$ photoanode of a dye-sensitized solar cell. Yb-doping improved $V_{\text{oc}}$ via its p-type dopant effect; shifts the energy level of the TiO$_2$ oxide film up and consequently increases the photovoltage. As more crystal defects introduced by increasing the concentration of Yb$_2$O$_3$ dopants; more photoinduced electrons were captured and hence photocurrent was decreased. The solar conversion efficiency of Yb-doped DSSC devices is lower than that of the undoped DSSCs.

### References


