Double-layered ZnO nanostructures for efficient perovskite solar cells

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To date, a single layer of TiO 2 or ZnO has been the most successful implementations of any electron transport layer (ETL) in solution-processed perovskite solar cells. In a quest to improve the ETL, we explore a new nanostructured double-layer ZnO film for mesoscopic perovskite-based thin film photovoltaics. This approach yields a maximum power conversion efficiency of 10.35%, which we attribute to the morphology of oxide layer and to faster electron transport. The successful implementation of the low-temperature hydrothermally processed double-layer ZnO film as ETL in perovskite solar cells highlights the opportunities to further improve the efficiencies by focusing on the ETL in this rapidly developing field.

1. Introduction

Zinc oxide (ZnO), an important II–VI semiconductor with a wide direct band gap of 3.37 eV and an exciton binding energy of 60 meV, has attracted significant attention because of its interesting properties, such as high infrared reflectivity and good transparency in the visible spectrum. It is inexpensive, abundant in nature and easy to prepare into complex nanostructures and morphologies due to its ease of crystallization and anisotropic growth, owing due to its strong polarity in the c-axis direction of the wurtzite structure. Moreover, ZnO has high electron mobility with reduced recombination losses as compared with TiO 2, making it particularly interesting to be an electron transporting layer (ETL) for solution-processed thin film photovoltaic applications, such as organic photovoltaics, colloidal quantum dot photovoltaics, dye sensitized solar cells and most recently in hybrid organic–inorganic perovskite solar cells. The state-of-the-art hybrid organic–inorganic perovskite (CH 3 NH 3 PbI 3 ) absorber-based solar cells show a remarkable efficiency of >15%, with numerous studies suggesting strong prospects for >20% in the near future.

ZnO has been successfully demonstrated both as a planar and a mesoporous electron transporting layer in perovskite solar cells, with most of the work based upon ZnO nanoparticles or nanorods. Nanoparticles have slower electron transport due to the presence of grain boundaries, and they also suffer from higher recombination. Nanorods, on the other hand, have an internal electrical field in the direction of the c-axis to facilitate charge transport and suppress the recombination of injected electrons. One-dimensional (1-D) TiO 2 or ZnO nanoarchitectures have recently been used as a substitute to the nanoparticles-based strategy to enhance perovskite and absorber infiltration into the mesoporous nanostructures, leading to efficient perovskite solar cells. However, the performance of these mesoporous devices is still inferior as compared to nanoparticle-based films, perhaps because a wide range of ZnO morphologies have yet to be explored.

Herein, we report on the low-temperature hydrothermal synthesis of a double-layered mesoporous ZnO film, consisting of a vertically aligned film of nanosheet arrays decorated by horizontally-arranged nanorods and its successful implementation as electron transporting layer in solution-processed mesoporous perovskite solar cells. The morphology of the double-layer structure was investigated in detail and found to influence the device performance. By combining faster electron transport provided by ZnO nanorods with better infiltration and contact of the perovskite absorber within the nanosheet array, we achieved perovskite solar cells with the power conversion efficiency of 10.35%.

2. Experimental

2.1 Hydrothermal growth of ZnO double-layered structures

The well-developed hydrothermal method was used to obtain ZnO double-layered structures. Initially, fluorine-doped tin oxide (FTO) glass substrates were thoroughly washed two to
three times with acetone, DI water and ethanol for efficient cleaning. FTO substrates were then treated with TiCl4 solution, followed by sintering at 450 °C for 40 minutes, and they were then finally cooled down to room temperature for further processing. This was followed by spin coating a very thin and compact blocking layer of ZnO onto the FTO substrates at 4000 rpm for 30 seconds and annealing in ambient atmosphere at 350 °C for 30 minutes.

To grow the double-layered structure on the above prepared substrates, a 100 mL solution containing a mixture of 0.06 M hexamethylenetetramine (HMTA) and zinc nitrate hexahydrate (Zn(NO3)2·6H2O) was used as a growth solution, based on a modified method reported elsewhere. The FTO substrates were horizontally placed inside the sealed reaction vessel having an equimolar solution of 0.06 M Zn(NO3)2·6H2O/HMT and heated to 90 °C in a laboratory oven for the double-layer growth. The double-layer coated FTO substrates were then removed from the vessel after 12 h of growth, washed with distilled water to remove the residual zinc salts and preserved in absolute ethanol. The detailed experimental parameters are shown in Table 1.

### 2.2 Perovskite solar cell fabrication

The perovskite solar cells were fabricated on the double-layered ZnO nanostructures using a sequential deposition method as reported elsewhere. Firstly, a 1 M PbI2 solution was prepared in DMF at constant temperature of 70 °C and spin-coated at 6000 rpm for 5 s on the as-grown double-layer films onto the ZnO blocking layer, followed by the complete drying of DMF for 30 minutes at 70 °C. In the second step, PbI2 coated films were dipped into a 10 mg mL−1 solution of CH3NH3I prepared in IPA for approximately 20 minutes, followed by rinsing in IPA and finally dried at 70 °C for 30 minutes. The spiro-OMeTAD, which was used as hole transporting layer, was prepared by spin coating the solution composed of 8.4 μl of 4-tert-butylpyridine, 80 mg of 2,2′,7,7′-tetraakis(N,N-di-p-methoxyphenyl-amine)-9,9′-spirobifluorene and 51.6 μl of bis(trifluoromethane)sulfonamide lithium salt (Li-TFSI) (154 mg mL−1 in acetonitrile), and the mixture was dissolved in 1 ml chlorobenzene solution for 30 s at 3000 rpm. Finally, a 90 nm thick silver film was evaporated as the back contact. The long term stability of the devices was automatically recorded in air every five hours for a total duration of 240 hours.

### 3. Results and discussion

In Fig. 1a, a schematic illustration of a ZnO-based double-layer structure composed of an overlayer of horizontally grown ZnO nanorods on top of the underlayer of nanosheets is illustrated. Moreover, in Fig. 1b, the cross-sectional FE-SEM image of the completed devices with the structures of FTO glass/ZnO compact layer/ZnO double-layer film & CH3NH3PbI3/spiro-OMeTAD/Ag, respectively, are demonstrated. Furthermore, Fig. 1c shows a representative low magnification FE-SEM view of cross-section, which verifies the uniformity of the fabricated films over a reasonably large scale.

In Fig. 2, we show plane-view FE-SEM images corresponding to samples prepared with molar concentrations of 0.02, 0.04, 0.06 and 0.08 M. The FE-SEM images reveal that the ZnO layers are nanostructured with well-developed grain boundaries and free surfaces. From the image in Fig. 2a, the ZnO film prepared at a low precursor concentration of 0.02 M appears to be composed mainly of vertically aligned nanosheets as an underlayer with a sparse overlayer of nanor-
ods. When the concentration is doubled to 0.04 M (Fig. 2b), the film shows a partial double-layered structure with the underlayer forming a network-like structure of nanosheets, while the overlayer contains horizontal ZnO nanorods with a diameter of about 800 nm. By further increasing the concentration to 0.06 M, we observe flower-like nanorods in the overlayer with a diameter of about 900 nm (Fig. 2c). Further increasing the solution concentration (0.08 M) produces more nanorods in the overlayer (Fig. 2d), which risks hindering the infiltration of the perovskite absorber down to the underlayer with negative consequences on solar cell performance. Interestingly, the underlayer morphology appeared to be rather insensitive to the precursor concentration over the investigated range, even as the morphology of the overlayer significantly changed.

XRD measurements (Fig. 3) were performed on the ZnO double-layer structures for samples prepared with molar concentration of 0.02, 0.04, 0.06 and 0.08 M. All the diffraction patterns feature a strong characteristic peak for the (002) plane of the hexagonal wurtzite structure of ZnO. The XRD data for ZnO double-layer structures indicate four reflection peaks, $2\theta = 31.63^\circ$, $34.41^\circ$, $36.25^\circ$, and $47.54^\circ$, corresponding to the (100), (002), (101), and (102) reflections of the hexagonal wurtzite structure and in agreement with the JCPDS card No. 36-1451. A sharp (002) diffraction peak indicates that the ZnO double-layer structures preferentially grow along the c-axis.3

The as-synthesized samples were fabricated into perovskite solar cells for measuring their J-V curves and external quantum efficiency (EQE), as shown in Fig. 4a and b, respectively. The detailed device parameters are presented in Table 2. As the concentration increases from 0.02 M to 0.06 M, short-circuit
current density \( (J_{sc}) \) shows an increasing tendency, reaching the maximum of 18.0 mA cm\(^{-2}\) with maximum EQE (Fig. 4b). In addition, when the concentration increases from 0.02 M to 0.06 M, open-circuit voltage \( (V_{oc}) \) increases from 0.83 V to 0.928 V and the efficiency \( (\eta) \) increases from 6.98% to 10.35%. With further the increase of concentration (0.08 M), \( J_{sc}, V_{oc} \) and fill factor (FF) all decrease, resulting in \( \eta \) of 8.11%. The changes in solar cell performance can be qualitatively explained on the basis of FE-SEM observations: At the optimum concentration of 0.06 M, the density of ZnO nanorods in the overlayer is sufficiently high to achieve a large interfacial area between ZnO and the perovskite absorber while also maintaining the good infiltration of the absorber into the double-layer. With the optimum perovskite infiltration and improved contact with ZnO nanorods, electron transfer to the ETL becomes more effective, resulting in an increase of \( J_{sc} \). On increasing the concentration to 0.08 M, \( J_{sc}, V_{oc} \) and FF decrease. We believe this might be caused by the decreasing gap between the nanorods, which can hinder the full infiltration of the perovskite absorber and reduce the effective interfacial area between the perovskite and ETL and possibly lead to more recombination.

The long term stability of the perovskite solar cells based on the 0.06 M type double-layered ZnO films was also tested by keeping the cells at a temperature of 45 °C and under long-term light soaking in ambient air at an intensity of 100 mW cm\(^{-2}\) as reported elsewhere. It was observed that photovoltaic efficiency maintains more than 80% of its initial value even after a period of 240 hours (Fig. 5). Notably, no significant decrease is observed for the \( J_{sc} \) values, which highlights the remarkable photostability of the devices. A slight decrease in the efficiencies is mainly attributed to the \( V_{oc} \) and FF values, which encourages further investigation.

4. Conclusions

In conclusion, a simple hydrothermal method was used to prepare double-layer ZnO nanostructures with nanosheet arrays at the bottom, decorated with horizontal nanorods. XRD analysis revealed that the double-layer ZnO nanostructures are highly crystalline (wurtzite structure) with a preferential (002) orientation. The number density of ZnO nanorods in the overlayer was found to be sensitively dependent on the concentration of the precursor, whereas the nanosheets in the underlayer remained unaffected. The performance of perovskite solar cells was found to improve with increasing ZnO nanorod density in the overlayer up to 10.35% at a concentration of 0.06 M, followed by decrease at higher concentrations. It is believed that an excessive number of ZnO nanorods negatively impacts the infiltration of the perovskite absorber into the mesoporous structure, and thus reduces the amount of perovskites and its effective interfacial area with the ZnO-based mesoporous ETL. The fabricated perovskite cells showed promising long term photostability even after 240 hours.

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References


