Complete coverage of perovskite materials over ZnO Nanorods with Multiwalled Carbon Nanotubes (MWCNTs) as Hole Transport Material (HTM)

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Abstract. In this research, ZnO nanorods (NRs) have been fabricated for perovskite solar cell (PSC) application. An issue about the use of ZnO material for PSC application is lower photovoltaic outputs than TiO2 material. Such outcome is due to unstable ZnO/perovskite interface. Other factor is due to partial coverage of the perovskite over the ZnO material. By using 1-step method and mixture of DMF and DMSO as the solvent for perovskite solution, complete coverage of the ZnO NR was achieved. Multiwalled carbon nanotubes (MWCNTs) and copper iodide (CuI) were used as hole transport materials (HTMs) for comparison purpose. The experiment and characterization were done in Shizuoka University, Hamamatsu campus, Japan. The ZnO NRs were grown by implementing 2-steps method of seed layer deposition by spin coating and NRs growth through chemical bath deposition. Methylammonium lead iodide (CH3NH3PbI3 or MAPbI3) perovskite was grown through 1-step method by mixing equimolar lead iodide (PbI2) and methylammonium iodide (CH3NH3I or MAI) in DMF and DMSO solvents (volume ratio of 7 to 1 for DMF and DMSO, respectively). The current-voltage (I-V) curve for both materials showed higher JSC and VOC for MWCNTs at 5.34 mA/cm2 and 0.21 V, respectively compared to CuI materials (JSC = 3.40 mA/cm2 and VOC = 0.14 V). Lower VOC is the result of higher series resistance due to non-passivated ZnO/MAPbI3 interface. Another factor to consider is recombination of electron and hole at the interface. MWCNT material is an alternative material to act as HTM because of high conductivity and lower electrical resistance compared to CuI. Complete coverage of the perovskite over ZnO material helped improving the production of photogenerated electrons.

1. Introduction

Perovskite solar cell (PCS) technology has developed from its first application of MAPbBr3 nanocrystalline in DSSC (dye sensitized solar cell) device by Kojima et al. [1] in 2009 with PCE (power conversion efficiency) of 3.8 %. Recent development has shown that TiO2 material is the ETM (electron transfer material) that deliver the highest PCE at 22.1 % by Yang et al. [2]. ZnO material is an alternative to TiO2 material because of its similar Fermi level bandgap with TiO2 material while possessing higher electron mobility. Despite such advantages over TiO2 material, the highest PCE of ZnO based PSC is found at 17.3 % by Li et al. [3]. One explanation about the lower PCE for ZnO
based PSCs is due to presence of defects in the ZnO/perovskite interface which increases the number of electron-hole recombination.

In order to reduce the electron-hole recombination in ZnO based PSCs, surface passivation can be done by applying a dopant on top of the ZnO ETM. Deposition of TiO$_2$ material was reported by many groups of researchers to form ZnO-TiO$_2$ core-shell structure as the ETM for PSC application [4-6]. The advantages of ZnO-TiO$_2$ structure compared to pure ZnO is larger surface area, higher impedance of charge-transfer resistance R$_{CT}$, and increased chemical stability which gives increased photovoltaic parameters. A research conducted by Wang et al. explored the possibility to coat ZnO material with SnO$_2$ to reduce hysteresis effect and stabilize the decomposition of MAPbI$_3$ perovskite[7]. Another material capable of passivating the surface of ZnO for PSC application is aluminium (Al)[8].

In this research, ZnO nanorods (NRs) was developed to provide direct electron pathway for photogenerated electrons. MWCNTs (Multiwalled carbon nanotubes) was utilized as HTM (hole transport material) because of the high conductivity and low resistivity. MWCNTs also provided protection for the perovskite material from water moisture. Although the use of MWCNTs have been reported by many researchers, most of them were applied for TiO$_2$ based PSCs[9-13]. This research fabricated MWCNTs as an HTM alternative other than Spiro-OMeTAD. Complete coverage of the perovskite over the grown ZnO NRs was achieved.

2. Experimental

2.1. Seed layer deposition

FTO substrates were cleaned ultrasonically through separate use of distilled water, acetone, and ethanol at 5 minutes each. The seed layer solution was made from 10 mL of 0.30 M zinc acetate dihydrate with 2-methanol as solvent. Ethanolamine was dropped 10 times into the seed layer solution. The seed layer solution was heated at 60 °C for 30 minutes. The seed layer was spin coated from the low speed of 500 rpm to high speed of 3000 rpm for 1 minute and then heated at 100 °C for 10 minutes to remove left over solution on top of the substrate. This cycle was repeated until 3 times and finally annealed at 350 °C for 1 hour.

2.2. ZnO NRs growth

The growth solution for the ZnO NRs was formed from mixture of equimolar 0.050 M zinc acetate dihydrate and HMT (hexamethylenetetramine) at 50 mL of distilled water solvent for each solution. The substrate containing spin coated seed were kept at vertical position. Chemical bath deposition method was used at 85 °C from room temperature. When the desired temperature was reached, the growth condition was kept for 3 hours. After the growth process was over, the samples were annealed at 350 °C for 1 hour.

2.3. Perovskite 1-step deposition

The perovskite solution was made from mixture of equimolar 1.2 M of PbI$_2$ and MAI in 1 mL DMF and DMSO solvents (volume ratio of DMF and DMSO were 7:1). The solution was heated at 100 °C for about 30 minutes. The perovskite solution was spin coated into the ZnO NRs grown substrates at 1000 rpm for 1 minute. During the spin coating, 200 – 300 μL of diethyl ether was dropped in order to remove leftover solution and smoothed the perovskite surface. The perovskite was heated at 100 °C for 30 minutes in low humidity environment inside a glovebox (less than 20 % humidity).

2.4. HTM deposition and PSC fabrication

Doctor blading method was applied to deposit the HTMs. CuI and MWCNT powders were grinded separately to form pastes with chlorobenzene as the solvent. Each HTM pastes were applied onto different substrates with the deposited perovskite. After the paste was dried, platinum plate was put on top of the HTM. The HTM was sandwiched between the perovskite and the Pt plate. Solar simulator was used to characterize the photovoltaic parameters.
2.5. Characterizations
Scanning electron microscopy (SEM) images of the samples were captured using SEM JOEL 7001F. The X-ray diffraction (XRD) chart was measured using type D5000 machine. Finally, The I-V characteristics was carried out using a calibrated solar simulator (JASCO CEP-25 BX solar cell evaluation system) under incident light intensity 1.5 AM, 100 mW cm\(^{-2}\).

3. Results and discussions
Complete coverage of the perovskite over ZnO NRs had been attempted before. However, usage of pure DMF as solvent for the perovskite solution resulted in wires or fibers of MAPbI\(_3\) perovskite. Such morphology left some parts of ZnO NRs’ surface not covered by the perovskite which contributed to short circuit device. Fast crystallization of the perovskite during the processing of the 1-step perovskite in pure DMF solution gave rise to formation of perovskite crystallites. When the perovskite solution was spin coated, the perovskite crystallites could not cover the whole surface of the ZnO NRs because the mixture of PbI\(_2\) and MAI have already formed the MAPbI\(_3\) crystallites before the solution was spin coated. One way to slowed down the crystallization of perovskite during the solution processing was done by mixing DMF and DMSO solvents. In this manner, the perovskite crystallites have not been converted completely and when the spin coating was finished, most if not all of the ZnO NRs’ surface was covered by the perovskite crystallites. SEM images for the perovskite using mixed DMF and DMSO solvents is shown in figure 1.

![SEM images](image1.png)

Figure 1. SEM images (a) upper view, and (b) cross section view of the ZnO/Perovskite interface with mixed DMF and DMSO solvents.

The XRD profile for the perovskite spin coated onto the ZnO NRs is shown in figure 2. There were two dominant MAPbI\(_3\) peaks in (110) and (220) directions which corresponded to growth in two-dimensional X and Y axis. Meanwhile, there were two peaks for ZnO NRs in (100) and (002) directions. Growth along the horizontal and vertical directions were represented in the (100) and (002) peaks, respectively. Stronger intensity of the (002) ZnO peak meant that the growth alongside the vertical direction was dominant or the ZnO NRs were vertically aligned.

HTM is an important part in a PSC device. Spiro-OMeTAD is one of the most commonly used HTM due to its ability to generate high efficiency PSCs. However, Spiro-OMeTAD is quite expensive and the need for other alternative HTMs that are more cost friendly while being able to deliver high efficiency. Cul is an alternative HTM that is often used for ZnO based PSCs. MWCNTs was compared with Cul in this research for PSCs application. A Pt plate was pressed on top of the HTM to form the metal contact. An insulator mask was used to prevent the Pt plate from touching the areas that were not covered with the HTM while a hole at about 0.25 cm\(^2\) was provided for calculation of photovoltaic process. Figure 3 shows the PSC configuration that was calculated.
Photovoltaic measurement of the PSCs can be seen in table 1. The PSC with MWCNTs have larger outputs compared to CuI based PSCs. Such outcome was expected because of higher conductivity of the MWCNTs compared to CuI. The generated holes could move faster from the perovskite to MWCNTs compared to the perovskite to CuI. Additional observations about the I-V curve can be seen in figure 4. The I-V curve shows that the shunt resistance ($R_{sh}$) for the PSC was low that the I-V curve exhibited nearly flat lines for both MWCNTs and CuI. Low $R_{sh}$ meant that there was a defect in the interfaces. It was possible that unstable ZnO/MAPbI$_3$ interface became the source for electron-hole recombination which gave less than desired results. Another source for interface defects was faulty deposition of the HTM by doctor blading where the HTM was spread unevenly in the active area. The application of Pt plate by pressing the plate onto the HTM could leave empty spaces along the HTM/Pt interface that lead to short circuit device.
Table 1. Photovoltaic parameters of the PSCs with CuI and MWCNTs.

| HTM     | J_sc (mA/cm²) | V_oc (V)  | FF    | PCE (%)  |
|---------|---------------|-----------|-------|----------|
| CuI     | 3.3953        | 0.1417    | 0.2835| 0.1364   |
| MWCNTs  | 5.3409        | 0.2055    | 0.3026| 0.3322   |

Figure 4. I-V curve of the PSCs with MWCNTs and CuI.

4. Conclusions
Complete coverage of MAPbI₃ perovskite over the ZnO NRs was done through preventing the finalization of perovskite crystallization before the spin coating was conducted. In this way, the perovskite was able to cover the ZnO NRs completely while still in the crystallization process. The slowing down of the perovskite crystallization was done through mixing of the perovskite solvents between DMF and DMSO. The photovoltaic outputs of MWCNTs and CuI were compared and calculated. MWCNTs delivered higher outputs due to higher conductivity and lower resistivity. Less than ideal photovoltaic parameters occurred due to defects between the interfaces.

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