Effects of Ethanol on Optimizing Porous Films of Dye-Sensitized Solar Cells

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ABSTRACT: Solvent, dispersant, and surfactant play different roles in forming porous films of dye-sensitized solar cells (DSSCs) when they are added into the paste. We investigate the influence of ethanol, acetylacetone, and Triton-X100 on the photoelectrode of DSSCs with orthogonal array design experiments. Stereoscopic morphologies of photoelectrodes scanned with atomic force microscopy (AFM) show that decreasing the amount of ethanol in TiO2 paste results in forming a more compact structure of the photoelectrode for DSSCs. The TiO2 photoelectrode made with 2.5 g of TiO2 nanoparticle powder dissolved in 20 mL of ethanol presents lower root-mean-square (rms) roughness calculated from AFM, and its corresponding performance in DSSCs shows higher photoelectric conversion efficiency, while the effects of acetylacetone and Triton-X100 on the performance of DSSCs are not very apparent. Optimized photoelectrode dyed with N719 shows increased light absorption. This may result from adsorbing more amount of dye on a larger inner area of the porous photoelectrode. We find that the DSSC with the photoelectrode made from 2.5 g of TiO2 nanoparticle powder dissolved in 20 mL of ethanol containing 0.8 mL of acetylacetone and 0.6 mL of Triton-X100 shows a large increase in short-circuit current density (Jsc) and a little improvement in open-circuit voltage (Voc). At the optimized point, photoelectric conversion efficiency of 6.1% is obtained.

1. INTRODUCTION

Since Gratzel et al.1 reported dye-sensitized nanocrystalline TiO2 solar cell (DSSC) efficiency up to 7% in 1991, this type of solar cell has attracted much academic and commercial interest. A typical DSSC is a sandwich structure that contains photoelectrode, dye, electrolyte, and counter-electrode. The characteristics of TiO2 nanostructured films or photoelectrodes have important influence on the whole performance of DSSCs. In previous studies, much work has been performed to increase the performance of DSSCs through the optimization and treatment of TiO2 photoelectrodes with complicated fabrication. A kind of highly efficient nanocrystalline TiO2 photoelectrode precursor paste is fabricated normally by hydrothermal autoclaving.2–4 There are also some other approaches, including screen-printing deposition,5,6 sol–gel methods,7–9 electrodeposition,10,11 chemical vapor deposition,12,13 and spray pyrolysis.14,15 After those, a post-treatment using TiCl4 solution results in enhanced interconnection of the TiO2 nanoparticles in the photoelectrode and, thus, improves energy conversion efficiency of DSSCs.16,17 However, the simple method of industrialization, which is also a very important requirement for DSSC application, has become one of the primary challenges for a long time. Nazeeruddin et al.18 reported an easier way to make thick films used as photoelectrodes of DSSCs without any obvious crack. In that way, solvent, dispersant, and surfactant are mixed with commercial TiO2 nanoparticle powder to change the paste, which can subsequently form a deposited layer with the “doctor blade” technique. The final photoelectric conversion efficiency of DSSCs largely depends upon the amount of dye adsorbed on the nanocrystalline TiO2 photoelectrode and the permeability of the electrolyte in this photoelectrode. Both points, the amount of dye adsorbed and the permeability of the electrolyte, depend upon the structure of the photoelectrode, which changes when the TiO2 paste is adjusted by different amounts of solvent, dispersant, and surfactant. To compare their impact on the performance of DSSCs and increase adsorption of dye on the nanocrystalline TiO2 photoelectrode, we investigated the effect of ethanol, acetylacetone, and Triton-X100 on the photoelectrode film of DSSCs with orthogonal array design experiments. The stereoscopic morphologies of different photoelectrodes were compared by atomic force microscopy (AFM), and root-mean-square (rms) roughness calculated from AFM was also studied. Ultraviolet–visible (UV–vis) absorption spectra were analyzed to compare adsorption of dyes. Photovoltaic parameters, short-circuit current density, Jsc and open-circuit voltage, Voc were also analyzed to compare the effects by adjusting the amount of ethanol, acetylacetone, and Triton-X100.

2. EXPERIMENTAL SECTION

2.1. Materials. TiO2 nanoparticles (P25, 20–30 nm; BET, 48 m2 g−1; Degussa AG, Germany), LiI (Acros), I2 (Beijing Yili Chemicals, China), and N719 (Solaronix, Switzerland) were used. Triton-X100, ethanol, acetylacetone, and propylene carbonate (PC) were purchased from Sinopharm Chemical Reagent Corporation (China). 4-tert-Butylpyridine was obtained from Acros. Fluorine-doped SnO2 conductive glass (FTO, transmission >80% in the visible spectrum; sheet resistance, 15 Ω square−1, Japan) was used. All of the reagents used were of analytical purity and used without further purification.

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2.2. Fabrication of Dye-Sensitized TiO2 Photoanode. A total of 2.5 g of TiO2 nanoparticles (P25) were dispersed in ethanol with different amounts of Triton-X100 and acetylacetone. The amounts of ethanol were 20, 40, and 60 mL, respectively. The amounts of acetylacetone were 0.4, 0.6, and 0.8 mL. The amounts of Triton-X100 were 0.2, 0.4, and 0.6 mL, as listed in Table 1. The above mixture was ground in an attritor mill for 3 days before using. Then, the prepared paste was spread on the transparent conducting glass with a "doctor blade" technique. All TiO2 films were sintered at 450 °C for 30 min. After cooling to 120 °C, the TiO2 photoanodes were immersed in the dye N719 ethanol solution overnight to complete the dye-sensitized process. Nanoporous TiO2 photoelectrodes (6–14 μm thick) were obtained. The thicknesses of the TiO2 films were measured by a profilometer (Form Talysurf Profiler-S4C, Taylor Hobson, U.K.).

2.3. Assembly of the DSSCs. The electrolyte composed of 0.5 M LiI, 0.04 M I2, and 0.5 M 4-tert-butypyridine in PC was employed for DSSCs. The sputtered Pt counter electrodes were pressed tightly on the prepared photoelectrodes. The electrolyte permeated through the photoelectrode because of capillary forces. For current—voltage characteristic measurements, a 1000 W xenon light source (Newport 91192) was used to simulate the solar emission (66.7 mW cm−2, AM 1.5) and a Keithley 2400 digital source meter unit was used to measure the current—voltage curves under the light. The light intensity was calibrated by a Si-1787 photodiode (spectral response range, 320–730 nm). The active area of DSSCs was controlled at 0.25 cm2 by a mask.

3. RESULTS AND DISCUSSION

3.1. Optimizing the Thickness of TiO2 Photoanode Films Fabricated with Different Amounts of Additives. In view of different TiO2 photoelectrodes showing different optimized thickness of films in the performance of DSSCs, we fabricated nine groups of photoelectrodes ranging from 6 to 14 μm. The different photoelectric conversion efficiencies of DSSCs are drawn in panels a–c of Figure 1, panels d–f of Figure 2, and panels g–i of Figure 3. The best photoelectric conversion efficiency of DSSCs was obtained from the trial number 3, and its photocurrent density—voltage curve of DSSCs is shown in Figure 4. The photoelectrode of trial number 3 shows the most...
optimal performance of DSSCs, $V_{oc} = 710 \text{ mV}$, $J_{sc} = 12.8 \text{ mA/cm}^2$, $FF = 0.57$, and $\eta = 6.1\%$. The best photoelectric conversion efficiencies ($\eta$) of DSSCs fabricated with different TiO$_2$ photoanodes are listed in Table 1.

3.2. AFM Studies of TiO$_2$ Photoanode Films with Different Amounts of Additives. The stereoscopic morphologies of optimized photoanodes from trial numbers 1–9, scanned by AFM (measured by SPM-9500J3, Shimadzu, Japan), are shown in panels a–i of Figure 5. To compare the degree of compact structure of the different photoanodes, each photoanode surface roughness was characterized by rms, which can be calculated from AFM. The rms roughnesses of the optimized photoanodes from trials numbers 1–9 are 29.0, 27.7, 25.1, 31.7, 26.8, 31.3, 34.8, and 35.4 nm, respectively. The relationship between the rms roughnesses and the best photoelectric conversion efficiencies of DSSCs fabricated is shown in Figure 6. To distinguish the influence of solvent, dispersant, and surfactant on the performance of DSSCs, three factors including ethanol, acetylacetone, and Triton-X100 were investigated and each factor has three levels as mentioned above. To compare three factors in optimizing photoanode films of DSSCs clearly, photoelectric conversion efficiencies of DSSCs at the same level of each factor were added and listed in Table 1. Changing the amount of ethanol shows the most important impact on optimizing DSSCs (Table 1). Because the low surface tension of ethanol results in a smooth film deposition, decreasing the amount of ethanol in the range of the investigated experiments can form a comparatively more compact porous photoanode. With the compact porous photoanode being distinct from the incompact porous TiO$_2$ photoanode made with a mass of ethanol in TiO$_2$ paste, the compact porous photoanode with a larger inner area can adsorb more amount of dye; therefore, it presented higher energy conversion efficiency of DSSCs. The most compact porous photoanode observed from the stereoscopic morphology of AFM can be seen in Figure 5c, which presents the highest energy conversion efficiency of DSSCs, while the most incompact porous photoanode observed from the stereoscopic morphology of AFM can be seen in Figure 5i, which presents the lowest energy conversion efficiency of DSSCs. The relationship between the rms roughness calculated from AFM and the energy conversion efficiencies of DSSCs is shown in Figure 6, which indicates the...
same tendency that the rougher the photoelectrode, the lower the energy conversion efficiency of DSSC.

3.3. Photocurrent Density/Voltage Characteristics of DSSCs with Different Amounts of Ethanol, Triton-X100, and Acetylacetone. Aggregated TiO$_2$ nanoparticles, which are dispersed in the solvent, easily form non-uniform and cracking films, which increases recombination between the electron and the tri-iodide across the conducting glass boundary and impedes transport of photoinduced electrons in photoelectrodes under the light. To form uniform and well-deposited film, acetylacetone and Triton-X100 were added in the process of making photoelectrodes. Acetylacetone is a well-known bidentate ligand, which has been employed to disperse TiO$_2$ in solution. Increasing the quantity of acetylacetone in TiO$_2$ paste in making photoelectrode shows the same effect in the range of our experiments, as seen in Table 1, but its effect for improving energy conversion efficiency of DSSCs is much less than decreasing the amount of ethanol in TiO$_2$ paste. As a non-ionic surfactant, Triton-X100 presents both sterical and electrostatic repulsion when added in solution. This non-ionic surfactant makes it easy to deposit TiO$_2$ on the FTO because of its aggregative stability. For this reason, increasing the amount of Triton-X100 in TiO$_2$ paste to make the photoelectrode improves energy conversion efficiency of DSSCs, to some extent. This result can be noticed in Table 1. In the range of our experiments, improving energy conversion efficiency of DSSCs by increasing the quantity of Triton-X100 in TiO$_2$ paste to make the photoelectrode is more important than increasing that of acetylacetone in TiO$_2$ paste but less important than decreasing the amount of ethanol in TiO$_2$ paste. Photoelectrodes with the best energy conversion efficiency of DSSCs of groups 3, 4, and 6 that stand for the optimized amount of ethanol, Triton-X100, and acetylacetone in TiO$_2$ paste, respectively, are selected from all nine trials. A large increase of short-circuit density, $J_{sc}$, on the performance of DSSC with photoelectrode 3 compared to photoelectrodes 4 and 6 is obviously achieved because of the enhancing of an excitation electron coupled with increased dye adsorption, as listed in Table 2. The open-circuit voltage, $V_{oc}$, on the performance of DSSC with photoelectrode 3 is a little higher than that with photoelectrodes 4 and 6, partly resulting from lower surface trap in TiO$_2$ photoelectrodes because the thickness of photoelectrode 3 is a little thinner than that of both photoelectrodes 4 and 6 while increased electron density caused a negative potential shift of the band edges.

3.4. UV−Vis Study of TiO$_2$ Photoelectrode Films with Different Amounts of Additives. Figure 7 provides the absorption spectra of N719 dyes adsorbed onto the optimized photoelectrodes: (a) group 3, (b) group 4, and (c) group 6.

$V_{oc}$, the open-circuit voltage of DSSC with photoelectrode 3 is a little higher than that with photoelectrodes 4 and 6, recorded on a UV−vis−near-infrared (NIR) spectrophotometer (Cary 5000, Varian). Table 2 lists their photovoltaic parameters. As expected, the metal-to-ligand charge-transfer absorption peaks appear around 530 nm in Figure 7. The thickness of photoelectrode 3 (8.5 μm) is thinner than the thickness of photoelectrode 4 (9.6 μm) and photoelectrode 6 (9.1 μm), but the increased adsorption of N719 dyes can be observed in Figure 7a because the quantity of dye adsorption on the photoelectrode relating to the effective inner area of the photoelectrode is proportional to the optical intensity of adsorption of the dye. It also demonstrates that the compact porous photoelectrode made with less amount of ethanol in TiO$_2$ paste has a larger inner area; therefore, it can adsorb more amount of dye and achieve higher energy conversion efficiency of DSSCs.

4. CONCLUSIONS

The effect of optimizing porous film of DSSCs by adjusting the amount of ethanol, acetylacetone, and Triton-X100 was investigated...
with orthogonal array design experiments. Ethanol shows the most important effect on the energy conversion efficiency of DSSCs. AFM stereoscopic morphology shows that decreasing the amount of ethanol can form a comparatively more compact porous photoelectrode with a larger inner area, which can adsorb more amount of dye in DSSCs, as demonstrated by UV–vis absorption spectra, therefore resulting in higher energy conversion efficiency. The relationship between the energy conversion efficiency and rms roughness calculated from AFM indicates the same tendency. Increasing the amount of acetylacetone or Triton-X100 can also improve the energy conversion efficiency of DSSCs, but they are less important than adjusting the quantity of ethanol. UV–vis absorption spectra and photovoltaic parameters indicated that the photoelectrode fabricated with less amount of ethanol was thinner but achieved a large increase in short-circuit current density, $J_{sc}$ and a little improvement in open-circuit voltage, $V_{oc}$. The process of decreasing the amount of solvent and avoiding cracking photoelectrodes with a certain amount of dispersant and surfactant at the same time may point out a convenient and efficient approach to making rapid progress in improving the energy conversion efficiency of DSSCs.

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