Fabrication And Characterization of $\text{Cs}_{0.33}\text{WO}_3$ Nanorod Combined Within Dye Sensitized Solar Cells For Near-Infrared Light Absorption

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Abstract

Near-infrared (NIR) light absorbing materials have been widely used in vehicle and building applications due to their transparent film structure with high absorption rate in NIR range and a high transmittance for the visible light. In this paper, Cesium-doped Tungstate ($\text{Cs}_{0.33}\text{WO}_3$) has been combined with dye-sensitized solar cell (DSSC) to convert the heat energy (absorbed from NIR light) into photocurrent. $\text{Cs}_{0.33}\text{WO}_3$ Nanorods were synthesized and used to prepare the active layer of the cell. The mesoporous Titanium dioxide (TiO_2) on FTO has also been used as the electron transport layer (ETL). This simple structure of $\text{FTO}/\text{TiO}_2/\text{Cs}_{0.33}\text{WO}_3$ resulted in a poor Fermi level alignment and a low voltage. However, a buffer layer made of Poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN-DOF) improved the Fermi level alignment and the quality of the interface in the modified structure of $\text{FTO}/\text{TiO}_2/\text{PFN-DOF}/\text{Cs}_{0.33}\text{WO}_3$ which improved the initial J_{sc} from $0.38 \mu\text{A}/\text{cm}^2$ to $0.45 \mu\text{A}/\text{cm}^2$ for the NIR range. In addition, the J_{sc} of this modified structure improved from $18.84 \mu\text{A}/\text{cm}^2$ to $27.56 \mu\text{A}/\text{cm}^2$ for the visible light. Finally, by using a P25-doped TiO_2 layer, the J_{sc} increased from $0.70 \mu\text{A}/\text{cm}^2$ to $31.12 \mu\text{A}/\text{cm}^2$ for both NIR and visible light, respectively.

Introduction

Nowadays, the development trend of solar energy tends to generate electricity from visible light. However, the radiant energy produced by near-infrared rays penetrates the atmosphere and irradiates the energy contained in the earth. Ultraviolet light has no role in energy generation in solar cells, the visible light contributes to 40% while the near-infrared light corresponds to 60% energy production. Therefore, using the potential of NIR light in energy generation seems logic and essential. In 2011, He et al. [1] simply added a thin layer of PFN-DOF alcohol/water-soluble polymer as the cathode interlayer in a PTB7:PC71 polymer solar cell to increase the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF) which led to a high-efficiency of 8.37%. Furthermore, they fabricated polymer-fullerene bulk heterojunction solar cells with lightweight and low-cost process and a record efficiency boosted from 8–10% of the threshold for commercial applications. In 2012, they successfully demonstrated efficient PSCs using a simple inverted structure, using PFN-DOF alcohol/water-soluble conjugated polymer compound to adjust the work function of ITO with authentication efficiency of 9.2% [2]. Since perovskite solar cells (PSC) mainly use planar and mesoporous TiO_2 as the electron transport layer (ETL), the inherent photocatalytic properties of TiO_2 cause the separation of perovskites. In order to improve this problem, Zhao et al. proposed to add bathocuproine (BCP) to ETL-free PSCs as an easy-to-deposit and light stable material, which increased the efficiency from 15.56–19.07% [3]. The efficiency retention of this structure is much higher without encapsulation of TiO_2 structure and is relatively high compared to 19.03% efficiency obtained by the addition of TiO_2 . In 2016, Jia et al. used ZnO (metal oxide) with high charge carrier mobility and polyethylenimine (PEI) polymer, which is conducive to film formation and forms a new type of cathode buffer layer (CBL) [4]. By this structure, they developed inorganic and trans-perovskite solar cells, ZnO:PEI BCP based on P3HT:PC61BM and PTB7-Th:PC61BM with efficiency

increased to 3.57% and 8.16%. In order to replace the TiO_2 electron transport layer, researchers are looking for low-temperature sintering ETL materials because high-temperature sintering is not suitable for flexible substrates. Ha et al. replaced TiO_2 with the C60-assisted polyethylenimine ethoxylated (PEIE) electron collecting layer as (spin-coated) and obtained 13.3% efficiency from this flexible perovskite solar cell [5]. In perovskite solar cells (PSCs), the basic light-absorbing layer MAPbI_3 absorbs the light mainly in visible range of 300–800 nm. In 2013, Koh's team [6] synthesized formamidinium cations ($\text{CH}(\text{NH}_2)^{2+}$) with a band gap of 1.47 eV instead of methylammonium cations (CH_3NH_3^+) by absorption measurements to synthesize FAPbI_3 perovskites. The receiving wavelength extends to longer wavelengths, which is a way to increase PCE. By enlarging the photo-absorption range in perovskite and DSSCs we can minimize the non-absorption range from visible to NIR and improve the photovoltaic performance of the cell. In 2017, Tao et al. [7] used IR806 dyes to form IR806-UCNCs crystals and combined that with perovskite for the first time to extend its absorption band. This up-converted NIR light (800-1000nm) broadband into visible light absorbed by perovskite. The device made by incorporating IR806-UCNC exhibited a power conversion efficiency of 17.49%, which is 29% increase in performance from the original device (13.52%).

1.1. Tungsten Oxide WO_x

The bandgap of Tungsten Oxide (WO_3) semiconductor is 2.6 ~ 2.8 eV with a cut-off wavelength of about 460 nm. The Tungsten Oxide particles are doped or reduced with cations, and with their large surface area they can collect a large number of free electrons, which gives them the characteristics of plasma resonance absorption of near-infrared light [8, 9]. Because Tungsten Oxide can form a stable Magneli phase (WO_{3-x}) ($0 < x < 1$) under oxygen-deficient conditions, it is non-stoichiometric structure and the oxygen vacancies on the surface form donor energy levels in the bandgap. Therefore, when Tungsten Oxide is reduced, free electrons are generated, and the surface Plasmon resonance is generated after light irradiation with the characteristic of absorbing NIR light. Because the size of tungsten oxide nanoparticles is much smaller than the wavelength of visible light, it can maintain the penetration of visible light. Moreover, WO_{3-x} has naturally a thermal insulation properties [10]. Because of its non-stoichiometric properties, WO_3 can withstand a certain amount of oxygen vacancies in its lattice to obtain different proportions of WO_{3-x} .

1.2 Cesium Tungstate Cs_xWO_3

$\text{Cs}_{0.33}\text{WO}_3$ has significant absorption in NIR and still maintains high visible light transmittance. So far, the synthesis of Cesium Tungstate is mostly based on the solid-state reaction method under high-temperature reducing atmosphere [11]. During 2010–2012, Guo et al and other researchers [12–13] found that by adjusting the ratio of ethanol and acetic acid for esterification reaction, the release of water can be controlled to synthesize Cs_xWO_3 nanorods, and the different ratios and temperature of the two solvents can be achieved. In 2014, Lee et al. [14] fabricated double-layer coating of Cesium Tungstate and reached has 10% transmittance at 1000nm in NIR region, 80% transmittance for 550nm wavelength in visible range.

1.3 Cesium Tungstate Cs_xWO_3 with core-shell structure

Cs_xWO_3 (CWO) is a NIR shielding material with viable application as a windows for houses and cars. However, the NIR shielding properties of CWO is not stable and degrades at humid/hot conditions and in alkaline environments, which hinders the further application of CWO. To solve this problem, Chen et al. [15] successfully prepared the CWO@ZnO core-shell structure through a simple thermal reduction method, and obtained high absorption of NIR light (NIR transmittance of 13.2%), high-visible light transmittance (63.9%) and humidity stability (~ 150 days), excellent stability even in alkaline (~ 50 minutes).

This paper focuses on hydrothermal method to synthesize Cesium Tungstate Nanorods that absorb near-infrared wavelengths. We aimed to form a component with a dye-sensitized cell (DSSC) structure to generate current in NIR region. Mesoporous Titanium dioxide (m-TiO_2) was used as ETL in a conventional perovskite cell as the main structure. PFN-DOF material has been used as buffer layer between the Cesium Tungstate and m-TiO_2 it has higher excited energy level (LUMO) as shown in Fig. 1. Finally, P25 (TiO_2) of the absorbing dye is added in DSSC.

Experimental Procedure

2.1 Synthesis of $\text{Cs}_{0.33}\text{WO}_3$

The $\text{Cs}_{0.33}\text{WO}_3$ synthesis has been performed as following steps:

The overall solvent is ethanol (60ml) and glacial acetic acid (48ml and 12ml) with volume ratio of 4:1.

1. Dissolved 0.3569g (0.0009mol) WCl_6 in 48ml ethanol to make 0.01875M, stir in the magnet until the solution is completely dissolved.
2. Added 0.0756g (0.00045mol) $\text{CsOH}\cdot\text{H}_2\text{O}$ (mole number ratio W:Cs = 0.5:1) then dissolve by magnet stirring.
3. Added 12ml of glacial acetic acid (20 vol%) to the solution and stir until the solution is uniform.
4. Moved the Teflon cup with the solution to the autoclave, and react in the autoclave at $240^\circ\text{C}/240\text{rpm}$ for 20hr until the reaction is complete.
5. After the reaction is completed, a blue $\text{Cs}_{0.33}\text{WO}_3$ suspension (ethanol phase) is obtained. The concentration of WCl_6 in the final solution is 0.015M, and the concentration of $\text{CsOH}\cdot\text{H}_2\text{O}$ is 0.0075M. Now it's time to wash the synthesized $\text{Cs}_{0.33}\text{WO}_3$ suspension by two-stage centrifugation. After that deionized water was added to the final suspension to prepare an aqueous solution of Cesium Tungstate (solid content: 10 wt%)

2.2 Preparation of working electrodes

Three different concentrations of PFN-DOF (0.5mg, 1mg and 2mg) precursor solution has been prepared: by adding 2 μl trace of glacial acetic acid in 1ml methanol solution DOF precursor fluid. Firstly, the FTO conductive glass ($7\Omega/\square$) was washed with dishwashing detergent solution through ultrasonic vibration

for 30 minutes to remove the oil stains, and then acetone and ethanol were used for 30 minutes ultrasonic vibration to clean the surface organic impurities and then was inserted into oven to dry. Finally, it was inserted into Plasma cleaner for 10 minutes to prepare a cell with 0.16cm^2 area size. Then, the FTO glass was coated on a spin-coater with a commercial TiO_2 slurry precursor (weight ratio TiO_2 Past: ethanol = 2:7). The coating condition was 1000rpm and 60s. The residual solution was completely volatilized by long-term rotation, and then Calcined in air at 500°C for 30 minutes to fully bond. Now the PFN-DOF precursor solution is applied with the coating conditions of 2000rpm and 60s for the second layer coating. This will be equipped with different concentrations of $\text{Cs}_{0.33}\text{WO}_3$ aqueous solution (0.09wt%, 0.11wt%, 0.13wt%) and will be doped relative to the $\text{Cs}_{0.33}\text{WO}_3$ aqueous solution with different concentrations of P25 (0.025wt%, 0.048wt%, 0.071wt%) and then is coated by spin-coating with 1000rpm and 30s coating conditions to achieve uniform dispersion of suspension. When the film thickness become complete, then it was shaken off to clean it from the remaining suspension at 3000 rpm and 10 seconds, and the same coating conditions were repeated to make $\text{Cs}_{0.33}\text{WO}_3$ film to reach the required film thickness.

2.3 Device Fabrication Procedure

Device fabrication is as explained in our previous publication [16]. The counter electrodes made of Pt were sputter deposited on FTO glass (40 mA, 60s) while the anodes were deposited using a $25\mu\text{m}$ -thick Surlyn film. These films were deposited as spacer and were pressed at 30 psi and 125°C within 20 s afterward. The electrolyte solution (0.4 M tetrabutyl-ammonium iodide, 0.3 M N-methylbenzimidazole, 0.4 M LiI, 0.04 M I_2 was added into a mixture of 3-methoxypropionitrile and acetonitrile (1:1, v/v)) and was then fed into cells via pre-drilled holes in Pt counter electrodes.

2.4 Characterization Methods

A dynamic light scattering analyzer (NanoPlus, Micromeritics) has been used for h-TAc particle size distribution. h-TAc crystallinity determined by X-ray diffraction (XRD) using Miniflex II – Rigaku with routine Cu K_α source. TiO_2 morphology was scanned by optical microscope (M835, M&T Optics) and FE-SEM- JSM-6700F, (JEOL) and the surface areas measured by N_2 adsorption-desorption isotherms at $T = 77\text{ K}$. The h-Tac has inorganic content, which is measured by thermogravimetric analyzer (TGA 2050, TA Instruments) $10^\circ\text{C}/\text{min}$ with a heat-up rate under N_2 flow. h-TAc composition have been extracted by FTIR spectrophotometer (Spectrum One, PerkinElmer). Nanoindentation has been used to extract the mechanical properties of the mesoporous film (MTS G200, Keysight Tech.). Dye adsorption measured by using 0.1M NaOH to desorb it and then measuring it's absorption rate using UV–Vis spectrophotometer (Lambda 850, PerkinElmer). The Current-density and Voltage curves (J-V characteristics) were obtained under 100 mW cm^{-2} irradiation with solar simulator (MFS-PV, Hong-Ming Technology). Electrochemical impedance spectroscopy (EIS-spectra) were measured for 50 mHz-100 kHz at 10mV potential perturbation by Zennium system, (Zahner).

2.5. Assembly of components

In order to avoid the working electrode and the counter electrode from being short-circuited, Surlyn with a thickness of 25µm was used as a spacer to create a gap between the two electrodes without direct contact. The heat press sealer has been used at a temperature of 125°C and a pressure of 30 psi for a duration of 20s. The two electrodes are bonded by Surlyn, and electrolyte is injected through the gap between the bonding, and finally, the PI tape paste is added to the holes to complete the component assembly. The assembly diagram is as shown in Fig. 3.

Results And Discussions

We performed few experiments to confirm the formation of nanorods before we evaluate the device characteristics. Figure 4a shows the XRD analysis performed on $\text{Cs}_{0.33}\text{WO}_3$ Nanorods. The detected XRD peaks indicate the nanorods formation with the main phase (200) which is in agreement with the main characteristic peaks of Cs-doped Tungsten bronze (Cs-doped WO_3) reported in literature [17, 18]. The water-controlled release process proposed by Guo et al. [11] has been used to synthesize $\text{Cs}_{0.33}\text{WO}_3$ nanorods with high IR light absorption and a high transmission rate for the visible light.

Figure 4b shows the TEM measurements that has been performed to confirm and detect the average length and width of the $\text{Cs}_{0.33}\text{WO}_3$ nanorods. These images confirm that the synthesized $\text{Cs}_{0.33}\text{WO}_3$ is a nanorod structure with an average length of 24–37 nm and a width of 8–12 nm.

3.1. Optimizing the $\text{Cs}_{0.33}\text{WO}_3$ concentrations

Three different concentration of $\text{Cs}_{0.33}\text{WO}_3$ nanorods has been synthesized with 0.09wt%, 0.11wt%, and 0.13wt%. Figure 5 shows the transmission rate (T at %) of the films prepared with different $\text{Cs}_{0.33}\text{WO}_3$ concentrations. The films show acceptable absorption rate in the infrared region. In the NIR wavelength region (850-1100nm), the transmission rate drops from 59–29% for the concentration of 0.09wt% $\text{Cs}_{0.33}\text{WO}_3$. When the concentration reaches 0.11wt%, the transmission rate in NIR range significantly drops from 48–18%. For $\text{Cs}_{0.33}\text{WO}_3$ concentration of 0.13wt%, the transmission rate only slightly reduces from 44–16%. According to this, the NIR light absorption is close to the optimum when the concentration is 0.11wt%.

Now, we aim to investigate using mesoporous Titanium dioxide (TiO_2) as the ETL with different concentrations of $\text{Cs}_{0.33}\text{WO}_3$ as the light-absorbing layer to explore the current-density characteristics of the device with focus on NIR range (850-1100nm) and visible range (400-1100nm) absorption. Figure 6a shows the average of current density measured under the irradiation of NIR light. When the concentration of $\text{Cs}_{0.33}\text{WO}_3$ is 0.11 wt%, the overall current value is $0.253 \mu\text{A}/\text{cm}^2$ and the best value of the overall current is $0.38 \mu\text{A}/\text{cm}^2$ (highest). Figure 6b shows the average current density obtained under irradiating of visible light which seems to be similar to Fig. 6a. In this case, when the concentration of $\text{Cs}_{0.33}\text{WO}_3$ is 0.11 wt%, the overall current value is $18.41 \mu\text{A}/\text{cm}^2$ and the best value of overall current is highest at $18.84 \mu\text{A}/\text{cm}^2$.

3.2. Optimizing the P25 concentration in Cs_{0.33}WO₃ layer

Xuechang. et al. [19] proposed the porous P25 (TiO₂) to increase the overall surface area and increase the photo-absorption DSSCs. Here we doped Cs_{0.33}WO₃ with three different concentration of P25 to enhance the current density under NIR and visible light irradiation. P25 has smaller particle size to fill the pores of the bottom side of the Cs_{0.33}WO₃ to block the recombination at the interface of electrolyte and ETL. The structure will be modified to FTO/TiO₂/PFN-DOF/Cs_{0.33}WO₃ with the optimized Cs_{0.33}WO₃ concentration of 0.11wt% and 1mg PFN-DOF interface layer. Here, we tested the different concentrations of P25(TiO₂) (0.025wt%, 0.048wt%, 0.071wt%) and measured the current density under NIR (850-1100nm) and visible light (400-1100nm) irradiation as presented in Fig. 7a and 7b, respectively. When 0.048wt% P25 is added to the optimized Cs_{0.33}WO₃ concentration of 0.11wt%, the total current density increases to 0.58 $\mu\text{A}/\text{cm}^2$ and the best current value raised to 0.70 $\mu\text{A}/\text{cm}^2$. Moreover, according to Fig. 7b, the trend of current density versus time under visible light irradiation is the same as that of NIR light with the total current density of 30.46 $\mu\text{A}/\text{cm}^2$ and the best value of 31.12 $\mu\text{A}/\text{cm}^2$. The results confirm that P25 addition to Cs_{0.33}WO₃ is feasible and effective in blocking the contact between the electrolyte and ETL.

3.2. adding the PFN-DOF buffer layer

Here, we proposed adding a layer of PFN-DOF as the buffer layer at the interface layer between the mesoporous TiO₂ as ETL and the active layer Cs_{0.33}WO₃ as the adsorbing electrolyte. The current density versus time of three different PFN-DOF concentrations (0.5PFN, 1PFN, 2PFN) have been discussed under the irradiation of NIR (850-1100nm) and visible light (400- 1100nm) irradiation. The LUMO level of PFN-DOF is as high as -2.14 eV, which facilitates electron extraction at the interface of Cs_{0.33}WO₃ and FTO electrode. The order matching is shown in Fig. 1. The active layer of Cs_{0.33}WO₃ absorbs NIR light and the excited electrons are transferred to FTO electrode through - 2.1eV CB value of PFN-DOF and the - 4.4 eV CB value of TiO₂. As shown in Fig. 8, 1mg of PFN-DOF reaches a current density of 0.38 $\mu\text{A}/\text{cm}^2$ and the highest best current of 0.45 $\mu\text{A}/\text{cm}^2$ under NIR irradiation. The trend of irradiating visible light is the same as that of NIR light with 26.81 $\mu\text{A}/\text{cm}^2$ and the best current value of 27.56 $\mu\text{A}/\text{cm}^2$.

In Table 1, we summarized the average current density measured for the cells with different concentrations of Cs_{0.33}WO₃, P25 doping concentrations and three different PFN-DOF concentrations as buffer layer irradiated under NIR and Visible light. This also indicates the highest values obtained in each case. It is observed that when 0.048wt% P25 is added to 0.11wt% cesium tungstate, the highest $V_{oc}=0.375\text{ V}$, $J_{sc}=0.030\text{ mA}/\text{cm}^2$ has been obtained .

Table 1

the average current of cells with different $\text{Cs}_{0.33}\text{WO}_3$ concentration, P25 doping and the added PFN-DOF buffer layer irradiated under NIR and Visible light.

Material	Concentration	J_{sc} (mA/cm ²) under NIR	J_{sc} (mA/cm ²) under Visible	Max J_{sc} (mA/cm ²) under NIR	Max J_{sc} (mA/cm ²) under Visible
$\text{Cs}_{0.33}\text{WO}_3$	0.09 %wt	0.21 ± 0.03	12.12 ± 0.18	0.29	12.36
	0.11 %wt	0.25 ± 0.04	18.41 ± 0.53	0.38	18.84
	0.13 %wt	0.24 ± 0.04	13.49 ± 0.34	0.34	13.79
P25	0.025 %wt	0.45 ± 0.05	27.5 ± 0.05	0.58	28.38
	0.048 %wt	0.58 ± 0.05	30.4 ± 0.05	0.70	31.11
	0.071 %wt	0.49 ± 0.03	28.02 ± 0.03	0.54	28.65
PFN-DOF	0.5	0.26 ± 0.02	22.57 ± 0.40	0.30	23.32
	1	0.38 ± 0.03	28.81 ± 0.44	0.45	27.55
	2	0.30 ± 0.03	24.00 ± 0.46	0.36	24.77

The performance parameters of the solar cells with different concentration of $\text{Cs}_{0.33}\text{WO}_3$, P25 doping and PFN-DOF buffer layer measured under visible light has been summarized in Table 2. The highest V_{oc} = 0.125 V and J_{sc} = 0.017 $\mu\text{m}/\text{cm}^2$ was measured for 0.11wt% optimized concentration of $\text{Cs}_{0.33}\text{WO}_3$. Doping with P25 has increased the V_{oc} to 0.37 V and the J_{sc} raised to 0.03 mA/cm². Moreover, the best voltage obtained by adding the PFN-DOF buffer layer (0.313 V) with the best J_{sc} = 0.025 mA/cm². The buffer layer promotes the carrier transport and enhances the electron extraction capability resulting in lower recombination rate at the interfaces which, in turn, increases the V_{oc} of the cell.

Table 2
, the device parameters of the cells with different concentrations of $\text{Cs}_{0.33}\text{WO}_3$, P25 doping and PFN-DOF buffer layer irradiated under **visible** light.

Material	Concentration	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
$\text{Cs}_{0.33}\text{WO}_3$	0.09 %wt	0.064	0.01	27.46	0
	0.11 %wt	0.125	0.017	32.86	0
	0.13 %wt	0.115	0.012	34.29	0
P25	0.025 %wt	0.40	0.027	52.08	0.01
	0.048 %wt	0.37	0.030	48.61	0.01
	0.071 %wt	0.30	0.028	52.08	0
PFN-DOF	0.5	0.313	0.02	47.80	0
	1	0.229	0.025	41.58	0
	2	0.135	0.024	24.41	0

3.3. Nyquist plots of the cells with different concentration of $\text{Cs}_{0.33}\text{WO}_3$, P25 doping and PFN-DOF buffer layer, measured by EIS, has been shown in Fig. 9. The impedance values extracted from these plots has been presented in Table 3. R1 is the impedance of the conductive substrate and the connectors, R2 and R3 are the resistance between the ETL/ $\text{Cs}_{0.33}\text{WO}_3$, and the $\text{Cs}_{0.33}\text{WO}_3$ /electrolyte, respectively. The results show that when $\text{Cs}_{0.33}\text{WO}_3$ concentration reaches 0.11wt%, both R2 and R3 have the lowest values of 20.86 Ω and 117.30 Ω . and R1 has the highest values compared to other two $\text{Cs}_{0.33}\text{WO}_3$ concentrations. On the other hand, The Nyquist plot of structures with P25 concentrations show that although the R2 value of this cell is comparable with the R2 of $\text{Cs}_{0.33}\text{WO}_3$ without P25 doping, the R3 (interface impedance) value is increasing for P25-doped $\text{Cs}_{0.33}\text{WO}_3$ since the electrolyte is not connected to ETL after adding the adding P25 layer. Finally, the Nyquist plots of the cells with PFN-DOF buffer layer shows a downward trend in the surface layer comparison, indicating that the PFN-DOF interface layer enhances the internal carrier transport at the interfaces.

Table 3
, the impedance parameters of the cells with different concentrations of $\text{Cs}_{0.33}\text{WO}_3$, P25 doping, and PFN-DOF buffer layer.

Material	Concentration	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)
$\text{Cs}_{0.33}\text{WO}_3$	0.09 %wt	23.90	34.82	169.0
	0.11 %wt	35.64	20.86	117.3
	0.13 %wt	14.36	21.98	126.3
P25	0.024 %wt	24.29	25.32	439.30
	0.048 %wt	16.35	17.11	412.40
	0.071 %wt	18.66	20.43	424.50
PFN	0.5	21.08	19.11	354.8
	1	15.93	12.80	293.4
	2	29.92	13.74	341.7

3.4. SEM images: SEM cross-sectional images of the films has been presented in Figs. 10 and 11. It is observed that the thickness of TiO_2 is between 1.1–1.3 μm and 400–500 nm (under high magnification: 200k). The thickness of 22nm, 35nm, 83nm has been measured for 0.5mg, 1mg, and 2mg of PFN-DOF buffer layer, respectively. Note that the best V_{oc} was measured for 1mg of PFN-DOF with thickness of 35 nm, which is in agreement with the literature measured 30-40nm of PFN-DOF film for the most efficient cell [20–22]. In addition, the SEM top view in Fig. 12 shows that the whole $\text{Cs}_{0.33}\text{WO}_3$ has many pores. In fact, we aimed to dope the $\text{Cs}_{0.33}\text{WO}_3$ with P25 to prevent the electrolyte from contacting the ETL.

Conclusion

In this paper, we proposed $\text{Cs}_{0.33}\text{WO}_3$ as the absorber layer for NIR light to enhance the total photo-generated current of a dye-sensitized solar cell by modifying the morphology and structure of its electron transport layer. The experimental results show two conclusions. The first buffer layer is PFN-DOF, which has a high LUMO value and promotes the electron transport at the interface to increase the overall current density of the cell. The second buffer layer is P25(TiO_2) doped with $\text{Cs}_{0.33}\text{WO}_3$ to fill the internal pores of $\text{Cs}_{0.33}\text{WO}_3$ to isolate contact of electrolyte and ETL to obtain higher photocurrent density. We conclude the following modified structures and the current density improvements from our experiments:

1. In $\text{Cs}_{0.33}\text{WO}_3$ element without PFN-DOF layer, when the concentration reaches 0.11wt%, the optimal current value is $0.38 \mu\text{A}/\text{cm}^2$ under NIR light, and $18.84 \mu\text{A}/\text{cm}^2$ under visible light. By adding the PFN-DOF buffer layer, the best current density of $0.45 \mu\text{A}/\text{cm}^2$ is obtained for 0.1mg PFN-DOF concentration irradiated under NIR light. In addition, the current density of $27.559 \mu\text{A}/\text{cm}^2$ has been obtained under

visible light conditions confirming that inserting PFN-DOF as buffer layer can effectively enhance the electron transport and increases the current density.

2. For a 0.048 wt% of P25, the best current density of $0.700 \mu\text{A}/\text{cm}^2$ obtained under NIR light and $31.11 \mu\text{A}/\text{cm}^2$ obtained under visible light which shows the small size of P25 particles fill the pores and directly impact on total current density of $\text{Cs}_{0.33}\text{WO}_3$ layer.

Declarations

Conflict of Interest: The authors declare that they have no conflict of interest.

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Figures

Figure 1

Schematic diagram of energy level for every layer in the device structure matching the $\text{Cs}_{0.33}\text{WO}_3$ layer.

Figure 2

$\text{Cs}_{0.33}\text{WO}_3$ preparation procedure.

Figure 3

Schematic diagram of component assembly and the resulted structure.

Figure 4

a) The XRD analysis, and, b) the TEM images of the nanorods.

Figure 5

The transmission rate of the cells with three different concentration of $\text{Cs}_{0.33}\text{WO}_3$ films and the FTO substrate.

Figure 6

The current density vs. time for different $\text{Cs}_{0.33}\text{WO}_3$ concentration irradiated under a) NIR, b) visible light.

Figure 7

Current vs. time for different concentrations of P25 under a) NIR, b) visible light.

Figure 8

Current density versus time for various concentration of PFN-DOF buffer layer under NIR and visible light.

Figure 9

Nyquist plots measured for different concentrations of $\text{Cs}_{0.33}\text{WO}_3$, P25 doping, and PFN-DOF buffer layer.

Figure 10

The SEM cross-sections of PFN-DOF buffer layer with different concentrations.

Figure 11

The SEM cross-sections of P25 layer with different concentrations.

Figure 12

The SEM top view of the $\text{Cs}_{0.33}\text{WO}_3$ layer with different concentrations of P25.