Solid-State Solar Energy Conversion from WO₃ Nano and Microstructures with Charge Transportation and Light-Scattering Characteristics

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Received: 19 November 2019; Accepted: 12 December 2019; Published: 17 December 2019

Abstract: Solar energy conversion devices composed of highly crystalline gel polymers with disk-WO₃ nanostructure and plate-WO₃ microstructures (D-WO₃ and P-WO₃, respectively) exhibited higher power conversion efficiency than those with a gel electrolyte. In this study, D-WO₃ and P-WO₃ were prepared using a hydrothermal process and their structural and morphological features were investigated for application in solar energy conversion devices. The P-WO₃ solid-state electrolyte significantly enhanced the cell performance owing to its charge transportation and light-scattering characteristics. The P-WO₃ solid-state electrolyte showed a power conversion efficiency of 6.3%, which is higher than those of the gel (4.2%) and D-WO₃ solid-state (5.5%) electrolytes. The electro-chemical impedance spectroscopy (EIS), intensity-modulated voltage spectroscopy (IMVS), diffuse reflectance, and incident photon-to-current conversion efficiency (IPCE) analysis results showed that the P-WO₃ solid-state electrolyte showed improved charge transportation and light scattering, and hence enhanced the cell performance.

Keywords: solid-state electrolyte; tungsten oxide (WO₃); hydrothermal; charge transportation; solar energy conversion; light scattering; dye-sensitized solar cell

1. Introduction

As an alternative to fossil fuel-based devices, dye-sensitized solar cells (DSSCs) are considered as one of the promising next-generation energy devices. DSSCs can be prepared easily at a low cost [1]. Among the electrolytes used in DSSCs, liquid-state electrolytes have been studied extensively due to their high efficiency (~12%) [2–10]. However, liquid-state electrolytes exhibit instability because of leakage and evaporation, and hence find limited DSSC applications.

Owing to their thermal and long-term stability, solvent independence, and environmental safety, solid-state electrolytes have gained significant attention [11–16]. However, solid-state electrolytes with highly crystalline polymers show lower mobility and ionic conductivity than liquid-state electrolytes. To reduce the polymer crystallization, additional inorganic nanofillers can be introduced [17]. In addition, this improves the free volume, thereby improving the ion conductivity and mobility of the solid electrolyte [18].

Introduction of the light-scattering effect is a simple method to enhance the light-harvesting capacity of solid-state DSSCs (ssDSSCs). Various studies have been carried out on introducing light scattering or photonic crystal layers within the photoanode [19,20]. On the other hand, at the...
photoanode, the nanomaterial-based light-scattering layer can undergo delayed charge transport due to the large number of grain boundaries, which limits the photovoltaic efficiency of ssDSSC. Hence, the use of nano or microstructured electrolytes is an efficient way to enhance the light-harvesting properties and to improve the short-circuit current density of ssDSSCs without inducing charge recombination.

In this study, we prepared a solid-state electrolyte consisting of disk-WO$_3$ (D-WO$_3$) nanostructures and plate-WO$_3$ (P-WO$_3$) microstructures for ssDSSCs. The D-WO$_3$ nanostructures and P-WO$_3$ microstructures were fabricated through the hydrothermal process. Manufactured D-WO$_3$ and P-WO$_3$ solid-state electrolytes were thoroughly characterized for material characteristics through scanning electron microscopy (SEM) and wide-angle X-ray scattering (WAXS), and for photovoltaic efficiencies by electrochemical impedance spectroscopy (EIS), incident photon-current conversion efficiency (IPCE) analysis, diffuse reflectance analysis, and intensity-modulated voltage spectroscopy (IMVS). As a control, a gel electrolyte was prepared without D-WO$_3$ nanostructures or P-WO$_3$ microstructures.

2. Experiment

2.1. Materials

Titanium isopropoxide, 4-tert-butylpyridine, poly (ethylene glycol) (PEG, $M_n=10000$ g/mol), lithium iodide (LiI), chloroplatinic acid, sodium tungsten dihydrate (Na$_2$WO$_4$·2H$_2$O), 1-methyl-3-propylimidazolium iodide (MPII), I$_2$, ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$), and titanium diisopropoxide bis (acetylacetonate) 75 wt% (Ti(acac)$_2$OiPr$_2$) were purchased from Sigma Aldrich (St Louis, MO, USA). Commercial nano-TiO$_2$ paste (Ti-Nanoxide, D20) and ruthenium (Ru) sensitizer (N719) were purchased from Solaronix (Aubonne, Switzerland). Acetonitrile, ethyl alcohol, chloroform, and 2-propanol were purchased from J.T. Baker. Fluorine doped tin oxide (F-SnO$_2$)-conducting substrates (FTO glass, TEC7) were purchased from Pilkington (Sandouville, France). All the chemicals and solvents were as received.

2.2. Preparation of Disk-WO$_3$ (D-WO$_3$) Nanostructures

The D-WO$_3$ nanostructures were synthesized via a facile one-step hydrothermal process. In brief, 0.79 g of Na$_2$WO$_4$·2H$_2$O was dissolved in 45 mL of deionized water ($>18$ MΩm) at 25 °C. Then, 1 mL of 10 M HCl was added to the as-prepared solution under constant stirring followed by the introduction of 0.2 g of ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$). After 2 min of stirring, 30 mL of deionized water ($>18$ MΩm) was added to the reaction mixture with stirring for 30 min. The as-prepared D-WO$_3$ precursor solution was transferred and heated for 3 h at 140 °C in a 100 mL Teflon-lined stainless-steel autoclave reactor. The as obtained precipitate was then thermally treated at 400 °C for 2 h in air condition to obtain the D-WO$_3$ nanostructures.

2.3. Preparation of Plate-WO$_3$ (P-WO$_3$) Microstructures

The P-WO$_3$ microstructures were prepared using a facile one-step hydrothermal process. In brief, 0.231 g of Na$_2$WO$_4$·2H$_2$O was dissolved in 30 mL of deionized water ($>18$ MΩm) under stirring at 25 °C followed by the introduction of 10 mL of 3 M HCl, resulting in a precipitate. After stirring for 30 min, the resulting solution was transferred and heated for 3 h at 140 °C in a 100 mL Teflon-lined stainless-steel autoclave reactor. The precipitate was filtered, washed with distilled water and ethanol several times to reduce the ions possibly remaining in the products, and was dried in air. The as obtained precipitate was then thermally treated at 400 °C for 2 h in air condition to obtain the P-WO$_3$ microstructures.

2.4. Preparation of the D-WO$_3$ and P-WO$_3$ Solid-State Electrolytes

The D-WO$_3$ and P-WO$_3$ solid-state electrolytes were prepared using the solution-casting method. First, 1g of PEG was dissolved in 10 mL of acetonitrile. The concentrations of D-WO$_3$ and P-WO$_3$ were fixed at 1 wt% relative to PEG. The molar ratio of the ether group of PEG to two iodine salts (LiI, MPII) was fixed at 20, and the iodine (I$_2$) content was fixed at 10 wt% with respect to the iodine salt.
(See Table S3). The solvent (acetonitrile) was completely evaporated by vacuum drying. As a control sample, a gel electrolyte was prepared using the same procedure without the D-WO$_3$ nanostructures and P-WO$_3$ microstructures.

2.5. Fabrication of Dye-Sensitized Solar Cells (DSSCs)

DSSCs with an active area of 0.4 cm$^2$ were prepared. A transparent FTO substrate was employed to prepare both the two electrodes (photoanodes and counter electrodes). For the photoanode, a Ti (IV) bis(ethyl acetoacetate) diisopropoxide solution was first spin-coated onto the FTO substrate and was then annealed stepwise to 450 °C and maintained at this temperature for 30 min. Then, a commercial nano-TiO$_2$ paste (Ti-Nanoxide, D20) was cast onto the FTO substrate using the doctor blade method followed by annealing at 450 °C for 30 min. The nanocrystalline TiO$_2$ photoanode (10 µm thickness) was sensitized overnight with 13 mg of a ruthenium dye (535-bisTBA, N719) dissolved in distilled ethanol (50 mL). Counter electrodes were prepared by spin coating a solution of 1 wt% H$_2$PtCl$_6$ in isopropanol onto the FTO substrate followed by annealing at 450 °C for 30 min. A dilute gel or solid-state electrolyte solution was cast onto a dye-adsorbed TiO$_2$ photoanode and was then evaporated for easy penetration through the nanopores of the TiO$_2$ photoanode. Then, a concentrated gel or solid-state electrolyte solution was cast onto the photoanode to minimize the time required for solvent evaporation and to prevent the formation of cavities between the photoanode and the counter electrode during the solvent evaporation. Then, both the photoanode and the counter electrodes were superposed together and were pressed between two glass plates in order to achieve slow solvent evaporation and to obtain a thin electrolyte layer. The cells were placed in a vacuum oven for the complete evaporation of the solvent for 24 h and were then sealed with an epoxy resin.

2.6. Characterization

The surface morphologies of the D-WO$_3$ nanostructures and P-WO$_3$ microstructures were observed using scanning electron microscopy (SEM) (Hitachi SU 8010, Hitachi High-Technologies Corporation, Abingdon, UK). Wide angle X-ray diffraction (WAXs) was carried out using a Rigaku 3-kW rotating-anode X-ray generator with Cu Kα radiation ($\lambda = 1.5406$ Å) operating at 30 kV and 100 mA. The two theta range was 15–65° and a scanning speed of 10°/min was used. Electrochemical impedance spectroscopy (EIS) measurements were carried out at the open-circuit voltage ($V_{oc}$) over the frequency range of $10^{-2}$–$10^6$ Hz with an amplitude of 10 mV. The incident photo to electron conversion efficiency (IPCE) spectra of the D-WO$_3$ nanostructures and P-WO$_3$ microstructures were obtained using a CE system (IVIUM Technologies, Eindhoven, Netherlands). The diffused reflectance spectra of the D-WO$_3$ nanostructures and P-WO$_3$ microstructures were recorded over the wavelength range of 400–800 nm using a ultraviolet (UV)-visible spectrophotometer (Hewlett-Packard, Hayward, CA, USA). Intensity-modulated voltage spectroscopy (IMVS) measurements were carried out on an electrochemical workstation equipped with a frequency response analyzer under a modulated red-light emitting diode (635 nm) driven by a source supply, which could provide both the direct current/alternating current (DC/AC) components of the illumination. Frequency was varied from $10^{-2}$ to $10^6$ Hz. Current density-voltage ($J-V$) measurements were carried out on a potentiostat (IVIUM Technologies, Eindhoven, Netherlands). The photovoltaic parameters of the nano and microstructures were determined using the following equations:

$$FF = \frac{V_{max}}{V_{oc}} \frac{J_{max}}{J_{sc}}$$

$$\eta = \frac{V_{max}}{P_{in}} \frac{J_{max}}{100} = \frac{V_{oc}}{J_{sc}} \frac{FF}{P_{in}} \frac{100}{100}$$

where $\eta$ is the solar power conversion efficiency (%), $J_{sc}$ is the short circuit current density, $V_{oc}$ is the open circuit voltage, $P_{in}$ is the incident solar light power, and $FF$ is the fill factor. $J_{max}$ and $V_{max}$ are the current density and voltage in the $J-V$ curves of the structures at the maximum solar power output, respectively.
3. Results and Discussion

To improve the charge transportation and light scattering properties of the solid-state electrolyte, we employed P-WO₃ microstructures to create charge pathways and a light-scattering center, as shown in Scheme 1. The ssDSSC performance was improved by the P-WO₃ solid-state electrolyte, which facilitated the movement of the redox I⁻/I₃⁻ couple and enhanced the light-scattering characteristics of the ssDSSC. In order to survey the effect of the P-WO₃ solid-state electrolyte on the DSSC performance, gel and D-WO₃ solid-state electrolytes were also prepared.

![Scheme 1. (a) Schematic of the dye-sensitized solar cells (DSSCs) fabricated in this study and the possible light scattering mechanisms of the (b) disk-WO₃ (D-WO₃) and (c) plate-WO₃ (P-WO₃) solid-state electrolytes.](image)

Figure 1 exhibits the SEM image of the D-WO₃ nanostructures and P-WO₃ microstructures. The D-WO₃ nanostructures showed an average diameter of 300 nm. The P-WO₃ microstructures on the other hand, were approximately 5 μm in length. Gel electrolytes without nanofillers are transparent and show low light-scattering features. However, the P-WO₃ solid-state electrolyte showed rough layers owing to its irregular morphology. These layers showed light-scattering properties. The diffuse reflectance plots of DSSCs fabricated with gel electrolyte, D-WO₃ solid-state electrolytes, and P-WO₃ solid-state electrolytes were also measured by spectrophotometer (Figure S1). Hence, the P-WO₃ solid-state electrolyte showed better light harvesting than the gel and D-WO₃ solid-state electrolytes.

The WAXS results of the D-WO₃ nanostructures and P-WO₃ microstructures prepared using the hydrothermal process are shown in Figure 2. To acquire more quantitative information, the average crystalline WO₃ size was calculated using the following Scherrer equation:

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

(3)

where \( D \) is the average crystalline WO₃ size, \( k \) is the shape factor of the nanostructure, \( \lambda \) is the X-ray wavelength, \( \beta \) is the full width at half maximum of the Bragg’s diffraction peak at half its maximum intensity, and \( \theta \) is half of the Bragg’s diffraction angle of the center of the peak [13]. Both the D-WO₃ nanostructures and P-WO₃ microstructures exhibited WAXS peaks at \( 2\theta = \) 16.4, 25.6, 30.4, 33.3, 34.1, 35.0, 38.8, 48.5, 49.1, 49.6, 52.6, 56.1, and 57.2 corresponding to the (002), (111), (031), (040), (200), (002), (022), (240), (042), (222), (311), and (113) planes, respectively. These peaks could be indexed to the typical pattern of orthorhombic WO₃ (ICPDS No. 43-0679) [21]. These results confirm the successful preparation of highly crystalline orthorhombic D-WO₃ nanostructures and P-WO₃ microstructures from the WO₃ precursor using the hydrothermal process. All the WAXS peaks of the D-WO₃ nanostructures synthesized via the hydrothermal process were relatively wide, indicating that these nanostructures showed smaller crystallite size than the P-WO₃ microstructures. The average WO₃ crystallite size of the D-WO₃ nanostructures was estimated to be approximately 300 nm (using Equation (3)). This result is consistent with the nanostructure size obtained from the previous SEM image.
counterelectrode, including the sheet resistance of the FTO substrate, $R_{s}$, the electrolytes, respectively. The electro-kinetic characteristics, i.e., the interfacial resistance characteristics ($R_{1}$) of the photoanode/sensitizer/electrolyte interface, and $C_{PE2}$ are the constant phase components of capacitance corresponding to $R_{1}$ and $R_{2}$, respectively.

The WAXS results of the D-WO$_3$ nanostructures and P-WO$_3$ microstructures prepared using the hydrothermal process were relatively wide, indicating that these nanostructures resulted in smaller crystallite size than the P-WO$_3$ microstructures. The average WO$_3$ crystallite size of the nanostructures was estimated to be approximately 300 nm (using Equation (3)). This result is consistent with the nanostructure size obtained from the previous SEM image. (Figure S2, 3)

The recombination kinetics of the three types of cells were characterized by using dark EIS and IMVS. Results have been reported previously [24]. To further understand the dynamics of charge transport, the highly crystalline polymer chain. In addition, the ionic diffusions within the P-WO$_3$ solid-state electrolyte was higher than those of the other electrolytes. Similar viscosity of the P-WO$_3$ solid-state electrolyte was lower than that of the gel electrolyte ($\lambda_{G}$ solid-state electrolytes were 97.6, 60, and 63.9 with the equivalent circuit. Because we used identical FTO substrates, photoanodes, and counter electrodes, the difference in the total interfacial resistance, which was related with the series interfacial resistance ($R_s$), $R_{1}$, and $R_{2}$, respectively, as calculated using the EIS data fitted with the equivalent circuit. Because we used identical FTO substrates, photoanodes, and counterelectrodes, $R_{2}$ is the charge transfer interfacial resistance of the photoanode/sensitizer/electrolyte.

EIS analysis was carried out at frequencies ranging from $10^{-2}$ Hz to $10^{-1}$ MHz with an AC amplitude of 0.02 V under 1 sun illumination. Figure 3a,b show the Nyquist plots and the equivalent circuit for the EIS spectra of the ssDSSCs employing the gel, D-WO$_3$ solid-state, and P-WO$_3$ solid-state electrolytes, respectively. The electro-kinetic characteristics, i.e., the interfacial resistance characteristics ($R_{s}$, $R_{1}$, $R_{2}$, and $W_s$) of the ssDSSCs are summarized in Table 1. $R_s$ is the series interfacial resistance including the sheet resistance of the FTO substrate, $R_{1}$ is the charge transfer interfacial resistance of the counterelectrode, $R_{2}$ is the charge transfer interfacial resistance of the photoanode/sensitizer/electrolyte.

**Figure 1.** Scanning electron microscope (SEM) image of (a) D-WO$_3$, (b) magnified D-WO$_3$, (c) P-WO$_3$, and (d) magnified P-WO$_3$.

**Figure 2.** Wide-angle X-ray scattering (WAXS) results of D-WO$_3$ and P-WO$_3$. 

- $2\theta$ values: 15, 22.5, 25, 29, 30.4, 33.3, 34.1, 35, 38.8, 48.5, 49.1
- WAXS peaks: (020), (002), (022), (040), (042), (200), (002), (022), (240), (042), (113)
- $\lambda$ is the X-ray wavelength,
- $\beta$ is the half width of the Bragg's diffraction peak at its maximum intensity,
- $k$ is the Bragg's diffraction angle of the center of the peak

- Scherrer equation: $D = \frac{k \lambda}{\beta \cos \theta}$
interface, and $W_s$ is the ionic diffusion within the electrolyte. CPE1 and CPE2 are the constant phase components of capacitance corresponding to $R_1$ and $R_2$, respectively [22,23]. The total interfacial resistances of the ssDSSCs with the gel, D-WO$_3$ solid-state, and P-WO$_3$ solid-state electrolytes were 97.6, 60, and 63.9 Ω, respectively, as calculated using the EIS data fitted with the equivalent circuit. Because we used identical FTO substrates, photoanodes, and counter electrodes, the difference in the $R_s$ and $R_1$ values was insignificant. Therefore, the difference in the total interfacial resistance, which was related with the $R_2$ value at the TiO$_2$ photoanode/sensitizer/electrolyte interface, of the three devices can be mainly associated to the solid-state electrolytes based on D-WO$_3$ and P-WO$_3$. The charge transfer interfacial resistances of the D-WO$_3$ ($R_2 = 42.9 \ \text{Ω}$) and P-WO$_3$ ($R_2 = 43.4 \ \text{Ω}$) solid-state electrolytes were lower than that of the gel electrolyte ($R_2 = 76.9 \ \text{Ω}$). This can be attributed to the enhancement in the continuous free volumes related to ion-mobility resulting from the interaction between the WO$_3$ nano or microstructures and the highly crystalline polymer chain. In addition, the ionic diffusions within the P-WO$_3$ solid-state electrolyte ($W_s$) were slightly larger than those of the other systems. This result indicates that the viscosity of the P-WO$_3$ solid-state electrolyte was higher than those of the other electrolytes. Similar results have been reported previously [24]. To further understand the dynamics of charge transport, the recombination kinetics of the three types of cells were characterized by using dark EIS and IMVS (Figures S2 and S3).

![Figure 3](image)

**Figure 3.** (a) Electro-chemical impedance spectroscopy (EIS) Nyquist plots of the DSSCs fabricated with the gel, D-WO$_3$ solid-state, and P-WO$_3$ solid-state electrolytes obtained under one sun illumination (AM 1.5, 100 mW cm$^{-2}$) and (b) equivalent circuit of DSSCs.

**Table 1.** Photovoltaic and electrochemical properties of the DSSCs and ssDSSCs fabricated with the gel, D-WO$_3$ solid-state, and P-WO$_3$ solid-state electrolytes under 1 sun illumination (AM 1.5, 100 mW cm$^{-2}$) $^a$.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ $^b$ (mA/cm$^2$)</th>
<th>$J_{sc}$ $^c$ (mA/cm$^2$)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
<th>$R_s$</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$W_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel</td>
<td>0.67 ± 0.2</td>
<td>11.1 ± 0.3</td>
<td>11.0</td>
<td>0.56 ± 0.02</td>
<td>4.2 ± 0.3</td>
<td>13.7</td>
<td>2.1</td>
<td>76.9</td>
<td>4.9</td>
</tr>
<tr>
<td>D-WO$_3$ solid-state</td>
<td>0.74 ± 0.1</td>
<td>11.6 ± 0.3</td>
<td>11.8</td>
<td>0.64 ± 0.02</td>
<td>5.5 ± 0.2</td>
<td>11.2</td>
<td>2.5</td>
<td>42.9</td>
<td>3.6</td>
</tr>
<tr>
<td>P-WO$_3$ solid-state</td>
<td>0.71 ± 0.1</td>
<td>14.6 ± 0.2</td>
<td>14.3</td>
<td>0.61 ± 0.02</td>
<td>6.3 ± 0.2</td>
<td>11.5</td>
<td>2.2</td>
<td>43.4</td>
<td>6.8</td>
</tr>
</tbody>
</table>

$^a$ A typical dye-sensitized solar cell had an active area of 0.40/cm$^2$ and was masked using an aperture with similar area during the solar cell performance measurements. The thickness of the TiO$_2$ photoanode was about 7 µm. $^b$ Determined from the J-V curves. $^c$ Determined from the incident photon-to-current conversion efficiency (IPCE) curves.

The IPCE analysis of the ssDSSCs provided quantitative information on their light-harvesting properties. Figure 4 exhibits the IPCE analysis of the ssDSSCs based on the gel, D-WO$_3$ solid-state, and P-WO$_3$ solid-state electrolytes. The P-WO$_3$ solid-state electrolyte-based DSSC exhibited a
maximum IPCE of 72% at a wavelength of about 540 nm while the gel electrolyte- and D-WO3 solid-state electrolyte-based ssDSSCs showed the IPCEs of 45% and 52%, respectively. This indicates that the P-WO3 solid-state electrolyte acted as an effective light-scattering center to enhance the scattering of the unabsorbed solar light back into the DSSC. Therefore, the P-WO3 solid-state electrolyte improved the light-harvesting capability of the DSSC through efficient utilization of incident light.

Solid-state electrolytes with D-WO3 nanostructures and P-WO3 microstructures were prepared for fabricating DSSCs. The photovoltaic properties of the D-WO3 and P-WO3 solid-state electrolyte-based DSSCs are shown in Figure 5. Also, the performance of the liquid electrolyte was evaluated in DSSCs under on sun (AM 1.5) illumination (Figure 4, Table S2). The photovoltaic characteristics including the open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and solar power conversion efficiency (η) of the DSSCs are listed in Table 1. The measurements were carried out under one sun illumination. As a control, a gel electrolyte was prepared using the same procedure without D-WO3 nanostructures or P-WO3 microstructures. The solid-state nanofiller ratio (1 wt%) was minimized to survey the effect of the morphology of the D-WO3 nanostructures and P-WO3 microstructures on the DSSC performance. The Jsc value of a device can be estimated by integrating its light harvesting, electron injection, and electron collection efficiencies using the following equation:

\[
J_{sc} = q \eta_{lh} \eta_{inj} \eta_{col} I_0
\]

where \( q \) is the elementary charge, \( \eta_{lh} \) is the light harvesting efficiency, \( \eta_{inj} \) is the electron injection efficiency, \( \eta_{col} \) is the electron collection efficiency, and \( I_0 \) is the solar light flux [25,26]. The solar power conversion efficiencies of the ssDSSCs prepared with the D-WO3 nanostructure- and P-WO3 microstructure-based solid-state electrolytes were found to be 5.5 and 6.3%, at 100 mW/cm², which is one of the highest values for ssDSSCs (Table S1). These values are approximately 1.3- and 1.5-fold higher than that of the gel electrolyte-based DSSC, respectively. This result demonstrates the importance of incorporating inorganic WO3 nanofillers in solid-state electrolytes. This enhancement in the DSSC performance with the incorporation the WO3 nanofillers can be attributed to their high Jsc and FF values. According to Equation (4), light-harvesting characteristics were responsible for the high Jsc value of the ssDSSC based on the P-WO3 solid-state electrolyte. Owing to the light-harvesting characteristics of P-WO3, the light utilization efficiency of the ssDSSC improved along with an improve in the Jsc value. These results are consistent with the IPCE results shown in Figure 4. In addition, the D-WO3 nanostructures and P-WO3 microstructures acted as nanofillers and decreased the crystallinity.
of the polymer electrolyte matrix, thus enhancing the continuous free volumes, charge-carrier mobility, and FF values of the ssDSSCs.

![Figure 5](https://www.mdpi.com/xxx/s1).

**Figure 5.** Current density-voltage (J-V) curves of the DSSCs fabricated with the gel, D-WO3 solid-state, and P-WO3 solid-state electrolytes obtained under one sun illumination (AM 1.5, 100 mW cm\(^{-2}\)).

4. Conclusions

The solar power conversion efficiency of the P-WO3 solid-state electrolyte-based ssDSSC was higher than those of the gel electrolyte- and D-WO3 solid-state electrolyte-based DSSCs. The ssDSSC fabricated with the P-WO3 solid-state electrolyte showed a solar power conversion efficiency of 6.3%, which is higher than those of the DSSCs with the gel (4.2%) and D-WO3 solid-state (5.5%) electrolytes. P-WO3 solid-state electrolytes offer enhanced charge transportation and light-scattering characteristics, can confine the incident light within the electrolyte/electrode, and limit the interfacial resistance, thereby increasing the cell performance. The results exhibited that the introduction of nano or microstructures within the non-electrode elements of DSSCs such as electrolytes can enhance the light-harvesting characteristic of the cells avoiding charge recombination, and hence increase their solar-energy conversion performance.

**Supplementary Materials:** The following are available online at [http://www.mdpi.com/2079-4991/9/12/1797/s1](http://www.mdpi.com/2079-4991/9/12/1797/s1), Figure S1: Diffuse reflectance plots of DSSCs fabricated with gel electrolyte, D-WO3 solid-state electrolytes, and P-WO3 solid-state electrolytes, Figure S2: EIS curves of DSSCs fabricated with gel electrolyte, D-WO3 solid-state electrolytes, and P-WO3 solid-state electrolytes measured at -0.65 V bias voltage in dark condition (100 kHz~10 mHz), Figure S3: IMVS of DSSCs fabricated with gel electrolyte, D-WO3 solid-state electrolytes, and P-WO3 solid-state electrolytes, Figure S4: J-V curves DSSCs fabricated with liquid electrolyte and P-WO3 solid-state electrolytes that were obtained under one sun illumination (AM 1.5, 100 mW cm\(^{-2}\)), Table S1: Comparison of photovoltaic parameters of DSSCs fabricated with polymer gel or solid-state electrolytes reported in the literature, Table S2: Photovoltaic parameters of DSSCs fabricated with liquid electrolyte and P-WO3 solid-state electrolytes that were obtained under one sun illumination (AM 1.5, 100 mW cm\(^{-2}\)), Table S3: DSSCs electrolyte formulations.

**Author Contributions:** Conceptualization, J.M.; formal analysis, W.S.; writing-review and editing, J.T.P. and H.J.

**Funding:** This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (NRF-2019R1C1C1002305, NRF-2019R1C1C1010283) and the Technology Innovation Program (20004627) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


8. Zhang, Q.; Li, C. TiO₂ Coated ZnO Nanorods by Mist Chemical Vapor Deposition for Application as Photoanodes for Dye-Sensitized Solar Cells. Nanomaterials 2019, 9, 1339. [CrossRef]


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