Application of Electrospun Nb:TiO₂ Nanofibers to Dye Sensitized Solar Cells

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The electrospun nanofibers of TiO₂ and Nb doped TiO₂ (NTO) were mixed into the TiO₂ mesoporous layer in the photoelectrodes of dye sensitized solar cells (DSCs) as a conductive agent, and their effects to the carrier mobility and photovoltaic characteristics were examined. From the time-transient spectra of photocurrent excited by the pulse laser irradiation, it was found that the diffusive velocity of photoexcited carriers was increased by the mixture of the bundle of electrospun nanofibers, and the increase resulted in the improvement of short-circuit current density and efficiency. The enhancement of carrier mobility was also observed due to the band bending at the interface of NTO/TiO₂. Thus, it was found that electrospun nanofibers of NTO were a good conductive agent for the accumulation of photoexcited carriers in dye/TiO₂ nanoparticles.

Key words: Electrospinning, Nanofibers, Dye Sensitized Solar Cells, Diffusion velocity, Nb doped titanium dioxide

1. INTRODUCTION

The electrospinning method[1-3] is a relatively simple and versatile technique for generating continuous ultrathin fibers, in which a polymer solution is injected from a small nozzle under an electric field as high as 1 kV/cm. The nonwoven cloth consisting of conductive electrospun nanofibers (ES-NFs) is applicable to a flexible and light-weight substrate instead of a transparent conductive oxide (TCO) layer with a glass substrate used in conventional dye sensitized solar cells (DSCs).

Furthermore, these one-dimensional nanostructure materials[4] such as nanotubes, nanowires, nanorods and nanofibers are known to be effective to improve the efficiency due to the improvement of carrier transport keeping the high interface area with electrolyte. Recently, ES-NFs of ITO[4] and TiO₂[5] which were treated to reduce the effect of grain boundaries within NFs were found to be effective to increase the efficiency. As a first step, we added bundles of ES-NFs of TiO₂ and Nb doped TiO₂ (NTO) as a conductive agent into the conventional photoelectrode of DSCs. TiO₂-NFs are expected to have many connections to TiO₂ nanoparticles in DSCs without making high potential barrier of carriers at the interface. NTO is well known as TCO with high transparency and conductivity having the same crystal structure of anatase[6,7]. By doping Nb atoms, the Fermi energy of TiO₂ is lowered without any large distortion of crystal lattice. Then, the band

bending at the interface between TiO₂ nanoparticles and NTO-NFs is expected to promote the carrier transfer at the interface[8,9].

In the present study, we added ES-NFs of TiO₂ and NTO to the dye-sensitized layer of mesoporous TiO₂ in conventional DSCs, and examined their effects to the photovoltaic characteristics. Furthermore, the effect for the carrier mobility was examined by the time-transient measurements[10-12] of photocurrent and photovoltage with a pulse laser irradiation.

2. EXPERIMENTAL

2.1 Structure of working electrodes

In this study, four types of structure shown in Fig.1 were adopted to the working electrode (WE) of DSCs. The fundamental type (DSC-1) consists of two mesoporous layers of TiO₂ nanoparticles with different diameter, the reflective layer and the dye-sensitized one, prepared by the squeegee method on an FTO/glass substrate. In DSC-2, FTO/glass substrate was covered by a buffer layer of NTO by the spin coating method to prevent the leakage of photoexcited carriers from FTO to the electrolyte. In DSC-3 and DSC-4, ES-NFs bundles of TiO₂ and NTO were mixed into the dye-sensitized layer in DSC-2, respectively.

2.2 Preparation of NTO buffer layer

The buffer layer of NTO was prepared by the spin coating method [13] on the FTO/glass substrate. The

Fig. 1 Structure of the working electrodes of DSCs used in the present study.

ethanol solutions of TiCl₄ (Wako, 16 %) and NbCl₅ (Wako, 95 %) were diluted by ethanol to get 0.15 M of titanium and niobium, respectively, under vigorous stirring for 2 h without being exposed to air. The two solutions were mixed to get 20 at% of Nb and stirred for 2 h, again. The mixed solution was stirred at 50 °C for 20 h in a closed vessel, and was spin-coated on the substrate at 2500 rpm in air for 1 min. Then, the films were calcined at 250 °C in air for 30 min and 540 °C for 1 h. The prepared NTO layer was confirmed to have anatase phase with Nb 6 at% by XRD and EDX.

2.3 Electrospinning method

For the preparation of TiO₂-NFs[1,2], titanium tetraisopropoxide (Ti[CH(CH₃)₂]₄, Wako) was added to an ethanol solution containing polyvinyl pyrrolidone (PVP; Wako, M_w ≈ 360,000) to get Ti concentration of 0.15 M. For NTO-NFs, ethanol solution containing PVP of niobium ethoxide (Nb(C₂H₅)₅, Wako) of which Nb concentration was 0.15 M was added to the above solution of Ti to get 6 at% of Nb, followed by magnetic stirring for 2 h.

The mixture was immediately loaded into a plastic syringe equipped with a 23 gauge stainless steel needle, and the sheet of nanofibers of TiO₂/PVP and NTO/PVP were prepared by an electrospinning apparatus (MECC, NANON-05) on a flat piece of aluminum foil. The electrospinning process was conducted in air under applied voltage 15 kV and feed rate 1.0 ml/h for 1 h. The sheet of TiO₂-NFs and NTO-NFs were obtained after successive calcination under 250 °C-30 min and 500 °C-2 h in air.

2.4 Preparation of DSC cell

As was shown in Fig.1, we adopted two-layer structure for the mesoporous TiO₂ layer of DSCs. The first "dye-sensitized layer" was prepared by the squeegee method with TiO₂ paste containing TiO₂ nanoparticles of PST-10R (JGC Catalysts and Chemicals, grain size ~ 10 nm). After drying at 80 °C for 10 min,

the first layer was covered with the second "reflective layer" by the squeegee method using the paste containing TiO₂ nanoparticles of SSP-20 (Sakai Chemical Industry). Although the grain size of the primary particles of SSP-20 was ~ 20 nm, they were aggregated to form secondary particles with a diameter of a few hundred nanometers. The films were calcined successively under 150 °C-5 min, 200 °C-10 min and 540 °C-30 min in air. For DSC-3 and DSC-4, the broken pieces of the electrospun sheet of TiO₂-NFs or NTO-NFs were mixed gently into the paste of PST-10R, respectively. Here, the volume ratio of mixed ES-NFs was set to ~10 % against the volume of the paste.

The prepared films were sensitized with N719 (0.3 mM in ethanol, Solaronix SA) at 50 °C for 20 h. Then, only the dye-sensitized layer consisted with smaller particles was colored by the dye, since the particles in SSP-20 with larger radius could hardly adsorb the dye on the surface. The cells were fabricated by a commonly used way with the electrolyte solution (Solaronix SA, R-50) and the counter electrode (CE) of FTO/glass covered by a platinum layer with a conventional sputtering method.

The photovoltaic measurements were carried out under simulated AM 1.5 illumination at 100 mW/cm² intensity (Bunkoukeiki, KP-3202).

2.5 Time-transient measurements

The time-transient measurements of photocurrent and photovoltage[10-12] were carried out with a second harmonics of Q-switched Nd:YAG pulse laser (Spectra Physics, GCR-130-10) with pulse width 7 ns, beam diameter 7 mm and wavelength 532 nm. A single pulse with 20 mJ/pulse was irradiated to WE under the illumination of white LED light so as to eliminate the influence of the trapping states of carriers. The power of LED light was controlled to get 400 mV of photovoltage under no irradiation of pulse laser.

In the time-transient photocurrent measurements, the potential between WE and CE was controlled to 400 mV

Fig. 2 SEM images of (a) a sheet of electrospun nanofibers of NTO and (b) magnification of nanofibers.

Fig. 3 SEM images of the cross section of WE of DSC, (a) the whole section and (b) the magnification of dye-sensitized layer.

Table I Summary of the photovoltaic parameters obtained for working electrodes with different structure.

	Structure of WE	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)	v_D (mm/s)	τ_c (s)
DSC-1	TiO ₂ /FTO	11.25	0.707	70.6	5.62	1.56	0.24
DSC-2	TiO ₂ /NTO/FTO	11.43	0.720	73.6	6.05	1.44	2.35
DSC-3	TiO ₂ =TiO ₂ -NFs/NTO/FTO	12.18	0.714	70.9	6.17	2.45	1.01
DSC-4	TiO ₂ =NTO-NFs/NTO/FTO	12.37	0.718	72.8	6.47	3.83	1.71

by a potentiostat (Hokuto Denko, HA-300, time constant = 1 μ s) to get zero output impedance equivalently. The output signal was monitored by a digital oscilloscope with several different scales. For the photovoltage measurements, the wires from CE and WE were connected directly to the oscilloscope. All the measurements were performed with a sufficient interval more than 10 min after the potential became stable.

3. RESULTS AND DISCUSSION

3.1 Structure of NFs and WE

The SEM images of prepared ES-NFs of NTO are shown in Figs. 2(a) and (b). It was found that the network of NTO-NFs with ~ 120 nm diameter was formed in the electrospun sheet, and each fiber consisted of the aggregation of NTO nanocrystals with the size of ~ 10 nm. Both TiO₂-NFs and NTO-NFs were confirmed to have crystal structure of anatase phase by XRD. The crystal size estimated from the width of the x-ray diffraction peak was consistent with the observation with SEM. The Nb concentration in NTO-NFs was obtained to be ~ 6 at% from EDX.

In Figs. 3(a) and (b), the cross-sectional SEM images were shown for WE of DSC. Although the NTO buffer layer was not clear in the figures since it was as thin as 70 nm, it was found that the dye-sensitized layer of 5.7 μ m thick was covered with the reflective layer of ~ 20 μ m. As shown in Fig. 3(b), broken pieces of the NFs bundles were scattered in the dye-sensitized layer.

3.2 Photovoltaic characteristics

In Table I photovoltaic parameters are summarized for WEs with different structure. The notation "=" means the mixture of NFs into the mesoporous layer of TiO₂. By the insertion of NTO buffer layer into DSC-1, short-circuit current density J_{sc} , open-circuit voltage V_{oc} and fill factor FF were increased, and consequently the efficiency η was increased from 5.62 % to 6.05 %. By mixing ES-NFs, it showed further increase to 6.17 % and 6.47 % for TiO₂-NFs and NTO-NFs, respectively.

To investigate the effect for the carrier mobility, the time variation of photocurrent was measured after the irradiation of laser pulse of 7 ns under a bias illumination. As shown in Fig. 4(a), the photocurrent rose rapidly at around 10 μ s after the pulse irradiation, and fell at 1-5 ms. The irradiated light from substrate side is absorbed by the dye in the dye-sensitized layer, and photoexcited carriers in the dye are injected immediately into TiO₂ with the order of femtoseconds[14]. If the photoexcitation in the reflective layer is negligibly small, the time t_D at which the photocurrent disappeared is considered to be the traveling time of the carrier injected near the interface between the dye-sensitized layer and the reflective layer. Here, t_D was defined as the time at which the

photocurrent decreased to half as shown in Fig. 4(a). We estimated the diffusion velocity of photoexcited carriers v_D under a potential gradient caused by the bias illumination simply with dividing the thickness of the dye-sensitized layer by t_D .

As shown in Table I, by mixing TiO₂-NF into the dye-sensitized layer (DSC-3) v_D increased by ~ 70 % from DSC-2. Further increase of ~ 165 % against DSC-2 was observed for the mixture of NTO-NFs (DSC-4). Although the amount of mixed NFs was small, the effect for the mobile characteristics was very large. This shows that the paths made by the ES-NFs are effective for the diffusive motion of photoexcited carriers, and J_{sc} and η were improved consequently. Since as-grown ES-NFs are the chain of nanocrystals as shown in Fig. 2(b), the carrier mobility considered to be limited by their grain boundaries. However, the barrier at the grain boundaries might be reduced when the bundles of NFs were calcined together with the TiO₂ nanoparticles in the mesoporous layer. As for NTO, it is known that the carrier mobility is dominated by the grain boundary scattering at low doping region less than 1 at% of Nb as in the case of polycrystalline TiO₂ films[15]. At higher doping region of 1-10 at%, however, optical phonon and ionized impurity scatterings are dominant at room temperature, while the grain boundary scattering is reduced due to the reduction

Fig. 4 Time-transient spectra of (a) photocurrent and (b) photovoltage after the irradiation of laser pulse under a bias illumination.

of potential barrier in grain boundaries[15]. A part of the large increase of v_D by mixing NTO-NFs will be attributed to the effect.

By the insertion of NTO buffer layer between FTO and TiO₂ mesoporous layer, the photocurrent was enhanced at a time region shorter than 100 μ s as indicated by t_E in Fig. 4(a). Simply multiplying the average velocity of the carrier v_D by t_E , the thickness of the region is estimated to be ~ 240 nm. This value might be related to the thickness of depletion layer of TiO₂ formed at the interface with NTO buffer layer. Although it is difficult to estimate the thickness since there are many unknown parameters such as carrier density and potential difference in the inhomogeneous medium of mesoporous layer, the enhancement of photocurrent should be attributed to the acceleration and the reduction of carrier recombination by the band bending near the interface between NTO buffer and TiO₂ mesoporous layer.

When mixing NTO-NFs (DSC-4), not only v_D but also the magnitude of photocurrent was increased. This may be due to the band bending at the interface between TiO₂ nanoparticles in the mesoporous layer and NTO-NFs as well as the reduction of the scattering at grain boundaries mentioned above.

The time-transient spectra of photovoltage are shown in Fig. 4(b). The open-circuit photovoltage increases with the accumulation of photoexcited electrons into FTO and TiO₂ mesoporous layer, and decreases by the recombination with iodide ions in the electrolyte etc. We estimated the lifetime of the electrons τ_e from the curves of attenuation after 10 ms in Fig. 4(b), and summarized in Table I. Since τ_e of DSC-1 was seriously improved by the insertion of NTO buffer layer, it was found that the leakage of electrons from the surface of FTO to the electrolyte was obstructed by the layer, and consequently V_{oc} and FF were improved.

However, τ_e was decreased when the bundles of ES-NFs were mixed into TiO₂ mesoporous layer. This may be due to the increase of the probability of leakage from the surface of ES-NFs as a consequence of the accumulation of electrons in the conducting path of NFs. Because of this reason, V_{oc} and FF were considered to be decreased.

4. CONCLUSION

The electrospun nanofibers of TiO₂ and NTO were mixed into the dye-sensitized layer of DSCs by ~ 10 vol% as a conductive agent, and their effects to the carrier mobility and photovoltaic characteristics were examined. From the time-transient spectra of photocurrent and photovoltage, the main reason for the increase of J_{sc} and η was attributed to the increase of diffusive velocity of photoexcited carriers v_D by ~ 70 % for the mixture of TiO₂-NFs and ~ 165 % for NTO-NFs. The large increase of v_D implies that ES-NFs can supply effective conducting paths for the carriers. In particular in NTO-NFs, the remarkable increase of v_D is considered to result from the reduction of the scattering effect at grain boundaries due to the increase of carrier density.

By the insertion of NTO buffer layer between FTO and TiO₂ mesoporous layer, photocurrent was enhanced at a time region shorter than 100 μ s after the pulse

irradiation implying the acceleration effect of carriers due to the band bending near the interface of NTO/TiO₂. Furthermore, the lifetime of the electrons τ_e was seriously improved because of the obstruction of the leakage of electrons from the surface of FTO to the electrolyte, and V_{oc} and FF were improved. However, by mixing ES-NFs, τ_e was reduced implying the increase of the leakage of electrons from the surface of ES-NFs.

Thus, it was found that ES-NFs of NTO were a good conductive agent for the accumulation of photoexcited carriers in dye/TiO₂ nanoparticles even when the amount of NFs was small. Because electrospinning technique allows the production of nonwoven clothes, the conducting NTO cloth is expected to be a self-standing substrate of flexible DSCs which reduces the weight and cost of conventional ones.

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