



Minimizing energy losses in perovskite solar cells using plasma-treated transparent conducting layers



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ARTICLE INFO

Article history:

Received 1 July 2015

Received in revised form 31 August 2015

Accepted 17 September 2015

Available online 25 September 2015

Keywords:

Plasma treatment

Blocking layer

Electron recombination

Perovskite solar cells

ABSTRACT

This study reports for increasing the efficiency of perovskite solar cells (PSCs) by modifying the surface of a fluorine-doped indium tin oxide (FTO) substrate using an atmospheric pressure plasma treatment. Surface modification of the FTO film involved several challenges, such as control of the blocking layer uniformity, removal of pinholes, and deposition of a dense layer. This strategy allows the suppression of charge recombination at the interface between the FTO substrate and hole conductor. Electrochemical impedance spectroscopy analysis showed that the plasma treatment increased the charge transfer resistance between the FTO and hole conductor from 95.1 to 351.1 Ω , indicating enhanced resistance to the electron back reaction. Analyses of the open-circuit photovoltage decay revealed that modification of the surface of the FTO substrate by plasma treatment increased time constant from 6.44 ms to 13.15 ms. The effect is ascribed to suppression of the electron recombination rate. PSCs based on the newly developed electrode had 39% higher efficiency than reference devices. The obtained results provide direct evidence in favor of the developed strategy.

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1. Introduction

Perovskite solar cells (PSCs) have attracted considerable interest as next-generation solar energy conversion devices because of their simple fabrication and high energy conversion efficiencies [1–5]. The theoretical maximum efficiency of PSCs, estimated to be around 33%, exceeds the appropriate parameter in conventional dye-sensitized solar cells (DSCs) [6]. To date, the best reported power conversion efficiencies are 15% for PSCs based on a $\text{CH}_3\text{NH}_3\text{PbI}_3$ sensitizer and 19.3% for cells based on a $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ sensitizer [2–5,7]. It has been shown that one of the losses of photo-injected electrons in DSCs and PSCs is the loss due to electron–hole recombination at the interface of the FTO substrate and redox electrolyte or at the FTO/hole transport material (HTM) interface. Indeed, the underlying FTO substrate is in contact with the electrolyte or HTM instead of an uncoated surface. Because the typical doping level ($N_d = 10^{20} \text{ cm}^{-3}$) of FTO yields a space charge layer width of around a few nanometers [8], the probability that electrons will tunnel across this thin barrier is very high, even if a built-in potential exists at the substrate surface. The probability of electron transfer from the FTO substrate is especially high under open-circuit conditions, because the gradient of free energy (the quasi-Fermi levels) for electrons in FTO and holes in the HTM is very large owing to an upward

shift of the quasi-Fermi level in FTO under illumination. The depletion region in FTO was derived from the Mott–Schottky plot, and “metallic” electron-transfer behavior was confirmed by electrochemical impedance spectroscopy (EIS) analysis [9]. Thus, PSC device performance can be further improved by significant suppression of electron transfer via the FTO substrate [10–13]. For this purpose, a 50–100-nm-thick TiO_2 blocking layer (BL) has been introduced by atomic layer deposition, spin-coating, spray pyrolysis, or thermal oxidation of a sputtered titanium film [14–16]. However, the proposed technologies suggest coverage of the FTO substrate with thick BLs. Expensive vacuum equipment and targets are drawbacks for the development of an economical and continuous process for device fabrication. Furthermore, for a high BL thickness, the photocurrent is reduced because of the formation of a region insufficient for electron transport from the bulk TiO_2 layer to FTO via the BL [17]. Therefore, the growth of a thin, uniform BL is still an issue for PSC technology.

Here, we present a novel strategy for increasing the efficiency of PSCs by using FTO transparent conducting layers modified by atmospheric pressure plasma treatment on glass substrates. Surface modification of the FTO film involves several challenges, such as control of the BL uniformity, removal of pinholes, and deposition of a dense layer. The developed technology allows the suppression of charge recombination at both the FTO substrate/hole conductor interface and the FTO/working electrode (WE) interface. PSCs based on the plasma-modified FTO layers demonstrate a power conversion efficiency of 2.09%, which is 105% higher than that of PSCs with conventional untreated FTO layers and without a mesoporous TiO_2 layer. Accordingly,

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the observed efficiency in PSC samples using a mesoporous TiO₂ layer was 39% higher.

2. Experimental section

2.1. Materials synthesis

The organometal halide perovskite sensitizer CH₃NH₃PbI₃ was synthesized using a previously reported method [1]. The precursor CH₃NH₃I was prepared by stirring equimolar amounts of methylamine (40% in methanol) and hydroiodic acid (57 wt.% in water) at 0 °C for 2 h. The precursor solution was evaporated on a rotary evaporator at 40 °C; then the precipitated CH₃NH₃I was washed three times with diethyl ether and dried under vacuum. Finally, CH₃NH₃PbI₃ was synthesized by stirring equimolar amounts of CH₃NH₃I and PbI₂ in γ -butyrolactone at 60 °C overnight.

To prepare the HTM, we used chlorobenzene and acetonitrile with a volume ratio of 1:0.1 as a solvent. The concentrations of 2,2',7,7'-tetrakis-(N,N-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD), lithium bis(trifluoromethane) sulfonamide salt, and 4-*tert*-butylpyridine in the mixed solvent were 170, 64, and 198 mM, respectively.

Methylamine (40% in methanol) was purchased from Tokyo Chemical Industry Co., and spiro-MeOTAD was provided by Merck. All other reagents and chemicals were purchased from Sigma–Aldrich unless otherwise stated and were ACS grade or higher.

2.2. Solar cell fabrication and characterization

FTO glass substrates (Pilkington, USA) were cut to dimensions of 1.6 × 1.6 cm² and patterned by etching with Zn powder and 2 M HCl. The etched substrates were cleaned with water, acetone, and ethanol in ultrasonic cleaner. Four types of WEs were prepared and compared. For WE 1, a TiO₂ BL/pristine FTO substrate was fabricated using a dip-coating method. The substrate was immersed in 40 mM TiCl₄ aqueous solution for 30 min and then rinsed with water and ethanol. Finally, the sample was sintered at 500 °C for 30 min. For WE 2, we used a plasma-treated FTO glass substrate. After cleaning, the FTO substrates were treated by atmospheric plasma under the following operating conditions: power of 150 W, Ar gas flow rate of 5 lpm, plasma treatment time of 1 min, and substrate moving speed of 5 mm/s. Finally, a TiO₂ BL was deposited on the plasma-treated FTO glass by the dip-coating method described above. WE 3 was prepared by depositing 1- μ m-thick mesoporous TiO₂ on the TiO₂ BL/pristine FTO sample. TiO₂ was deposited by spin-coating at 4000 rpm for 30 s. For this purpose, TiO₂ paste (Dyesol 18NR-T) was diluted in anhydrous ethanol with a weight ratio of 1:3. Finally, the film was sintered in air at 500 °C for 30 min. The sintered TiO₂ film was immersed in 40 mM aqueous TiCl₄ solution at 70 °C for 30 min. After cleaning, the sample was annealed at 500 °C for 30 min. WE 4 consists of a 1- μ m-thick mesoporous TiO₂ film deposited on a TiO₂ BL/plasma-treated FTO substrate. The mesoporous TiO₂ layer was fabricated as described above. The prepared electrodes were coated with a perovskite precursor solution and heated at 100 °C for 15 min. Subsequently, all the electrodes under study were coated with the HTM solution using spin-coating at 4000 rpm for 30 s. The samples were left in the dark in air before sputtering of 60 nm Au counter electrodes to complete the solar cells.

2.3. Measurements

The surface morphologies of the FTO and BLs were characterized using a high-resolution scanning electron microscope (HRSEM) (Jeol JSM 7000F). The water contact angles were measured using a drop shape analyzer (DSA 100, KRÜSS GmbH). The photocurrent–voltage (*J*–*V*) characteristics were assessed using an IviumStat device under 1000 W/m² illumination intensity using a sun. 3000 solar simulator

consisting of a 1000 W mercury-based Xe arc lamp and AM 1.5 G filters. The incident-photon-to-current efficiencies (IPCEs) were measured in the spectral range of 300 to 800 nm using an IPCE system for DSCs (Ivium Technologies.). Calibration was conducted using a PECS102-calibrated silicon photodiode as a standard. A diode laser with variable power and modulation control (Coherent Labs, 10 mW, 623 nm) was used as the light source. Illumination was always incident on the WE side of the solar cell. The intensity was measured using a calibrated Si photodiode. The impedance spectrum of the PSCs was measured under constant light illumination (100 mW cm⁻²) biased under open-circuit conditions and under dark with different bias voltages at frequencies of 100 kHz to 100 MHz with a perturbation amplitude of 10 mV.

3. Results and discussion

The aim of this study was to fabricate a uniform, dense, and pinhole-free TiO₂ BL to improve the efficiency of PSCs by surface modification of FTO transparent conducting substrates through an atmospheric pressure plasma treatment. A TiO₂ BL was fabricated on the FTO glass substrate by a sequence of processes, as shown in Fig. 1. Fig. 1a–d shows HRSEM images of the pristine FTO, plasma-treated FTO, TiO₂ BL on the pristine FTO, and TiO₂ BL on the plasma-treated FTO, respectively. No visible differences were observed in the surface morphology of the FTO layer before and after plasma treatment. We observed, however, that the surface became superhydrophilic after plasma treatment [18]. Fig. 2a, b shows images of the water contact angles for the pristine and plasma-treated FTO samples, respectively. The obtained data show that plasma treatment of the surface changes the water contact angle from 83.4° to 0°, which indicates superhydrophilicity. The superhydrophilic surface provides favorable conditions for uniform and pinhole-free coverage from the aqueous TiCl₄ solution. Therefore, we treated the FTO surface with plasma to address those issues. Fig. 1c, d shows HRSEM images of TiO₂ BLs formed on the pristine and plasma-treated FTO glasses, respectively. The surface of the BL on the pristine FTO is not uniform and exhibits many microcracks and pinholes (yellow dotted loops) as presented in Fig. 1c, which formed because of the hydrophobicity of pristine FTO surface. The existence of naked FTO sites is well known to increase the dark current, which negatively affects device efficiency [19]. Shunting via the substrate significantly decreases the open-circuit voltage (*V*_{oc}) [8]. However, the change in the surface properties of the FTO substrate under plasma treatment yields uniform pinhole-free coverage of the substrate with tightly connected small seeds of TiO₂ BL. A pinhole-free, uniform, and tight BL is important for optimal solar cell operation because it enhances the suppression of charge recombination at the interface. In addition, such a BL increases the effective surface area for perovskite adsorption, enhancing the light harvesting efficiency.

The transmittances of the samples at wavelengths of 350–800 nm were estimated. Transmittance spectra are shown in Fig. 3. The transmittances of the pristine FTO, plasma-treated FTO, pristine FTO/BL, and plasma-treated FTO/BL at 550 nm were estimated to be 65.61%, 65.98%, 68.72%, and 70.98%, respectively. These numbers demonstrate that plasma treatment of the FTO surface enhances the transmittance of the FTO/BL structure compared to the pristine FTO/BL. The increase in the transmittance of the FTO/BL structure can be explained by effective scattering enhancement in the TiO₂ nanoparticle structure, which can be assigned to Rayleigh scattering [20]. The Rayleigh scattering is the elastic scattering of electromagnetic waves induced by particles with sizes much smaller than the wavelength (particle size < 1/10 wavelength). We estimated the transmittances of samples at the wavelengths of 350–800 nm, and, in particular, at the wavelength of 550 nm. The particle size was estimated as ~25 nm from SEM image. This value satisfies the requirement of Rayleigh scattering. Since the Rayleigh scattering intensity is inversely proportional to the fourth power of wavelength ($\sim \lambda^{-4}$) and the short wavelength is scattered

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