Optimization of Experimental Parameters for the Performance of Solid-state Dye-sensitized Solar Cells

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The effects of various sample parameters for solid-state dye sensitized solar cells were studied with carrier dynamics measurements and electrochemical measurements. Although many parameters and processes have been decided based on the experience of researchers, the chemical and physical reasons for the selections have not been clarified. We studied the effect of the generally utilized materials and processing such as the blocking layer, titanium oxide thickness, surface treatment, and the selection of dyes and hole transfer materials. Based on our findings, we were able to rationally optimize the structure of the solid-state dye sensitized solar cells in terms of cell performance or the lifetime of charge carriers.

Keywords Solid-state dye-sensitized solar cell

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Introduction

Because dye-sensitized solar cells (DSCs) have become an established system as a photovoltaic device, many researchers have moved on to the research field of developing perovskite solar cells. However, there is still a need for advancements in the study of DSCs consisting of all solid materials for commercialization. All solid DSCs (sDSCs) have been extensively studied in the last decade and it seems that most of the appropriate combinations of materials and fabrication techniques have been already examined. However, the selection of materials and the fabrication methods and their parameters have been mostly determined by experienced researchers. That is, explanations of the physics/chemistry behind them are still lacking.

For example, the optimization of the thickness of a TiO₂ layer is necessary to compromise the maximization of the amount of adsorbed dyes and the collection of the electrons transported inside; only a limited number of dyes and hole transfer materials (HTMs) were implemented for the actual device; various additives or surface treatments were necessary; and a TiO₂ blocking layer is always necessary, different from the DSCs with liquid electrolytes, etc.

To study the effects of dyes, HTMs and surface treatments, time-resolved dynamics studies have been utilized and such effects have been clarified from the direct information of excited carriers such as their injection and recombination processes.

As mentioned above, even though there are still many empirical parameters for preparation of sDSCs, the effect of each process has not been understood well. Therefore, for this paper we studied such empirical parameter from the viewpoint of their effects on the charge carrier and we would like to pave the way to select the parameters based on rational reasons.

Figure 1 shows a typical structure of sDSCs, which typically consists of a blocking layer, a porous TiO₂ layer, a dye layer, a hole transfer layer and a counter electrode. We investigated the sample parameter for each layer mostly by using the

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Fig. 1 Schematic drawing of the structure of a typical solid-state dye sensitized solar cells (BL, blocking layer; HTM, hole transfer material; CE, counter electrode).
complete structure of sDSCs under the same conditions of the structure and the combination.

**Experimental**

**Blocking layer**

The cleaned FTO glass were coated with 0.15 M titanium disopropoxidebis(acetylacetonate) (Aldrich) in a 1-butanol solution by the spin-coating method (3000 rpm/30 s) by a spin coater (MS-B100, MIKASA Co., Ltd.), which was heated at 130°C for 5 min. After the coated film was cooled down to room temperature, the same process was repeated twice with 0.3 M titanium disopropoxidebis(acetylacetonate) solution in 1-butanol. After repeating the coating procedure three times, the FTO glass with the TiO2 precursor solutions were heated at 500°C for 30 min.

**TiO2 layer**

A commercial TiO2 paste (PST-18NR, JGC Catalysts and Chemicals Ltd.) was diluted with ethanol (25 wt%) and the paste was coated by the spin coater. After that, it was cooled down after heating for 5 min at 180°C. After the process was repeated four times, it was placed in a furnace for 30 min at 500°C. The thickness of the TiO2 layer was ca. 1.0 μm.

**Dye adsorption**

The substrate was placed into 0.3 mM cis-bis(isothiocyanato)-2,2′-bipyridyl-4,4′-dicarboxylato(4,4′-di-nonyl-2′-bipyridyl)-ruthenium(II) (Z907, Aldrich)/ethanol solution and left for a day. After that, it was washed with ethanol.

**Treatment procedure and building of the electrode**

The Z907-sensitized TiO2 samples were put into an acetonitrile solution containing Li(CF3SO2)2N (6 mg mL–1, Aldrich) and 4-tert-butylypyridine (TBP) (30 mg mL–1, Aldrich) for 5 min and dried in air flow. After Li salt and TBP were treated, poly-(3-[N,7,7]-tetrakis(N′,N′-dime-thoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD, Aldrich) in chlorobenzene (83 mg mL–1) was spin-coated onto the Z907-sensitized TiO2 films (600 rpm for 12 s followed by 3000 rpm for 40 s. Then, the films were placed in a high vacuum chamber (4 × 10–4 Pa). Gold was subsequently deposited onto either P3HT or Spiro-OMeTAD layers as a counter electrode.

**Measurement methods and equipment**

For the carrier dynamics measurements, we utilized the transient absorption (TA) method. The pump light source was the second harmonic of an Nd:YAG laser (532 nm, a pulse width of 5 ns, SureliteII, Continuum, Electro-Optics Inc.) and the probe light was detected by a fiber optic spectrometer (USB2000+, Ocean Optics, Inc.) with the wavelength range of 350 – 890 nm. The diameters of the pump and probe beams were 3.0 and 2.5 mm, respectively. The current density-voltage (J-V) measurements were performed using a Keithley 2400 source meter in the dark and under AM 1.5 G irradiation (100 mW cm–2) with a Pecell solar simulator PEC-L10.9 In CV measurements, FTO/TiO2, a platinum and Ag/AgCl (sat. KCl) were employed as a working electrode, a counter electrode and a reference electrode, respectively. The supporting salt was 0.1 M Na2SO3. In Li+ treatment, the FTO/TiO2 electrode was immersed into an acetonitrile solution containing Li(CF3SO2)2N (6 mg mL–1, Aldrich) for 5 min.

**Results and Discussion**

**Blocking layer**

First, we studied the effect of the blocking layer since it has been believed that the blocking layer is useful to decrease recombination processes and current losses at the FTO/TiO2 interface and it has been always utilized for sDSC, although it has not always been used for the DSCs with liquid electrolytes. The dark current was compared in the presence and absence of the layer (Fig. 2). Since the rectification property was incomplete without the blocking layer, the J-V curve showed a slope by applying the voltage, while only a small constant drift current was observed in a wide range of the applied potential in the presence of the blocking layer. It means that there was an ohmic contact between FTO and HTM in the absence of the blocking layer, which was prevented by adding it.

**TiO2 layer thickness**

This is also one of the empirical parameters, which has not been clearly understood even though it is also a critical parameter for the efficiency. By increasing the thickness, more dyes can be loaded on the TiO2 layer and it is beneficial for the light harvesting; however, the efficiency of the charge collection is lowered by increasing the thickness due to the recombination of carriers during the travel inside the film.
Thus, in order to find the best condition for the charge collection, the thickness dependence was investigated by changing the coating cycles. The film thicknesses for different cycles (2, 4, 5, and 6 cycles) were 0.50, 1.00, 1.25, 1.50 μm, respectively. The J-V curve was measured for these samples as shown in Fig. 3. As can be seen in the curves, by changing the cycles, the short-circuit current ($J_{sc}$) increased until the cycle number of 4, and then it decreased with additional cycles. Thus, for the optimal charge collection, it is assumed that the optimal thickness is 1.00 μm.

To understand why there is an appropriate thickness, we studied the carrier dynamics observed at the probe wavelength of 785 nm, which was assigned to the holes transferred to P3HT. In Fig. 4, under the open circuit condition, the holes decay due to the recombination with the electrons in the conduction band of the TiO₂. As you could see by the fitting with an exponential function, the obtained decay times were 9.2 ± 0.3 × 10², 9.1 ± 0.4 × 10², 7.7 ± 0.2 × 10² and 6.9 ± 0.2 × 10² μs for coatings of 2, 4, 5 and 6 cycles, respectively. With an increase in the cycles, the lifetime of the holes became shorter, which means that the probability of the recombination increased when the film became thicker. This is because of an increase in the surface area of nanoporous TiO₂. However, the recombination probability does not matter in this case because $V_{oc}$ was not influenced by changing the thickness in this range. It means that the lifetime of the photo-generated carriers was long enough for the collection of carriers to the circuit.

The next thing we need to think about is the charge collection efficiency; it was reported that the thickness <1.50 μm does not affect the charge collection efficiency. Conversely, the surface area of TiO₂ needs to be increased for light harvesting. Thus, there is a contradicting parameter; a thicker layer is better to increase light absorption and a thinner layer is necessary for charge collection efficiency. It means that the thickness of 1.00 μm was the optimal thickness to balance the light absorption efficiency and the charge collection efficiency.

Li⁺ treatment

This treatment is a general treatment for the semiconductor substrates of DSCs, and has been often used and it is believed that it is effective for the removal of defects of the TiO₂ surface but the effect has not been fully clarified. The J-V curves are shown in Fig. 5(a) with and without the treatment. In the figure, clearly $J_{sc}$ was improved while $V_{oc}$ was suppressed. Due to the large enhancement of the photocurrent, the final efficiency is usually improved; it was doubled in this experiment. In general, it is believed that, by capping the defects with Li cations, more electrons can stay in the conduction band, which lowers the Fermi energy and $V_{oc}$ decreases correspondingly.

To study the effect of this treatment, cyclic voltammetry (CV) was measured for a bare TiO₂ electrode with and without the Li cation treatment and the results are shown in Fig. 5(b). The general shape of the CV curve for a TiO₂ particulate film was reported before. As can be seen in the CV in the reference, by polarizing negatively, there is a cathodic peak, corresponding to the accumulation of electrons inside the trap states (deep and shallow states) appears, and a non-symmetrical peak is observed by sweeping reversely, which corresponds to the release of the electrons. It is believed that this irreversibility is caused by the resistance to move the electrons once accumulated inside the film.

In our experiment, as shown in Fig. 5(b), it was found that there is a peak at around ~0.4 V, which corresponds to the deep trap state. On the other hand, by applying the Li cation treatment, the peak totally disappeared, which means the defect arising from the deep state was eliminated by the Li cations. Furthermore, the peak at around ~1.0 V corresponding to the accumulation of the electrons in the shallow states and the Fermi energy shifted negatively (upward). This means that shallow states were capped with Li cations and more electrons could stay at the higher energy states. From these results, the Li cation treatment works well to eliminate both the deep and shallow trap states, which would provide more electrons in the conduction band, causing the increase in the photocurrent.
Selection of sensitizer

The selection of the sensitizer is also one of the issues, and also the Li+ and TBP treatments sometimes give different effects. Here we show the effect of the treatments for the most general sensitizers of DSCs; ruthenium dyes with different functional groups, Z907 and N3 (Fig. 6). Without treatments, the efficiencies for both dyes were similar, but the treatments enhance both the photocurrent and photovoltage in case of Z907 as a sensitizer. However, they gave little effect for the cell with N3. Since the difference of Z907 and N3 is the alkyl functional groups connected to Z907, it could be understood that the combination of the treatments and alkyl-chain enhanced the efficiency. It is possible that the alkyl-chain was aligned well at the interface to keep the optimal distance from the dyes and the HTM.

Hole transfer material (HTM)

There are several variations for the hole transfer materials such as P3HT, Spiro-OMeTAD, and so on. However, the selection of the materials is an empirical parameter, though the work function for different HTMs is well studied. The difficulty is that $V_{oc}$, which is theoretically determined from the difference between the HOMO level of the HTM and the conduction band edge of TiO$_2$, is quite different from the actually measured values obtained from the complete cells. Here, we studied the most frequently used HTMs recently, P3HT and Spiro-OMeTAD.

Here we show an example when we use P3HT and Spiro-OMeTAD as HTMs. In Fig. 7(a), the band alignment of TiO$_2$ and the HTMs is shown. From the energy levels, $V_{oc}$ should have 0.90 and 1.02 V, respectively, for P3HT and Spiro-OMeTAD. However, $V_{oc}$ were 0.75 and 0.80 V, respectively (Fig. 7(b)). The differences of the expected and experimental values were much larger for Spiro-OMeTAD. As a result, the measured $V_{oc}$ of Spiro-OMeTAD was even lower than that of P3HT, which is one of the reasons why P3HT has been utilized. Furthermore, P3HT has a higher hole mobility and is less expensive.

We measured TA spectra of sDSCs to study their carrier dynamics and they are shown in Fig. 8. To assign the TA band, the TA spectrum was measured only for TiO$_2$/Z907. Based on the previous research, we could observe the dye bleach response from 400 – 650 nm, and correspondingly, a dye cation peak was observed in the range 630 – 900 nm. The bleach and dye cation peaks decayed with the same decay time and it is assumed that the recombination between the electrons at the conduction band of TiO$_2$ and the dye cation is the dominant cause of the decay. When the HTMs are used, the holes in the dye cation are transferred to HTMs within picoseconds. In this case, the peak in the range 650 – 900 nm corresponds to the P3HT cation, including a small amount of the dye cation as a minor component. Similarly, for Spiro-OMeTAD, the response corresponding to the dye cation was quite reduced because of the hole transfer to Spiro-OMeTAD, instead, the transferred holes in Spiro-OMeTAD were observed around 500 nm as an absorption.

We also observed the carrier dynamics of sDSCs by using the TA method with the probe wavelength of 785 nm (Figs. 9(a) – 9(c)).
For TiO$_2$/Z907 only, the response corresponds to the dye cation decay due to the recombination between electrons in TiO$_2$ and the dye cation (dye recombination). For TiO$_2$/Z907/P3HT, the decay corresponds to the recombination between the holes in P3HT and the electrons in TiO$_2$, including the dye recombination as a minor component. For TiO$_2$/Z907/Spiro-OMeTAD, the decay corresponds to only the dye recombination. In addition, the holes in Spiro-OMeTAD were monitored at the 488 nm absorption band, corresponding to the recombination between the holes in Spiro-OMeTAD and the electrons in TiO$_2$ (Fig. 9(d)). The dye recombination for TiO$_2$/Z907 and TiO$_2$/Z907/Spiro-OMeTAD showed a similar decay. However, the decay for TiO$_2$/Z907/P3HT was much longer and was extended into 1 ms. This indicates that the holes are efficiently transferred to the P3HT layer and the lifetimes of electrons and holes were extended. For TiO$_2$/Z907/Spiro-OMeTAD, the hole lifetime was much shorter (120 μs) than the case for TiO$_2$/Z907/P3HT. This would be the reason why $V_{oc}$ was much lower than the expected value.

**Figures**

Fig. 7 (a) The energy diagram of the TiO$_2$, Z907 and HTMs (P3HT and Spiro-OMeTAD), and the theoretical open circuit voltage is shown in the figure. (b) J-V curves for sDSCs consisted of P3HT and Spiro-OMeTAD as HTMs.

Fig. 8 Transient absorption spectra for sDSCs without HTMs (a) consisted of P3HT (b), and Spiro-OMeTAD (c) as HTMs.

For TiO$_2$/Z907 only, the response corresponds to the dye cation decay due to the recombination between electrons in TiO$_2$ and the dye cation (dye recombination). For TiO$_2$/Z907/P3HT, the decay corresponds to the recombination between the holes in P3HT and the electrons in TiO$_2$, including the dye recombination as a minor component. For TiO$_2$/Z907/Spiro-OMeTAD, the decay corresponds to only the dye recombination. In addition, the holes in Spiro-OMeTAD were monitored at the 488 nm absorption band, corresponding to the recombination between the holes in Spiro-OMeTAD and the electrons in TiO$_2$ (Fig. 9(d)). The dye recombination for TiO$_2$/Z907 and TiO$_2$/Z907/Spiro-OMeTAD showed a similar decay. However, the decay for TiO$_2$/Z907/P3HT was much longer and was extended into 1 ms. This indicates that the holes are efficiently transferred to the P3HT layer and the lifetimes of electrons and holes were extended. For TiO$_2$/Z907/Spiro-OMeTAD, the hole lifetime was much shorter (120 μs) than the case for TiO$_2$/Z907/P3HT. This would be the reason why $V_{oc}$ was much lower than the expected value.

**Conclusions**

It is still difficult to prepare all-solid-state dye sensitized solar cells without prior knowledge because most of the parameters such as thicknesses, treatments, material selection, etc. are decided by the experienced researchers. Based on the information of charge carrier, we could clarify how each
parameter affects the device. We studied the effects of TiO2 blocking layers, the thickness of TiO2 blocking layer, surface treatments, and the selection of materials. This kind of complicated device consisting of various combinations of materials requires rational reasons to prepare the device for further improvement. Our study would support the development of new devices with various combinations of materials.

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