Investigation on the Performance of Perovskite Solar Cells Based on All-oxide Charge Transport Layers

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Abstract. A perovskite solar cell with NiO and ZnO as charge transport layers was successfully fabricated. Intramolecular exchange technology was used to improve the morphology of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films. Doping was used to improve the conductivity of the NiO layer. X-ray diffractometer and scanning electron microscopy were used to analyze CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films. A solar simulator with a digital source meter and quantum efficiency measurement system were used to test devices performance. The perovskite solar cells with FTO/p-NiO/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/n-ZnO/Ag structure, have optimal PCE of 11.02% and long-term stability at 25 °C and 30 ± 2% humidity. This provides the possibility for the application of perovskite solar cells in the atmospheric environment.

Introduction

Various countries in the world have stepped up their efforts to develop new energy sources, due to issues such as the energy crisis and environmental pollution. Recently, a new type of solar cell using an organic-inorganic hybrid halide perovskite as a light absorber has attracted the attention of many scientific researchers, which has the advantages of excellent performance, simple structure, and low preparation cost. The photoelectric conversion Efficiency has increased rapidly from 3.8% \cite{1} to over 25.2% \cite{2} in the past 10 years. The hole-transport materials currently used in such perovskite solar cells are usually organic polymers, such as Spiro-OMeTAD, P3HT \cite{3}, PCBM \cite{5}, DEH \cite{6}, etc. Among them, spiro ometad device has the best performance, but the price is more expensive, 10 times of gold, which greatly improves the device cost, and the long-term stability of organic materials also needs to be further tested. Therefore, the development of high-efficiency and low-cost inorganic materials has become one of the important research directions of this kind of new solar cells.

NiO is a p-type transparent oxide semiconductor with a wide band gap (E\textsubscript{g} of 3.6 ~ 4.0 eV) and excellent performance. It has been successfully used as a hole-collecting and electron-blocking layer in dye-sensitized solar cells and organic solar cells. Compared with organic hole materials, NiO-based devices show better stability and comparable conversion efficiency \cite{7}. Compared with TiO\textsubscript{2}, ZnO has a close band structure and higher electron mobility, which is 100 times that of TiO\textsubscript{2} \cite{8}. This enables photo-generated electrons to be more effectively injected into their conduction bands, and to transmit quickly to reduce electron losses and increase photocurrent. In addition, ZnO materials have the advantages of simple preparation, diverse morphology, and high crystal quality. These properties make ZnO the most ideal substitute for TiO\textsubscript{2}.

In this work, NiO was used to replace the expensive and poorly stable Spiro-OMeTAD as the hole transport layer, and ZnO was used to replace TiO\textsubscript{2} with low electron mobility as the electron transport layer. A perovskite solar cell with p-NiO/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/n-ZnO simple sandwich structures were constructed and studied for their performance.
Experiment

Preparation of NiO and ZnO Materials

Preparation of NiO material: 1.45 g of nickel nitrate (Ni(NO$_3$)$_2$ • 6H$_2$O) was dissolved in 100 mL of ethanol solution, and 0.2 mL of acetylacetone (C$_5$H$_8$O$_2$) was added at the same time, and stirred on a magnetic stirrer for 24 h to obtain a uniform NiO solution.

Preparation of ZnO material: 1.45 g of zinc acetate hexahydrate was dissolved in 60 mL of isopropanol, and the temperature was raised to 62 °C by using a water bath heating method while continuously stirring to obtain transparent solution A. 0.69 g of potassium hydroxide was dissolved in 35 mL of isopropanol, and heated and stirred on a magnetic stirrer for 1 hour to obtain a transparent solution B. Solution B was slowly injected into solution A with a syringe, and a white precipitate appeared after a period of reaction. The precipitate was centrifuged and washed twice with isopropanol, and then dissolved with dry isopropanol to obtain a uniform ZnO suspension.

Fabrication of Perovskite Solar Cells

The fabrication of perovskite solar cells is referred to the literature. The PSCs were fabricated with an inverted structure of FTO/NiO/CH$_3$NH$_3$PbI$_3$/ZnO/Ag. The FTO substrate was cleaned with sonication in acetone, detergents, deionized water and IPA for 20 min, respectively. Then it was dried using N$_2$ flow and treated with UV-ozone for 15 min. The NiO was coated on the FTO by spincoating at 3000 rpm for 30 s and then was annealed at 330 °C for 30 min. The PbI$_2$(DMSO) complex solution was spin-coated onto the PEDOT:PSS-coated ITO substrate at a speed of 3000 rpm for 30 s, resulting in the formation of semitransparent faint yellow PbI$_2$(DMSO) thin film. Then, the CH$_3$NH$_3$I solution was dropped onto PbI$_2$(DMSO) thin film quickly after the spinning for 3 s at a spin speed of 5000 rpm and spin-coating for 40 s. The resulted thin film were placed on heater table, among which about 10 ml toluene solution was dropped, covered by glass dish and annealed at 100 °C for 90 min. The ZnO layer was spincoated subsequently at a speed of 3000 rpm for 30s, and finally a 100 nm Ag counter electrode was thermally deposited at a pressure of ~4 × 10$^{-6}$ mbar. The active area of PSCs is 0.09 cm$^2$. The fabrication process of PCBM-based PSCs was similar to that of ZnO-based PSCs.

Performance Characterization Method

The structural properties of perovskite films were characterized by X-ray diffractometer (XRD, Bruker Advance D8), using Cu K$_\alpha$ radiation (λ=0.1546 nm). The surface morphology of the f perovskite films was analysed by scanning electron microscopy (SEM, JEOL JSM-6700F). Photocurrent-voltage (J-V) curves of PSCs were measured using a solar simulator (Zolix, AM 1.5G) with a digital Source Meter (Keithley 2420) and a light intensity of 100 mW/cm$^2$ calibrated by using Si-reference cell. The scanning direction was located from -1.5 V to +1.5 V at a scanning speed of 0.3 V/s if without special illustration. Incident photon-to-electron conversion efficiency (IPCE) spectra of PSCs devices were measured using the quantum efficiency measurement system (Zolix, Beijing).

Results and Discussion

High-quality Perovskite Films

High-quality perovskite films are a prerequisite for obtaining high-performance devices. In this work, CH$_3$NH$_3$PbI$_3$ thin films were prepared by intramolecular exchange technology. Figure 1 shows the SEM morphology and XRD pattern of the CH$_3$NH$_3$PbI$_3$ thin films prepared based on the intramolecular exchange technology. A set of diffraction peaks related to tetragonal perovskite crystals are shown at 14.08°, 28.4°, 31.82° and 40.66°, which can be attributed to (110), (220), (310) and (224) crystal plane diffraction. The stronger intensity of the diffraction peaks on the (110) and (220) crystal planes, indicating that the growth of the perovskite crystals has a preferential orientation, and the sharp diffraction peaks indicate that a well-crystallized perovskite film is formed. In addition,
except for the diffraction peaks of CH$_3$NH$_3$PbI$_3$, there are no diffraction peaks from PbI$_2$(DMSO) or CH$_3$NH$_3$I, which proves that CH$_3$NH$_3$I can completely react with PbI$_2$(DMSO) and leaves no CH$_3$NH$_3$I or PbI$_2$(DMSO).

Figure 1. SEM morphology and XRD pattern of the CH$_3$NH$_3$PbI$_3$ thin films.

The CH$_3$NH$_3$PbI$_3$ thin films are composed of large crystals around 500 nm and have no observable pinholes. The large crystal size indicates that the high crystallinity of the perovskite films is favorable for charge transport and collection to occur in the single crystal grains in the vertical direction without grain boundary interference, as shown in Figure 1 (a).

**Element-doped NiO-based Perovskite Solar Cells**

Pure NiO has poor conductivity, resulting in low battery short-circuit current and low fill factor. Doping is one of the effective ways to improve the conductivity of NiO. We have tried to use single-doped and co-doped NiO thin films of metal elements such as Ag and Li to improve its conductivity, and constructed perovskite solar cells with FTO/NiO/CH$_3$NH$_3$PbI$_3$/PCBM/Ag structure. The effects of doping modification on the optical and electrical properties of NiO films and the effects of modified NiO films on the solar properties of perovskite were studied.

Figure 2. J-V curves of different element-doped NiO-based perovskite solar cells.

The results show that doping can effectively improve the light transmittance and hole mobility of NiO thin films, and can promote the subsequent perovskite thin films to have better crystal quality and coverage, lower film roughness and larger grain size. Compared with undoped or mono-doped NiO, the co-doping of Li and Ag shows a synergistic effect, which makes NiO films have higher conductivity, higher hole mobility, and better interfacial energy with perovskite level matching. Figure 2 shows the optoelectronic properties of different element-doped NiO-based perovskite solar cells. Perovskite solar cells with 1 at% Ag and 1 at% Li co-doped NiO films as the hole transport layer have an open circuit voltage ($V_{oc}$) of 1.05 V, a short-circuit current density ($J_{sc}$) of 17.69 mA/cm$^2$, a fill factor ($FF$) of 0.72, and a maximum power conversion efficiency ($PCE$) of 12.75%, significantly higher than 9.34% of pure NiO-based devices.

**The Performance of Perovskite Solar Cells Based on All-Oxide Charge Transport Layers**

Based on the research of NiO-based perovskite solar cells, we optimized the CH$_3$NH$_3$PbI$_3$ thin films by intramolecular exchange technology, modified the interface of NiO layer and ZnO layer by means
of doping and modification, and constructed planar perovskite solar cells with FTO/p-NiO/CH₃NH₃PbI₃/n-ZnO/Ag structure. When NiO thickness is 70 nm and ZnO thickness is 60 nm, the best device performance is obtained. As shown in Figure 3(a), $V_{oc}$ is 0.98 V, $J_{sc}$ is 16.96 mA/cm², $FF$ is 0.66, and $PCE$ reaches 11.02%. Figure 3(b) shows the external quantum efficiency (EQE) of the device. The EQE integrated current density on the AM 1.5G spectrum is consistent with the corresponding $J_{sc}$ value measured by $J-V$ curve.

Table 1. Photoelectric conversion parameters of different element-doped NiO-based perovskite solar cells.

| Sample     | $J_{sc}$ (mA/cm²) | $V_{oc}$ (V) | FF   | PCE (%) |
|------------|-------------------|--------------|------|---------|
| NiO        | 15.52             | 1.02         | 0.59 | 9.34    |
| Li:NiO     | 15.51             | 1.05         | 0.71 | 11.56   |
| Ag:NiO     | 16.13             | 1.04         | 0.70 | 11.74   |
| Ag,Li:NiO  | 17.69             | 1.05         | 0.72 | 12.75   |

Figure 3. Device performance of FTO/NiO/CH₃NH₃PbI₃/ZnO/Ag planar perovskite solar cells.

(a) $J-V$ curve, (b) EQE curve

(b) Figure 4. Stability of the all-oxide charge transport layers device in atmospheric environment without package.

(c) (a) Normalized $V_{oc}$, (b) Normalized $J_{sc}$, (c) Normalized $FF$, (d) Normalized $PCE$

Figure 4 shows the device performance tested in an unpackaged environment at 25 °C and 30 ± 2% humidity. Perovskite solar cells based on NiO and ZnO metal oxide as charge transport layers still
maintain 80% of their original efficiency after 30 days. The decay relation of photovoltaic parameters with time, $V_{oc}$, $J_{sc}$, $FF$ and $PCE$, are shown in Figure 4. Compared with devices with organic charge transport materials, perovskite solar cells with inorganic metal oxide materials such as NiO, ZnO as charge transport layers show better water resistance and resistance to oxygen degradation, and have better stability [9].

Conclusion

In summary, we optimized the CH$_3$NH$_3$PbI$_3$ thin film by intramolecular exchange technology, and used NiO and ZnO oxides as charge transport layers to construct a planar perovskite solar cell with all-inorganic charge transport layers. The co-doping of Li and Ag makes the NiO film have higher conductivity, higher hole mobility, and better interfacial energy. The perovskite solar cells with FTO/p-NiO/CH$_3$NH$_3$PbI$_3$/n-ZnO/Ag structure, have optimal $PCE$ of 11.02% and better stability in atmospheric environment.

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