

Reverse Bias Boosted Photovoltaic Performance of Perovskite Solar Cells

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Introduction

Perovskite materials and perovskite solar cells (PSCs) still face the problem of instability. Except oxygen and humidity that can be excluded by encapsulation, intrinsic instability of perovskites under light and heat stimuli and the ion migration inside the device are more critical. Among these problems, the PSC under reverse bias is still relatively less studied.

Herein, it was found that the photovoltaic performance of some PSCs can be significantly improved by reverse bias. Specifically, the open-circuit voltage (V_{oc}) can be markedly improved with an average increment of 30 mV, while short-circuit current density (J_{sc}) and fill factor (FF) remain constant. The phenomenon is first reported here. Electrical characterizations, including Nyquist plots, Mott-Schottky curves and so on, also confirmed this positive effect of reverse bias. It was found that halide ions in the perovskite, especially iodine ions, can migrate into the electron transport layer, e.g., tin oxide (SnO_2) under reverse bias. More importantly, the interaction between halide ions and Sn^{4+} has been confirmed, which may help to passivate oxygen vacancies and change the energy level of the SnO_2 layer.

Results and Discussion

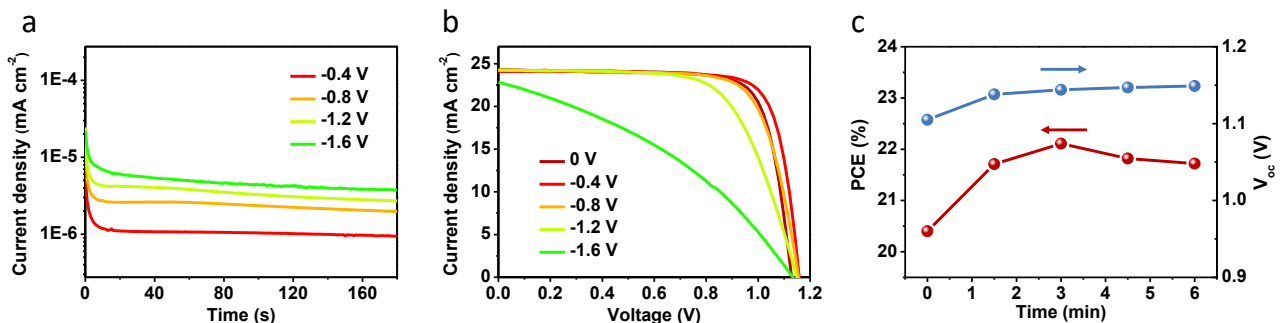


Figure 1. (a) Current of the reverse-biased PSCs as a function of time; (b) J - V curves of a typical PSC after reverse biasing at different voltage for 3 min; (c) PCE and V_{oc} of the PSCs after reverse biasing at -0.4 V for different time.

When the PSC with a structure of ITO/ SnO_2 / $\text{FA}_{0.945}\text{MA}_{0.025}\text{Cs}_{0.03}\text{Pb}(\text{I}_{0.975}\text{Br}_{0.025})_3$ /Spiro-OMeTAD/Ag is subjected to moderate reverse bias, the reverse current first decreases and then tends to be stable (Figure 1a), which is consistent with reports in the literature [1]. In addition, the current grows with the increase of the reverse bias. It is because both electronic and ionic currents should be promoted under higher electric field. Moreover, it is found that the photovoltaic performance of the cell changes obviously after the cell is subjected to different reverse voltage for 3 min. As shown in Figure 1b, the device performance is significantly improved after the reverse biasing at -0.4 V, especially the V_{oc} . Specifically, the efficiency (V_{oc} , J_{sc} and FF) of the PSC increases from the initial 20.50% (1.112 V, 24.24 mA cm⁻² and 76.02%) to 21.95% (1.157 V, 24.09 mA cm⁻² and 78.78%). However, when the reverse bias exceeds -0.8 V, the device performance will gradually degrade, which is consistent with the results reported in the literature [1,2]. It may

result from ion migration, phase segregation and the formation of highly conductive shunts due to silver melting or metal migration induced by reverse bias [1,2]. Besides, the effect of reverse-bias loading time on device performance is also investigated. As shown in Figure 1c, with the increase of loading time of the reverse bias at -0.4 V, the V_{oc} grows first and gradually remains stable. In contrast, the efficiency peaks at 3 min and then decreases as the loading time increases.

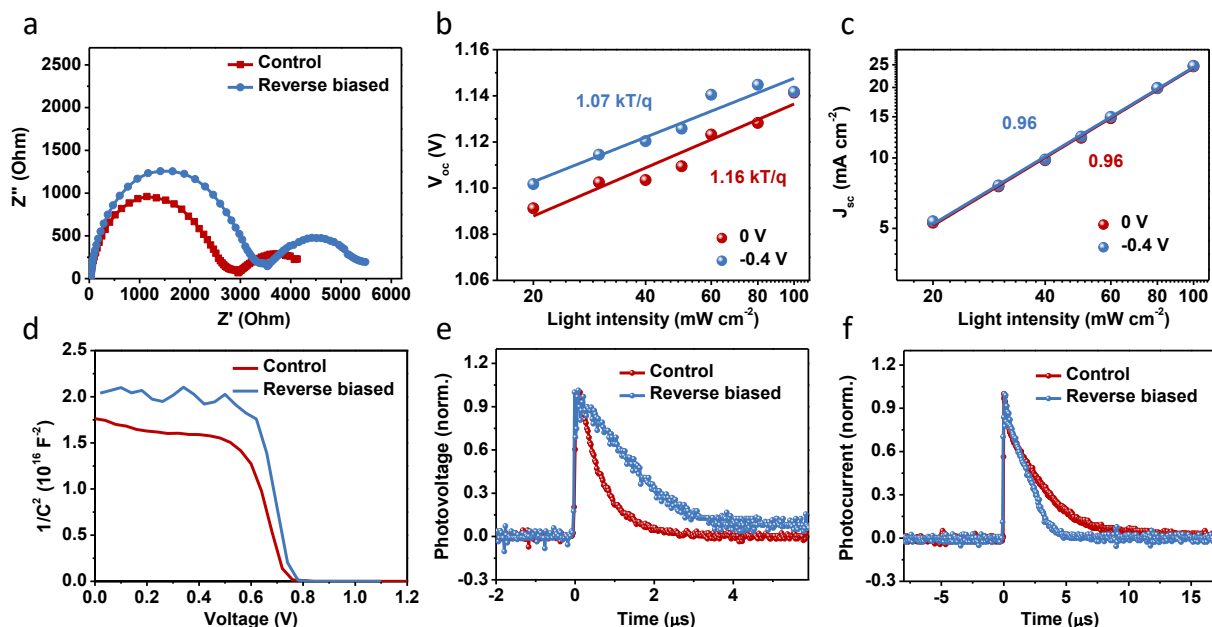


Figure 2. (a) Nyquist plots of the PSC before and after reverse biasing at -0.4 V for 3 min; the light-intensity dependence of (b) V_{oc} and (c) J_{sc} measurement related to pristine and reverse biased PSC; (d) Mott-Schottky curves, (e) transient photovoltage decay curves and (f) transient photocurrent decay curves of the PSCs before and after reverse biasing.

Electrochemical impedance spectroscopy (EIS) is employed to study carrier dynamics in PSCs. As shown in Figure 2a, recombination resistance (R_{rec}) assigned to low-frequency increased obviously in the PSCs after reverse biasing. It indicates that the charge carrier recombination within the cell is suppressed. Additionally, it is found that the charge transfer resistance (R_{ct}) ascends, which is not conducive to the carrier transport. It may be caused by the forward bias applied during EIS measurement. Figure 2b shows V_{oc} versus light intensity of the PSC before and after reverse biasing. It suggests that the V_{oc} values increase obviously after reverse bias, irrespective of the light intensity. More importantly, the deviation between the slope and the value of (kT/q) decreases significantly after reverse bias, indicating that the trap-assisted recombination is suppressed [3]. In contrast, the slopes between J_{sc} and light intensity are almost identical and very close to 1 (Figure 2c), suggesting that the bimolecular recombination in the PSC is negligible and not affected by the reverse bias [3]. In addition, the Mott-Schottky curves are obtained in dark via capacitance-voltage measurement to reveal the mechanism for improved V_{oc} and efficiencies. As shown in Figure 2d, the built-in field (V_{bi}) of the reverse biased cell is much higher than its initial value, indicating an increased driving force for charge separation and extended depletion region for suppressing the carrier recombination. The larger slope indicates the decreased interfacial charge density, which has an inversely proportional relationship to the slope [4]. It should be attributed to the ion migration, improved energy level alignment, and accordingly reduced interfacial defects, which will be discussed below. Besides, the transient photovoltage and photocurrent decays were measured at open and short circuit, respectively. It is apparent that the photovoltage decay was slowed down, but the decay of photocurrent was accelerated after reverse biasing (Figure 2e and Figure 2f). It indicates that the recombination of charge carriers was suppressed, and charge extraction and transport were improved within the cells.

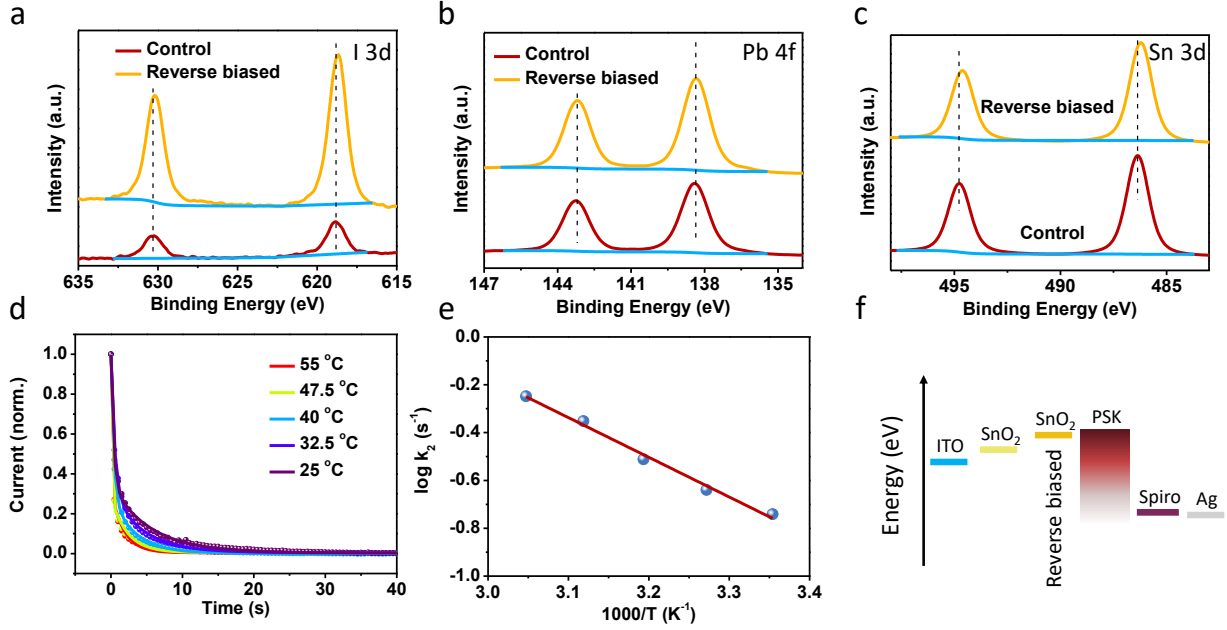


Figure 3. XPS spectra of (a) I 3d, (b) Pb 4f and (c) Sn 3d; (d) current decay with temperature and (e) the Arrhenius plot of the time constant; (f) energy level diagram of perovskite solar cells before and after reverse biasing.

Figure 3 a-c show the X-ray photoelectron spectroscopy (XPS) spectra of the SnO_2 layers before and after reverse biasing. Note that the SnO_2 films are derived from complete PSCs. The result shows that the intensity of I 3d peaks in reverse biased sample is much stronger than that of control sample, while the differences in Pb 4f and Sn 3d are negligible. Note that I 3d and Pb 4f peaks in the control sample should be attributed to residual lead iodine. The results suggest that reverse bias contributes to the increase of iodine content in SnO_2 layers. It should be ascribed to the directional migration of iodine ions within PSCs under the electric field caused by reverse bias. Also, the movement of peak locations of I 3d and Sn 3d was observed after reverse biasing. It further confirms that the migrated iodine ions would interact with SnO_2 , which may help to passivate the oxygen vacancies on the surface of SnO_2 particles.

Figure 3d shows the data of reverse biased PSCs under different temperature. They can be well fitted by the following equation.

$$I = I_0 + I_1 \exp(-k_1 t) + I_2 \exp(-k_2 t) \quad (1)$$

It has been reported that the capacitance of PSCs is very small [5]. Therefore, the rapid decrease at the beginning of the current-time ($I-t$) curves should be attributed to the capacitive effect of PSCs, corresponding to the small value of k_1 . The following part of the slow decay should result from ion migration under reverse bias. Accordingly, the Arrhenius plot of current decay velocity k_2 and the inverse time constant calculated from the $I-t$ curve are shown in Figure 3e. The activation energy calculated from the slope of the curve is 0.17 eV, which is much lower than the activation energy of various mobile ions in perovskites [6]. Only the activation energies of iodine ions and iodine interstitials match this value [7,8]. It further confirms our speculation that iodine ion migration can occur in PSCs under reverse bias. Figure 3f shows the energy level diagram of PSCs after reverse biasing. Given the XPS results and improvement in efficiency and V_{oc} , we hypothesize that the conduction band of SnO_2 layers will move upward under reverse bias to form a better energy level alignment with perovskite.

References

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