Semi-Transparent and Stable Solar Cells for Building Integrated Photovoltaics: The Confinement Effects of the Polymer Gel Electrolyte inside Mesoporous Films

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ABSTRACT: The semi-transparent solar cells are promising to be applied in building integrated photovoltaic (BIPV) and tandem solar cells. In this study, we fabricate semi-transparent and stable solar cells for BIPV by utilizing a poly (ethylene oxide) electrolyte and controlling the size of TiO2 nanoparticles and the thickness of the TiO2 film. The power conversion efficiency of the semi-transparent (over 50% transmittance at 620–750 nm) and quasi-solid solar cells is 5.78% under standard AM1.5G, 100 mW cm−2. The higher conductivity and smaller diffusion resistance of the quasi-solid electrolyte inside the mesoporous TiO2 film indicate the confinement effects of the polymer electrolyte inside a mesoporous TiO2 film. The unsealed semi-transparent and quasi-solid solar cell retains its initial efficiency during 1000 h irradiation in humid air.

1. INTRODUCTION

Dye-sensitized solar cell (DSC) is a kind of photochemical cell, which simulates plant photosynthesis. The outstanding advantages of DSCs are green, abundant raw materials and color choice, as well as low energy consumption in production and high power generation under weak light. Currently, the world’s highest power conversion efficiency (PCE) reaches approximately 15%† under standard AM1.5G (100 mW cm−2) and about 28%‡ under weak light (1000 Lux). Weak light power generation of DSCs is promising to be applied at room light conditions. Therefore, DSCs are more promising among the third-generation thin-film solar cells and are still a hot topic in the research field. As a third-generation thin-film solar cell, DSCs can be made into a semi-transparent solar cell which greatly increases its application field. The advantages of semi-transparent solar cells are mainly of two aspects: on the one hand, the semi-transparent solar cell can combine the glazing windows with a building to form household intelligent windows, realizing the solar cell-building integration and saving the space immensely. Meanwhile, it also has the function of shading, which not only weakens the glare but also provides a broad view. Solar cell-building integration is a distributed form, which largely saves the area of cultivated land, unlike a large-area photovoltaic station. On the other hand, we can combine the semi-transparent DSCs with other solar cells to make a tandem solar cell.

The composition of DSCs is as follows: photoanode, counter electrode,3−9 and electrolyte. However, the main problem of DSCs is that the liquid electrolyte leaks easily and has poor stability. Therefore, the stability problem must be solved to achieve industrialization. The development of a solid or quasi-solid electrolyte is a very important direction in the future.10 In our previous study, polymer as a gelatin liquid electrolyte to fabricate a quasi-solid DSC exhibited commendable performance. The electrically conductive function of high-molecular-weight poly (ethylene oxide) (PEO) was investigated when it was used to gelate liquid electrolyte to fabricate polymer gel electrolytes for DSCs.11 Our previous study found that the diffusion coefficient of I3−/I− decreased constantly, while the conductivity of the polymer gel electrolytes increased initially and then decreased.11 So far, these two inconsistent behaviors have not been solved and are understudied. In addition, the properties and performance of PEO in semi-transparent DSC devices have not been reported until now.

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To overcome the above problems, here, we designed and prepared a green, semitransparent, and quasi-solid DSC (QS-DSC) by utilizing the quasi-solid electrolyte and controlling the size of TiO₂ nanoparticles and the thickness of the TiO₂ film. We find the confinement effects of the polymer electrolyte inside a mesoporous TiO₂ film. The PCE of the semi-transparent (over 50% transmittance at 620–750 nm) and quasi-solid solar cell is 5.78% under standard AM1.5G, 100 mW cm⁻². In addition, QS-DSC exhibits long-term stability.

2. RESULTS AND DISCUSSION

Compared with the traditional liquid electrolyte, the fluidity of the quasi-solid electrolyte is very poor, which is close to that of the solid state as shown in Figure 1a. The quasi-solid electrolyte can decrease the leakage of the electrolyte and increase the stability of the devices. We controlled the size of TiO₂ nanoparticles and the thickness of the TiO₂ film for preparing semi-transparent DSCs. A clear outside view can be seen through the whole device of quasi-solid DSCs as shown in Figure 1b.

The morphology of the mesoporous TiO₂ film is shown in Figure 2a. The size of the TiO₂ nanoparticle selected is approximately 30 nm. Larger TiO₂ particles will lead to poor transparency of the TiO₂ film. TiO₂ particles are stoutly connected to each other by sintering ethyl cellulose as a binder at 500 °C, which is favorable for electron transfer from the TiO₂ film to the electron collector (fluorine-doped tin oxide, FTO). The size of mesopores in the TiO₂ film is about 60–250 nm. Many materials and reactions may exhibit peculiar properties in mesoporous spaces (confined spaces). The cross section is shown in Figure 2b. The thickness of the FTO layer is about 600 nm and that of the mesoporous TiO₂ film is 4.5 μm. In addition, the thickness of the film is very uniform. The interior is full of mesopores. The morphology of the quasi-solid electrolyte was analyzed by scanning electron microscopy (SEM), as shown in Figure 2c. A wrinkled film is observed on the surface of the quasi-solid electrolyte. After magnification, the channels exist on the surface of the PEO film, as shown in Figure 2d. These channels are beneficial to the diffusion and transport of I⁻.

The absorptivity and transmittance of six devices (FTO, FTO/3 μm TiO₂, FTO/7 μm TiO₂, FTO/3 μm TiO₂ + N719, FTO/7 μm TiO₂ + N719, Pt counter electrode, and QS-DSC) were compared, as shown in Figures 3a and S1. As shown in Figure 3a, the transmittance of FTO between 400 and 750 nm is all above 80%. The transmittance of FTO/3 μm TiO₂ and FTO/7 μm TiO₂ from 350 to 400 nm (ultraviolet range) is below 40%, which is conducive to avoiding the harm caused by ultraviolet. In addition, the transmittance at 500–750 nm (visible range) exceeds 50%, which is conducive to meeting indoor light requirements. The transmittance of the Pt counter electrode at 450–750 nm is above 60%. The QS-DSC exhibits over 50% transmittance at 620–750 nm. In addition, the trend of absorption is consistent with that of transmittance as shown in Figure S1. The PCE of QS-DSCs was measured under 1 sun illumination. According to Figure 3b, with irradiation from the front, QS-DSC based on the 3 μm TiO₂ film showed a PCE of 2.49%, with $V_{oc} = 0.677 \text{ V}$, $J_{sc} = 6.25 \text{ mA/cm}^2$, and FF = 59.00%. QS-DSC based on the 7 μm TiO₂ film showed a PCE of 5.78%, with $V_{oc} = 0.736 \text{ V}$, $J_{sc} = 11.00 \text{ mA/cm}^2$, and FF = 71.60%. When irradiated from the rear, QS-DSCs based on the 7 μm TiO₂ film showed a PCE of 3.76%, with $V_{oc} = 0.710 \text{ V}$, $J_{sc} = 7.77 \text{ mA/cm}^2$, and FF = 68.20%. Semi-transparent DSCs can collect light from both sides, which will increase the PCE. In addition, semi-transparent DSCs can also be used in tandem solar cells.

We tested the conductivity and electrochemical impedance of the polymer electrolyte. The schematic diagram of the test devices is shown in Figure 4a. The results of conductivity are shown in Figure 4b. We can see that the conductivities of the quasi-solid electrolyte between the two electrodes without the TiO₂ mesoporous film and with the TiO₂ mesoporous film are 121.1 and 234 μS/cm, respectively. Compared to that of the quasi-solid electrolyte without a TiO₂ mesoporous film, the conductivity of the quasi-solid electrolyte inside the TiO₂ mesoporous film increases by 93.23%. The results indicate that the TiO₂ mesoporous film increases the conductivity of the quasi-solid electrolyte because of the confinement effects. In order to further confirm the confinement effect of the quasi-solid electrolyte inside mesoporous films, we tested the electrochemical impedance of two kinds of devices. According to the results of electrochemical impedance spectra of these two device structures, their equivalent circuits are drawn, as shown in the inset of Figure 4c. The series impedances of these two devices are 9.5 and 10.3 Ω cm⁻², respectively. The first arc corresponds to charge-transfer resistance in the interface between the Pt counter electrode and quasi-solid electrolyte, while the second arc corresponds to the diffusion resistance of the quasi-solid electrolyte.
electrolyte. It can be seen from Figure 4c that the diffusion resistance of the quasi-solid electrolyte without a mesoporous TiO$_2$ film is $635 \, \text{Ω cm}^2$. The diffusion resistance of the quasi-solid electrolyte inside the TiO$_2$ mesoporous film is $114 \, \text{Ω cm}^2$. The results indicate that the diffusion resistance of the quasi-solid electrolyte inside the TiO$_2$ mesoporous film decreases obviously, which further proves that the quasi-solid electrolyte exhibits the confinement effect in the mesoporous film. The stability of unsealed QS-DSCs during light-emitting diode (LED) irradiation in humid air is shown in Figure 4d. We find that the PCE of unsealed QS-DSCs does not decrease after 1000 h, whereas the PCE of DSCs based on the liquid electrolyte decreases from 4.0 to 0.07% after 36 h. Thus, QS-DSCs exhibit a very good stability compared with DSCs based on the liquid electrolyte.

3. EXPERIMENTAL SECTION

3.1. Materials. The chemicals used are as follows: PEO ($M_w = 2 \times 10^6$ g mol$^{-1}$, Aldrich), iodine (I$_2$, Guangdong Xilong Chemicals, China, analytically pure), 1,2-dimethyl-3-propyl imidazolium iodide (DMPII, Shanghai Cheng Jie Chemicals, China, 99%), lithium iodide (LiI, Shanghai Macklin Biochemical Co., Ltd 99%), 3-methoxypropionitrile and N-methyl-benzimidazole (NMBI, Alfa Aesar, 99%), 3-methoxypropionitrile (MePN, Alfa Aesar, 99%), titanium dioxide (TiO$_2$, OPV Tech Co., Ltd), FTO conductive glass (15 Ω, OPV Tech Co., Ltd), platinum electrode (OPV Tech Co., Ltd), and N719 dye (OPV-N719-Y, OPV Tech Co., Ltd). All materials were used without further purification.

3.2. Preparation of the Quasi-Solid Electrolyte. The preparation of the quasi-solid electrolytes mainly involves the following two steps. First, a liquid electrolyte was prepared, which was composed of 0.1 mol L$^{-1}$ LiI, 0.1 mol L$^{-1}$ I$_2$, 0.6 mol L$^{-1}$ DMPII, and 0.45 mol L$^{-1}$ NMBI. MePN was used as a solvent. Second, the PEO reagent was slowly added to the prepared liquid electrolyte. The whole mixing system was heated under constant stirring. Thus, a quasi-solid electrolyte was prepared, with a weight ratio of 7.5% relative to the liquid electrolyte.

3.3. Preparation of Quasi-Solid DSCs. Cleaning of FTO conductive glass: the 15 Ω FTO conductive glass was successively put into the detergent, deionized water, and anhydrous ethanol for ultrasonic cleaning. The time of each ultrasonic cleaning was 5 min.

3.4. Preparation of Photoanodes. TiO$_2$ was printed onto the cleaned FTO conductive glass by screen-printing. One and three layers of titanium dioxide films were prepared. The one-layer and three-layer titanium dioxide films are about 3 and 7
μm, respectively. The area of each photoanode film is 0.19 cm². Then, the printed photoanode films were burned at 500 °C. After cooling to 50°–60 °C, the photoanode films were immersed in N719 dye solution (1.26 × 10⁻⁴ mol L⁻¹, anhydrous ethanol as the solvent) for 20 h. After being immersed, the photoanode films were removed. The N719 dye adsorbed on the surface of films was washed away with anhydrous ethanol. Then, anhydrous ethanol was dried. Thus, photoanode films were obtained.

3.5. Assembling of the Quasi-Solid DSCs. First, two slender tapes were pasted on both sides of the photoanode film. Then, a small amount of quasi-solid electrolyte was added to the photoanode film. The platinum electrode was placed on the quasi-solid electrolyte. Thus, quasi-solid DSCs were assembled.

3.6. Characterizations. The EIS test of quasi-solid DSCs was performed by an electrochemical workstation (CHI760 Chenhua, China), with an initial voltage of ~0.7 V, a high frequency of 10⁶ Hz, and an amplitude of 0.005 V. A solar simulator (IVS, PV Measurements, Inc., USA) was used to determine the dark current, stability, and PCE of the quasi-solid DSCs. The thickness of the film was measured by a step tester (D-100, USA-KLA). The conductivity of the quasi-solid electrolyte was measured by a conductivity meter (DDSJ-308A, Shanghai Precision Scientific Instrument Co., Ltd.), with an electrode constant (K = L/S) of 0.017. Absorption and transmission data of components were collected by a visible spectrophotometer (722E, Shanghai Spectrum Instrument Co., Ltd.).

ASSOCIATED CONTENT
Supporting Information
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Notes
The authors declare no competing financial interest.

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