Effect of the post-annealing temperature on the thermal-decomposed NiO_x hole contact layer for perovskite solar cells

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A hysteresis-less inverted perovskite solar cell (PSC) with power conversion efficiency (PCE) of 13.57% was successfully achieved based on the thermal-decomposed NiO_x hole contact layer, possessing better electron blocking and hole extraction properties for its suitable work function and high-conduction band edge position. Herein, the transparent and high-crystalline NiO_x film is prepared by thermal-decomposing of the solution-derived $\text{Ni}(\text{OH})_2$ film in our study, which is then employed as hole transport layer (HTL) of the organic–inorganic hybrid PSCs. Reasonably, the post-annealing treatment, especially for the annealing temperature, could greatly affect the $\text{Ni}(\text{OH})_2$ decomposition process and the quality of decomposed NiO_x nanoparticles. The vital NiO_x HTLs with discrepant morphology, crystallinity and transmission certainly lead to a wide range of device performance. As a result, an annealing process of $400^\circ\text{C}/2\text{h}$ significantly promotes the photovoltaic properties of the NiO_x layer and the further device performance.

Keywords: NiO_x ; hole transport layer; thermally decomposing; annealing temperature; perovskite solar cell.

1. Introduction

Nowadays, the organic–inorganic hybrid PSCs have been demonstrated to be promising and suitable candidates for the silicon and organic photovoltaics owing to their higher efficiency, lower cost and easier preparation process.^{1,2} The extraordinary optoelectronic properties of excellent light harvesting characteristic, superior carrier mobility and long carrier lifetime undoubtedly assist this great performance promotion of the perovskite solar cells (PSCs) with a promising power conversion efficiency (PCE) from 3.8% to 22.1% rapidly.^{1,3–7} For the conventional perovskite devices, apart from the core of perovskite light absorber, charge extraction property of the carrier transporting materials (CTLs) also plays a very important role in the integrated photovoltaic devices.⁸ Currently, the poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) polymer (PEDOT:PSS), 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) and poly(3-hexylthio-phenene-2,5-diyl) (P3HT) are the familiar organics serving as the hole transport layers (HTLs) in the devices.^{9–12} Reasonably, the low processing temperature and processability in solution are the typical

advantages for these organic materials in the application of device fabrication. However, disappointingly, some serious defects of high acidity, hygroscopicity and complexity are inevitably harmful to the long-term stability of the resulting devices, which has been already demonstrated in organic photovoltaics and light emitting diodes (LEDs).¹³

In response, lots of stable metal oxides, such as Cu_2O , WO_3 , V_2O_5 , MoO_3 , or NiO_x have also been demonstrated to possess excellent hole transport property and can act as appropriate candidates for the organic materials.^{14–22} Moreover, the inorganics possess such great advantages of easy accessibility of raw materials, low-cost and simple synthesis and rough storage condition. Importantly, their low-cost and simple fabrication can largely contribute to the large-scale industrialization. There in numerous works have focused on the NiO -based planar heterojunction PSCs, and several different methods have also been reported to deposit efficient NiO hole transport films.^{14,15,23} Particularly, Zhu *et al.* recently reported that a highest PCE of 18.8% was demonstrated by the device with a structure of $\text{FTO}/\text{NiO}/\text{MAPbI}_3/\text{C}_{60}/\text{SnO}_2/\text{Ag}$ and a simple solution-derived method of NiO .¹⁴ The suitable work function and high-conduction band edge position of NiO also provide the crucial electron blocking and

hole extraction properties for further device performance. Nevertheless, both synthetic method and post-treatment have a great effect on the fabrication process and resulting film quality for the devices.

In view of the great effect of post-annealing treatment on the decomposition of $\text{Ni}(\text{OH})_2$ and the resulting NiO_x properties, the PSCs with a structure of $\text{FTO}/\text{NiO}_x/\text{MAPbI}_3/\text{PCBM}/\text{Ag}$ were fabricated in our work, in which the essential NiO_x film was obtained from the solution-derived $\text{Ni}(\text{OH})_2$ film under a certain post-annealing. Results indicate that the annealing temperature has a strong impact on the optoelectronic properties of the NiO_x films. Especially, the 400°C -annealing process can not only achieve the complete decomposition from $\text{Ni}(\text{OH})_2$ to NiO_x , but the HTL possesses good crystallinity, original surface topography and great transmission, contributing to excellent hole extraction and electron blocking properties as mentioned. Briefly, the optimized device achieves a champion PCE as high as 13.57% in this work.

2. Experimental

2.1. Synthesis of $\text{Ni}(\text{OH})_2$ precursor

First, 12.885 g nickel(II) chloride hexahydrate was dissolved into 0.1 L deionized water, and the 10 M-NaOH solution was added into the green solution with the increasing pH to 10. The mixture was dramatically stirred for over 5 min. The resulted viscous solution was then centrifuged at 9900 rpm for 6 min to obtain the incipient precipitation.^{15,17,20} Furthermore, the above precipitation was washed by deionized water, and the clear supernatant extract was collected as the $\text{Ni}(\text{OH})_2$ precursor with a concentration of 5 mg mL^{-1} .

2.2. Preparation of the perovskite precursor

Before the solar cell fabrication, 2.3 g PbI_2 and 0.8 g $\text{CH}_3\text{NH}_3\text{I}$ (Xi'an Polymer Light Technology Corp.) were completely dissolved into a mixture of 3.5 mL *N,N*-dimethylformamide (DMF, Alfa-Aesar) and 1.5 mL dimethyl sulfoxide (DMSO, Alfa-Aesar) to prepare the precursor as our previous reports.^{15,16,24,25} After that, the precursor was stirred at 70°C for over 5 h, and then filtered through a TPFE filter ($0.45 \mu\text{m}$) twice before use.

2.3. Solar cell fabrication

First, the patterned FTO/glass substrate was cleaned by the sonication in deionized water, acetone and ethanol, successively. The FTO substrate was dried by compressed N_2 flow and put through a UV-ozone treatment of 15 min before use. Then the above $\text{Ni}(\text{OH})_2$ precursor was spin-coated on FTO/glass substrate at the speed of 3000 rpm for 30 s for a certain thickness, followed by baking at 150°C for 10 min, and annealed to obtain the requisite NiO_x HTL. The NiO_x

coated substrate was then transferred into a nitrogen-filled glovebox for the upper perovskite deposition. The perovskite layer was spin-coated at a low speed of 1000 rpm for 5 s and then a higher speed of 3000 rpm for 30 s, during which 0.13 mL chlorobenzene was continuously dripped onto the spinning film. After that, the wet film was baked at 70°C for 2 min and then 100°C for 10 min. After cooling, a PCBM (American Dye Sources) film was coated on perovskite by spin-coating a chlorobenzene solution of 20 mg mL^{-1} at 1500 rpm for 45 s. Finally, the substrate was transferred into an evaporator, and a 120 nm-thick silver electrode was evaporated onto the PCBM film to complete the device fabrication with a mask of 0.07 cm^2 .

2.4. Characterization

As-prepared $\text{Ni}(\text{OH})_2$ precursor was diluted and observed by transmission electron microscopy (TEM, JEM-2100, JEOL., Japan). X-ray diffraction (XRD) analysis was performed to acquire the crystal structure characterization of the samples from a D/max 2400 X Series X-ray diffractometer (Rigaku, Japan). The UV-VIS absorption spectra of the films were obtained from a JASCO V-570 UV/VIS/NIR spectrometer. Field emission scanning electron microscopy (SEM, JSM-6390, JEOL Inc., Japan) was used to obtain microscopic morphologies of the annealed films. Transient steady-state fluorescence spectrometer (Edinburgh FLS980) was employed to complete the measurement of their steady photoluminescence. For the devices, the current density-voltage (J - V) measurement was completed by a PVIV-201V I-V Station (Newport Oriel), and the light source applied in our experiment was a sunlight simulator with an OF 450 W Xe arc lamp and an AM1.5G filter (Newport Oriel). All J - V curves were scanned from -0.1 V to 1.2 V or vice versa at a scanning rate of 0.1 V s^{-1} . The external quantum efficiency (EQE) spectra was recorded by a Qtest Station 1000ADX system (Growthtech. Inc) in air without bias light.

3. Results and Discussion

Figures 1(a) and 1(b) exhibit the TEM and high-resolution TEM (HRTEM) images of the as-prepared $\text{Ni}(\text{OH})_2$ precursor. Obviously, the $\text{Ni}(\text{OH})_2$ nanomaterial possesses regular sheet structure, and the space between two adjacent fringes is determined to be 0.21 nm, which can be well ascribed to its (011) plane. Meanwhile, the electron diffraction of the diluent precursor, in Fig. 1(c), also clearly reveals a superior crystallinity from a set of diffraction rings. Then XRD patterns of the NiO_x samples with different post-annealing treatments (300, 400, and $500^\circ\text{C}/2 \text{ h}$) are shown in Fig. 1(d). The consistent identical diffraction peaks at 37.2° , 43.3° , 62.8° , 75.4° and 79.4° are clearly observed, which can be well ascribed to the (111), (200), (220), (311), and (222) planes of NiO with a complete decomposition process.¹⁵ According to the Debye-Scherrer equation $D = 0.89\lambda/(\beta \cos \theta)$, we can

Fig. 1. (a) TEM image, (b) HRTEM image, (c) electron diffraction of the as-prepared $\text{Ni}(\text{OH})_2$ precursor, (d) XRD patterns, and (e) absorption edges of the NiO_x films on quartz substrates with post-annealing treatments.

predict that the average crystalline sizes of NiO_x nanoparticles are bound to increase with the temperature rise and a better crystallinity correspondingly. As a contrast, the results of absorption coefficient as a function of photonenergy, as shown in Fig. 1(e), suggest that all band gaps of the annealed NiO_x samples are determined to be ~ 3.76 eV, matching well with our previous reports.^{16,17}

Figure 2 presents the top-view SEM images of the annealed NiO_x films. Coinciding with the XRD results in Fig. 1(d), the post-annealing treatment can achieve a complete decomposition from $\text{Ni}(\text{OH})_2$ to NiO_x . The 300/400 °C-annealing processes can still remain the but same for the adhesive structure with the original $\text{Ni}(\text{OH})_2$ surface. Inversely, there exists a certain fine distinction for the 500 °C-annealed film in that the nanoparticles are obviously more independent and estranged with each other, which may

reduce the photovoltaic and charge extraction properties (demonstrated below). Certainly, the better crystallinity and bigger grains of the 500 °C-annealed sample are also well consistent with the mentioned XRD results.

The transmission spectrum of the annealed NiO_x HTLs are shown in Fig. 3(a). It reveals that all transparent films possess high-light transmission property of over 82% in the major visible region. Especially for the 400 °C-annealed sample, it is obvious that the slightly more transparent film can provide more energy source for the perovskite light-harvester. In order to demonstrate the superior charge extraction of the obtained HTLs, PL spectra characterization of the perovskite films coated on NiO_x layers is shown in Fig. 3(b), and the results demonstrate that the 400 °C-annealed film possesses a better hole extraction property than the others. The suitable grain size and unbroken structure of

Fig. 2. Top-view SEM images of the annealed NiO_x films coated on FTO/glass substrates.

Fig. 3. (a) Transmission spectra of the annealed NiO_x films on FTO/glass substrates and (b) their corresponding PL spectra of the perovskite films coated on NiO_x HTLs.

the film surface largely contribute to a better contact of perovskite and NiO_x materials for the promising device performance.

Figure 4(a) shows the top-view SEM image of the perovskite absorber coated on NiO_x film, which exhibits a good crystallinity of MAPbI_3 film with an average size of ~ 300 nm and a full coverage. The corresponding cross-sectional SEM image of a typical PSC device with a structure of

FTO/ NiO_x /CH₃NH₃PbI₃/PCBM/Ag is shown in Fig. 4(b), in which a MAPbI_3 layer (~ 340 nm), a PCBM layer (~ 80 nm) and a silver electrode (~ 120 nm) were successively deposited onto the NiO_x film. Further, the relative energy levels of the solar cell are presented in Fig. 4(c), where the big barrier between the conduction bands of NiO_x and perovskite enables an effective blocking of the electron transport from perovskite absorber to NiO_x and a reduced carrier

Fig. 4. (a) SEM image of the MAPbI_3 film coated on the NiO_x layer, (b) cross-sectional view SEM image of a typical device, (c) corresponding schematic band diagram of the solar cell, (d) J - V curves, (e) EQE spectra, and (f) a steady state PCE with a bias voltage of the devices based on NiO_x HTLs.

Table 1. Photovoltaic parameters for the PSCs based on NiO_x films with different annealing temperatures.

Annealing condition	Scan direction	V _{oc} (V)	J _{sc} (mA cm ⁻²)		FF (%)	PCE (%)
			J-V	EQE		
300°C/2 h	J _{sc} → V _{oc}	1.003	15.34	15.42	73.75	11.34
	V _{oc} → J _{sc}	1.006	15.25		69.99	10.75
400°C/2 h	J _{sc} → V _{oc}	1.029	17.58	17.77	74.99	13.57
	V _{oc} → J _{sc}	1.031	17.74		70.67	12.92
500°C/2 h	J _{sc} → V _{oc}	0.954	14.29	13.05	59.24	8.08
	V _{oc} → J _{sc}	1.006	14.19		57.87	8.26

recombination. Figure 4(d) indicates that the device based on the 400°C-annealed NiO_x film has an obvious performance superiority. Compared with the others, the device shows larger open circuit voltage (V_{oc}) of 1.029 V, higher short circuit current density (J_{sc}) of 17.58 mA cm⁻², greater fill factor (FF) of 74.99% and better PCE of 13.57%. The summary of the photovoltaic parameters of devices is listed in Table 1 in detail. The EQE spectra of the devices are shown in Fig. 4(e), including the integral current densities as a function of wavelength. Obviously, the EQE of the device based on 400°C-annealed NiO_x film overweighs the others in the whole region, which can be explained by its slightly higher transmission and the better hole extraction properties as demonstrated in Fig. 3. Moreover, the integral J_{sc} value from the EQE spectra is roughly comparable with that obtained from the J-V curve (17.77 mA cm⁻² versus 17.58 mA cm⁻²). As presented in Fig. 4(f), the steady state PCE of our best device based on the 400°C-annealed film was successfully measured to be 12.3%, which is very useful to estimate the reliability of the J-V scans in our research.²³

Figure 5 exhibits statistical distributions of photovoltaic parameters for 24 devices measured under the same test conditions of AM 1.5 simulated sun light for their reproducibility. Distinctly, the performance targets of 300/500°C-annealed samples vary in a wide range. In contrast, the devices based on the 400°C-annealed films exhibit a much narrow distribution of the parameters and larger average J_{sc}, V_{oc}, FF and PCE than the others for a better device performance.

4. Conclusions

Efficient hybrid PSCs have been fabricated based on the thermal-decomposed NiO_x HTLs, which were prepared by decomposing the solution-derived Ni(OH)₂ films by a suitable post-annealing treatment. It is obvious that the annealing process has an important effect on the Ni(OH)₂ decomposition process and the surface topography, crystallinity, transmission of the resulting NiO_x films. By comparison, the annealing process of 400°C/2 h can achieve a complete decomposition from Ni(OH)₂ to NiO_x, which possesses superior transmission and hole extraction properties as demonstrated. Briefly, a promising PCE of 13.57% with a steady-state output of 12.3% was successfully achieved by the device based on NiO_x film annealed in 400°C for 2 h.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgments

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Fig. 5. Photovoltaic parameters of the devices based on NiO_x HTLs with post-annealing treatments.

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