

Research Article

Enhanced Efficiency of Dye-Sensitized Solar Cell by High Surface Area Anatase-TiO₂-Modified P25 Paste

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How to improve the conversion efficiency and the stability of dye-sensitized solar cells (DSSCs) are two major problems. Furthermore, reduction of the manufacturing cost of DSSCs and large-scale manufacture are also very important factors. As a raw material, commercial P25 would be used for large-scale manufacture of TiO₂ paste with simple preparation procedure. However, there are several drawbacks for P25 such as the low surface area of P25 powder and the poor connectivity among particles in film using tradition P25 paste without modification. In this paper, we introduced a simple modified method by adding high surface area anatase TiO₂ into pure P25 paste. The photoelectric conversion performances of DSSCs based on these photo-electrodes were tested. The results show that the open-circuit voltage, the fill factor and the energy conversion efficiency of the modified electrode were increased. It is found that the modified P25 films have fast electron transportation and a slow charge recombination. We conclude that through adding the anatase TiO₂ nanoparticles to the P25 paste with high surface area, it can not only improve the particles connectivity among inside the films, but also enhance the efficiency of DSSCs.

1. Introduction

Titanium dioxide (TiO₂) is a very important semiconductor; it has outstanding physicochemical properties, such as heat resistance, high refractive index, and wide band gap. TiO₂ nanocrystallites have been investigated widely in photocatalytic degradation, sensors, dye-sensitized solar cells (DSSCs) [1, 2], and so on. With the shortage of fossil fuels and an increasing demand for energy, developing new types of cheap and environmentally friendly energy sources is becoming more and more important. Dye-sensitized solar cells (DSSCs) as a new-generation solar cell was developed in the early 1990s and it has attracted extensive attention attributed to its high conversion efficiency, low production cost, stable performance, and the simplicity of the process [3]. DSSCs would be the most effective way of the utilization of solar energy and one of the most promising technologies [4].

DSSCs operate similarly as photosynthesis which takes place in leaves. DSSCs consist of mesoporous TiO₂ thin film photoanode, a nonaqueous electrolytic solution of the redox

couple I⁻/I₃⁻, and a platinized transparent conductive glass as a counter electrode. When the DSSCs are illuminated by sunlight, the dyed molecules will be excited by light absorption. Then the photon-generated electrons will be injected into mesoporous TiO₂ thin film. Simultaneously the oxidized dye molecules will accept electrons from I⁻ in electrolyte to return to the ground state. The electrons in the mesoporous TiO₂ thin film will be collected by the transparent conductive oxide electrodes and flow through the external circuit to the counter electrode. To complete the reverse reaction of the redox couple, a counter electrode must be used to provide the electrons to I₃⁻. Through these processes, solar energy is converted into electric energy [5]. In order to realize future commercial production, extensive studies have been performed on each component of DSSCs, such as synthesis of TiO₂ film, types of dye sensitizer, the composition of electrolyte solution, and counter electrode.

The mesoporous TiO₂ thin film photoanode is one of the main components of DSSCs and it plays a key role in

photovoltaic performances. It is well known that a photoelectrode with high efficiency should possess large surface area, high light-harvesting efficiency, rapid electron transport, and low electron recombination [3]. It is well known that after modifications are always needed for TiO₂ film because of the insufficient connectivity between TiO₂ particles in the film. The poor connectivity would lead to low electron transport rate and high electron recombination hence reducing the conversion efficiency of DSSCs [6]. Among many after-modifications, TiCl₄ posttreatment is widely used. By this modification, an extra layer of TiO₂ will grow onto the surface of the former TiO₂ film to enhance the connectivity [7]. Yu et al. adopted a similar method by modifying the conventional porous TiO₂ with a titanium organic sol [8]. On the other hand, we need to design simple methods to prepare TiO₂ film for mass production. TiO₂ film via hydrothermal method [9] achieved the highest efficiency, while a several layers and steps are needed, which limits its large-scale manufacture. In this paper, we adopted a P25 paste for mass production and introduced a new method to modify it for enhancing the connectivity of particles. The preparation of the P25 paste via bead mill is simple and just one layer and one step are needed to prepare TiO₂ film, which can be easily used for the large-scale manufacture. Furthermore, the modification by adding high surface area anatase TiO₂ into pure P25 paste could cement the P25 nanoparticles together, which could enhance the connectivity of particles to improve the efficiency. The performances of DSSCs using modified paste were tested and compared to unmodified ones. It is showed that the open-circuit voltage, the fill factor, and the energy conversion efficiency of the modified electrode were increased. It is found that the modified P25 films have a rapid electron transport rate and a slow charge recombination rate.

2. Experimental Section

2.1. Materials. The commercial P25 powders (P25, 20–30 nm, surface area 50 m²/g) [10] was purchased from Degussa. Ethylene glycol (EG), citric acid (CA), propylene carbonate (PC), anatase TiO₂, ethanol, and nitric acid were all purchased from Sinopharm Chemical Reagent Corporation (China). Distilled water (18.25 MΩ) was prepared in our laboratory. Fluorine-doped SnO₂ conductive glass (FTO, sheet resistance 10–15 Ω sq⁻¹) was purchased from Asahi glass, Japan. Iodine (I₂, 99.8%) was obtained from Beijing Yili chemicals, China. Lithium iodide (LiI, 99%), 4-tertbutylpyridine (TBP), and guanidine thiocyanate (GNCS) were purchased from Acros. The Ru dye, cis-di(thiocyanato)-bis(2,2'-bipyridyl)-4,4'-dicarboxylate ruthenium(II) (N719), was purchased from Solaronix, Switzerland [11]. All the reagents used were of analytical grade.

2.2. Preparation of P25 Paste. The unmodified P25 paste (Sample 1) was prepared by a bead-mill method. 5.6 g of P25 powder was ball-milled with 13 mL of EG for 24 h, and then 12.6 g of CA was added to the above mixture for another 24 h; the processes were done at room temperature [10].

The first modified P25 paste (Sample 2) was prepared by adding 0.56 g of anatase TiO₂. 5.04 g of P25 powder and

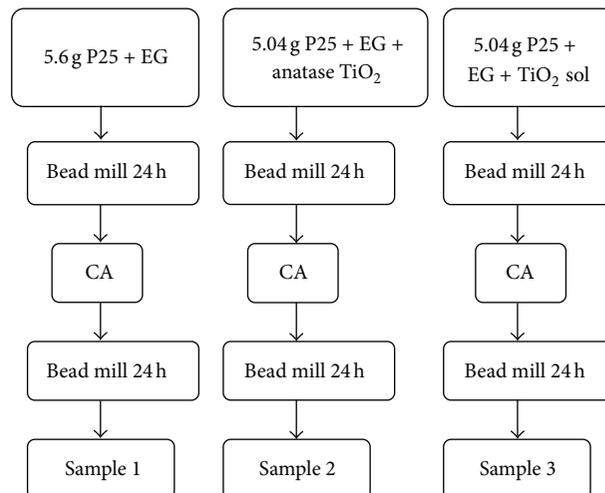


FIGURE 1: The steps for synthesizing anatase pastes.

0.56 g of anatase TiO₂ (197 m²/g) powder were ball-milled with 13 mL of EG for 24 h, then 12.6 g CA was added to the mixture for another 24 h; the processes were done at room temperature [10].

The second modified P25 paste (Sample 3) was prepared by adding TiO₂ sol. The TiO₂ sol was prepared by a hydrothermal method. Typically, 10 mL of TTIP is mixed with 2.1 g acetic acid, and then using an ultrasonicator ultrasonicated for 15 min. The previous solutions were added drop-wise to 50 mL of distilled water, under vigorous stirring for 1 hour. Then 0.68 mL of nitric acid was added to the previous mixture solution and stirred for 6 h at 80°C. 10 mL of transparent sol was obtained by evaporation of the water. The preparation of the P25 paste modified with TiO₂ sol (Sample 3) was analogous to Sample 2. 0.56 g of anatase TiO₂ in Sample 2 was replaced by 2 mL of TiO₂ sol in Sample 3. The flow diagrams for synthesizing these P25 pastes are shown in Figure 1.

2.3. Preparation of Photoelectrodes and DSSCs. The TiO₂ pastes were coated onto FTO substrates by doctor-blading, respectively, and then they were sintered at 500°C for 30 min. In order to ensure the TiO₂ mesoporous films with similar thickness, we pasted two layers of adhesive tapes on the edge of FTO; the film with a thickness of about 14.3 μm was formed. The mesoporous TiO₂ photoelectrodes were pre-heated at 120°C for 30 min; after cooling down, the electrodes were washed with ethanol to remove the remaining small glass fragments. Afterwards, they were immersed in a 0.5 mM ethanolic N-719 solution for 24 h at room temperature to allow complete dye adsorption [11]. After taking them out, the redundant dye molecules on the electrodes were washed away by ethanol for several times, and then the electrodes were dried with a hair dryer. The dye-adsorbed TiO₂ electrode was assembled into a cell holder, a drop of electrolyte solution was injected into the photoelectrode, and a clamp was used to press together the photoelectrode and a counter electrode (a platinum-sputtered F-SnO₂ glass). The electrolyte solution

was composed of 0.05 M LiI, 0.03 M I₂, 0.1 M 1-propyl-3-methylimidazolium iodide, 0.1 M GNCS, and 0.5 M 4-tert-butylpyridine in a mixed solvent of acetonitrile and PC (volume ratio: 1/1). A sandwich-type DSSC configuration was fabricated [6].

3. Results and Discussion

3.1. Photovoltaic Performances of DSSCs. The photocurrent-voltage characteristics of three DSSCs were measured by a CHI660C electrochemical Workstation (CH Instruments, Shanghai, China) at room temperature. Figure 2 shows the photocurrent density and photovoltage characteristics of three DSSCs. The resulting photovoltaic parameters derived from the J - V are shown in Table 1.

When we compare the photovoltaic performance parameters of the TiO₂ films modified by anatase TiO₂ or TiO₂ sol to the original P25 film without modification, as shown in Figure 2, we can observe that the open-circuit voltage (V_{oc}) and fill factor (FF) of Samples 2, 3 have been increased, and the short-circuit photocurrent density (J_{sc}) slightly reduced, but the energy conversion efficiency increased. The fill factor (FF) was calculated using (1) and the cells' overall energy conversion efficiency (η) was estimated by (2). In (1), the V_{max} and J_{max} are voltage and current density for maximum power output, respectively. In (2), the P_{in} is the intensity of the incident light (82.9 mW/cm²) [8]:

$$FF = \frac{V_{max}J_{max}}{V_{oc}J_{sc}}, \quad (1)$$

$$\eta = \frac{V_{oc}J_{sc}FF}{P_{in}}. \quad (2)$$

The charge recombination can be estimated by the magnitude and onset of dark current. Recombination reaction happens between electron at conduction band of semiconductor and redox couple in electrolyte, which is described by the following [9]:



Figure 2(b) shows the dark current-voltage characteristics of the photoanodes with and without modification. The dark current measurement suggested that the modified photoanodes had a slower photoelectrons recombination rate. It is noteworthy to see that the P25 photoelectrode modified with TiO₂ sol TiO₂ produces the lowest dark current, while the P25 photoelectrode without modification produces the highest dark current at the same potential about 0.6 V. These observations reflect a higher recombination at the P25 photoelectrode (Sample 1) than the P25 photoelectrode modified with anatase TiO₂ (Sample 2) and TiO₂ sol (Sample 3), which is supported by EIS measurements in Section 3.2.

3.2. EIS and OCVD Analyses. In order to confirm the speculation that modification is beneficial to retard electron recombination and facilitate electron transport, electrochemical impedance spectroscopy (EIS) measurements were carried out to investigate the kinetics of the electrochemical processes

TABLE 1: J - V Parameters for Sample 1, 2, and 3.

DSSCs	V_{oc}/mV	$J_{sc}/mA\ cm^2$	FF	$\eta/\%$
Sample 1	727	9.00	0.64	5.32
Sample 2	737	8.66	0.71	5.50
Sample 3	749	8.72	0.70	5.53

TABLE 2: Parameters obtained by fitting the impedance spectra of DSSCs using the equivalent circuit in Figure 3.

DSSCs	R_1/Ω	R_2/Ω	R_3/Ω	F_{max}/Hz	τ_e/ms
Sample 1	13.24	7.902	20.47	5.486	0.0290
Sample 2	18.84	5.109	19.11	4.542	0.0351
Sample 3	16.36	9.709	18.93	4.542	0.0351

of DSSCs. The impedance spectra of DSSCs based on the three films (Sample 1, Sample 2, and Sample 3) under one-sun illumination were measured at the frequency range of 10⁻¹-10⁵ Hz at the open circuit, respectively. Figure 3(a) shows the Nyquist plots which exhibit two semicircles, including a large semicircle at low frequencies and a small one at high frequencies; the plots were fitted with an equivalent circuit [12] (shown in the inset of Figure 3(a)). The equivalent circuit consisted of R_1 which is ascribed to the sheet resistance of FTO and contacting resistance, R_2 which is ascribed to the contact resistance between the FTO and TiO₂ film and the charge transfer resistance at the interfaces of the redox electrolyte/Pt counter electrode, and R_3 which is ascribed to the charge transport resistance of the accumulation/transport of the injected electrons within TiO₂ film and the charge transport resistance at the TiO₂/redox electrolyte interfaces. CPE1 and CPE2 are constant phase elements of the capacitance corresponding to R_2 and R_3 , respectively [4]. As shown in Table 2, the paste modified with TiO₂ sol exhibits the lowest values of R_3 among the three types of DSSCs, which implies the most efficient charge-transfer process at the interface of TiO₂/electrolyte interfaces and across TiO₂ film. By adding small particles into the paste, it could cement the TiO₂ nanoparticles together so the electron pathways would be widened [8]. Consequently, the overall efficiency would be increased by the enhanced electron transfer efficiency.

The Bode phase plots of EIS spectra, as shown in Figure 3(b), display the frequency peaks of the charge transfer process at different interfaces of three different DSSCs. The characteristic low frequency peak (f_{max}) is located at 5.486 Hz for Sample 1, 4.542 Hz for Sample 2 and Sample 3. Table 2 shows the electron lifetime for recombination (τ_e) of DSSC. The electron lifetime in DSSCs is determined by the characteristic frequency peak in the low frequency (f_{max}) according to the following [13]:

$$\tau_e = \frac{1}{2\pi f_{max}}. \quad (4)$$

We can notice that the DSSCs' electron lifetimes using the modified pastes were longer than that without modification, which implies that the modified pastes could improve the electron lifetime. The longest electron lifetime is due to

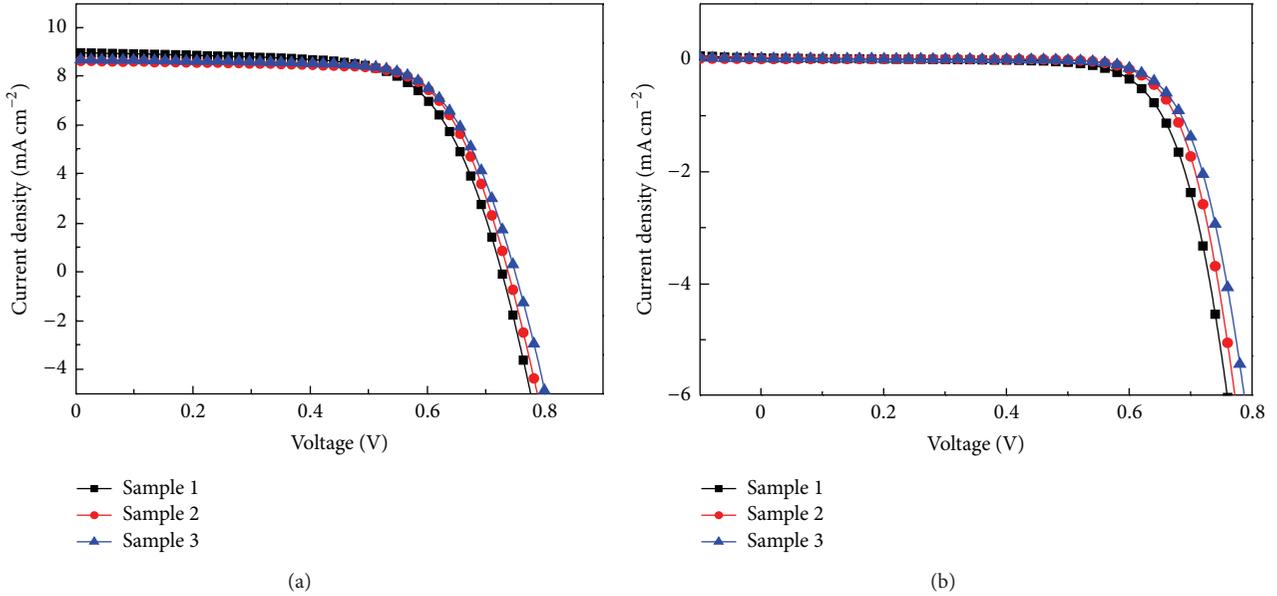


FIGURE 2: Current density-voltage characteristics of DSSCs based on the P25 photoanode (Sample 1), the photoanodes modified by anatase TiO_2 (Sample 2), and TiO_2 sol (Sample 3) measured under simulated sunlight (a) and under dark (b).

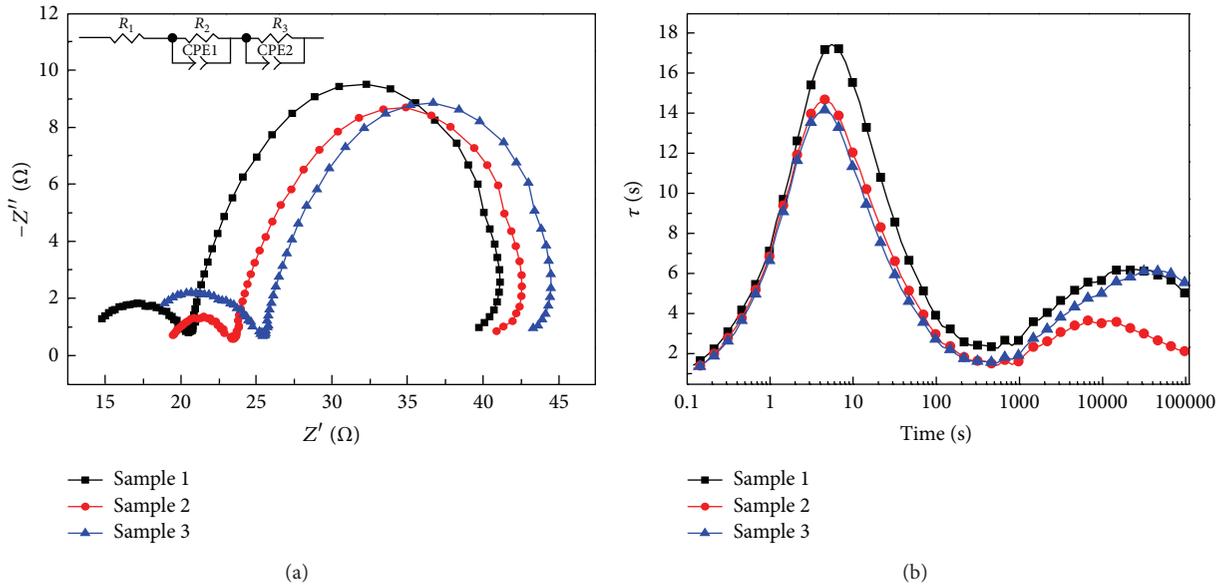


FIGURE 3: EIS spectra of DSSCs based on the P25 photoanode, the photoanodes modified by anatase TiO_2 and TiO_2 sol: (a) Nyquist plots, (b) Bode phase plots.

the lowest recombination between electrons injected from the excited dye and I_3^- .

The open-circuit voltage decay (OCVD) technique was employed for investigating the electron lifetime (τ_e), which is conducted by turning off the illumination on DSSC in a steady state and monitoring the subsequent decay of V_{oc} . The electron lifetime was calculated by the following equation, where k_B is the Boltzmann constant, T is the

absolute temperature, and e is the positive elementary charge [14, 15]:

$$\tau_e = \frac{k_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1}. \quad (5)$$

Figure 4(a) shows OVCD spectra of DSSCs based on the P25 photoanode, the photoanodes modified by anatase TiO_2 and TiO_2 sol, respectively. Figure 4(b) shows the electron

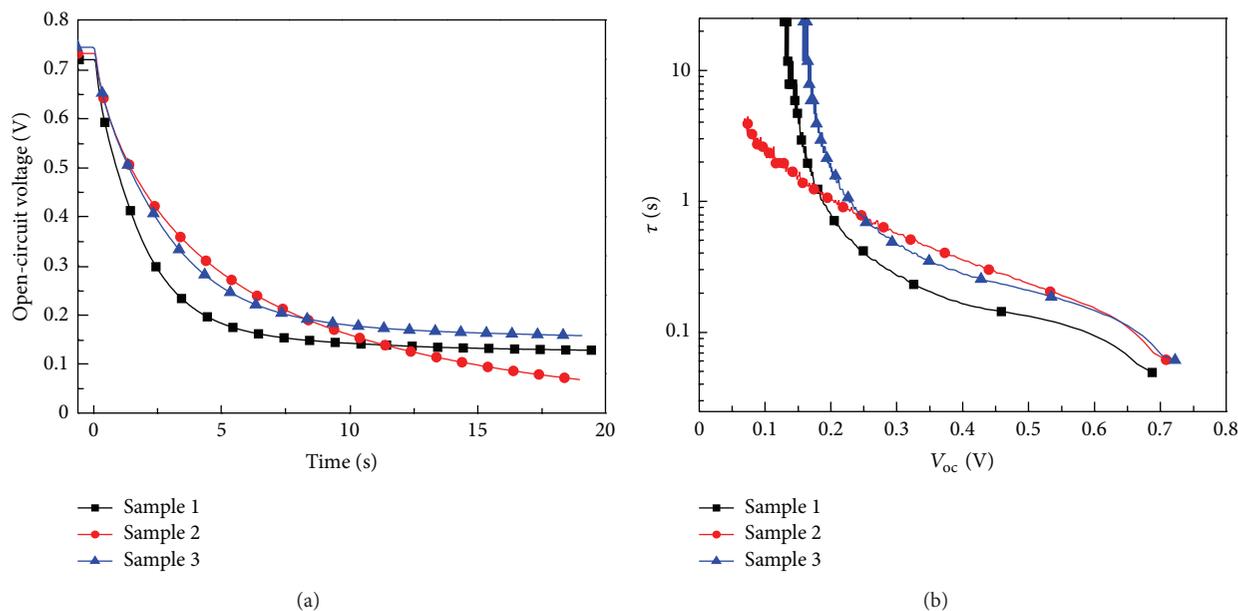


FIGURE 4: (a) OCVD spectra of DSSCs based on the P25 photoanode, the photoanodes modified by anatase TiO_2 and TiO_2 sol respectively, (b) The electron lifetime spectra of these DSSCs.

lifetime spectra of these samples. As shown in Figure 4(b), we could note that the variation trend of the electron lifetime measured by OCVD is the same as the EIS results. The electron having longer electron lifetime and faster transfer rate would be a result of additional electron pathways in the TiO_2 film [16]. As a result, the TiO_2 pastes modified with high surface anatase TiO_2 could improve the performance of the TiO_2 films in DSSCs.

4. Conclusion

In summary, we have successfully fabricated three kinds of modified P25 pastes and investigated them in DSSCs photoanodes. We employed high surface area anatase TiO_2 to improve the connectivity among the TiO_2 particles. The photoelectric measurement results showed that the modified cells have low charge transport resistance and long electron lifetime; it is assigned that the rapid electrons transport rate delays the process of their recombination. The photoelectric measurement results showed that open-circuit voltage (V_{oc}), the fill factor (FF), and the energy conversion efficiency all have remarkably increased. We conclude that through the addition of extra anatase TiO_2 in P25 paste, the electron pathways inside TiO_2 film would be enlarged, which would result in high photoelectric parameters. In brief, we introduce a simple and effective strategy, which provides a good way to improve the overall energy conversion efficiency of DSSCs.

Conflict of Interests

The authors do not have any conflict of interests in their submitted paper.

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