



Effect of MnTiO₃ surface treatment on the performance of dye-sensitized solar cells

Kokn-Nara Bae^a, Suk In Noh^a, Hyo-Jin Ahn^{b,*}, Tae-Yeon Seong^{a,**}

^a Department of Materials Science and Engineering, Korea University, Seoul 136-713, South Korea

^b Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul 139-743, South Korea

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ABSTRACT

We investigate the effect of MnTiO₃ surface treatment on the performance of dye-sensitized solar cells (DSSCs). The MnTiO₃-treated TiO₂ sample reveals a smoother surface with fewer cracks than the bare TiO₂ sample. It is shown that the MnTiO₃ is an amorphous layer (~2 nm thick). The MnTiO₃-treated TiO₂ sample exhibits higher absorbance across the wavelength region of 450–800 nm than the bare TiO₂ sample. The MnTiO₃-treated sample gives the higher point of zero charge than the bare sample. Measurements show that the open-circuit voltage and the short circuit current are 0.64 and 0.67 V and 12.3 and 15.7 mA/cm² for DSSCs with the bare and MnTiO₃-treated TiO₂ electrodes, respectively. The MnTiO₃ treatment improves the cell efficiency by about 25%.

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1. Introduction

Dye-sensitized solar cells (DSSCs) work under the principle of sensitization known as Grätzel cells, which entails decoupling light absorption from charge carrier transport in a solar cell [1–3]. Conventional DSSCs consist of nanoporous semiconductors (working electrode), sensitizer (dye molecules), catalyst (counter electrode) and electrolyte of redox couple. DSSCs based on nanoporous electrodes (commonly TiO₂) are of considerable interest because of their low cost, impressive efficiencies, and less toxic manufacturing process [4,5]. However, DSSCs exhibit lower conversion efficiency than silicon solar cells, because of the problems, such as charge recombination, cell leakage, long-term stability, low scalability, etc. Among them, charge recombination is a particularly serious problem, causing a significant degradation in the performance of DSSCs. For nanoporous TiO₂ electrode where electrons are in close proximity to holes, interfacial charge recombination serves as one of the major problems [6,7]. Thus, to suppress the recombination in the nanoporous TiO₂, surface treatment processes were employed. For example, surface treatments using Al₂O₃, SiO₂, ZrO, ZnO, and MgO were performed to minimize charge recombination [8–11]. These metal oxides on the electrode could separate the injected electrons from the oxidized electrolyte, which can slow the recombination at the TiO₂ surface and consequently improve the cell performance.

Manganese titanate (MnTiO₃) was shown to exhibit strong absorption in the visible wavelength region, which could be beneficial to a solar energy system [12,13]. Furthermore, the conduction band edge and the surface pH of MnTiO₃ are higher than those of TiO₂ [14]. The higher conduction band edge of the MnTiO₃ is helpful for reducing the recombination and the basic pH at the electrode surface can attract more dye molecules. In this work, we investigate a way of improving the efficiency of DSSCs through reduction in the charge recombination and increase in the light absorption by treating the electrode surface using MnTiO₃. DSSCs were also fabricated using MnTiO₃-treated nanoporous TiO₂ electrodes (Fig. 1) and their characteristics were studied.

2. Experimental

A TiO₂ paste was prepared by combining TiO₂ nanoparticles (Degussa, P25) with hydroxypropyl cellulose (HPC, Aldrich), acetyl acetone, and distilled water. Nanoporous TiO₂ films were deposited onto transparent conducting glass substrates (F-doped SnO₂, 8Ω/□, Pilkington) using TiO₂ paste by screen printing. The films were dried in air, followed by calcination at 500 °C for 1 h. The MnTiO₃ treatment was performed by dipping the samples into a mixture of 0.2 M TiCl₄ (Aldrich) and MnCl₂ (Aldrich) solutions for 30 min, followed by rinsing with DI water, and then sintering at 500 °C for 30 min in air. Finally, the films were soaked into 0.5 mM Ru(dcbpy)₂(NCS)₂ (N719, Solaronix) in an ethanolic solution for 24 h at room temperature, and then washed with ethanol and dried in air. The counter electrode was produced by coating FTO glass substrates with a 5 mM solution of chloroplatinic acid hexahydrate

* Corresponding author.

** Corresponding author. Tel.: +82 2 3290 3288; fax: +82 2 928 3584.

E-mail addresses: hjahn@seoultech.ac.kr (H.-J. Ahn), tyseong@korea.ac.kr (T.-Y. Seong).

($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aldrich) in isopropanol. The coated substrates were heated at 450°C for 30 min. A 0.6 M BMII-based iodine solution was used as an electrolyte [15].

The structure of the samples was analyzed by X-ray diffraction (XRD, Bruker D8-Advance with $\text{Cu K}\alpha$ radiation). The presence of the MnTiO_3 was examined by X-ray fluorescence spectroscopy (XRF, Shimadzu XRF-1800). The morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi SU70), atomic force microscopy (AFM, SIS Nanostation II), and transmission electron microscopy (TEM, FEI Tecnai F20). Light absorption was analyzed by UV–vis spectrophotometer (Shimadzu, UV-1800). The current–voltage (I – V) characteristics of DSSCs were investigated under AM 1.5 simulate sunlight using a 150 W xenon lamp (LAB 50).

3. Results and discussion

Fig. 2(a) shows XRD patterns obtained from the bare- TiO_2 and MnTiO_3 -treated TiO_2 films. The characteristic diffraction peaks (indicated by the solid squares) are originated from the FTO substrate (JCPDS card No. 46-1088). The surface treatment causes no apparent shift in the diffraction peaks due to the presence of a small amount of Mn. The average grain sizes of the bare and MnTiO_3 -treated TiO_2 samples were calculated by the equation

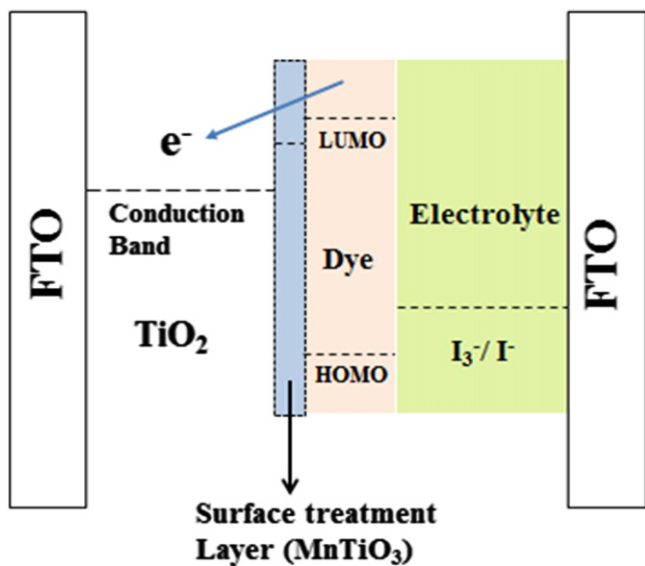


Fig. 1. Schematic diagram of a dye-sensitized solar cell.

[16], $D = 0.9\lambda / (\beta \cos \theta)$, where $\lambda_{(\text{CuK}\alpha)}$ and β are the X-ray wavelength and the full width at half maximum (FWHM), and θ the Bragg angle. The average sizes of the bare and MnTiO_3 -treated TiO_2 electrode at the main peak (101) were 26.6 and 28.2 nm, respectively. The MnTiO_3 treated sample shows slightly larger size. It is noted that there are no peaks related to MnTiO_3 phases. This may be due to the presence of a small amount of MnTiO_3 . However, the presence of Mn was confirmed by XRF measurement, as shown in Fig. 2(b). The Mn peak is clearly seen at 63 degree.

Fig. 3(a) and (b) exhibit FESEM images of the bare and MnTiO_3 -treated TiO_2 samples. Comparison shows that the MnTiO_3 -treated TiO_2 sample reveals fewer cracks (marked 'C') than the bare TiO_2 sample. Besides, comparison of the higher magnification images (Fig. 3(c) and (d)) shows that the MnTiO_3 -treated TiO_2 sample contains larger particles than the bare sample. The root-mean square (RMS) roughness was measured to be 86.2 and 67.4 nm for the bare and MnTiO_3 -treated samples, respectively. This implies that the MnTiO_3 treatment causes a smoother surface by filling the cracks (Fig. 3(a) and (b)). Fig. 3(e) and (f) reveal high resolution TEM images obtained from the bare and MnTiO_3 -treated TiO_2 samples. A comparison clearly shows that there is an amorphous layer (~ 2 nm thick) (as indicated by the arrows) on the treated TiO_2 sample, which is believed to be a MnTiO_3 layer. The MnTiO_3 effectively connects the TiO_2 particles, which facilitates the migration of the photo-injected electrons to the TiO_2 conduction band. Consequently, the internal resistance was reduced by efficient electron migration in the TiO_2 electrode [17].

Fig. 4(a) shows UV–vis absorption spectra from the dye-loaded films. The MnTiO_3 -treated TiO_2 sample reveals higher absorbance across the 450–800 nm wavelength region than the bare TiO_2 sample. This means that the MnTiO_3 treatment causes the dye molecules to more effectively attach to the TiO_2 electrode. Since the N719 dye molecules terminated with carboxyl group ($-\text{COOH}$) are connected to the metal oxide surface, the pH of the metal oxides is important for chemisorption between sensitizer and semiconductor. The dye molecules adhere more efficiently to the oxide electrodes if the pH of the oxide electrodes were more basic than the pH of the bare electrode [18]. The point of zero charge (pH_{ZPC}) that is known as the surface charge is used to represent the pH of the metal oxide. The point of zero charges of the bare and the MnTiO_3 -treated TiO_2 samples were calculated to be 5.80 and 7.83, respectively, [14] showing that the MnTiO_3 -treated sample gives higher pH_{ZPC} than the bare sample. Consequently, the MnTiO_3 treatment would increase the amount of the dye molecules adhering to the electrode.

Fig. 4(b) exhibits the I – V characteristics of DSSCs fabricated with and without the MnTiO_3 treatment. Measurements show that the open-circuit voltage (V_{OC}), the short circuit current (J_{SC})

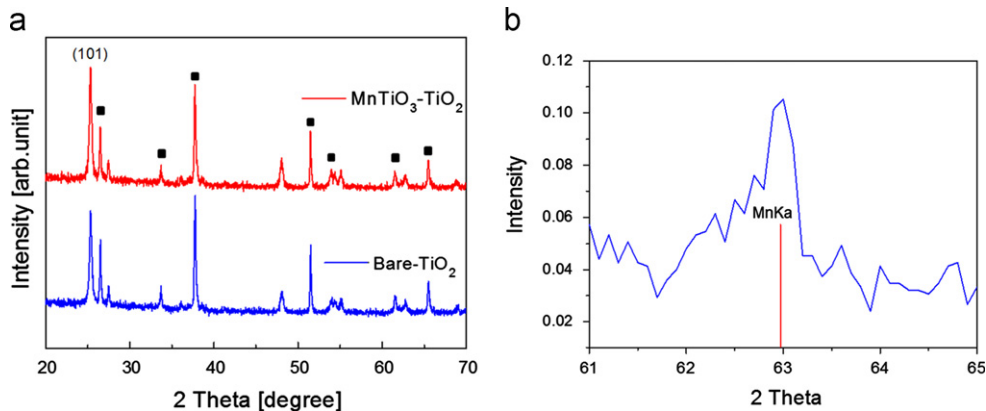


Fig. 2. (a) XRD patterns from bare and MnTiO_3 -treated TiO_2 films. (b) An XRF result of a MnTiO_3 -treated TiO_2 film.

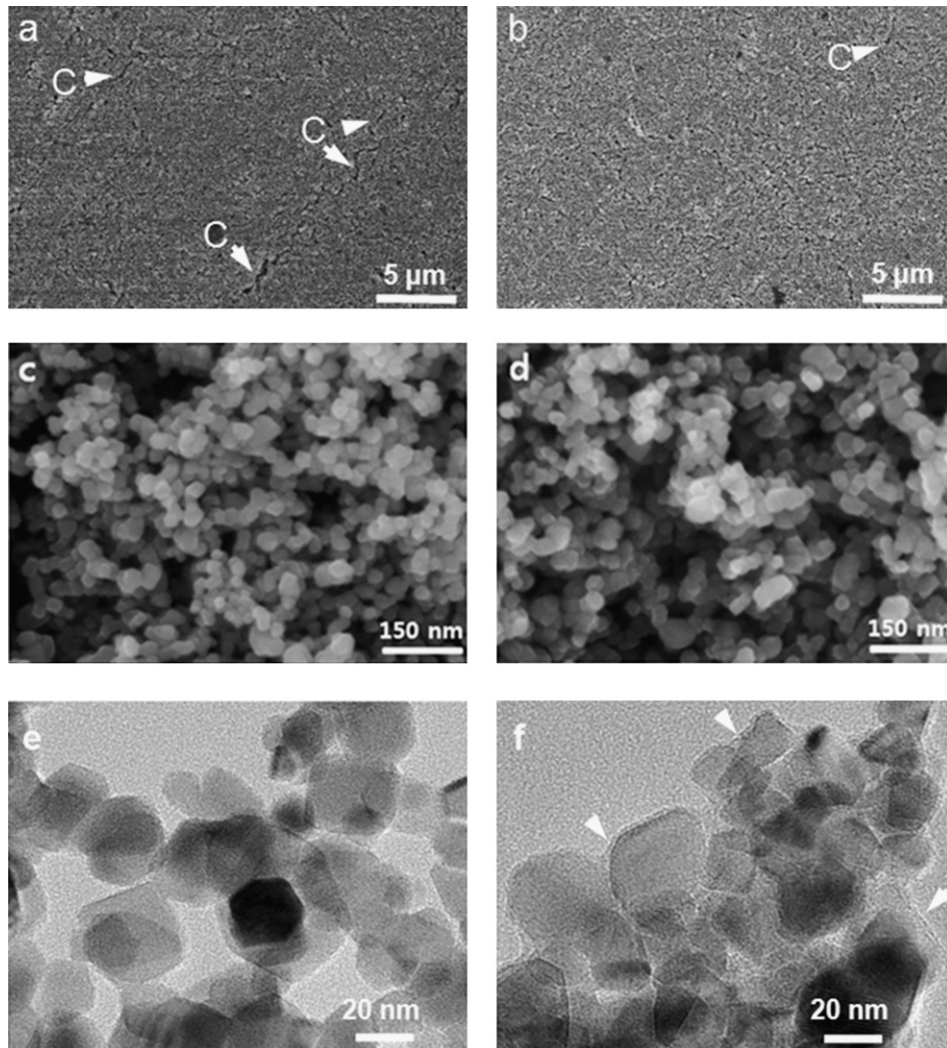


Fig. 3. SEM images of (a) bare and (b) MnTiO₃-treated TiO₂ samples. Higher magnification SEM images of (c) bare and (d) MnTiO₃-treated TiO₂ samples. High resolution TEM images obtained from (e) bare and (f) MnTiO₃-treated TiO₂ films.

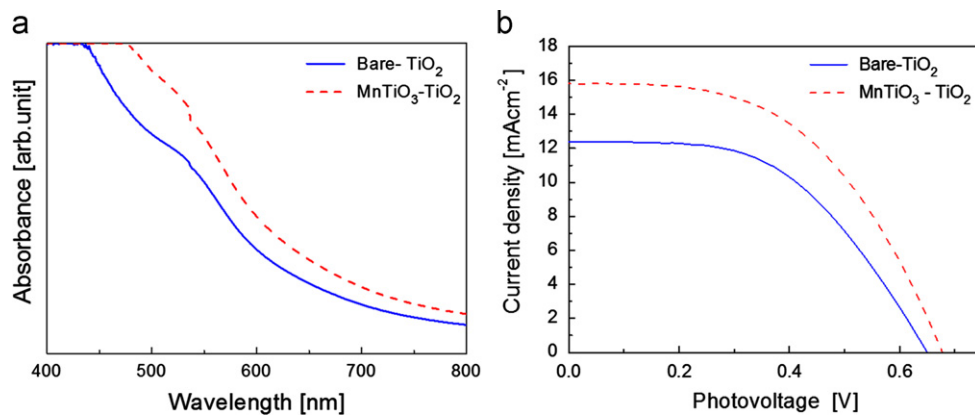


Fig. 4. (a) UV-vis absorption spectra of dye-loaded samples. (b) *I*-*V* characteristics of DSSCs with and without MnTiO₃ surface treatment.

and the fill factor are 0.64 and 0.67 V, 12.3 and 15.7 mA/cm², and 0.51 and 0.52 for the DSSCs with the bare and MnTiO₃-treated TiO₂ electrodes, respectively. A comparison demonstrates that after the MnTiO₃ treatment, the cell efficiency (η) is improved by about 25% (from 4.29% to 5.37%) due to the increase in J_{SC} and V_{OC} . The enhancement in J_{SC} of the MnTiO₃-treated sample can be explained as follows. First, it can be related to an increase in the

amount of the absorbed dye due to the increase in the pH of the surface-treated layer. Second, the improvement can be attributed to the decrease in the density of surface cracks (Fig. 3(b)) and the more efficient connections between the TiO₂ particles due to the amorphous MnTiO₃. The improved V_{OC} can be explained as follows. The conduction band edge (E_{CB}) of the MnTiO₃ (-4.04 eV) is higher than that of the TiO₂ (-4.21 eV). Thus, the

higher E_{CB} for the surface-treated layer suppresses recombination and back transfer between the TiO_2 electrode and the electrolyte.

4. Summary

We demonstrated a method of modifying TiO_2 electrode surface regions using $MnTiO_3$. The $MnTiO_3$ layer was used as a blocking layer to reduce the recombination and back transfer between the TiO_2 electrode and the electrolyte. The $MnTiO_3$ -treated sample gave the higher point of zero charge ($pH_{ZPC}=7.83$) than the bare sample ($pH_{ZPC}=5.80$), namely, the $MnTiO_3$ -treated sample was more basic than the bare sample. DSSCs with the $MnTiO_3$ -treated sample showed higher open-circuit voltage of 0.67 V and higher short circuit current of 15.7 mA/cm², leading to about 25% higher cell efficiency compared to DSSCs with the bare electrodes. This indicates that the $MnTiO_3$ treatment could represent a promising processing tool for the fabrication of high-performance DSSCs.

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