Improving the hole extraction by hexadecylbenzene modification for efficient perovskite solar cells

Lisha Xie, Xiaoyu Deng, Chengbo Li and Feng Hao*

School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 610054, China.

*Corresponding author e-mail: haofeng@uestc.edu.cn

Abstract. In highly efficient halide perovskite solar cells (PSCs), nickel oxide (NiOx) have been widely used as an inorganic hole transport layer (HTL). However, the solution-processed NiOx films always have pinholes, along with inferior contact with perovskite layer. Herein, a surfactant of hexadecylbenzene (HAB) was applied to improve the hole extraction from perovskite to NiOx HTL. With the modification of HAB, a high quality perovskite layer was obtained. Due to the enhanced hole extraction, the HAB modified device showed a higher short-circuit current density ($J_{sc}$) and a power conversion efficiency of 17.11%. Therefore, this work offers a novel strategy in interfacial engineering for high-efficiency PSCs.

1. Introduction

Perovskite solar cells (PSCs) have attracted great attention in recent years due to their easy fabrication, low-cost process and excellent power conversion efficiency (PCE). The certified PCE has increased from 3.8% to 25.5%, which benefits from novel thin film deposition, device structure design and material innovation [1-3]. However, efficient PSCs are usually achieved on the mesoporous normal structure with titanium dioxide (TiO$_2$). These mesoporous structure devices are faced with high annealing temperature and serious hysteresis, which inhibits its application. Moreover, these devices also show poor stability. Inverted planar devices exhibit great promise in terms of negligible hysteresis, application on flexible substrates and low-cost fabrication. In inverted device, poly (3, 4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS), poly (triarylamine) (PTAA) and nickel oxide (NiOx) are usually used as hole transport layer (HTL). Due to hygroscopic and acidic properties of PEDOT: PSS, poor stability and low performance are observed in PEDOT: PSS-based PSCs. Because of the complex synthesis, PTAA is hardly used on large scale devices. Thanks to the excellent stability of NiOx, NiO$_x$ HTL has attracted much attention in recent years [4].

When deposited by solution method, NiO$_x$ films exhibited low film coverage and pinholes. In addition, the conductivity of NiO$_x$ film does not match with perovskite, which reduces effectively used of photo-generated carrier. Great efforts have been made in the improvement of NiO$_x$ films. It has been proved that surface modification is a promising strategy to improve the morphology of perovskite and the hole transport ability. Chen confirmed that alkali metal chloride as a modifier for NiO$_x$ can significantly inhibit the interfacial recombination. Meanwhile, the improvement of open-circuit voltage ($V_{oc}$) and the inhibition of ion diffusion were observed in alkali metal chloride modified devices. Song
introduced different small molecules at the top of Cu: NiOx HTL to achieve excellent performance HTL, such as glycine, cysteine and mercaptoethylamine chlorate [5].

In this work, for the purpose of improving charge transport, a surfactant of hexadecylbenzene (HAB) was applied as surface modifier for NiOx. The crystallinity and absorbance of perovskite along with the charge transport between HTL and perovskite were improved remarkably. Based on HAB modified HTL, devices with structure of FTO/HTL/MAPbI3/[6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/polyethylenimine (PEI)/Ag were fabricated. Compare with control device, it was seen that an enhancement of $J_{sc}$ in HAB modification device, and the PCE of HAB modified device increased from 15.53% to 17.11%. With a series of carrier dynamics tests, it was found that the HAB modified device showed faster carrier transmission, more effective carrier extraction, and inhibited non-radiative recombination.

2. Device fabrication

PSCs were fabricated on FTO conducting glass. NiOx layer was deposited as our previous work. HAB was dissolved in isopropanol (IPA) ($3.0 \text{ mg mL}^{-1}$), spin-coated at 3000 rpm for 30 seconds on NiOx substrates. Perovskite film and electron transport layer (ETL) were deposited as our previous work [6]. A metal mask was used to defined the devices effective area of 0.096 cm$^2$.

3. Results and discussion

The effect of HAB on charge transport were investigated. The steady-state photoluminescence (PL) spectra for NiOx/HAB/perovskite (PSK), NiOx/PSK and PSK films were shown in Figure 1a. It was obviously that the PL intensity quenched efficiently in NiOx/PSK and NiOx/HAB/PSK samples. And the PL intensity in NiOx/HAB/PSK samples exhibited the lowest, which indicated that HAB can promote carrier transport. In addition, the time-resolved photoluminescence (TRPL) test was carried out to understand the electron extraction behaviour. As shown in Figure 1b, by fitting the life constant of TRPL, the process of rapid decay and slow decay could be observed. Table 1 listed the detail fitting parameters. The $\tau_1$ of the original perovskite film was 14.41 ns. When coated on NiOx or NiOx/HAB subtract, $\tau_1$ were shortened to 9.06 ns and 0.59 ns. And $\tau_2$ of the original perovskite film was 285.76 ns, $\tau_2$ was also shortened to 147.74 ns and 125.90 ns when coated on NiOx or NiOx/HAB subtract, respectively. These results confirmed that carrier transport from perovskite to NiOx was promoted by HAB modification. Obviously, the hole mobility of NiOx films prepared by solution method was not meeting the requirement of devices. The enhancement of the hole transport capability was undoubtedly beneficial to balance the charge transport so as to get high device performance. In order to verify that HAB could boost hole transport, the conductivity of hole only devices based on FTO/HTL/Ag structure was tested. According to Figure 1c, it was demonstrated that the conductivity of NiOx film was $4.7 \times 10^4 \text{ s cm}^{-1}$, however, in HAB modified NiOx film a higher conductivity of $5.3 \times 10^4 \text{ s cm}^{-1}$ was obtained. The increase of conductivity indicated that the introduction of HAB on NiOx could improve the conductivity of hole [7].

Figure 1. (a) PL spectra; (b) TRPL spectra; (c) J-V curve for conductivity measurements of control NiOx film and NiOx/HAB film.
Table 1. Summary the fitted carrier lifetimes from TRPL.

| Film                | A₁(%) | τ₁(ns) | A₂(%) | τ₂(ns) |
|---------------------|-------|--------|-------|--------|
| PSK                 | 4.78  | 14.41  | 94.87 | 285.76 |
| NiOₓ/PSK            | 5.75  | 9.06   | 93.79 | 147.74 |
| NiOₓ/HAB/PSK        | 0.44  | 0.59   | 94.38 | 125.90 |

J_sc and fill factor (FF) were the main limiting factors of high efficiency PSCs based on NiOₓ HTL. The fundamental reason was that the low crystallinity of perovskite and the poor contact between NiOₓ and perovskite. X-ray diffraction (XRD) was used to analyzed the crystallinity of perovskite films. As shown in Figure 2a, the typical peaks at 14.28 °, 28.60 ° and 32.02 ° were corresponded to (110), (220) and (310) planes of MAPbI₃ films. It could be seen that the diffraction peaks intensity increased obviously in perovskite films deposited on the HAB modified substrate. In addition, XRD patterns displayed no PbI₂ peak and the intensity of the diffraction peak was externally high, which indicated that the perovskite film had high crystallinity and phase purity. As shown in Figure 2b, due to the better crystallinity of perovskite, the absorption of perovskite film on NiOₓ/HAB substrate increased slightly. These results suggested that the surface modification of HAB on NiOₓ was beneficial to the growth of perovskite thin films.

Based on the above results, the photovoltaic performance of inverted PSCs was investigated in detail. Figure 3a displayed the J-V characteristics under AM 1.5 G simulated sunlight, the key parameters of the device were summarized in Table 2. The increase of PCE in HAB modified PSCs was mainly attributed to the improvement of J_sc. The PCE of the control device was only 15.53% with V_oc of 1.01 V, J_sc of 19.39 mA cm⁻², FF of 79.53%. While the PCE, V_oc, J_sc, FF of HAB modified PSCs were 17.11%, 1.01 V, 21.05 mA cm⁻² and 81.40%, respectively. To evaluate the stable power output of the device, the steady-state output photocurrent at the maximum power point was carried out (Figure 3b). The stable PCE and J_sc of the HAB modified device were 16.61% and 19.31 mA cm⁻², while the control device was 15.38% and 17.88 mA cm⁻². Incident photon-to-electron conversion efficiency (IPCE) spectra of HAB modified and control devices were showed in Figure 3c. It was showed that both devices exhibited similar absorption range, but higher external quantum effect (EQE) was achieved in the HAB modified device during the absorption range. A higher integrated current density (J_int) value of 19.89 mA cm⁻² was observed, which was consistent well with the J_sc value and the absorption spectrum.
Figure 3. (a) the $J$-$V$ curves of devices; (b) the steady-state photocurrent and output power of devices; (c) the IPCE spectrum and the $J_{int}$ of the devices.

Table 2. Detail photovoltaic parameters for PSCs.

|            | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|------------|----------------------|--------------|--------|---------|
| control F  | 19.45                | 1.01         | 76.55  | 15.09   |
| control R  | 19.39                | 1.01         | 79.53  | 15.53   |
| HAB F      | 20.92                | 1.01         | 81.40  | 17.11   |
| HAB R      | 21.05                | 1.01         | 79.01  | 16.72   |

To explain the improvement of device performance, charge recombination was investigated. According to the literature, the effect of Shockley-Read-Hall recombination is not apparent, when the slope of $V_{oc}$ dependence on light intensity curve is close to 1. As shown in Figure 4a, the $J$-$V$ curves under different light intensities were performed. It was observed that the slope of HAB modified device was $1.61 \frac{k_B T}{q}^{-1}$, which was smaller and closer to 1 than the control device ($1.84 \frac{k_B T}{q}^{-1}$). This result suggested that the trap-assisted charge recombination was effectively suppressed. In addition, the interfacial properties between HTL and perovskite were studied by Mott-Schottky curve. As shown in Figure 4b, the flat-band potential ($V_{bi}$) value of HAB sample was 0.130 V, which was higher than the control device (0.119 V). And the doping density in HAB modified device was increased, so as improve the charge collection efficiency [8].

Figure 4. (a) $V_{oc}$ dependence on light intensity curve; (b) Mott-Schottky curve at 1 kHz for device.

4. Conclusion
In summary, an interface modification was developed. By using a surfactant HAB as surface modifier, the hole transport ability had been improved significantly. Moreover, higher crystallinity and absorbance of perovskite layer was observed when prepared on the HAB modified substrate. Based on HAB
modified HTL, structure of FTO/HTL/MAPbI3/PCBM/PEI/Ag were fabricated. Attributed to the enhancement of $J_{sc}$ in HAB modified device, the PCE had reached to 17.11%. After a series of carrier dynamics tests, the HAB modified device exhibited faster carrier transmission, more effective carrier extraction, and well inhibit the non-radiative recombination. Therefore, this work offers insights into surface engineering for realizing high-efficiency PSCs.

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