

Short communication

Low-temperature oxygen plasma treatment of TiO₂ film for enhanced performance of dye-sensitized solar cells

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Abstract

The effects of low-temperature O₂ plasma treatment of a TiO₂ film are studied with the objective of improving the performance of dye-sensitized solar cells (DSSCs). X-ray photoelectron spectra (XPS) reveal that the ratio of titanium dioxide to titanium sub-oxides is increased in the O₂ plasma-treated TiO₂ film, compared with that of the untreated TiO₂ film. This increase suggests that the oxygen vacancies in the film are effectively reduced. The near-edge X-ray absorption fine structure (NEXAFS) spectra results agree with the XPS result. It is proposed that there is a correlation between the shifts of the peaks in the NEXAFS spectra and the adsorption of N719 dye on the TiO₂ particles. A DSSC having an O₂ plasma-treated, 4 μm thick TiO₂ film electrode renders a short-circuit photocurrent of 7.59 mA cm⁻², compared with 6.53 mA cm⁻² for a reference cell with an untreated TiO₂ electrode of the same thickness. As a result of these changes, the solar-to-electricity conversion efficiency of the O₂ plasma-treated cell is found to be 4.0% as compared with 3.5% for the untreated cell. This improvement in the performance is rationalized on the basis of increased N719 dye adsorption on to the TiO₂, due to the reduction in the number of oxygen vacancies caused by the oxygen plasma treatment.

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1. Introduction

It is known that titanium can exist in sub-oxide forms, such as TiO and Ti₂O₃, in a nanocrystalline TiO₂ film. The oxygen vacancies due to such sub-oxides are surface defects from the perspective of DSSCs. Because of the large surface-to-volume ratio of the nanocrystalline TiO₂ film, these surface defects are expected to influence significantly the performance of the cell. Altering the surface structure of the TiO₂ film is one of the strategies adopted for improving the solar-to-electricity conversion efficiency [1–4].

A photoelectron conductive TiO₂ film usually suffers a small oxygen loss [5], which results in the formation of dominant surface defect states. These surface states are known to be located in the inter-band region and cause slow charge transport in a

TiO₂ film, owing to their trapping and de-trapping of electrons [6–8]. The oxygen vacancies, acting as electron scavengers, facilitate the recombination of injected conduction band electrons with the I₃⁻ ions in the electrolyte. In addition, inter-band surface defects can also increase light absorption in the visible region. The oxygen vacancy states are found to exist at about 0.75–1.18 eV below the conduction band edge of TiO₂ [9], and thus can be excited by visible wavelengths of around 506 and 614 nm from the valence band, respectively. Optical absorption by these surface states does not contribute to the photocurrent in a DSSC. Therefore, to reduce the recombination of injected electrons and the light absorption by the surface states, it is necessary to reduce the number of oxygen vacancies, which are detrimental to the functioning of a DSSC, as mentioned above.

It is known that the oxygen vacancies in a TiO₂ film can be reduced by exposing it to an O₂ atmosphere [10–13]. Aronson et al. [14] demonstrated, through AES and XPS analyses that the oxidation of a TiO₂ film in an O₂ plasma produces a uniform and stoichiometric TiO₂ surface layer of reproducible

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composition [14]. Gan et al. [15] reported that O₂ plasma treatment had profound effects on the surface cleanliness, the local atomic structure, and the stoichiometry of TiO₂ (1 1 0). The reduction and re-oxidation of TiO₂ (0 0 1) has also been investigated by NEXAFS [16].

This paper reports the results of low-temperature O₂ plasma treatment of TiO₂ films and the consequent improvement in the performance of DSSCs using such films. To the best of our knowledge, this is the first report concerning the effects of O₂ plasma treatment of TiO₂ films on the performance of the pertinent DSSCs. The objective of the O₂ plasma treatment is to decrease the number of oxygen vacancies in the TiO₂ film and thereby facilitate the transfer of electrons through it to the substrate.

2. Experimental

2.1. Preparation of TiO₂ film and its O₂ plasma treatment

A thin layer of non-porous TiO₂ was deposited on cleaned fluorine-doped tin oxide (FTO) mounted on glass that was purchased from Libbey–Owens–Ford (TEC 8, 75% transmittance in the visible spectrum), using 5% titanium(IV) butoxide in ethanol by spin coating at 3000 rpm, followed by annealing at 450 °C. A porous TiO₂ film with a thickness of approximately 4 μm was formed on this coated substrate by the doctor-blade technique, as follows. A TiO₂ colloidal mixture was prepared by grinding together for 10 min in a mortar 1.2 g of TiO₂ (P25, Degussa), 0.42 mL of 2,3-pentanedione, 0.24 g of poly(ethylene glycol) (Mw. 10,000), and 8 mL of water. Then, 0.24 g of poly(ethylene oxide) (PEO, Mw. > 1,000,000) was added to the contents of the mortar along with an additional 6 ml of water, and the mixture was ground for another 10 min. The paste obtained was then placed in a container and stirred well for 24 h. From this colloidal mixture, a TiO₂ film was made on the above pretreated FTO glass using the doctor-blade technique. The film was dried at 70 °C for 10 min before removing the tape used for regulating the thickness of the film, and then annealed at 450 °C for 30 min. The thickness of the TiO₂ film was approximately 4 μm, as judged by the thickness of the scotch tape used for preparing it.

The TiO₂ film was placed on the sample platform of a plasma source ion implantation (PSII) device which was built in-house as described elsewhere [17]. The typical plasma process was carried out at a base pressure of 1.33×10^{-1} Pa and a radio-frequency (rf) power of 50 W. The pressure of the working gas, i.e., oxygen, was regulated by a mass-flow controller. The TiO₂ film was treated with the oxygen plasma for 5 min.

2.2. Dye sensitization of TiO₂ film and fabrication of pertinent DSSC

The resulting plasma-treated TiO₂ film was sensitized with N719 dye by immersion for 24 h in an ethanolic solution of the N719 dye (0.3 mM of (Ru(II)L₂(NCS)₂:2TBA, where L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, Solaronix SA).

A two-electrode sandwiched DSSC was fabricated according to the procedure described elsewhere [18]. The DSSC had an active area of 0.4 cm × 0.4 cm. The electrolyte consisted of 0.05 M I₂, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-hexylimidazolium iodide, and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile. Another DSSC was prepared as a reference cell under identical conditions, but without oxygen plasma treatment.

2.3. Characterization of O₂ plasma-treated TiO₂ film and the DSSC

The XPS spectra of the TiO₂ films were obtained using a PHI-5800 (Physical Electronics, Eden Prairie, MN). NEXAFS spectra measurements were performed on the soft X-ray beamline 7B1 (KIST beamline) of the Pohang Light Source (PLS), operating at 2.5 GeV with a maximum storage current of 200 mA. The spectra were simultaneously collected in the electron yield mode in a vacuum of less than 2.0×10^{-6} Pa. The resolution of the photon energy was more than 0.2 eV. An HP 8453A diode array spectrophotometer was used for estimating the amounts of dye adsorbed on the TiO₂ films. For time-of-flight secondary ion mass spectrometry (TOF-SIMS) data, a Physical Electronics model PHI 7200 TOF-SIMS/SALI instrument was used with a Cs⁺ ion gun operated at 8 keV, at an ion current of 10 nA. The operating spot size was 50 μm in diameter. Charge neutralization was employed when the modified TiO₂ film was analyzed. The photocurrent–voltage measurements were carried out with a Keithley 2400 source-measure unit under AM 1.5 G conditions, with a 1000 W Xenon lamp and a KG-5 filter. The light intensity was adjusted to 100 mW cm⁻² using a silicon solar cell.

3. Results and discussion

3.1. XPS studies of O₂ plasma-treated and untreated TiO₂ films

The 4 μm thin TiO₂ film was treated with a low-temperature O₂ plasma, as described above. Though 10–12 μm films are usually required to achieve high solar-to-electricity conversion efficiencies, we employed only a very thin layer of TiO₂ film to enhance the influence of the O₂ plasma on the performance of the DSSC. The low-temperature, oxygen plasma-treated TiO₂ films and untreated TiO₂ films were characterized by XPS. The alteration of the TiO₂ surface after O₂ plasma treatment was evidenced by the XPS spectra. Fig. 1a and b shows the Ti 2p region of the spectra of the untreated TiO₂ film and the O₂ plasma-treated one, respectively. Three main peaks were resolved for the sub-regions, Ti 2p_{1/2} and Ti 2p_{3/2}, in the figures. Table 1 gives the deconvoluted values obtained from Fig. 1 only for the Ti 2p_{3/2} sub-region. The presence of Ti₂O₃ and TiO peaks indicate the non-stoichiometric nature of the TiO₂ surface. The surface stoichiometry was determined by calculating the relative peak areas of TiO, Ti₂O₃ and TiO₂ as a % with respect to the total area of the Ti 2p peak. The ratios of the relative peak areas of TiO₂ to Ti₂O₃ + TiO are compared in Table 1.

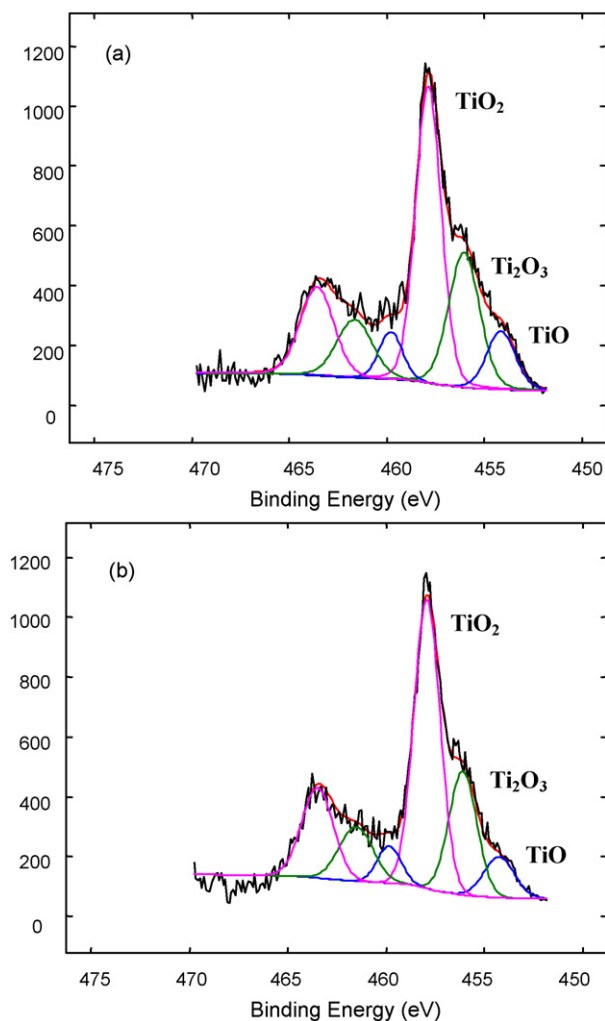


Fig. 1. XPS spectra of (a) untreated and (b) O_2 plasma-treated TiO_2 films.

The data reveal that the relative peak area ratio of TiO_2 to Ti sub-oxides increases from 1.30 to 1.62 after the O_2 plasma treatment, which indicates a change from a non-stoichiometric toward a stoichiometric TiO_2 film, and that the composition of TiO_2 in the film increases with respect to the sum of the compositions of Ti_2O_3 and TiO . This result implies that some of the lower oxidation states of the titanium in the film are oxidized and the oxygen vacancies in the film are filled by exposing the film to the O_2 plasma; this alteration of the surface is beneficial for enhancing the binding of dye molecules to the TiO_2 particles, as can be understood from the discussion given below.

Table 1

Relative peak areas in % with respect to the total area of the Ti $2p_{3/2}$ region and ratios of the relative peak areas for untreated and low-temperature O_2 plasma-treated TiO_2 films

Oxides (Ti $2p_{3/2}$, eV)	Untreated film (%)	Treated film (%)
TiO (454.2)	8.4	6.8
Ti_2O_3 (456.1)	21.4	19.4
TiO_2 (457.9)	38.7	42.6
$TiO_2/(Ti_2O_3 + TiO)$	1.30	1.62

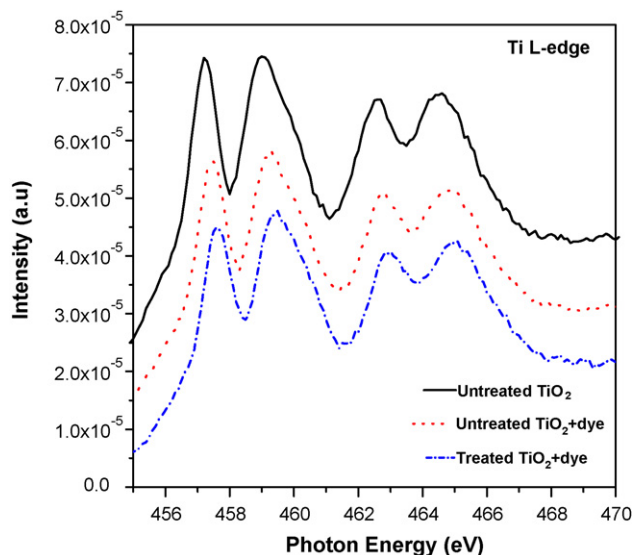


Fig. 2. NEXAFS spectra of Ti L edge for (a) untreated TiO_2 film, (b) untreated TiO_2 film with N719, and (c) O_2 plasma-treated TiO_2 film with N719 dye.

3.2. NEXAFS studies of O_2 plasma-treated and untreated TiO_2 films

Supporting evidence for the XPS analysis was obtained from the NEXAFS spectra. NEXAFS data is generally associated with surface/adsorbate interactions [19,20], especially for species with π -orbitals [21]. Fig. 2 compares the Ti L edge NEXAFS spectra of the three TiO_2 film samples, i.e., an untreated TiO_2 film (sample 1), an untreated but N719-coated TiO_2 film (sample 2), and an O_2 plasma-treated and then N719-coated TiO_2 film (sample 3). Sample 3 was prepared by coating N719 dye immediately after the O_2 plasma treatment to minimize the contact of the plasma-treated surface with air. The two doublets observed between 455 and 470 eV are characteristics of TiO_2 [22,23]. It can be seen that the two doublets of sample 3 are shifted slightly to higher energies relative to those of samples 2 and 1. The doublets of sample 2 also show a slight shift to higher energies with respect to the doublets of sample 1.

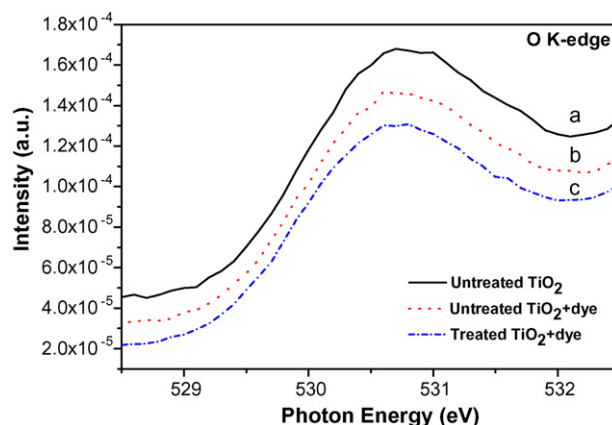


Fig. 3. NEXAFS spectra of O K-edge for (a) untreated TiO_2 film, (b) untreated TiO_2 film with N719 dye, and (c) O_2 plasma-treated TiO_2 film with N719 dye.

In Fig. 3, only one set of peaks, corresponding to one set of doublets of the O K-edge of the same three samples (as in Fig. 2) is observed. The set of peaks is located between 529 and 532 eV. Careful observation of this figure indicates that the peak of sample 3 is shifted discernibly toward a lower energy relative to the peaks of samples 2 and 1. The peak of the untreated but dye-coated TiO₂ film in turn shows a slight shift to lower energies with reference to the peak of the untreated TiO₂ film. These discernible shifts were confirmed by drawing tangents to the peaks. This shift behaviour is exactly opposite to that observed in the case of the Ti L edge NEXAFS spectra (Fig. 2) of the same three TiO₂ film samples.

In the absence of other NEXAFS information from the literature on a N719-coated TiO₂ film, it is concluded that both of the patterns of the shifts in Figs. 2 and 3 can be correlated not only with the stoichiometric changes in the TiO₂ film due to the O₂ plasma treatment, but also with an associated increase in N719 dye adsorption, because O₂ plasma treatment of the dye-coated TiO₂ film induces a further shift in the peaks relative to those of the dye-coated TiO₂ film.

3.3. Supporting evidence for NEXAFS analysis through absorption spectra and TOF-SIMS depth profiles

This phenomenon pertaining to the NEXAFS spectra regarding the N719 dye adsorption is supported by the absorption spectra in Fig. 4 and the TOF-SIMS depth profile in Fig. 5. That is to say, the O₂ plasma treatment enables a stronger binding between the N719 dye molecules and the surface of the treated TiO₂ film, as compared with that between the N719 dye molecules and the surface of the untreated TiO₂ film. Fig. 4 presents the absorption spectra of the N719 dye, obtained by desorbing it into 10 mM KOH from the plasma-treated and untreated TiO₂ films with dimensions of 2.0 cm × 2.0 cm and each with a thickness of 4 μm. This figure clearly shows that there is an increase in the adsorption of the N719 dye on the plasma-treated TiO₂ film, which supports our interpretation of the NEXAFS results that the O₂

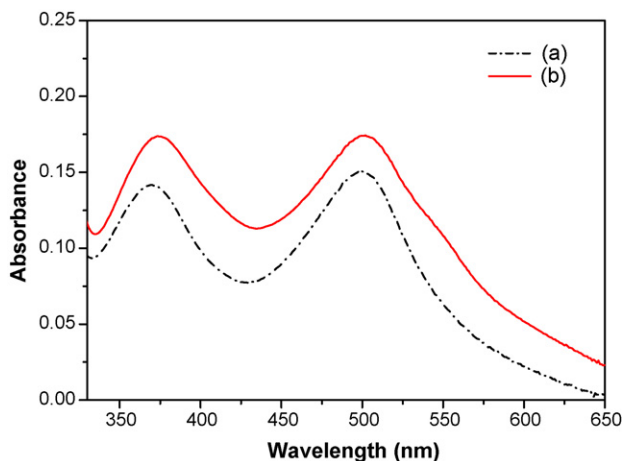


Fig. 4. Absorption spectra of N719 dye desorbed from (a) untreated TiO₂ film and (b) O₂ plasma-treated TiO₂ film.

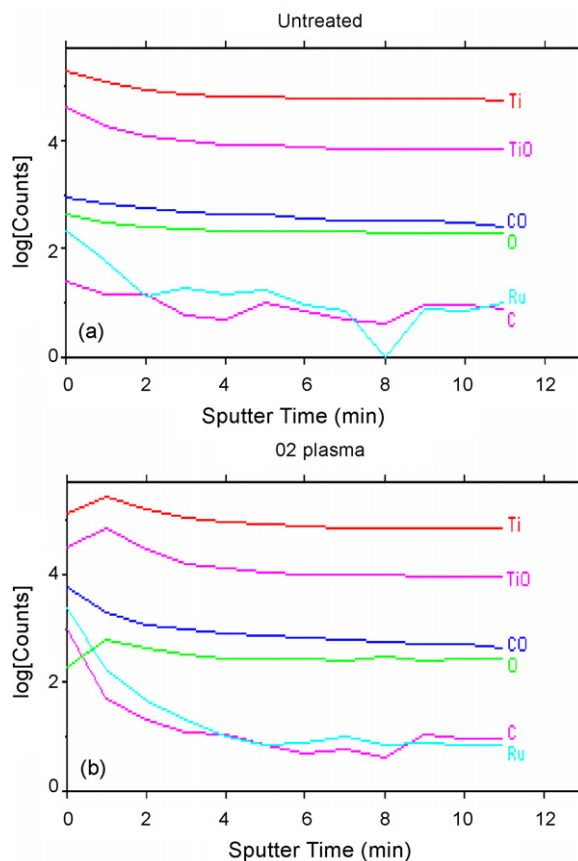


Fig. 5. TOF-SIMS depth profiles of untreated and O₂ plasma-treated TiO₂ films.

plasma-treated TiO₂ interacts more strongly with the N719 dye.

Fig. 5 presents the TOF-SIMS depth profiles of the dye-coated TiO₂ film and the dye-coated as well as low-temperature O₂ plasma-treated TiO₂ film. The distribution of six species, namely, O⁺, Ti⁺, TiO⁺, C⁺, CO⁺ and Ru⁺, of the TiO₂ films are compared. The first three species are associated with TiO₂ and the other three with the N719 dye adsorbed on the TiO₂ film. It is noted that after a sputtering time of less than 3 min the distribution of Ru⁺, CO⁺ and C⁺ in the O₂ plasma-treated TiO₂ film is considerably higher than that in the plasma-untreated TiO₂ film (the distribution of the species is represented on the log scale). This higher distribution of the dye-representing species indicates that the quantity of the N719 dye on the O₂ plasma-treated TiO₂ film is more than that on the plasma-untreated TiO₂ film.

3.4. Photocurrent–voltage curves of DSSCs with O₂ plasma-treated and untreated TiO₂ films

The increased dye uptake of the O₂ plasma-treated TiO₂ electrode (Fig. 4) leads to enhanced light harvesting and thereby increased photocurrent for the corresponding DSSC. Fig. 6 compares the photocurrent voltage (*J*–*V*) curves of the DSSCs made with the O₂ plasma-treated and untreated TiO₂ films with thicknesses of approximately 4 μm as the working electrodes. The short-circuit photocurrent density (*J*_{sc}), open-circuit volt-

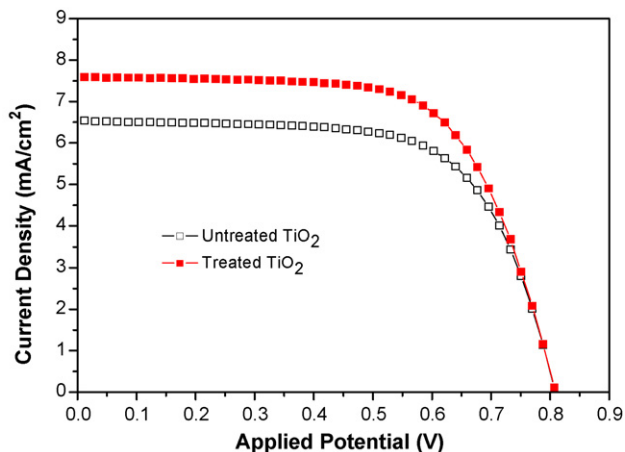


Fig. 6. J - V curves of DSSCs with untreated (open square) and O_2 plasma-treated (solid square) $4\ \mu\text{m}$ thin TiO_2 films. Light intensity is $100\ \text{mW cm}^{-2}$.

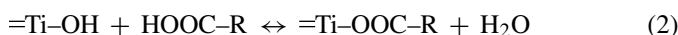
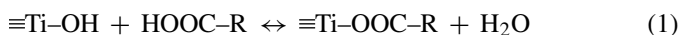
age (V_{oc}), fill factor (FF) and solar-to-electricity conversion efficiency (η) of the cells are summarized in Table 2. The J_{sc} of the DSSC with the O_2 plasma-treated working electrode is increased to $7.59\ \text{mA cm}^{-2}$, as compared with the J_{sc} value of $6.53\ \text{mA cm}^{-2}$ for the cell made with the untreated TiO_2 film, while the V_{oc} and FF values are essentially the same for both cells. Reduction of oxygen vacancies should lead to an increase in the value of the V_{oc} for the DSSC with plasma-treated TiO_2 film. This, however, does not happen here. It is known that the anchoring groups of the dye upon adsorption transfer most of their protons to the TiO_2 surface, charging it positively, and thereby move the Fermi level of TiO_2 positively [24]. In the present case, as the number of adsorbed dye molecules increases with plasma treatment, more H^+ ions are expected to be released from the dye, moving the Fermi level of plasma-treated TiO_2 more positively, compared with that of an untreated TiO_2 film. This positive shift in the Fermi level of the treated TiO_2 offsets the otherwise possible enhancement in the V_{oc} for its DSSC.

Due mainly to the increase in J_{sc} , the DSSC made with the O_2 plasma-treated TiO_2 film shows a higher solar-to-electricity conversion efficiency of 4.0%, as compared with 3.5% for the cell prepared with the untreated TiO_2 film. The increase in J_{sc} is consistent with the increased amount of N719 dye adsorption.

When the thickness of the TiO_2 film is increased to approximately 8 and $12\ \mu\text{m}$ and the films are treated with low-temperature O_2 plasma, the J_{sc} of the DSSC increases to 11.02 and $11.79\ \text{mA cm}^{-2}$, respectively. That is to say, doubling or tripling of the thickness of the TiO_2 film from $4\ \mu\text{m}$ does not yield proportionate increases in J_{sc} . This disproportionate increase in J_{sc} suggests that the upper portion of the TiO_2

layer is essentially affected by the low-temperature O_2 plasma treatment.

From the above results, it is clear that the adsorption of the N719 dye on the TiO_2 film increases with decreasing number of oxygen vacancies. The reason for the increased dye uptake by the TiO_2 film after the O_2 plasma treatment is not certain at this point, but can be explained on the basis of the electrostatic interaction between the oxidation state of titanium on the TiO_2 surface and the $-\text{COO}^-$ groups of the N719 dye molecules. The electrostatic interaction between the Ti^{4+} sites of the plasma-treated TiO_2 and $-\text{COO}^-$ groups of the dye is expected to be stronger than that between the coordinatively unsaturated Ti^{3+} sites of the untreated TiO_2 and the $-\text{COO}^-$ groups of the dye. The dye attachment reactions can be represented by Eqs. (1) and (2) as follows:



where $\equiv\text{Ti}-\text{OH}$ and $=\text{Ti}-\text{OH}$ stand for the hydroxylated TiO_2 surfaces of the Ti^{4+} and Ti^{3+} adsorption sites, respectively, and $\text{HOOC}-\text{R}$ represents the N719 dye with TiO_2 -anchoring carboxylic acid groups. The increased electrostatic interaction in the case of Eq. (1), which is attributable to the higher oxidation state of Ti^{4+} , as compared with that of Ti^{3+} of Eq. (2), causes its equilibrium constant to be larger than that of Eq. (2); this may explain the increased dye adsorption in the case of the O_2 plasma-treated TiO_2 sample. This is supported by a recent study by Aizawa et al. [25] of formic acid adsorption on the TiO_2 surface [25]. They reported that among the three types of configuration of the adsorbed formates, the one coordinated with two Ti^{4+} ions is energetically more stable and thus more abundant than the other two configurations involving oxygen vacancies. A similar phenomenon would be expected to occur in the case of the N719 dye, which suggests that a TiO_2 surface with less oxygen vacancies takes up more dye molecules.

Oxygen ion bombardment induces competition between the sputtering of oxygen ions from the oxide surface and oxygen implantation in the oxygen vacancies [26], depending on the rf power of the plasma; however, the low-temperature O_2 plasma surmounts the adverse effects of the sputtering process and implants oxygen atoms in the oxygen vacancies, as is evident from the filling of oxygen vacancies in the TiO_2 film. Moreover, O_2 plasma treatment can diminish the amount of carbon [15] on the surface of a TiO_2 film prepared with colloid-containing polymers. In the case of the untreated TiO_2 film, the residual carbons on the surface can block dye adsorption. This may be another reason for the higher dye adsorption of the O_2 plasma-treated TiO_2 film.

The best performance is observed for the DSSC made with the TiO_2 film subjected to O_2 plasma treatment for a period of 5 min at an rf power of 50 W. All of the results discussed above pertain to these conditions. We performed a simple stability test for the O_2 plasma promoted DSSC (i.e., the DSSC made with a plasma-treated TiO_2 film) and compared the results with the stability of an ordinary DSSC. Though the photocurrents of both of the cells decrease considerably over a period of 360 h, the O_2

Table 2
Characteristics of DSSCs with untreated and low-temperature O_2 plasma-treated TiO_2 films

Films	J_{sc} (mA cm^{-2})	V_{oc} (V)	η (%)	FF
Untreated	6.53	0.81	3.5	0.66
Treated	7.59	0.80	4.0	0.66

plasma promoted DSSC shows consistently higher J_{sc} values than the untreated one during this period. We also observed the effects of treating the TiO₂ surface by O₂ plasma source ion implantation (PSII) at negative voltages of -1 and -5 kV for periods of 30 s to 3 min, and noted that PSII at best leaves the $J-V$ curves unaltered at -1 kV after 3 min of treatment as compared with the $J-V$ curves obtained with an ordinary DSSC. This result implies that low-temperature O₂ plasma treatment is better than PSII for improving the performance of a DSSC.

We have previously investigated on the effects of various other gas plasmas [27], such as those of Ar, H₂, N₂ and CF₄. Under the same plasma conditions, CF₄ apparently caused damage to the TiO₂ surface, whereas low-temperature Ar, H₂ and N₂ plasmas brought about essentially no changes in the stoichiometry of TiO₂. Only the low-temperature N₂ plasma showed a favourable effect with respect to the photocurrent of the DSSC, but to a lesser extent than the low-temperature O₂ plasma treatment reported here.

It should be emphasized that we used only a 4 μm thick TiO₂ film as the photo anode and that a solar-to-electricity conversion efficiency of about 4% was obtained for a DSSC that employed this unusually thin film electrode. The focus in this research was primarily to understand the effects of O₂ plasma treatment of the TiO₂ film on DSSC performance. Further research employing a 12 μm thick TiO₂ film under optimum O₂ plasma treatment conditions is necessary to achieve higher efficiency for a DSSC. Research in this direction is currently in progress.

4. Conclusions

The XPS spectra of low-temperature O₂ plasma-treated and untreated TiO₂ films have revealed that the ratio of TiO₂ to Ti₂O₃ + TiO increases from 1.30 for the untreated TiO₂ film to 1.62 for the O₂ plasma-treated film. This suggests that there is a reduction in the number of oxygen vacancies in the O₂ plasma-treated TiO₂ film and therefore an increase in the amount of stoichiometric TiO₂. Owing to this change, a DSSC with the O₂ plasma-treated TiO₂ film electrode shows a relative increase of 10% in the J_{sc} , as compared with that of a cell with an untreated TiO₂ film electrode. This improvement is attributed to an increase in the adsorption of the N719 dye in the case of the O₂ plasma-treated TiO₂ film, as verified by absorption spectra and TOF-SIMS analysis. The patterns of the shifts in the NEXAFS spectra, due to O₂ plasma treatment, are correlated not only with the stoichiometric changes in the TiO₂ film, but also with the associated increase in the adsorption of N719. It is found that the O₂ plasma treatment of the TiO₂ film is more effective in enhancing the performance of a DSSC than when employing other types of plasma such as those with Ar, N₂, H₂, and CF₄.

Acknowledgments

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