Surface modification of dye-sensitized solid-state solar cells by plasma jet

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Abstract. Surface treatment of dye-sensitized solid-state solar cells (DSSSCs) by atmospheric pressure plasma jet was carried out to improve its characteristics using Ar/O₂ as process gas. It is a dry process and a low energy consumption method for surface modification of DSSSCs due to its generation at atmospheric pressure. Active species and radicals were generated by the atmospheric pressure plasma jet. Because these were flown by the gas, the TiO₂ surface was modified. The important parameters of DSSSCs, such as, the short circuit photocurrent densities (J_sc) and the open circuit photovoltage (V_oc) were measured by the solar cell evaluation system. Surface condition of DSSSCs was analyzed by an X-ray photoelectron spectroscopy (XPS), Ultraviolet Visible Absorption Spectroscopy (UV-VIS) and Scanning Electron Microscope (SEM). As a result, solar conversion efficiency of DSSSCs increased by 22.5% after 15min of dry treatment compare with before treatment.

1. Introduction

The dye-sensitized solar cells (DSSCs) which were invented by Grätzel are well known as clean and low cost photovoltaic devices due to their simple structure and use of low cost materials [1-5]. DSSCs have the disadvantage of leaks and deterioration of electrolytic solution. The dye-sensitized solid-state solar cells (DSSSCs) could have the potential to be alternatives to the existent DSSCs [6-8]. DSSSCs use CuI as solid electrolyte, which does not leak from the cell and does not deteriorate. However, solar conversion efficiency of DSSSCs is lower than that of a conventional DSSCs efficiency [9].

One method for surface treatments of DSSCs is using chemicals [10-12]; wet process, which makes the process expensive and potentially harmful to the human body. TiO₂ surface modification by low pressure plasma treatment has been carried out, and an increase of the solar conversion efficiency has been reported using the RF-plasma [13-16] and vacuum deposition [17-21]. Modification methods in atmospheric condition, dielectric barrier discharge (DBD) [22, 23], corona discharge [24], and plasma jet [25-27], have been also reported. By using atmospheric pressure plasma, there is the advantage that does not require a vacuum device. It is necessary to apply about 30 kV for DBD and corona discharge [23, 24]. In this study, Surface treatment of DSSCs by atmospheric pressure plasma jet was studied to improve its efficiency. The discharge gap of atmospheric plasma jet was set at 2.1 mm. Thus only a relatively low voltage is required to energize the discharge which furthermore leads to a reduced...
electricity consumption. Effect on the DSSSCs by plasma exposure was investigated by using the solar cell evaluation system, an X-ray photoelectron spectroscopy (XPS), Ultraviolet Visible Absorption Spectroscopy (UV-VIS) and Scanning Electron Microscope (SEM).

2. Experimental setup for TiO$_2$ surface modification

Figure 1 shows the experimental setup for DSSSC sample surface modification by atmospheric pressure plasma jet. Atmospheric pressure plasma was generated between two electrodes. The high voltage electrode was made of tungsten wire (0.8 mm in diameter) and was fixed to the center of the glass tube, while the grounded electrode was an Aluminum-tape wrapped around a glass tube (5.0 mm outer diameter, 3.2 mm inner diameter). The plasma jet electrode was energized by an AC high voltage power supply. The process gas was fed through the glass tube from gas cylinders.

DSSSC sample and the plasma jet electrode were placed into a chamber to control the ambient gas. An Ar/O$_2$ mixture (5.00 + 0.25 L/min.) was used as the process gas. Additionally, the process gas can be humidified (relative humidity 65%) to confirm the water vapor effect on modification of DSSSC. The frequency of AC high voltage was set at 16.1 kHz. The distance between electrode and sample was fixed to 13 mm. The size of the TiO$_2$ sample was 0.5 cm$^2$. After the plasma exposure treatment, the sample TiO$_2$ sample was soaked to dye again for about 18 hours (N719 Ruthenium-based dye). I-V characteristics and various parameters of the sample were measured under simulated solar light (Air Mass 1.5) using a solar cell evaluation system (JASCO, CEP-25BX). The UV-VIS (UV-1600PC, SHIMADZU) was used to measure the dye absorption quantity. The XPS (ESCA-3400, SHIMADZU) was used to analyze chemical composition of the TiO$_2$ surface. TiO$_2$ surface before and after treatment was observed by the SEM (JEOL, JSM-7001F).

3. Result and discussion

3.1. Photovoltaic measurements

Figure 2 and Table 1 shows a comparison of photocurrent voltage (I-V) characteristics between untreated DSSSCs and treated DSSSCs. Treatment time of sample surface was 5, 10 and 15 min. The target sample was attached in the chamber and relative humidity in chamber was 0%. Three samples were treated simultaneously each time.
Table 1. Characteristics of untreated and treated DSSCs.

| Treated time | J_{SC} [mA/cm^2] | V_{OC} [V] | FF | η_{C} [%] |
|--------------|------------------|------------|----|----------|
| Untreated    | 4.25             | 0.54       | 0.69| 1.60     |
| 5            | 4.32             | 0.55       | 0.70| 1.65     |
| 10           | 4.82             | 0.49       | 0.71| 1.67     |
| 15           | 5.35             | 0.51       | 0.72| 1.96     |

As shown in Figure 2 and Table 1, the short circuit photocurrent density (J_{SC}) and the solar conversion efficiency (η_{C}) of untreated TiO_2 sample were 4.25 mA/cm^2 and 1.60%, respectively. J_{SC} and η_{C} measured for the DSSSCs sample treated for 15 min. were increased to 5.35 mA/cm^2 and 1.96% respectively, which corresponds to an increase with 25% and 22.5%. However, the open circuit photovoltage (V_{OC}) decreased. Fill factor (FF) was not changed because J_{SC} was increased and V_{OC} was decreased. Conversion efficiency was improved with increasing treatment time.

3.2. Effect of humidity on the surface modification of DSSSCs

The dry treatment (dry process gas with relative humidity 0%), and the wet treatment (humid process gas with relative humidity 65%) were carried out to compare the effect of humidity. Figure 3 shows a comparison of the conversion efficiency between the dry treatment and the wet treatment. The dry treatment improved the conversion efficiency with about 20% after 15 min treatment time. The wet treatment decreased the conversion efficiency with about 45% after 15 min treatment time.
3.3. Dye adsorption quantity

Dye adsorption quantity of TiO$_2$ surface versus treatment time are shown in Figure 4. After Dry treatment, dye adsorption quantity increased with about 5%. On the other hand, after Wet treatment, dye adsorption amount decreased with about 20%. Hydrophilic group modification could be occurred both treatments (result will be next session). However, humidity in process gas inhibited the dye adsorption and decreased the conversion efficiency.

![Figure 4](image1)

**Figure 4.** Dye adsorption versus treatment time for dry and wet treatment. Applied voltage was set at 5.0 kV. The analysis of dye adsorption amount using UV-VIS. Solid line corresponds to the dye adsorption amount after the dry treatment. The broken line corresponds to the dye adsorption after the wet treatment.

3.4. XPS analysis

Ti 2p and O 1s XPS spectra of TiO$_2$ sample surface treated for 15 min with AC high voltage are shown in Figure 5. Table 2 shows the stoichiometry value of the atomic content of Ti 2p and O 1s peak.

Figure 5 shows the XPS spectra of Ti 2p on the TiO$_2$ surface after the dry treatment (15 min.). Ti 2p spectra has been analyzed for four peaks, i.e. Ti$^{4+}$ 2p$_{1/2}$, Ti$^{3+}$ 2p$_{1/2}$, Ti$^{4+}$ 2p$_{3/2}$, and Ti$^{3+}$ 2p$_{3/2}$. The surface stoichiometry was determined by calculating the relative peaks area as ratio of the total Ti 2p and O 1s in XPS spectra. The Ti$^{3+}$ surface state in Ti 2p XPS spectra increased from 3.27% to 3.9% after 15 min of Ar/O$_2$ plasma treatment. O 1s XPS spectra was measured as well as Ti 2p to investigate the surface reaction. Figure 6 shows the XPS spectra of O 1s. The Ti$_2$O$_3$ peak in O 1s was increased from 27.01% to 32.19% after 15 min of Dry treatment. Ti$^{4+}$ $\rightarrow$ Ti$^{3+}$ reduced reaction could be occurred at TiO$_2$ sample surface [28-30]. Part of TiO$_2$ surfaces were changed to Ti$_2$O$_3$ as shown in Figure 6. This surface reaction determined the increase of the electric conductivity of the DSSSCs sample surface and consequently, solar conversion efficiency was improved.

![Figure 5](image2)

**Figure 5.** (a) XPS spectra of Ti 2p before treatment. (b) XPS spectra of Ti 2p after 15 min treatment. Solid line shows analysis of four peaks, dotted line shows original peak.
Table 2. XPS relative peak areas of Ti2p and O1s before and after treatment.

|       | Ti$^{4+}$ 2p$_{1/2}$ | Ti$^{4+}$ 2p$_{3/2}$ | Ti$^{3+}$ 2p$_{1/2}$ | Ti$^{3+}$ 2p$_{3/2}$ | TiO$_2$ | Ti$_2$O$_3$ |
|-------|----------------------|----------------------|----------------------|----------------------|---------|-------------|
| Untreated [%] | 29.52              | 67.21                | 2.39                 | 0.88                 | 72.99   | 27.01       |
| 15 min [%]  | 29.61              | 66.48                | 2.93                 | 0.97                 | 67.81   | 32.19       |

3.5. SEM analysis
As shown in Figure 7, the photos of TiO$_2$ surface before and after treatment were taken by a SEM. Treated sample was treated by Dry treatment. Treatment time was 15 min.

![Figure 6. XPS spectra of TiO$_2$ and Ti$_2$O$_3$ before and after 15 min treatment. Applied voltage was set at 5.0 kV. After 15min Dry treatment, Ti$_2$O$_3$ peak was increased with 5% after treatment. Solid line corresponds to untreated sample. The broken line corresponds to Dry treated sample.](image)

![Figure 7. (a) FESEM image of Untreated TiO$_2$ surface. (b) FESEM image of Dry treated TiO$_2$ surface. Magnification was 30000.](image)

No significant change on the TiO$_2$ surface was observed. After plasma treatment by atmospheric plasma jet, TiO$_2$ surface was changed not as physical appearance but only as chemical composition.

4. Conclusions
Surface modification of dye-sensitized solid-state solar cell using plasma jet was carried out and the following conclusions were obtained:
1. The current density was increased and conversion efficiency was improved with about 20% after 15 min of the dry treatment. It could be due to the increase of dye adsorption quantity and the electron conductivity of the DSSSCs samples.
2. Conversion efficiency and dye adsorption quantity were decreased after the wet treatment. Inhibition of dye adsorption due to humidity occurred.
3. XPS analysis showed the Ti$_2$O$_3$ peak increase in TiO$_2$ surface. Electron conductivity and conversion efficiency increased due to the reduction action of Ti$_2$O$_3$ from TiO$_2$.  

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4. SEM analysis showed no significant change before and after the plasma treatment. TiO$_2$ surface was changed but only as chemical composition not as physical appearance.

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