Surface treatment of dye-sensitized solid-state solar cells using atmospheric pressure plasma jet

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INTRODUCTION

The dye-sensitized solar cells (DSSCs) which were invented by Grätzel are well known as clean and low cost photovoltaic devices, even, DSSCs has the disadvantage of leaks and deterioration of electrolytic solution [1]. The dye-sensitized solid-state solar cells (DSSSCs) could have the potential to be alternatives to the existent DSSCs. DSSSCs use CuI as solid electrolyte, which is not leaked from the cell and is not deteriorated. However, solar conversion efficiency of DSSSCs is lower than that of conventional DSSCs efficiency [2].

TiO_2 surface modification by low pressure plasma treatment has done, and increase of the solar conversion efficiency has reported. By using atmospheric pressure plasma, there is the advantage that does not require a vacuum device or can be processed with low power consumption. Surface treatment of dye-sensitized solid-state solar cells by atmospheric pressure plasma jet was studied to improve its efficiency. Effect on the DSSSCs by plasma exposure was investigated by photovoltaic measurements and XPS.

METHODS

(1) Experimental setup

Figure 1 shows the experimental setup for TiO_2 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 in outer diameter). The plasma jet electrode was powered with an AC high voltage power supply. The process gas was fed through the glass tube from gas cylinders. DSSSCs sample and the plasma jet electrode were placed into a chamber. 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%). The frequency of AC high voltage was set at 16.1 kHz. Table 2 shows the experimental conditions.

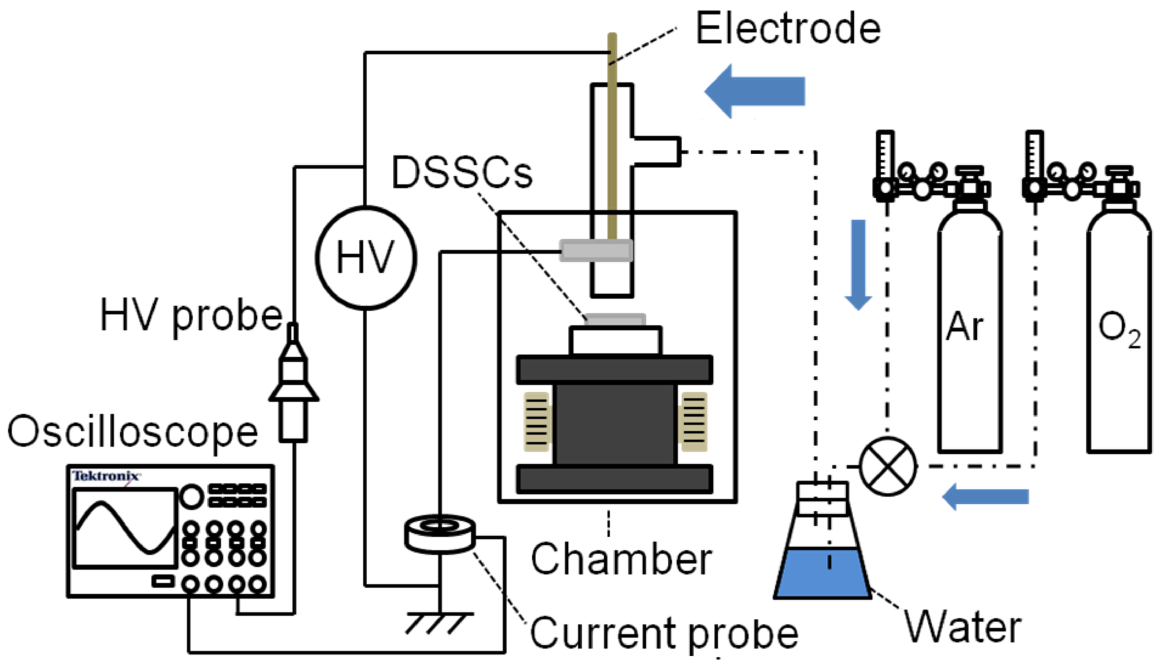


Fig. 1 An experimental setup for TiO_2 sample surface modification.

Table 1 Experimental conditions.

Carrier gas	Ar, O_2
Discharge voltage [kV]	5.0
Power source	AC
Distance between cathode and sample [mm]	13
Treatment time [min.]	0, 5, 10, 15
Flow rate [L/min.]	Ar : 5.0 O_2 : 0.25
Frequency [kHz]	16.1
Relative humidity [%]	0, 65

RESULT

(1)Photovoltaic measurements

Figure 2 shows a comparison of photocurrent voltage (I-V) characteristics between untreated DSSSCs and treated DSSSCs. The size of the TiO_2 sample was 0.5 cm square. After the plasma exposure treatment, the sample TiO_2 sample was soaked to dye again for about 18 hours. The kinds of dye is N719 which Ruthenium-based dyes. I-V characteristics were measured under simulated solar light (AM 1.5, 100mW/cm²) using a solar cell evaluation system (JASCO, CEP-25BX). 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%. 3 samples were made each treatment time.

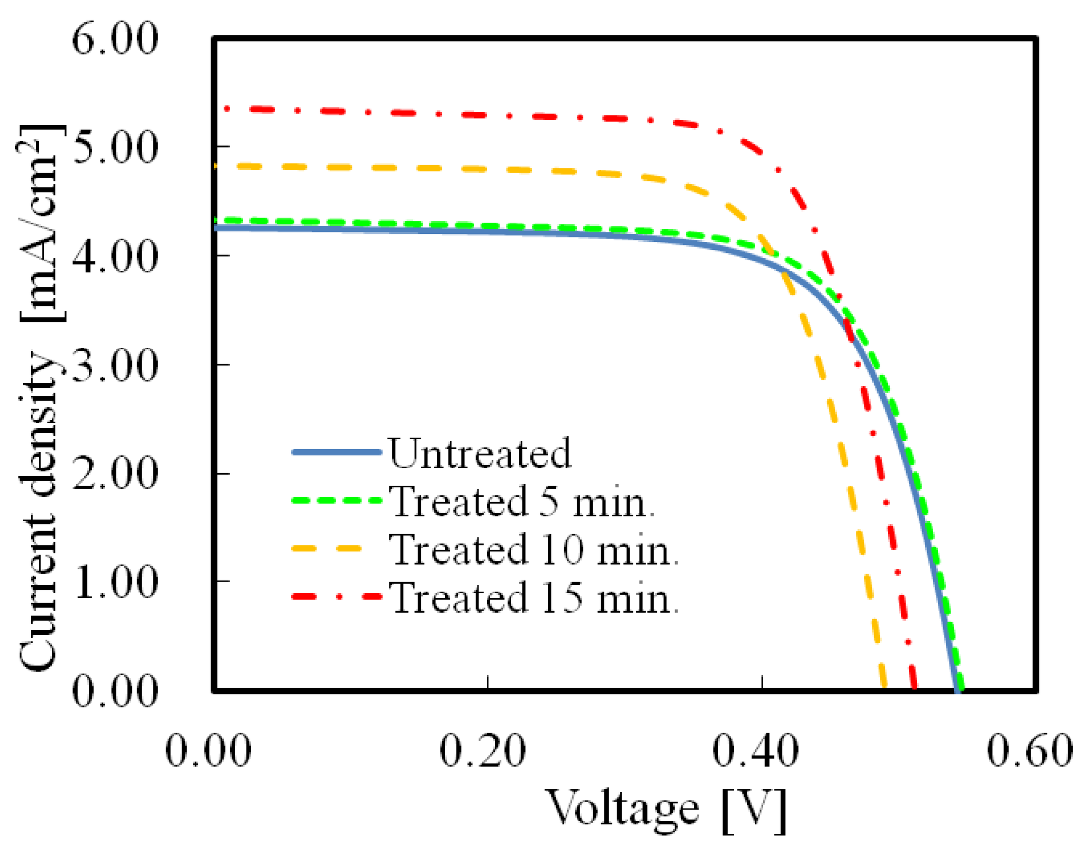


Fig. 2 I-V characteristics before and after various treatment times (5, 10 and 15 min.).

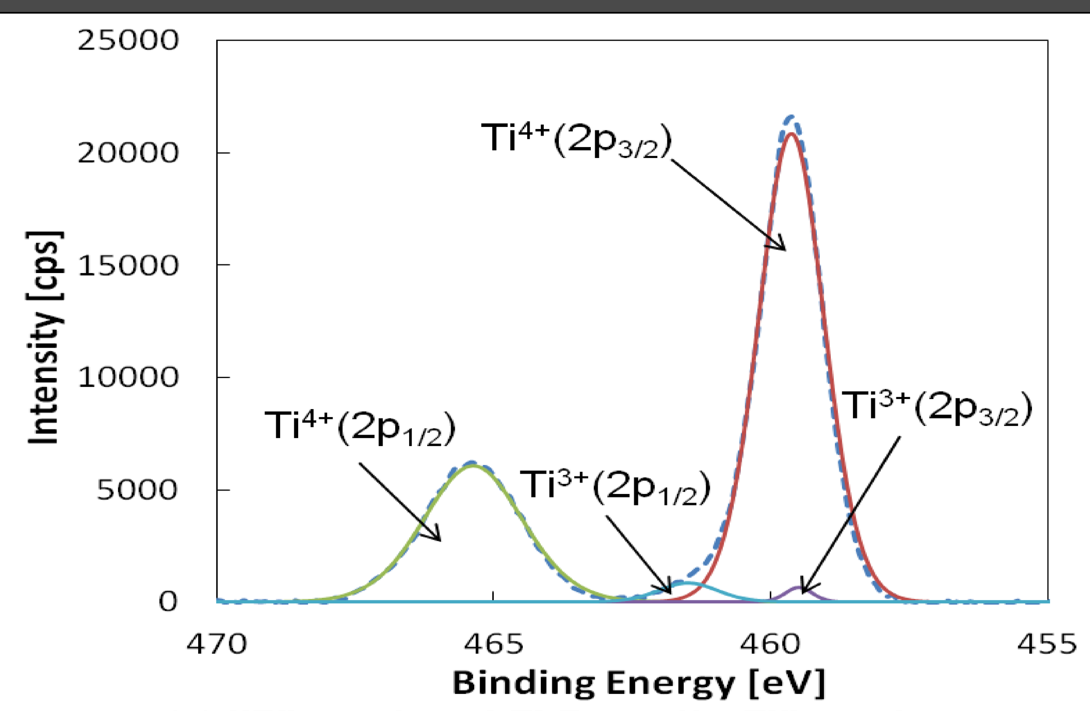
Table 2 Characteristics of no treated and treated DSSCs.

Treatment time [min.]	J_{sc} [mA/cm2]	V_{oc} [V]	FF	η [%]
No treated	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

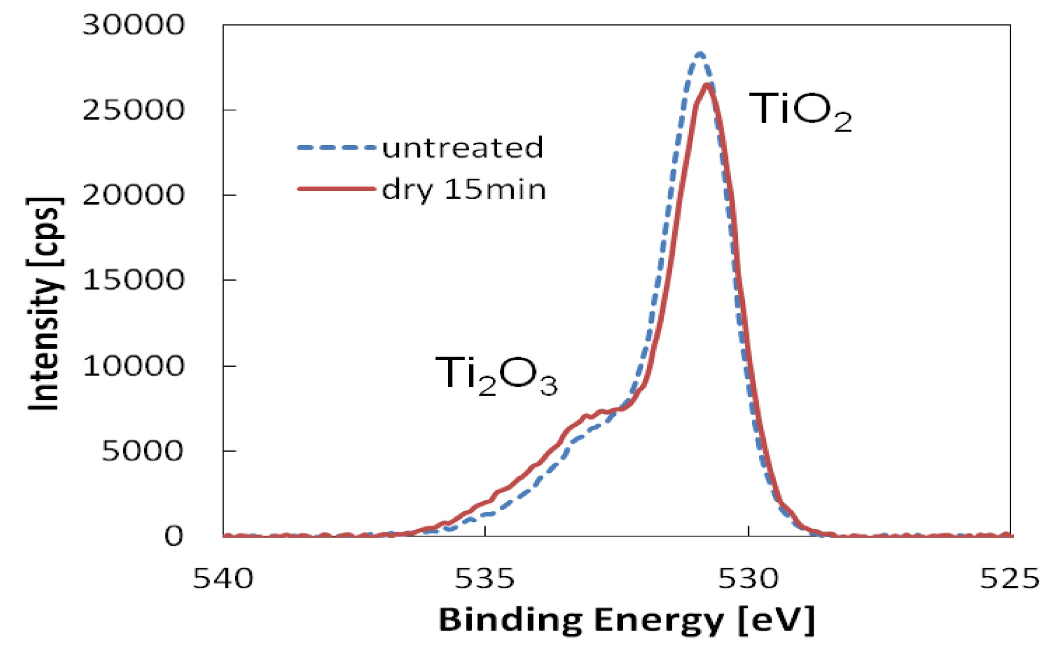
As shown in Figure 2 and Table 2, the short circuit photocurrent density (J_{sc}) and solar conversion efficiency (η) of untreated TiO_2 sample were 4.25 mA/cm² and 1.60%, respectively. Jsc and η measured for the DSSSCs sample treated for 15 min. were 5.35 mA/cm² and 1.96% respectively. However, the open circuit photovoltage (V_{oc}) decreased and fill factor (FF) was not changed. Efficiency was improved with increasing treatment time.

(2) XPS analysis

Ti 2p and O 1s XPS spectra of TiO_2 sample surface treated for 15 min are shown in Figure 3. Figure 3 (a) shows the XPS spectra of Ti 2p on the TiO_2 surface without plasma treatment (15 min.). Ti 2p spectra had analyzed with 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 was increased from 3.27% to 3.9% after 15 min of Ar/O_2 plasma treatment. O 1s XPS spectrum was measured as well as Ti 2p to investigate surface reaction. The Ti_2O_3 peak in O 1s was increased from 27.01% to 32.19% after 15 min of Ar/O_2 plasma treatment. $Ti^{4+} \rightarrow Ti^{3+}$ reduced reaction could be occurred at TiO_2 sample surface. Part of TiO_2 surfaces were changed to Ti_2O_3 as shown in Figure 3 (b). This surface reaction resulted the increase of the electric conductivity of the DSSSC sample surface and consequently, solar conversion efficiency could be improved.



(a) XPS spectra of Ti 2p on the TiO_2 surface (treated 15 min.).



(b) XPS spectra of O 1s on the TiO_2 surface (treated 15 min.).

Fig. 3 Ti 2p and O 1s peaks of TiO_2 sample surface by XPS.

(3) Effect of humidity

The Improvement rate of conversion efficiency was compared Dry treatment with Wet treatment as shown in Figure 4. 3 samples were made each treatment time. Dry treatment was used dry process gas (relative humidity 0%). Wet treatment was used humid process gas (relative humidity 65%). Dry treatment was improved the conversion efficiency. Improvement rate was increase about 20% after 15 min Dry treatment. Wet treatment was worsened the conversion efficiency. After 15 min Wet treatment, improvement rate was decreased about 45%.

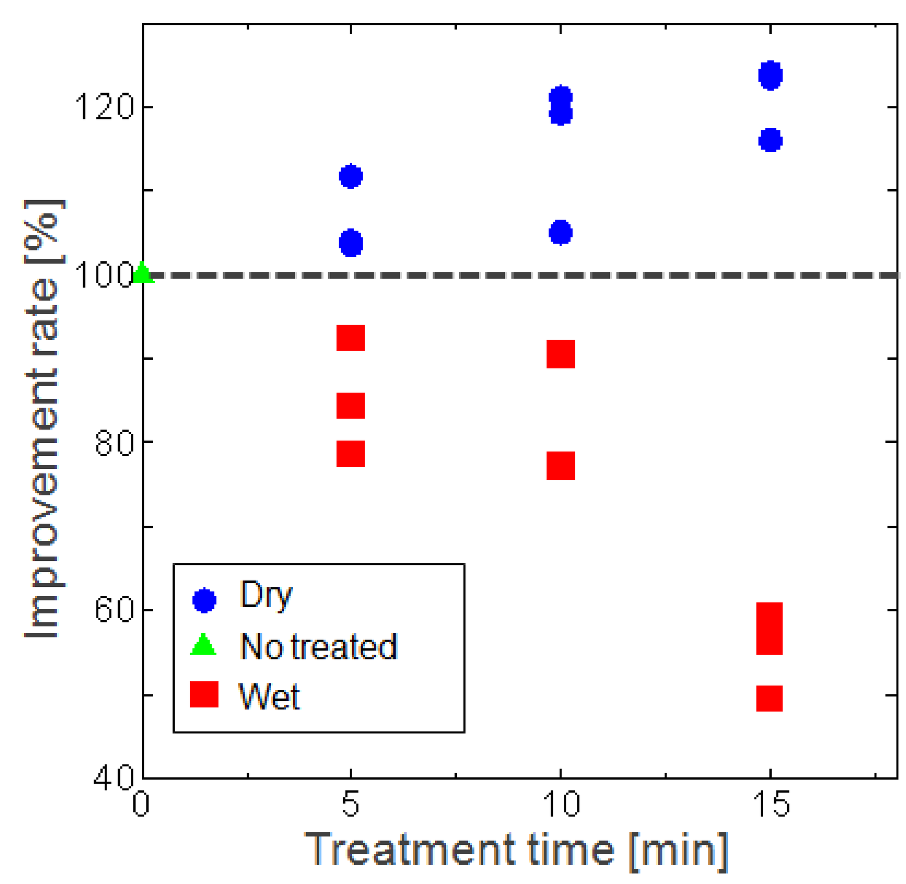


Fig. 4 Effect of humidity in the carrier gas.

CONCLUSIONS

In this study, the following conclusions were obtained.

1. The DSSSCs surface modification using atmospheric pressure plasma jet made the conversion efficiency of DSSSCs improve.
2. The electric conductivity of the DSSSC sample surface was increased after 15min plasma treatment.
3. Humidity in the carrier gas was worsened conversion efficiency of DSSSCs.

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