Development of flexible perovskite solar cells by the low-temperature fabrication of TiO$_2$ electron transport layers

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Flexible and light-weight perovskite solar cells (PSCs) have been considered due to the expectation of low production cost and wide application ranges. Low temperature processes are required in the fabrication of flexible perovskite solar cells because flexible substrates cannot resist process temperatures over 150 ºC. An electron transport layer (ETL) is commonly titanium-oxide (TiO$_2$) formed by high temperature sintering (>400ºC). The formation of ETL is crucial for flexible PSCs in order to complete the entire low-temperature process. Here, we have employed our original single crystalline TiO$_2$ nanoparticles with high purity of brookite phase (BK TiO$_2$ NPs), and could form TiO$_2$ ETLs below 150 ºC. We succeeded to fabricate flexible PSCs on polyethylene naphthalate (PEN) substrates with the power conversion efficiency of 13.08% (in reverse scan). The present work provides us a good finding to realize the low-cost flexible PSCs in the future.

Keywords : Perovskite solar cell, Titanium-oxide, Low temperature process

I. INTRODUCTION

In the recent years, perovskite solar cells (PSCs) have become an emerging star in a photovoltaic field because of its rapidly enhanced energy conversion efficiency and low-cost solution process. Flexible and light-weight PSCs have been considered due to the cost reduction and wide application ranges. Anatase titanium-oxide (TiO$_2$) is commonly used as an electron transport layer (ETL) of PSCs, but generally requires high temperature sintering (>400ºC) to get good opt-electrical properties. This becomes a barrier for low-cost and roll-to-roll processes in the mass production because flexible substrates generally require low temperature processes. We employ our original single crystalline TiO$_2$ nanoparticles with high purity of brookite phase.
(BK TiO$_2$ NPs), and the power conversion efficiency of 14.92% (in reverse scan) was obtained in planar PSCs on glass substrates with low temperature processes (<180°C). This work indicates that the BK TiO$_2$ NPs enable us to fabricate PSCs on flexible plastic substrate in low temperature processes. Here, we demonstrated the fabrication of flexible PSCs formed on indium tin oxide / polyethylene naphthalate (ITO/PEN) substrates covered by the BK TiO$_2$ NPs.

II. EXPERIMENTAL METHODS

Fig. 1 shows the structure of flexible PSCs on ITO/PEN substrates formed by the entire low temperature processes at 140°C or lower. The PSCs have a so-called planar structure without mesoporous layers. ITO/PEN substrates were purchased from Peccell technologies, Inc. (Tokyo, Japan). In some of the substrates, the surface of ITO were coated by thin sputtered TiO$_2$. The ITO/PEN substrates were cleaned sequentially in a sonication bath in commercial detergent and water, deionized water, and ethanol; each step was 15 min. The cleaned ITO/PEN substrates were then dried in nitrogen atmosphere and treated with UV-ozone for 30 min.

The BK TiO$_2$ NPs (100 nm thick) layer was formed as ETLs by spin-coating the synthesized noncolloidal suspension of pure-phase BK TiO$_2$ NPs on the ITO/PEN substrates in three coating cycles at 5000 rpm for 30 s, then dried at 100 °C for 5 min and further annealed at 140 °C for 1 h.

The precursors of triple-cation perovskite consist of formamidinium iodide (FAI), methylammonium bromide (MABr), cesium iodide (CsI), lead bromide (PbBr$_2$), and lead iodide (PbI$_2$); all were obtained from TCI (Tokyo, Japan). The stock solutions of FAI (1 M), PbI$_2$ (1.1 M), MABr (0.2 M), and PbBr$_2$ (0.2 M) were mixed in anhydrous DMF: DMSO (4:1), and 1.5 M CsI solution in DMSO was added to get a concentration of 5% Cs. The precursor solution was deposited on the BK TiO$_2$ NPs layer by spin-coated in three steps: 0 rpm for 15 s followed by 1000 rpm for 10 s and 6000 rpm for 20 s. In the third step, 500 μL of chlorobenzene was dripped 10 s before the spin-coating step stop. The deposited solution was then annealed at 100 °C for 60 min. Expected chemical formulation of the triple-cation perovskite was thus Cs$_{0.05}$(FA$_{0.83}$MA$_{0.17}$)$_{0.95}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$. The thickness was about 350 nm.

For the hole-transport layer (HTL), a spiro-OMeTAD precursor solution was prepared from dissolving spiro-OMeTAD (200.77 mg; Merck, Germany), in 2340 μL of chlorobenzene, and doped by lithium salt (23.4 mg), cobalt (7.3 mg), and 4-tert-butylpyridine (70.2 μL; Sigma-Aldrich). This precursor was deposited by spin-coating on the perovskite layer at 3000 rpm for 30 s. The thickness was about 200 nm.

Finally, a gold electrode was formed by thermal evaporation at a thickness of 80 nm on the HTL layer.

III. RESULTS AND DISCUSSION

We carried out the fabrication of PSCs with the BK TiO$_2$ NPs ETLs on the flexible TiO$_2$/ITO/PEN and ITO/PEN substrates by the entire low temperature processes at 140°C or lower. Table 1 shows the photovoltaic performance of these flexible PSCs, in comparison with PSCs formed on fluorine-doped tin oxide/Glass (FTO/Glass) substrates. On the FTO/Glass substrates, the BK TiO$_2$ NPs ETLs were formed at 180°C. The values in table 1 were obtained from the voltage-current characteristics measured in reverse voltage scans. The photovoltaic conversion efficiency (PCE) of 13.1% was obtained by the PSC on the flexible TiO$_2$/ITO/PEN substrates. The PCE was lower than 14.9% of the PSC on the FTO/Glass substrates, but the flexible substrates do not show significant negative effects. The results provide us a
good finding to realize the low-cost flexible PSCs in the future.

Fig. 2 shows the voltage–current characteristic of the PSCs on flexible TiO$_2$/ITO/PEN and FTO/glass substrate, measured in forward and reverse voltage scans. Both of the PSCs show relatively large hysteresis characteristics. Probably, the interface between the BK TiO$_2$ NPs and the perovskite layers is not properly formed and charges are trapped there.

On the other hand, the PSC shows lower performance on the ITO/PEN substrates without sputtered thin TiO$_2$. Probably, the BK TiO$_2$ NPs layers were not uniformly coated and pinholes were formed between the ITO and the perovskite layers. Therefore, the perovskite layers might directly touch the ITO at the pinholes. The current leak paths through the pinholes result in the reduction of FF. If the BK TiO$_2$ NPs can be coated without pinholes, the sputtered TiO$_2$ layers may not be necessary.

Table 1. Photovoltaic performance of PSCs with the BK TiO$_2$ NPs ETLs formed on the flexible TiO$_2$/ITO/PEN and ITO/PEN substrates, in comparison with FTO/Glass substrates. These values were obtained from the voltage-current characteristics measured in reverse voltage scans.

| Substrate         | Direction of voltage scan | Jsc (mA/cm$^2$) | Voc (V) | FF  | PCE (%) | Rs (ohm) |
|-------------------|---------------------------|-----------------|---------|-----|---------|----------|
| TiO$_2$/ITO/PEN   | Reverse                   | 17.1            | 0.95    | 0.80| 13.1    | 64.3     |
| ITO/PEN           | Reverse                   | 11.9            | 0.97    | 0.57| 6.51    | 91.4     |
| FTO/Glass         | Reverse                   | 20.5            | 1.04    | 0.70| 14.9    | 47.1     |

Jsc: Short circuit current density, Voc: Open circuit voltage, FF: Fill factor, PCE: Photovoltaic conversion efficiency, Rs: Series resistance

Fig. 3 shows the incident photon to current conversion efficiency (IPCE) of the same PSCs. The IPCE of the flexible PSC exhibits lower spectral response from 400 nm to 800 nm and the large reduction below 400 nm. This causes the lower current density (Jsc) of the PSC on the flexible TiO$_2$/ITO/PEN substrate than that on the FTO/glass substrate.

Fig. 4 show the optical transmittance spectra of the ITO/PEN substrates with and without the BK TiO$_2$ NPs coating. These two spectra are identical, so the BK TiO$_2$ NPs layers cause no extra absorption. The transmittance spectra show abrupt reductions below 400 nm because of the absorption of PEN, but relatively high above 450 nm.

Fig. 2. Voltage–current characteristic of PSCs with the BK TiO$_2$ NPs ETLs on flexible TiO$_2$/ITO/PEN and FTO/glass substrates, measured in forward and reverse voltage scans.

Fig. 3. The IPCE spectra of PSCs with the BK TiO$_2$ NPs ETLs on flexible TiO$_2$/ITO/PEN and FTO/glass substrates.

The large reductions below 400 nm in the IPCE resulted from the absorption of the ITO/PEN substrates. On the other hand, the substrate shows relatively high transmittance above 450 nm. Therefore, the lower IPCE from 400 nm to 800 nm was not cause
by the absorption of the substrate. The surface of ITO is quite flat, although FTO generally has a rough surface due to the crystal structures. The rough surface of front side layers causes the scattering of incident light and enhances the light absorption in photovoltaic layers, so-called light-trapping effect.\(^7\) Probably, the lower IPCE is caused by less light-trapping effects due to the flat surface of ITO compared with FTO.

Fig. 5 shows the photograph of the flexible PSC with and without the BK TiO\(_2\) NPs coating. The transparent and low-reflective BK TiO\(_2\) NPs layers on ITO/PEN substrates by the absorption of the substrate. The surface of ITO is quite flat, although FTO generally has a rough surface due to the crystal structures. The rough surface of front side layers causes the scattering of incident light and enhances the light absorption in photovoltaic layers, so-called light-trapping effect.\(^7\) Probably, the lower IPCE is caused by less light-trapping effects due to the flat surface of ITO compared with FTO.

Fig. 5 shows the photograph of the flexible PSC on the BK TiO\(_2\) NPs/TiO\(_2\)/ITO/PEN substrate. The flexible PSC could be bended by external force and the photovoltaic performance is maintained after bending. The bendable and light-weight flexible PSCs can be put on objects with curved surfaces and expand the application ranges of PSCs.

Fig. 4. Transmittance spectra of ITO/PEN substrates with and without the BK TiO\(_2\) NPs coating.

Fig. 5. Photograph of the flexible PSC on the BK TiO\(_2\) NPs/TiO\(_2\)/ITO/PEN substrate bended by external force.

IV. SUMMARY

1. We successfully demonstrated the fabrication of PSCs with the BK TiO\(_2\) NPs ETLs on the flexible TiO\(_2\)/ITO/PEN substrates by the entire low temperature processes at 140°C or lower.
2. The BK TiO\(_2\) NPs layers are not uniformly formed at the present. The sputtered thin TiO\(_2\) layers are necessary to suppress the leak current between ITO and perovskite layers through the pinholes in the BK TiO\(_2\) NPs layers.
3. Flexible perovskite solar cells on ITO/PEN substrates exhibited a little lower performance than those on glass substrates because of lower light-trapping effect and the optical absorption of the PEN below 400 nm.
4. The flexible PSC could be bended by external force and the photovoltaic performance is maintained after bending.
5. The results provide us a good finding to realize the low-cost flexible PSCs in the future. The bendable and light-weight flexible PSCs expand the application ranges of PSCs.

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