



Effects of tetrabutoxytitanium on photoelectrochemical properties of plastic-based TiO₂ film electrodes for flexible dye-sensitized solar cells

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ABSTRACT

The flexible DSSCs based on conducting plastic substrates are fabricated using electrodes made of tetrabutoxytitanium (TBOT) mixed with P25 TiO₂ nanoparticles at low temperature. To investigate the effects of TBOT on the flexible dye-sensitized solar cells, electrochemical impedance spectroscopy (EIS) is performed in the dark and under illumination conditions. Resistances for electron transport through TiO₂, charge-transfer resistance related to the TiO₂/redox electrolytes interface recombination, electron transport time and electron lifetime are quantified under different weight ratios of TBOT/P25. Additionally, the photovoltaic characteristics *I*–*V* curves and incident photon to current conversion efficiencies (IPCE) of flexible anodes made of different weight ratios of TBOT/P25 are obtained as well. It is found that the electrode under weight ratio 0.17 has the smallest inherent resistance, longest electron transport time and electron lifetime, lowest recombination rate and best performance with conversion efficiency 3.94%. These results indicate that after the weight ratios of TBOT/P25 is optimized, TBOT could enhance the interconnection between the TiO₂ particles, improve the conductivity of the electrode and decrease the charge recombination. Above results demonstrate that adding TBOT to TiO₂ is an easy and efficient method to improve the performance of the flexible DSSC fabricated at low temperature.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have promoted intense research in the decades due to their low cost, highly efficient conversion of visible light into electricity and eco-friendly production [1]. Generally, the substrate used for TiO₂ film electrode in DSSC is conducting transparent glass, and high-temperature sintering process over 450 °C is applied to enhance the interconnection between nanoparticles and substrate, remove the organic residue and improve the performance of the cell. In recent years, lightweight plastic-type DSSCs have attracted much attention because of drastic reduction in cost and more extensive applications such as cellular phones, ID cards, or watches. Unlike glass-based DSSCs, the plastic-based DSSCs need low-temperature sintering technique below 150 °C due to the decomposition of the plastic at high temperature. Therefore, the main problems of plastic-based DSSCs should be overcome are low-quality interconnections between the TiO₂ nanoparticles, and the larger inherent resistance and increased recombination sites with low dye coverage caused by the organic residue in the TiO₂ electrode.

Several methods have been developed to prepare TiO₂ films at low temperature, such as hydrothermally prepared TiO₂ colloid [2,3], electrophoretic deposition of TiO₂ nanoparticles using a solution of TiO₂ dispersed in *t*-butyl alcohol and acetonitrile [4,5] applying mechanical compression to a TiO₂ nanoparticle-dispersed ethanol or water solution [6,7], chemical vapor deposition with UV irradiation [8], lift-off/transfer technique [9] and chemical sintering with ammonia [10]. Besides these methods, adding titanate, such as titanium isopropoxide (TTIP) to the TiO₂ paste is an easy and efficient way to enhance the interconnection between nanoparticles and improve the performance of DSSCs fabricated at low temperature [11]. The hydrolyses of titanate can make interconnection from one particle to another via O–Ti–O bonds and make possible electrical conduction as well [12].

In this study, tetrabutoxytitanium (TBOT) mixed with P25 TiO₂ nanoparticles was used to prepare porous TiO₂ film electrodes on flexible ITO/PET substrates. And the weight ratio of TBOT/P25 was also optimized. In order to estimate the effects of TBOT to the prepared flexible anodes, electrochemical impedance spectroscopy (EIS) was used in the study, which is a steady state method measuring the current response to the application of an ac voltage as a function of the frequency. An important advantage of EIS over other techniques is the possibility of using tiny ac voltage amplitudes exerting a very small perturbation on the system. EIS is a useful technique which is widely employed to

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investigate the kinetic process occurring in the DSSCs, especially in the dark condition. Kern et al. used impedance under open circuit condition to study the effect of the TiO₂ layer thickness, cell thickness, and charge transfer resistance of the counter electrode (CE) [13]. Wang et al. applied EIS technique to investigate the influence of the nature of the hole transport materials (HTM) on the photovoltaic figures of merit, and derived the electron lifetime, as well as the electron diffusion coefficient and charge collection efficiency [14]. Wang et al. used EIS to study electronic and ionic processes in DSSCs [15]. In our case, EIS was used in the dark and under illumination condition, and the resistance, electron lifetime, charge transport time and chemical capacitance in flexible DSSCs were obtained. With these data, the effects of TBOT on the low-temperature fabrication of flexible DSSCs were discussed.

2. Experimental

2.1. Materials

Tetrabutoxytitanium (TBOT), acetonitrile and anhydrous ethanol were obtained from Sinopharm Chemical Reagent. Co., Ltd; Lithium iodide (LiI), iodine (I₂) and propylene carbonate (PC) were obtained from Alfa Aesar; 4-*tert*-butylpyridine (TBP) was obtained from Aldrich, and P25-TiO₂ was obtained from Degussa, Germany.

2.2. Preparation of flexible TiO₂ photoanodes and cell assembly

A modified method in the literature [16] was used to prepare TiO₂ paste and carry out the electrode fabrication on the flexible ITO/PET substrate. Briefly, Degussa P25-TiO₂, TBOT (instead of TTIP which was used in the literature) and ethanol were mixed at different weight ratios and dispersed by magnetic stirring in closed bottles for 24 h. The obtained paste was spread on flexible ITO/PET by doctor blading technique. The thickness of all the films was controlled to be ~4 μm by one layer Scotch tape when the paste was coated. The ethanol evaporated in

the air at room temperature, and then the films were heated at 60 °C for more than 4 h. The heat-treated films were immersed in 0.3 mM of *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutyl-ammonium) (known as N719, Solaronix) in ethanol solution for more than 10 h.

The dye-sensitized TiO₂ electrode and sputtered Pt counter electrode on ITO/PET were assembled into a sandwich type cell. The electrolyte, which was composed of 0.5 M lithium iodide, 0.05 M iodide and 0.1 M 4-*tert*-butylpyridine in 1:1 acetonitrile-propylene carbonate, was injected into the interspaces between the photoanode and the counter electrode.

2.3. Instrumentation and measurements

Structure phase analyses of P25 and product of TBOT hydrolysis were performed on Bruker D8-advance X-ray diffractometer (XRD) with Cu K_α radiation ($\lambda = 0.15418$ nm).

To estimate the dye adsorbed amount on the TiO₂ films, the sensitized electrode was separately immersed into a 0.1 M NaOH solution in a mixed solvent (water:ethanol = 1:1), which resulted in the desorption of N719. The absorbance of the resulting solution was measured by a UV-3600 UV-vis spectrophotometer (Shimadzu, Japan). The dye adsorbed amount was determined by the molar extinction coefficient of 1.41×10^4 dm³ mol⁻¹ cm⁻¹ at 515 nm as reported previously [17].

The electrochemical impedance spectra (EIS) measurements were carried out by applying different bias under illumination or in dark condition, and recorded over a frequency range of 0.05–100 kHz with ac amplitude of 10 mV. The obtained spectra were fitted with Z-View software (v2.1b, Scribner Associate, Inc.) in term of appropriate equivalent circuit [15]. For the photoinduced open circuit voltage decay (OCVD) measurements, the cell was first illuminated to a steady voltage, and then the illumination was turned off using a shutter, the open circuit photovoltage decay curves were recorded. The above two measurements were carried out on a CHI-604C electrochemical analyzer (CH Instruments) combined with Xe lamp as the light source. The cells were

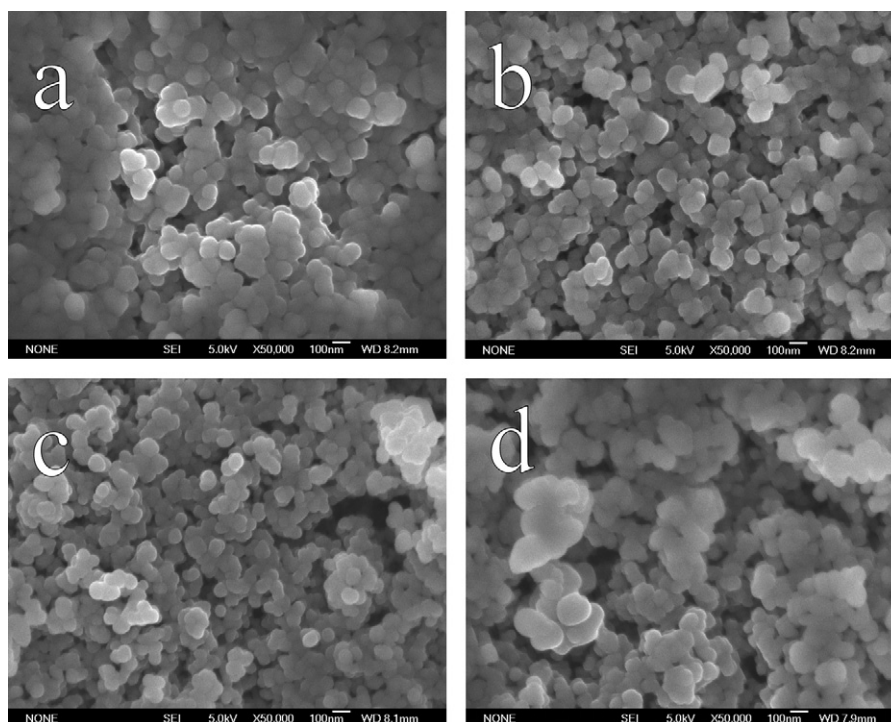


Fig. 1. SEM images of TiO₂ electrodes prepared in different TBOT/P25 weight ratios (a) 0 (b) 0.08 (c) 0.17 and (d) 0.34.

illuminated by light with energy of a 100 mW cm^{-2} from a 350 W Xe light source. A computer-controlled Keithley 2400 sourcemeter was employed to collect the current–voltage (I – V) curves.

3. Results and discussion

3.1. Photovoltaic performance

The main effects of TBOT in the paste are not only to control the viscosity, but also bind the TiO_2 nanoparticles and enhance the adhesion between P25 particles and flexible ITO/PET substrate.



According to reaction (1), O–Ti–O bonds would be formed between the nanoparticles, making electrical conduction possible across those bonds from one particle to another [12]. After the byproduct $\text{C}_4\text{H}_9\text{OH}$ of the reaction was evaporated by long time low-temperature treatment, organic residues, which enlarge the resistance and lower the absorption of dye, did not exist in the film electrode.

To optimize the weight ratios of TBOT with respect to P25 powder for preparation of the film, the properties of electrodes made of different weight ratios of TBOT/P25 were investigated. Fig. 1 shows the SEM images of TiO_2 electrodes prepared in different TBOT/P25 weight ratios. As shown in Fig. 1, when the weight ratio was 0, i.e., without adding any TBOT to the paste, the P25 particles were dispersed homogeneously with clear boundaries between particles, indicating the poor interconnection between P25 particles. Although P25 can make a good adhesion to the substrate [18], the electrode made of paste without TBOT can easily crack, which is another evidence that the interconnection property between the particles was weak. When the weight ratio of TBOT/P25 increases from 0 to 0.34, the interconnections between TiO_2 nanoparticles are enhanced gradually, and the particles aggregate once the TBOT/P25 ratio reaches 0.34. O–Ti–O bonds between the particles would be formed and interconnected P25 particles appear due to TBOT hydrolysis. Good interconnection makes the electron transfer from one particle to another easier and lowers the resistance of the film. However, with the increased ratio of TBOT/P25, the product of TBOT hydrolysis causes two drawbacks to the electrode. One is that the size of TiO_2 particles became larger, which could decrease the surface of electrode, lower dye loading and reduce photoelectrons. The other one is that the hydrolysis of TBOT is amorphous as the XRD shown in Fig. 2. Unlike P25 containing 70% anatase TiO_2 , which is favorable for DSSCs, the amorphous hydrolysis of TBOT decreases the photoresponse and the excited photoelectrons [19]. The typical I – V curves of all the cells are illustrated in Fig. 3, and the average values of parameters for four cells [dye loading, open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and efficiency (η)] are summarized in Table 1. In the range of 0–0.17 of the weight ratio of TBOT/P25, V_{oc} , J_{sc} , FF and η increase and the best performance η 3.94% is obtained when the ratio achieves 0.17. This is mainly due to the improved conductivity and lowered resistance of the film. However, the decreasing dye loading makes the performance decline when the weight ratio increases to 0.34. The normalized incident photon to current conversion efficiencies (IPCE) are shown in Fig. 4. The electrode made of 0.17 weight ratio of TBOT/P25 shows

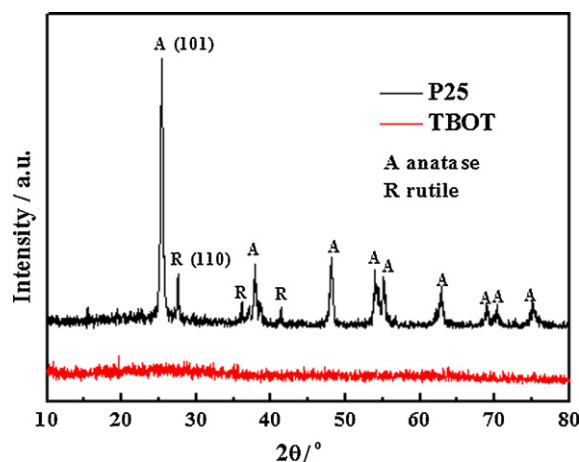


Fig. 2. XRD of P25 and hydrolysis of TBOT.

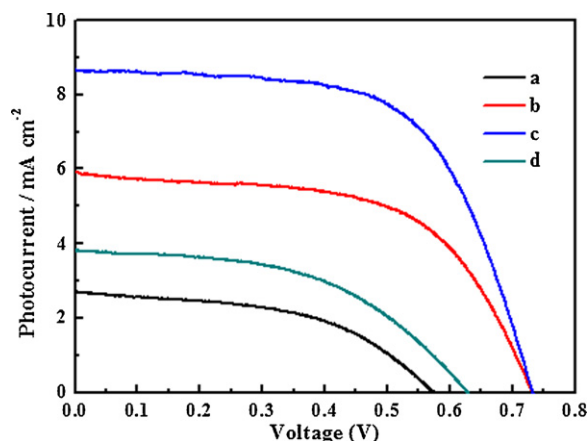


Fig. 3. I – V curves of TiO_2 electrodes prepared in different TBOT/P25 weight ratios (a) 0 (b) 0.08 (c) 0.17 and (d) 0.34.

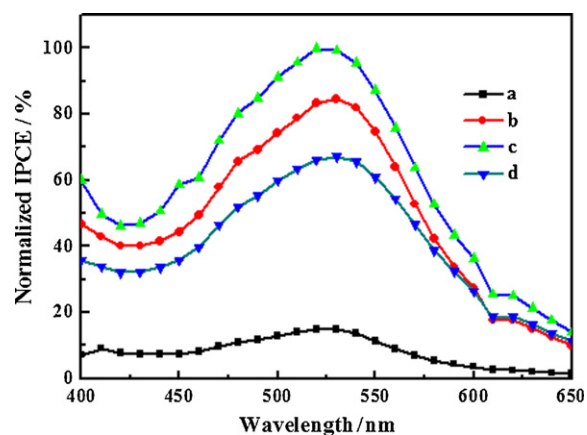


Fig. 4. Normalized IPCE of TiO_2 electrodes prepared in different TBOT/P25 weight ratios (a) 0 (b) 0.08 (c) 0.17 and (d) 0.34.

Table 1

The photovoltaic characteristics of TiO_2 electrodes prepared in different TBOT/P25 weight ratios.

Weight ratio of TBOT/P25	Dye loading ($10^{-8} \text{ mol cm}^{-2}$)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
0	4.71 ± 0.28	0.574 ± 0.011	2.70 ± 0.08	0.50 ± 0.01	0.77 ± 0.05
0.08	4.47 ± 0.22	0.731 ± 0.005	5.91 ± 0.39	0.59 ± 0.02	2.53 ± 0.26
0.17	4.03 ± 0.20	0.732 ± 0.008	8.67 ± 0.31	0.62 ± 0.02	3.94 ± 0.31
0.34	3.89 ± 0.17	0.628 ± 0.012	3.81 ± 0.14	0.50 ± 0.01	1.20 ± 0.22

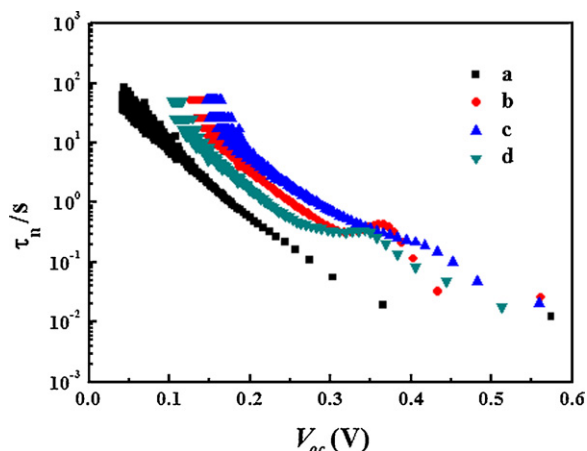


Fig. 5. Open circuit photovoltage decay curves (OCVD) of cells made of TiO₂ electrodes prepared in different TBOT/P25 weight ratios (a) 0 (b) 0.08 (c) 0.17 and (d) 0.34.

the highest IPCE value, and the value decreases with the order of weight ratio 0.08, 0.34 and 0. The IPCE curves are consistent with the performances of the corresponding cells in Fig. 3, where the electrode made of 0.17 weight ratio of TBOT/P25 displays the best efficiency.

3.2. Open circuit photovoltage decay curves (OCVD)

The open-circuit voltage decay (OCVD) curves can show the main information of interfacial recombination processes between the photoinjected electrons in the TiO₂ electrode and electrolyte under the dark state [20]. Under the present open-circuit and dark state conditions, the electron transport resistance in the TiO₂ film does not affect the OCVD measurements because there is no current flow through the cell; and the electron lifetime (τ_n) in DSSCs can change with the cell's open circuit voltage (V_{oc}) due to the shift of semiconductor's Fermi level [20]. Therefore, the effects of the electron traps on the recombination reaction can be qualitatively explained by analyzing the shapes of $\tau_n \sim V_{oc}$ relation curves. The electron lifetime (τ_n) can be derived from the OCVD measurements according to Eq. (1):

$$\tau_n = -\frac{k_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1} \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature, e is the electron charge.

Fig. 5 shows the $\tau_n \sim V_{oc}$ relation curves of cells made of TiO₂ electrodes prepared in different TBOT/P25 weight ratios. As shown in Fig. 5, the electron lifetimes τ_n show an exponential dependence on the V_{oc} , and make a good agreement with the photovoltaic performance of the corresponding cells, i.e., in the region of declined V_{oc} , the cell made of bare P25 has the shortest electron lifetime τ_n , while the one prepared in 0.17 TBOT/P25 weight ratios shows the longest τ_n . This phenomenon about electron lifetime is understandable according to Zaban's suggestion [20]. In Zaban's model, which could explain the shape of $\tau_n \sim V_{oc}$ curve qualitatively, the electron lifetime is mainly affected by the surface state traps in the nanoparticulated TiO₂ film. In our case, as Fig. 1 indicates, the bare P25 electrode has poor interconnections between nanoparticles, large numbers of traps exist in the surface state of TiO₂ nanoparticles. The internal trapping decreases the electron lifetime due to the electron captured by the traps. With the increased weight ratio of TBOT/P25, the interconnections between nanoparticles are enhanced, and the area is reduced. These factors result in good electron transfer and less electron traps. Consequently, the electron lifetime is increasing

with incremental weight ratio of TBOT/P25. However, the reducing surface lowers the dye loading on the TiO₂ electrode (shown in Table 1), and the amorphous TiO₂ phase from TBOT hydrolysis reduces the photoresponse of TiO₂ electrode. These mean the less photo-excited electrons with further adding TBOT. As a consequence the electron lifetime becomes shorter when adding weight ratio of TBOT/P25 to 0.34. Additionally, in the absence of blocking layer, the OCVD measurements include the electron transfer from the substrate (shunting), thus the comparisons of OCVD curves not only include the recombination from the surface state traps on TiO₂ particles but also the recombination from the conducting ITO/PET substrates [21]. From the comparisons of OCVD, we can infer that the recombination rate in electrode made of ratio 0.17 is the lowest one, while the bare P25 electrode has the largest one.

3.3. Electrochemical impedance spectra (EIS) under illumination condition

To further understand the effects of TBOT on the performance of the cells, electrochemical impedance spectra (EIS) of cells made of TiO₂ electrodes prepared in different TBOT/P25 weight ratios are observed, and Nyquist plots of different DSSCs are shown in Fig. 6.

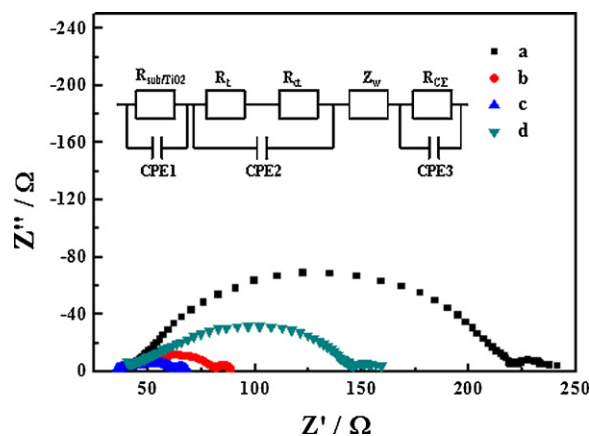


Fig. 6. Electrochemical impedance spectra (EIS) of cells made of TiO₂ electrodes prepared in different TBOT/P25 weight ratios (a) 0 (b) 0.08 (c) 0.17 and (d) 0.34. Inset: the equivalent circuit of DSSC. R_{sub/TiO_2} is the resistance of electron transfer at substrate/TiO₂ interface, R_t is resistance for electron transport through TiO₂, R_{ct} is resistance for charge-transfer process related to the TiO₂/redox electrolytes interface recombination, Z_w is diffusion resistance of I₃⁻ in the electrolyte, R_{CE} is the charge transfer resistance at counter electrode.

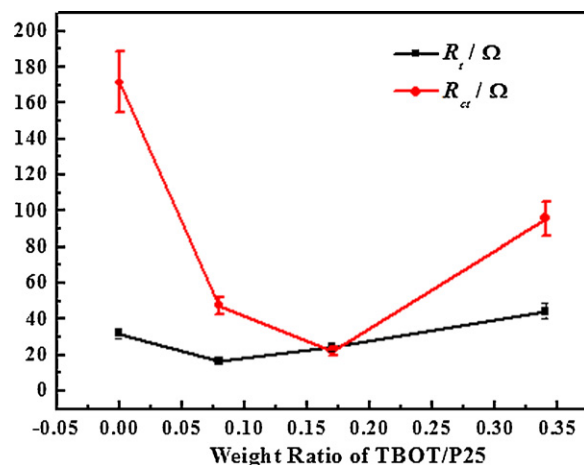


Fig. 7. Plots of R_t and R_{ct} as functions of different TBOT/P25 weight ratios under illumination condition.

In Nyquist plots, the arc observed in middle frequencies, which depends strongly on applied potential, results from the charge transfer resistance of the recombination process and the chemical capacitance of the TiO_2 film. The electron transport resistance is manifested as a linear feature in high frequency region. An equivalent circuit [15] was used to estimate different parts of the cells. Here, R_t and R_{ct} are used to describe the resistances for electron transport through TiO_2 and charge-transfer process related to the TiO_2 /redox electrolytes interface recombination respectively. The values of fitted elements are shown in Fig. 7. As Fig. 7 illustrates, under illumination condition with applying open circuit voltages, the R_{ct} results show good agreement with those obtained from the I - V curves and OCVD measurement. With increasing ratio of TBOT/P25, R_{ct} shows a decreased trend firstly due to the improvement of charge transfer, and 0.17 ratio has the smallest one then R_{ct} becomes larger when the ratio >0.17 due to the reduced dye loading and less photoelectrons as discussed above. R_t has a similar behavior with R_{ct} . Although the smallest R_t was obtained at ratio of 0.08 instead of 0.17, obviously here R_{ct} is the determinant factor, and it makes the inherent resistance of whole cell system smallest and the performance of the cell best at the ratio of 0.17.

3.4. Electrochemical impedance spectra (EIS) in the dark condition

Electrochemical impedance spectra (EIS) were also used to investigate the electron dynamics in DSSCs in the dark condition. What should be noted is that there are different processes that occur in the dark and under illumination conditions. At open circuit voltage and under illumination, no net current flowing exists through the cell. All the injected electrons are recaptured by I_3^- before being extracted to the external circuit. Meanwhile, the oxidized dye is regenerated by I^- , the processes of the sensitized electron injection, dye regeneration, and electron recapture by I_3^- convert the absorbed photon energy to heat. The counter electrode is kept at equilibrium due to no net current flowing through it. However, in the dark condition under forward bias, electrons transport through the TiO_2 network and react with I_3^- . At the same time, I^- is oxidized to I_3^- at the counter electrode. The net current density can be large depending on the applied bias voltage.

Since the R_t is inversely proportional to the density of electrons at the transport level, it is expressed in terms of Boltzmann

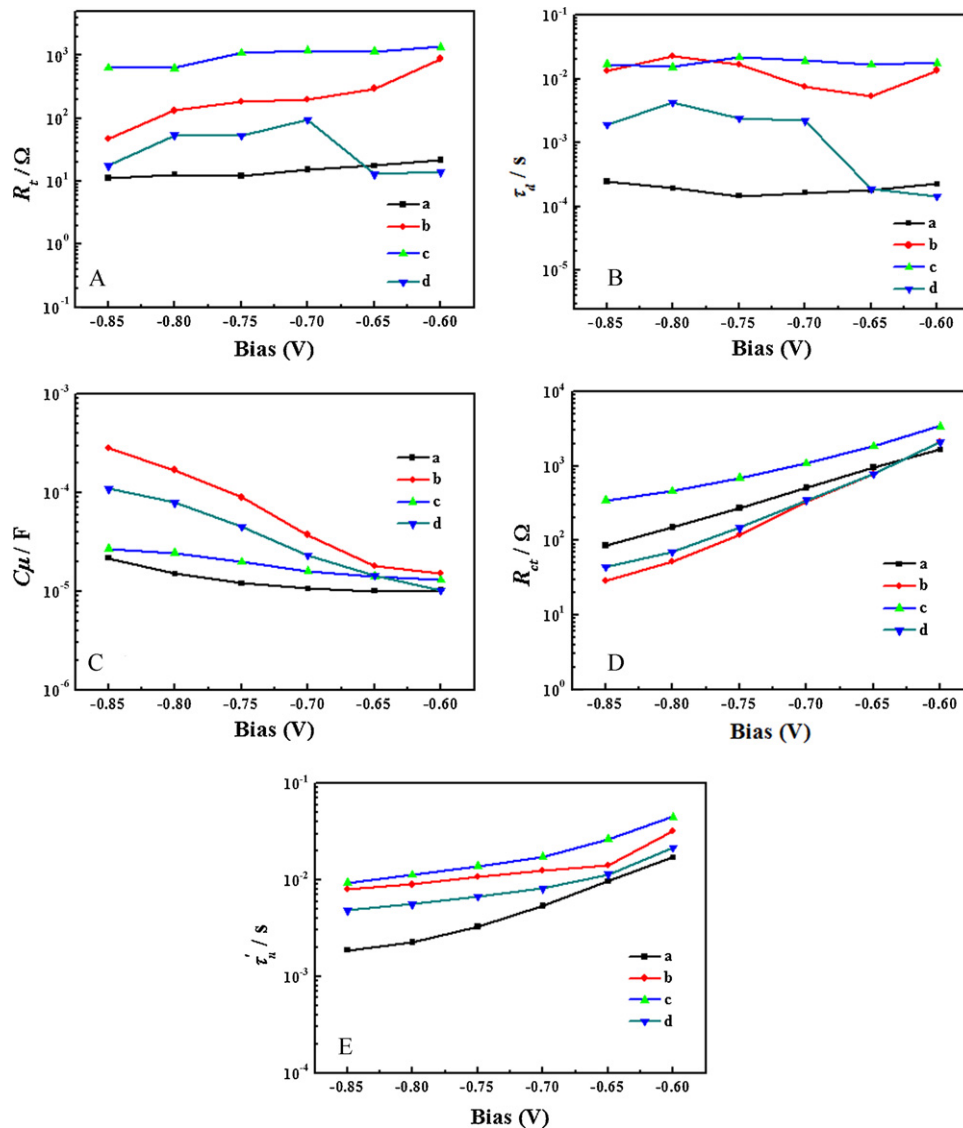


Fig. 8. Plots of R_t (A), τ_d (B), C_{μ} (C), R_{ct} (D) and τ_n' (E) of electrodes containing different TBOT/P25 weight ratios (a) 0 (b) 0.08 (c) 0.17 and (d) 0.34 as functions of bias in the dark condition.

distribution Eq. (2):

$$R_t = R_0 \exp\left(-\frac{nE_F - E_c}{k_B T}\right) = R_0 \exp\left(-\frac{E_{F,redox} - E_c}{k_B T}\right) \exp\left(-\frac{nE_F - E_{F,redox}}{k_B T}\right) \quad (2)$$

where R_0 is constant, nE_F is quasi Fermi level of the electrons in photoanode, E_c is the conduction band edge and $E_{F,redox}$ is the redox potential of the electrolyte [14].

Obviously, R_t relates to the conduction band edge of TiO_2 electrode. Given the redox potential of the electrolyte keeping invariable, the V_{oc} , which depends on the energy difference between the quasi Fermi level of the electrons in photoanode and redox potential of the electrolyte, should be reflected through the R_t . As shown in Fig. 8(A), the plots of R_t -Bias are in good agreement with the corresponded V_{oc} . According to Eq. (2), the energetic position of the energy TiO_2 conduction band edge E_c relative to the redox potential of the electrolyte can be to make comparisons directly. The plots of R_t -Bias shows the relative position following the order $c > b > d > a$, which is the same order of V_{oc} . So it can be concluded that the conduction band edge shifted positively with the increasing ratio of TBOT/P25 due to the increased electron density in the conduction band, and shifted negatively when the ratio is more than 0.17. Furthermore, the electron transport time:

$$\tau_d = R_t C_\mu \quad (3)$$

can be obtained by the fitted R_t and chemical capacitance C_μ . The plots of τ_d and C_μ as functions of bias are shown in Fig. 8(B) and (C). Clearly, the order of the electron transport time τ_d of different TiO_2 electrodes is consistent with R_t , and this should be due to the balance relationship of enhancing conductivity between TiO_2 particles and reduced surfaces.

R_{ct} plots obtained from impedance measurements in the dark condition are presented in Fig. 8(D). The electron lifetimes τ'_n can be calculated from Eq. (4):

$$\tau'_n = R_{ct} C_\mu \quad (4)$$

The electron lifetimes τ'_n of different TiO_2 electrodes can be observed in Fig. 8(E). Apparently, R_{ct} and τ'_n decrease exponentially with applied bias, which indicates R_{ct} strongly depends on the applied bias. As shown in Fig. 8(E), the electron lifetimes can be compared directly due to the same applied bias in the dark condition. In this case, at the same bias, the conduction energy is constant, and the electron lifetime depends mainly on the recombination rate. Therefore, application of a given bias produces a fix electron concentration in the conduction band for all the cells, and the lifetimes are inversely proportional to the rate constant of electron transfer to the oxidized redox species in electrolyte [22]. In Fig. 8(E), the lifetimes decrease in the order $c > b > d > a$, which indicates the recombination rate constant increases in the opposite order. This result is in excellent agreement with the OCVD technique described before.

4. Conclusions

The effects of TBOT amount in P25 TiO_2 electrode for flexible DSSC was studied with EIS and OCVD techniques. EIS technique

quantified the resistance for electron transport through TiO_2 , charge-transfer resistance related to the TiO_2 /redox electrolytes interface recombination and electron transport time. The electron lifetime was also observed by both EIS and OCVD measurements. The TiO_2 film with weight ratio of 0.17 showed the smallest system resistance under illumination, longest electron transport time and electron lifetime, and the lowest recombination rate. Therefore the TiO_2 film with weight ratio of 0.17 achieved best performance with open circuit voltage 0.732 V, short circuit current density 8.67 mA cm^{-2} , fill factor 0.62 and conversion efficiency 3.94% under 100 mW cm^{-2} irradiation. This result indicates adding optimal amount TBOT to TiO_2 film is an efficient method to improve the performance of the low-temperature prepared electrode for flexible DSSC.

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