

Enhanced photoelectric efficiency by surface modification of TiO₂ thin film using various acidic species

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(Received 16 December 2009 • accepted 19 May 2010)

Abstract—This study examined the photoelectric conversion efficiency of the dye-sensitized solar cell (DSSC) when the surface of a nanometer-sized TiO₂ film, which was prepared using the solvothermal method, was modified by five acid compounds. The TiO₂ film exhibited an anatase structure with an average particle size in the range of 10-15 nm, and the maximum absorption band was shown in the UV-visible spectrum around 360 nm. The surface colors of the carboxylic acid-modified TiO₂ films were changed to light or dark with differing energy conversion efficiencies. Particularly, the conversion efficiency was considerably enhanced from approximately 6.25% for the non-modified TiO₂ film to approximately 7.50% for the film treated by acetic acid of 1.0 mole, with the N719 dye under 100 mW/cm² of simulated sunlight. FT-IR analysis of the films after N719 dye adsorption confirmed that the IR spectrum of the modified TiO₂ showed a sharp and strong band at 500 cm⁻¹, which was assigned to a metal-O bond, due to the formation of a new Ti-O bond between the O of COO⁻ and the Ti atom, which was relatively weaker in the non-modified TiO₂. Furthermore, these results were in agreement with an electrostatic force microscopy (EFM) study showing that the electrons were transferred rapidly to the surface of the acetic acid-modified TiO₂ film, compared with that on the non-modified TiO₂ film.

Key words: DSSC, Carboxylic Acids, Enhancement of Photovoltaic Efficiency, EFM, FT-IR

INTRODUCTION

Dye-sensitized solar cells (DSSC) have been studied extensively due to their low cost, less toxic manufacturing, easy scale-up, light weight and potential use of flexible panels, compared to conventional p-n junction devices [1-3]. DSSC consists of a sensitizing dye, transparent conducting substrates (F-doped tin oxide), nanometer-sized TiO₂ film, iodide electrolyte, and counter electrode (Pt or carbon) [4,5]. When a dye molecule absorbs light, electrons on the highest occupied molecular orbital (HOMO) are excited to an electronically excited state: the lowest unoccupied molecular orbital (LUMO). When a dye molecule absorbs light, it leads to the excitation of electrons on the highest occupied molecular orbital (HOMO) to an electronically excited state, the lowest unoccupied molecular orbital (LUMO). The excited dye molecule injects an electron into the conducting band of the TiO₂ film. The oxidized dye is restored by electron donation from the reducing ions in the electrolyte, usually an organic solvent containing a redox system. The donated electron is in turn regenerated by the reduction of conjugated ions in electrolytes. The circuit is completed by electron migration through an external load [6-9].

The following four factors influence the photoelectric performance of the DSSC. 1) The electron transfer time from the dye to TiO₂ electrons must be shorter than the recombination time between the generated electrons and holes in the dye. 2) The conduction band of the TiO₂ semiconductor should be higher than the LUMO energy of the dye. 3) The electrons on the conduction band of TiO₂ should not be combined with the oxidation-reduction electrolytes. 4) The

dye molecule should not decompose during the passage of electrons from the electrolyte, so that this reaction has a strong influence on the cell lifetime. The most important factor for increasing the DSSC efficiency is the strong interaction between the dye and the TiO₂. If the dye molecules are stably coordinated onto the surface of the TiO₂ film in structural or energy divisions, the electrons generated at the LUMO of the dye can be passed to the surface of TiO₂ without the partial loss of any electrons, which eventually raises the photoelectric efficiency. Additionally, the perfect combination of the dye on the TiO₂ surface can depress the by-reaction between the TiO₂ surface and the electrolytes, thereby increasing the cell life. However, no research has yet been conducted on modification of the thin TiO₂ film surface in order to improve the photovoltaic efficiency in DSSC.

Therefore, this study tried to enhance the photoelectric conversion efficiency of DSSC by modifying the surface of the nanometer-sized TiO₂ film, which was prepared using the solvothermal method, by five acid compounds with carboxyl group. The synthesized sample was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible and Fourier transform infrared (FT-IR) spectroscopy, and electrostatic force microscopy (EFM) analysis. The photovoltaic performance of six types of TiO₂/dye (N719) solar cell was evaluated from the overall conversion efficiency, fill factor (FF), open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}).

EXPERIMENTAL

1. Preparation and Characteristics of Nanometer-sized TiO₂

TiO₂ particles were prepared using the solvothermal method, according to the following procedure. Titanium tetraisopropoxide (TTIP,

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99.95%, Junsei Chemical, Tokyo, Japan) was used as the titanium and ethanol as the solvent. TTIP (1.0 mol) was added to 200 mL of ethanol and stirred homogeneously for 2 h. Acetic acid was added and the pH was maintained at 3.0 for rapid hydrolysis. The final solution was stirred homogeneously and moved to an autoclave for thermal treatment. TTIP was hydrolyzed during thermal treatment at 200 °C for 8 h under a nitrogen environment at a pressure of approximately 10 atm. The resulting precipitate was washed with distilled water until pH=7.0 and then dried at 100 °C for 24 h.

The synthesized TiO₂ powder was examined by XRD (X-ray Diffractometer, MPD, PANalytical, Yeungnam University, Korea) with nickel-filtered CuK α radiation (30 kV, 30 mA) at 2θ angles ranging from 5 to 70°, a scan speed of 10 min⁻¹ and a time constant of 1 s. The sizes and shapes of the TiO₂ particles were measured by high-resolution TEM (Transmittance Electron Microscopy, H-7600, Hitachi, Yeungnam University, Korea) operated at 120 kV. The UV-visible spectra were obtained with a Cary 500 spectrometer (Varian, Yeungnam University, Korea) with a reflectance sphere over the special range of 200 to 800 nm. The surface states and electric properties of the TiO₂ film were determined by EFM analysis (resolution; 0.1 nm (X-Y), 0.01 nm (Z), Veeco Co., National Center for Nanomaterials Technology, Pohang, Korea).

2. Manufacturing Dye-sensitized Solar Cell (DSSC)

As shown in Fig. 1, to prepare the TiO₂ thin film, a slurry was produced by mixing 5.0 g nanometer-sized TiO₂ powder with 10 mL alcohol after sonication for 24 h at 1,200 W/cm². The TiO₂ was fabricated by twice coating onto a fluorine-doped SnO₂ conducting glass plate (Hartford FTO, ~30 ohm/cm², 80% transmittance the in

visible region) by using a squeeze printing technique to give an approximate thickness of 10.0 μ m. The film was treated by heating at 450 °C for 30 minutes to remove the alcoholic solvent. The surface modification of the TiO₂ film by five acids (acetic acid, formic acid, benzoic acid, pivalic acid, and ammoniac acid) with carboxyl group in comparison with base compound (ammonia; NH₃)-modification is important. The acid concentrations were maintained at 1.0 mole, with an immersion time of 1 h. The modified thin film electrode was immersed in a 3.0 \times 10⁻⁴ M N719 dye solution at room temperature for 24 h, rinsed with anhydrous ethanol and dried. A Pt-coated FTO electrode was placed over the dye-adsorbed TiO₂ electrode, and the edges of the cell were sealed with a sealing sheet (PECHM-1, Mitsui-DuPont Poly Chemical). The redox electrolyte consisted of 0.50 mol KI, 0.05 mol I₂, and 0.5 mol 4-tert-butylpyridine as a solvent. Modification of the acidic or ammonia achieved a variety of colors for the acquired film electrodes. Treatment with benzoic and pivalic acids produced bright colors, whereas acetic acid and ammonia produced a dark color. This result suggested that the interaction between the TiO₂ film and dye molecules differed according to the variation in chemical properties induced by the surface modification. However, the formic acid modification did not induce any color change. The photocurrent-voltage (I-V) curves (Sun2000 solar simulator, ABET technology, Yeungnam University, Korea) were used to calculate the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and overall conversion efficiency of the DSSC. The I-V curves were measured under white light irradiation from a xenon lamp (max. 150 W, Newport). The incident light intensity and active cell area were 100 mW/cm² and 0.40 (0.8 \times 0.5) cm²,

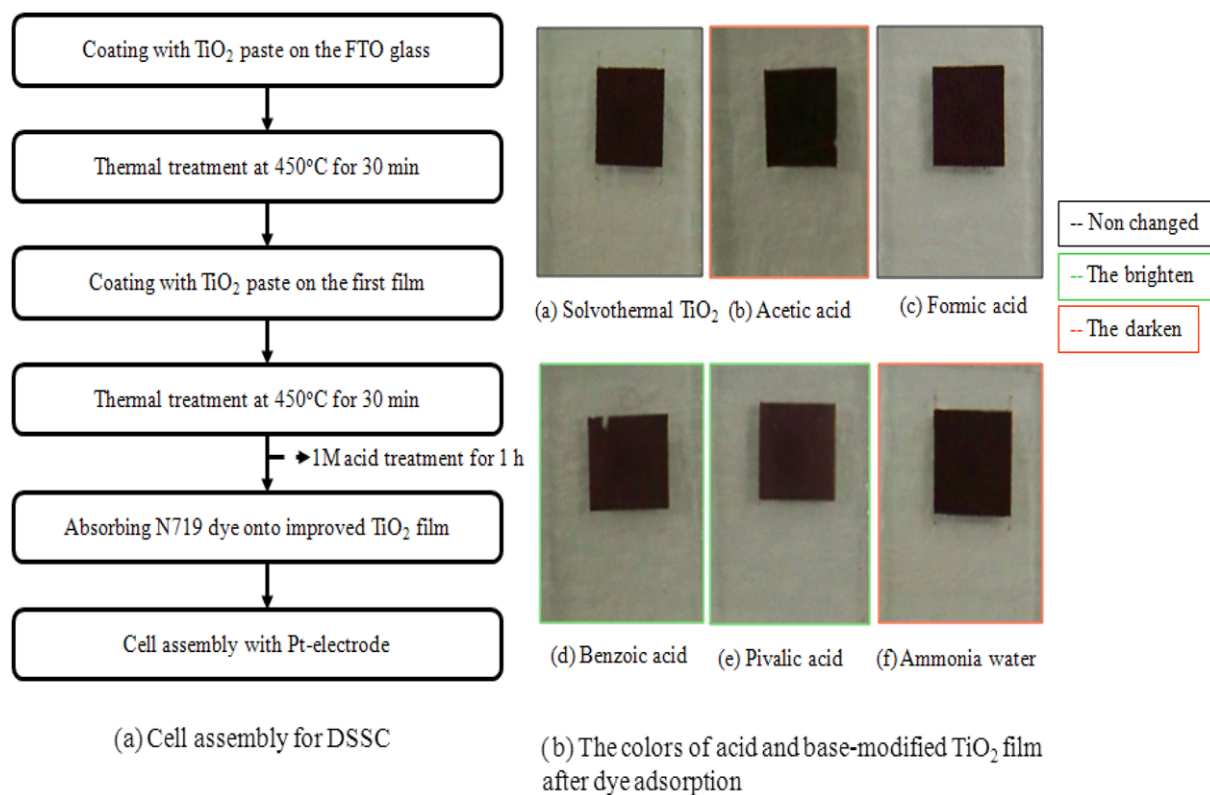


Fig. 1. Cell assembly (a) for DSSC with modification by various acids and ammonia onto nanometer-sized TiO₂ prepared using the conventional solvothermal method and the colors (b) of the acid- and ammonia-modified TiO₂ films after dye adsorption.

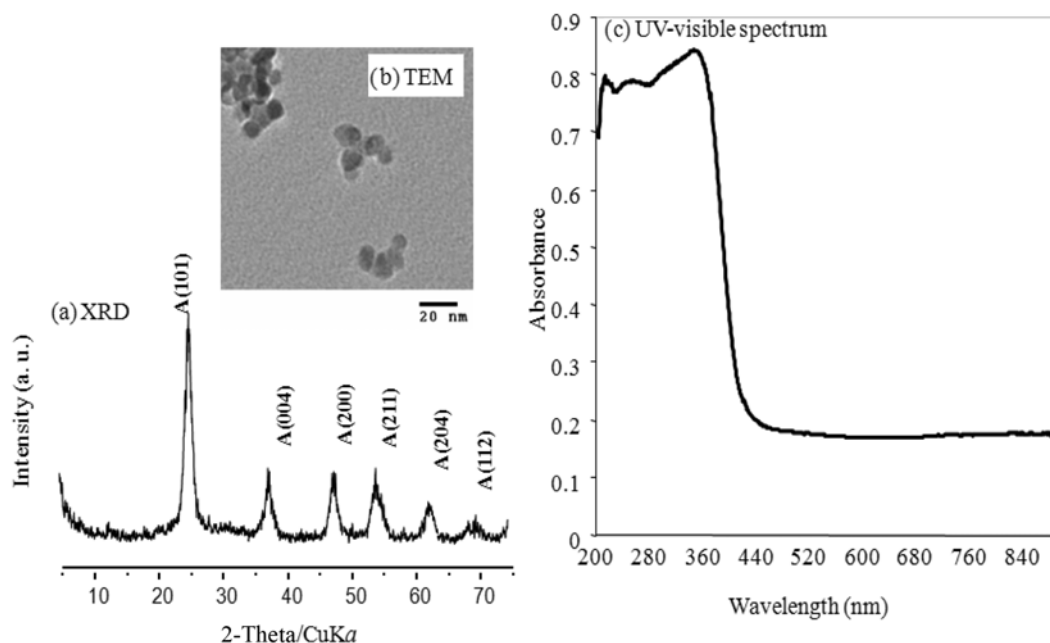


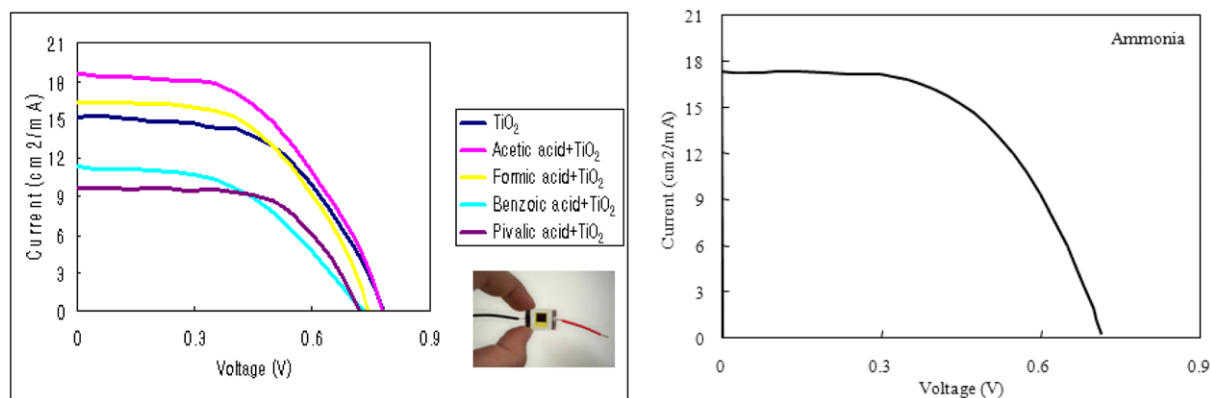
Fig. 2. XRD pattern (a), TEM image (b), and UV-visible spectrum (c) of TiO_2 prepared using the conventional solvothermal method.

respectively.

RESULTS AND DISCUSSION

Fig. 2 shows the XRD pattern, TEM image, and UV-visible spectrum of the TiO_2 nanometer-sized powder prepared by the solvothermal method. The anatase structure showed peaks at 25.3 , 38.0 , 48.2 , 54 , 63 , and $68^\circ 2\theta$, which were assigned to the (d_{101}), (d_{004}), (d_{200}), (d_{105}), (d_{211}), and (d_{204}) planes, respectively [10]. The full width at half maximum (FWHM) of the peak at $25.3^\circ 2\theta$ was 1.593° . Scherrer's

equation [11], $t=0.9\lambda/\beta\cos\theta$, where λ is the wavelength of the incident X-rays, β the FWHM height in radians, and θ the diffraction angle, was used to estimate the crystalline domain size as 14.7 nm. The upper photos of Fig. 2 show TEM images of the particle shape of TiO_2 . A relatively uniform mixture of rhombic and spherical particles with sizes ranging from 10 to 15 nm was observed. The UV-visible spectrum of the TiO_2 was obtained to determine the relationship between the solar energy conversion efficiency and spectroscopic property, as shown on the right. The absorption band for the tetrahedral symmetry of Ti^{4+} normally appears at approximately



Working electrode	Dye	Photo-efficiency (%)	Fill factor	J_{sc} (mA/cm ²)	V_{oc} (v)
TiO_2	N719	6.25	0.65	15.15	0.78
Acetic acid- TiO_2	N719	7.50	0.65	18.66	0.77
Formic acid- TiO_2	N719	6.86	0.66	16.36	0.74
Benzoic acid- TiO_2	N719	4.78	0.64	11.30	0.73
Pivalic acid- TiO_2	N719	4.42	0.67	9.57	0.71
Ammonia- TiO_2	N719	7.05	0.69	17.34	0.71

Fig. 3. The photoelectric efficiency as indicated by I-V curves in DSSC for the acid- and ammonia-modified TiO_2 films.

350 nm, with strong band intensity. The band gaps in a semiconductor material are closely related to the wavelength range absorbed, where the band gap decreases with increasing absorption wavelength. In our previous report [12], we confirmed that the solvothermal modification significantly shortened the band gap of the TiO₂ semiconductor and showed the better photo-activity.

The photoelectric properties were measured with a voltmeter and amperemeter (Sun2000 solar simulator, ABET technology, Yeungnam University, Korea) with a variable load. The voltmeter above power failure and a lock-in amplifier were used. A 150 W illuminant Xenon lamp was employed as a radiation source at an AM-1.5 radiation angle. The intensities of light were measured using a power analyzer and thermal smart-sensor. The FF and solar energy conversion efficiency (η) are calculated using Eqs. (1) and (2), respectively [13,14].

$$FF = I_{max} \times V_{max} / I_{sc} \times V_{oc} \quad (1)$$

$$\eta (\%) = P_{out} / P_{in} \times 100 = I_{max} \times V_{max} / P_{in} \times 100 = I_{sc} \times V_{oc} \times FF \quad (2)$$

Fig. 3 shows the I-V curves of six samples of TiO₂ modified by

five acids and ammonia. The FF, V_{oc} , J_{sc} , and overall energy efficiency were determined from the equations described above. A DSSC assembled with non-modified TiO₂ had a V_{oc} of 0.78 V and a J_{sc} of 15.15 mA/cm² at an incident light intensity of 100 mW/cm². The power conversion efficiency of the non-modified TiO₂ anatase structure was 6.25%. The efficiencies were enhanced with the modifications of acetic acid (7.50%), formic acid (6.86%), and ammonia (7.05%), but were decreased with the modifications of benzoic acid (4.78%) and pivalic acid (4.42%), due to their three-dimensional hindrance resulting from their larger molecules, and the electron-withdrawing effect. In particular, the efficiency enhancement reached 7.50% in the DSSC made from the acetic acid-modified TiO₂ film, with a J_{sc} of 18.66 mA/cm² and a V_{oc} of 0.77 V. This result confirmed that the modified TiO₂ with the light- and electron-donating acids is a better material in DSSC than the non-modified TiO₂.

Fig. 4 shows the interfacial binding energy between the dye molecules (N719) and the surface of the modified TiO₂ films, which was examined by FT-IR spectroscopy. Generally, the efficiency of the charge injection process is strongly dependent on the bonding structure of the dye molecules adsorbed on the TiO₂ film. In addition,

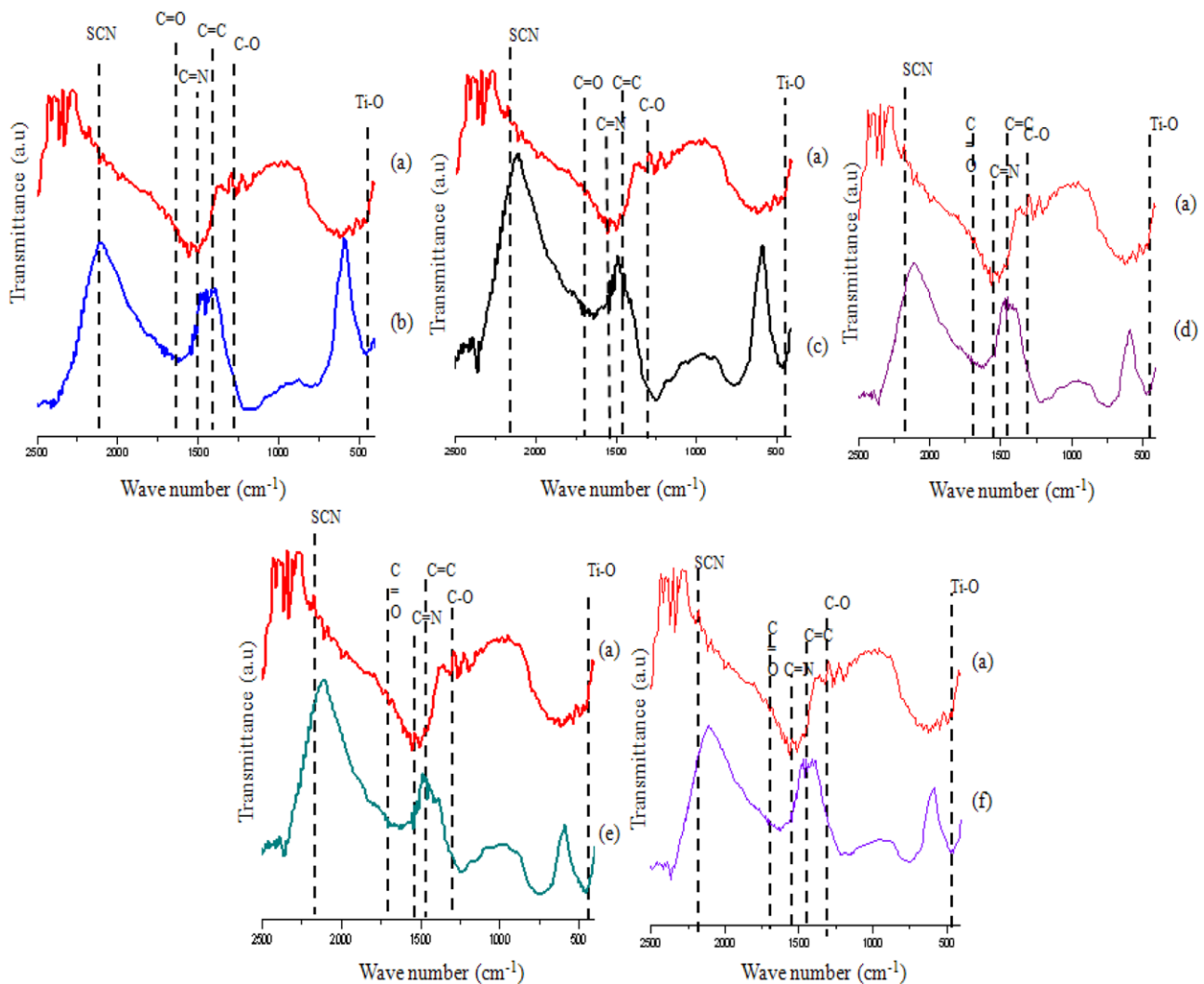
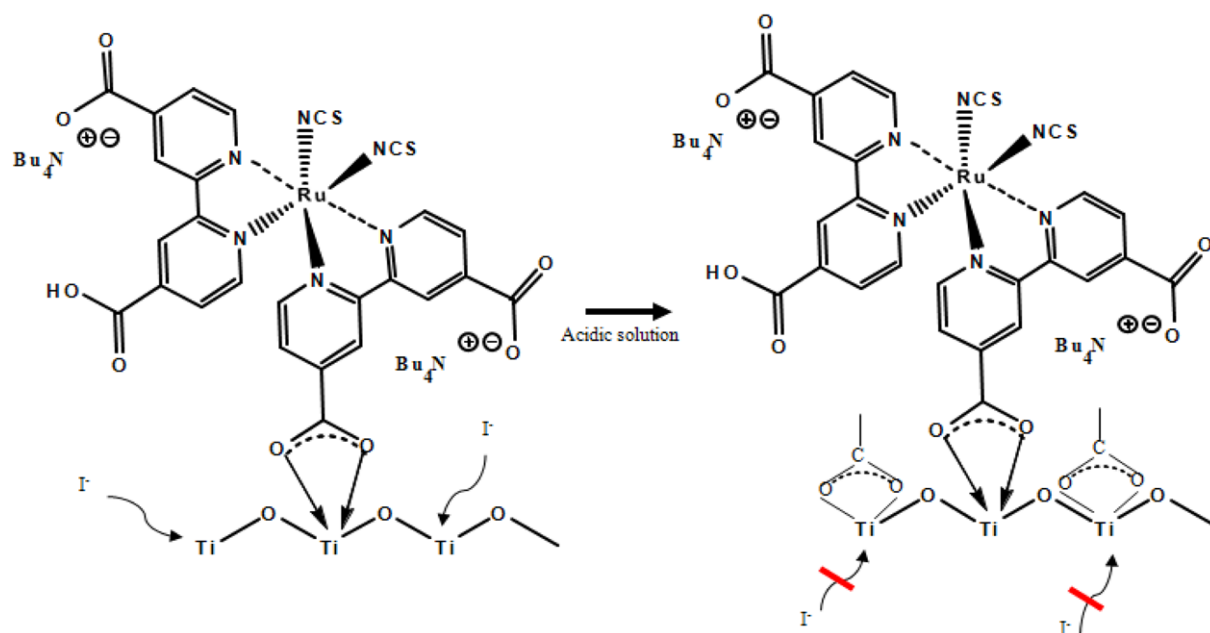


Fig. 4. FT-IR spectra on acid and ammonia-modified TiO₂ films after N719 dye adsorption: (a) non-modified, (b) ammonia-modified, (c) acetic acid-modified, (d) formic acid-modified, (e) benzoic acid-modified, and (f) pivalic acid-modified TiO₂ films.



Scheme 1. The interaction model between dye molecules and TiO_2 surface treated by carboxylic acid solution.

electron transfer in a DSSC is strongly affected by electrostatic and chemical interactions between the TiO_2 surface and the adsorbed dye molecules. Regarding the specific adsorption for FT-IR, the absorptions around 2,100-2,200 and 1,550 cm^{-1} were assigned to the SCN and C=N stretching bonds, respectively. The IR spectra showed absorption at 1,000-1,200 and 1,610-1,650 cm^{-1} , which were assigned to the C-O and C=O stretching modes, respectively. For the acetic and formic acid-modified TiO_2 films, the C=O band was decreased but the C-O band was increased because it was transferred to the C-O stretching mode due to bidentate coordination of the N719 dye on the surface of the TiO_2 films. On the other hand, the C=O band was rather significant on the benzoic and pivalic acid-modified TiO_2 films. This suggested that coordination of the N719 dye on the non- and the benzoic and pivalic acid-modified TiO_2 films was mainly due to the contribution of the monodentate and partially to that of the bidentate linkage. The bond between COO^- and the surface of the acetic and formic acid-modified TiO_2 films was assumed to be strong due to the perfect bidentate linkage. Furthermore, the IR spectrum of the acetic and formic acid-modified TiO_2 films showed a strong band at 500 cm^{-1} , which was assigned to a metal-O bond, due to the formation of a new Ti-O bond between the O of COO^- and the Ti atom, which was relatively weaker in the non-modified TiO_2 . Therefore, the acetic and formic acid-modified TiO_2 films had a better surface morphology than the non-modified TiO_2 film, resulting in an increase in I_{sc} due to the transportation of electrons.

As suggested in the beginning, the most important factor for increasing the DSSC efficiency is the strong interaction between the dye and the TiO_2 . Typically, when DSSC is driven, holes are created in the HOMO of the dye, because of electron transferring from the HOMO to the LUMO of the dye, and so the electrons move to the surface of TiO_2 . The holes are filled again by electron of electrolyte, where the information has to be considered seriously; it prevents reduction of the TiO_2 surface by the electrolyte, not the dye HOMO

reduction. If the surface of TiO_2 is reduced by the electrolyte, the TiO_2 surface is difficult trying to get the electrons from the dye and the conclusion is the photoelectric efficiency drop. In this study, in the DSSC cell assembly process, the TiO_2 photovoltaic efficiency is improved with doing the acidic treatment. We consider as shown in Scheme 1 that the TiO_2 surfaces, do not absorb dye, are blocked by carboxylic acid materials of small size, and the reaction between the electrolyte and the TiO_2 surface is depressed; however, the result is the opposite with the larger acid molecules. Consequently, interaction between the dye and the TiO_2 is increased relatively as a result of FT-IR.

The analytical method of EFM was used to determine the electron transfer on the different surface morphology in a higher electric current. Typically, the presence of a conductor and non-conductor within a nanometer-leveled film in the visual image can be distinguished by atomic force microscopy (AFM) using the modified EFM image. The power strength of the image between the samples and tips is measured while traversing voltage to the AFM tip bias. The presence of conducting and non-conducting areas in the sample can be determined from the responses of the AFM tip. [15] The phase changes periodically with the tip vibrating power cycle according to the charge and magnetic orientation. Consequently, the differences between the conducting and non-conducting surfaces are indicated by the amplitude and phase changes, and the change in width is expressed as the contrast of the image and roughness values (Ra). An Ra value in the phase is represented by the electrostatic field gradient. Therefore, the larger Ra value severely when tips specific in many areas of current are used. The Ra value can be determined indirectly by changing the twitch of the tip, according to the following equation [16,17].

$$\text{Ra} = 1/L_x L_y \int_0^{L_y} \int_0^{L_x} |f(x,y)| dx dy$$

Where $f(x, y)$ is the surface relative to the center plane and L_x and

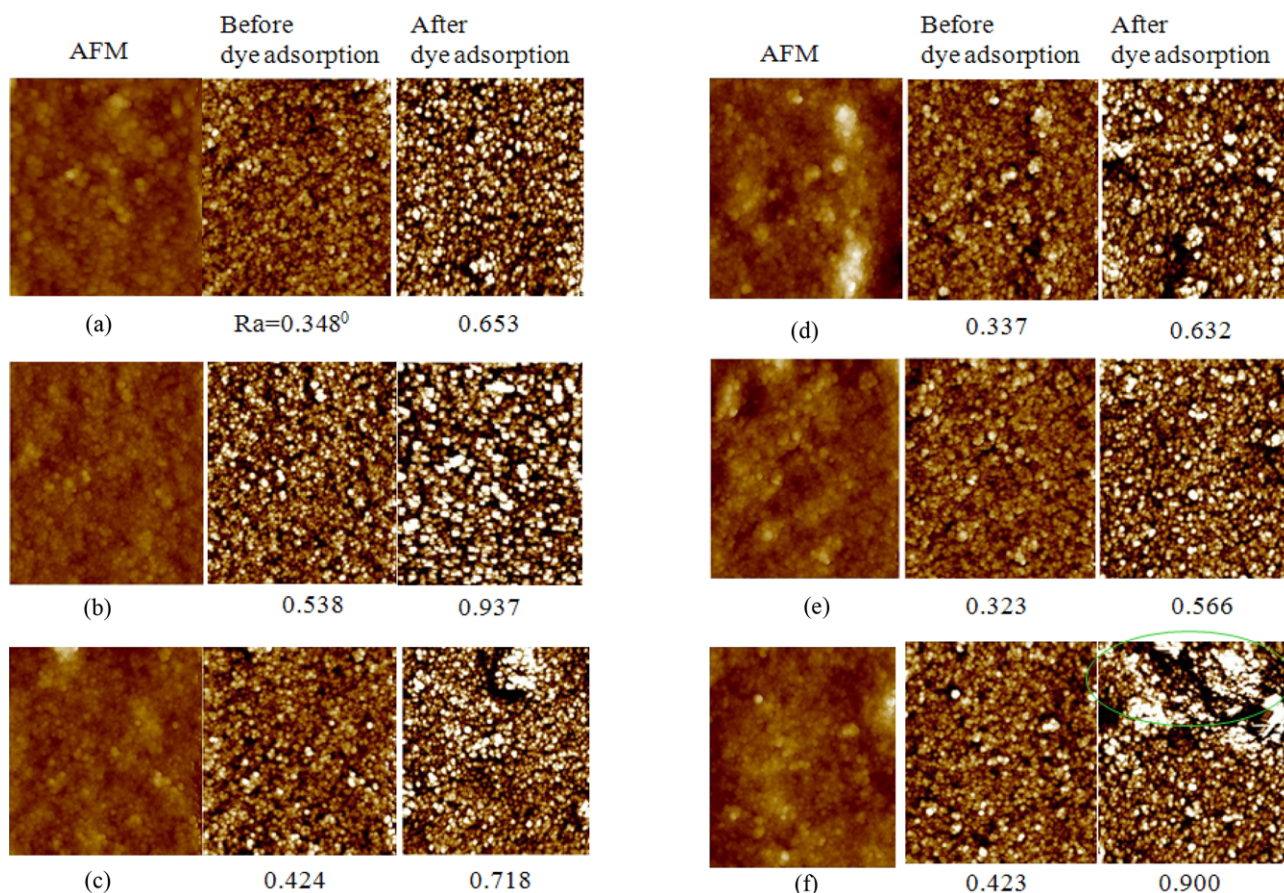


Fig. 5. AFM and EFM images of non- and acid-modified TiO₂ with and without N719 dye adsorption: (a) non-modified, (b) acetic acid-modified, (c) formic acid-modified, (d) benzoic acid-modified, (e) pivalic acid-modified, and (f) ammonia-modified TiO₂ films.

L_y are the dimensions of the surface.

Fig. 5 shows AFM and EFM images of six types of TiO₂ film before and after absorption of N719 dye in light condition. All TiO₂ films were 4.0 μm thick. When traversing at a voltage of 3.0 eV, the phase change was a maximum of 3.0 degrees in both samples. The phase difference is the difference in electrostatic force between phases, so that a bright image in the figure generally indicates the flow of charge [18]. When the five types of modified TiO₂ film were measured under light conditions, the images in the EFM photos were brighter than in the AFM photos, and in particular, the images were brighter with the adsorbing dye. The acetic and formic acid-modified TiO₂ films showed a more significant result after the adsorbing dye compared to the non-, and the benzoic and pivalic acid-modified TiO₂ films. In the ammoniac acid modification, unfortunately, the TiO₂ particles were exfoliated from the FTO surface, indicating that the effectiveness of the ammonia-modification was only temporary, and that this effectiveness would decrease long-term. Fig. 5 also shows the averaged Ra value of the six types of TiO₂ film, with and without dye adsorption, in the light condition. The non-modified TiO₂ film did not have a significant value before dye adsorption, but The Ra value was increased by 0.348 degrees from 0 degrees for the non-modified TiO₂ film before dye adsorption to 0.653 degrees after dye adsorption. Otherwise, the Ra value in the acetic acid-modified TiO₂ film was 0.937, which was 1.5-fold greater than that of the non-modified sample. These results revealed the good mobility

of the electrons flowing onto the surface of the TiO₂ film modified with the five types of acid, especially acetic acid.

CONCLUSION

Nanometer-sized TiO₂ was modified by using five acids in a cell assembly procedure to enhance the solar energy conversion efficiency. The performance on non-modified TiO₂ film in DSSC was compared with those of the five modified TiO₂ films. The acetic acid-modified TiO₂ DSSC showed excellent solar energy conversion efficiency compared to that of the non-modified TiO₂ and of that modified by the other four acids. In 100 mW/cm² simulated sunlight, the performance of the acetic acid-modified TiO₂ DSSC was as follows: solar energy conversion efficiency=7.50%, V_{oc} =0.77 V, J_{sc} =18.66 mA/cm², and FF=0.66. The electron density and electron flow on the DSSC films were explained by using roughness analysis based on the EFM images. Electrons were transferred more rapidly to the surface of the acetic acid-modified TiO₂ film than in the case of the non-modified TiO₂ film. Additionally, the FT-IR analysis results indicated that the interaction between the TiO₂ surface and dye molecules was strengthened by the acetic acid modification.

ACKNOWLEDGEMENT

This research was supported by the Basic Science Program through

the National Research Foundation of Korea (NRF) funded by Ministry of Education, Science and Technology (2009-0064865), for which the authors are very grateful.

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