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Enhanced Efficiency of Inverted Perovskite Solar Cells by Passivating Hole Transport Layer with POSS †

Bo-Tau Liu * and Hong-Ru Lin

Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan; M10615023@yuntech.edu.tw
* Correspondence: liubo@yuntech.edu.tw; Tel.: 886-5-552-4710; Fax: 886-5-531-2071

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Abstract: The energy crisis and environmental pollution are attracting increasing attention, which made many countries implement a series of preferential policies for renewable energy. Among them, solar photovoltaic technology, which can convert solar light into electrical energy, is one of the most feasible methods for renewable energy. It not only improves environmental problems but also reduces dependence on fossil fuels. In recent years, perovskite solar cells has reviewed promising potential in solar photovoltaics owing to low process energy consumption, large-scale production, low cost, simple fabrication process, light weight, flexibility, etc. Polyhedral oligomeric silsesquioxane (POSS) featuring a hollow-cage or semi-cage structure is a new type of organic-inorganic hybrid nanoparticles. POSS combines the advantages of inorganic components and organic components to become one of the most important materials. When POSS is well dispersed in the polymer matrix, it can effectively improve the thermal, mechanical, magnetic, acoustic, and surface properties of the polymer. In this study, the POSS was spin-coated as a ultra-thin passivation layer to optimize a nickel-oxide hole layer, which made perovskite solar cells feature high open circuit voltage. Experimental results showed that Coating an appropriate POSS amount to form an ultra-thin passivation layer could effectively suppress the surface defects of perovskite layers, reduce the recombination of the electron and hole, and increase the short-circuit current. As a result, the power conversion efficiency increased from 13.30 to 15.58%, enhanced by 17%.

Keywords: polyhedral oligomeric silsesquioxane; perovskite solar cell; passivation layer; NiO_x

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1. Introduction

Owing to lightweight, low cost, simple fabrication, high optical absorption coefficient, and large charge carrier diffusion length, perovskite solar cells (PSCs) have been regarded as one of the most promising photovoltaic technologies and increase rapidly in power conversion efficiency (PCE) from 3.8 to 25.2% in a very short period of time [1–4]. Compared to conventional PSCs, inverted cells with a device structure of transparent conductive oxide/hole transport layer (HTL)/perovskite/electron transport layer (ETL)/top metal electrode feature advantages of low-temperature processability and potential for flexible devices [5,6]. Among the device structure, HTL and ETL serve as auxiliary layers to extract charges from the perovskite layer, deliver the charges to the electrodes, and block the opposite charge transfer [7–10].

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is commonly used for the HTL of inverted PSCs. However, PEDOT:PSS possesses insufficient electron-blocking ability, high hygroscopicity, and poor chemical stability [11–13]. NiO_X, being in favor of hole transport and blocking electrons efficiently, is one of the most potential alternatives to PEDOT:PESS [14]. Moreover, NiO_X leads to higher open-circuit voltage (V_{OC}) of PSCs due to its energy level being more suitable to that of $CH_3NH_3PbI_3$ ($MAPbI_3$). To reduce interfacial loss, a passivation layer has been inserted between the perovskite layer and the charge transport layer to decrease interfacial defects and charge recombination [15,16]. Recently, several materials, such as sodium dodecylbenzenesulfonate [17] and polystyrene [18] have been reported to passivate NO_x and improve crystal size of perovskite. Although they revealed enhanced efficiency, the studies about how to improve the NO_x HTL for PSCs are still few. It remains a challenge to develop new passivation techniques for the NO_x HTL of PSCs.

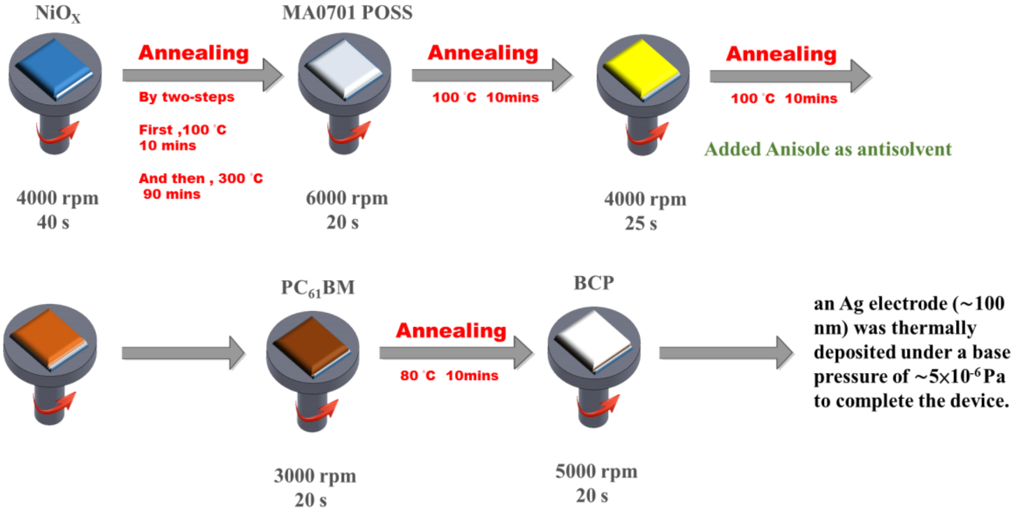
Besides mechanical properties, polyhedral oligomeric silsesquioxane (POSS) has showed its advantage to improve Li batteries [19], light emitting diodes [20], and PSCs [21,22] due to stable electrochemical properties. In this study, we are the first to attempt to use POSS to passivate NO_x. The PSCs with fluorine-doped tin oxide (FTO)/NO_x/POSS/$MAPbI_3$/$PC_{61}BM$/Bathocuproine (BCP)/Ag structure were fabricated. The effect of the POSS amount on photovoltaic properties was analyzed. The result showed that the POSS passivation improved significantly crystal size of perovskite, short circuit current (J_{SC}), and PCE. At 0.01-wt% POSS, the PCE increase from 13.3 to 15.58%, an enhancement of 17%. This enhancement was mainly due to the increase of the J_{SC} from 18.0 to 20.5 mA/cm^2, an increase of 13%.

2. Materials and Methods

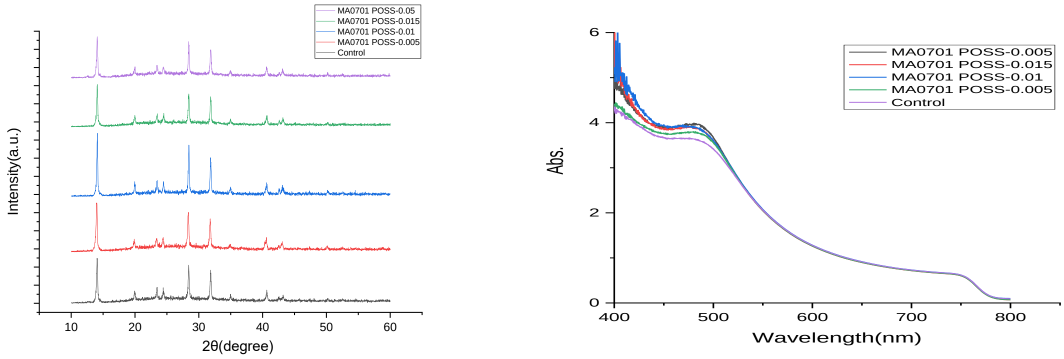
2.1. Synthesis of NO_x Solution

0.87 g of nickel nitrate hexahydrate and 0.12 g of ethylene diamine were mixed into 5 mL of ethylene glycol monomethyl ether as. The solution was sealed with parafilm and stirred overnight at 550 rpm and 60 °C. The color of the solution gradually changed from dark green to dark blue, resulting in a 0.6 M NO_x solution.

2.2. Device Fabrication

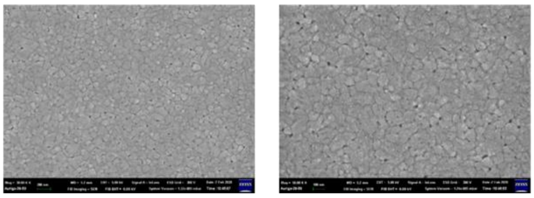


3. Results

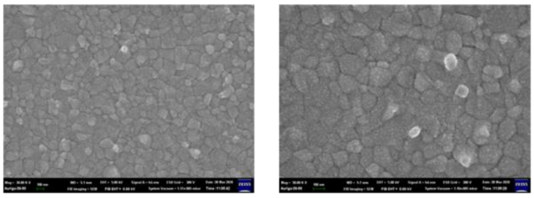


(**a**) (**b**)

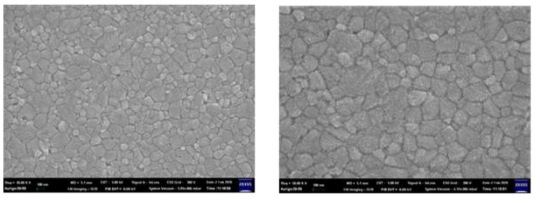
Figure 1. XRD patterns (**a**) and UV-Vis curves of the $MAPbI_3$ layers over the POSS layers fabricated with various concentrations.



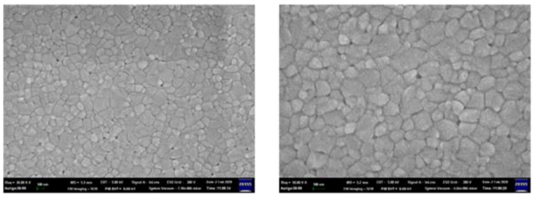
(a) Perovskite (b) Perovskite



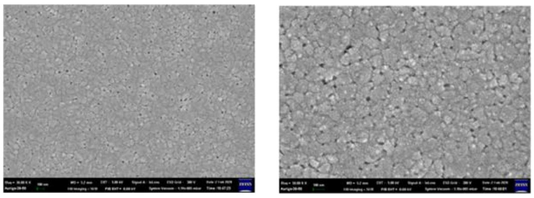
(c) Perovskite + MA0701 POSS-0.005 (d) Perovskite + MA0701 POSS-0.005



(e) Perovskite + MA0701 POSS-0.01 (f) Perovskite + MA0701 POSS-0.01



(g) Perovskite + MA0701 POSS-0.015 (h) Perovskite + MA0701 POSS-0.015



(i) Perovskite + MA0701 POSS-0.05 (j) Perovskite + MA0701 POSS-0.05

Figure 2. SEM images of the $MAPbI_3$ layers over the POSS layers fabricated with various concentrations: (**a**,**b**) 0, (**c**,**d**) 0.005, (**e**,**f**) 0.01, (**g**,**h**) 0.015, (**i**,**j**) 0.05 wt%.

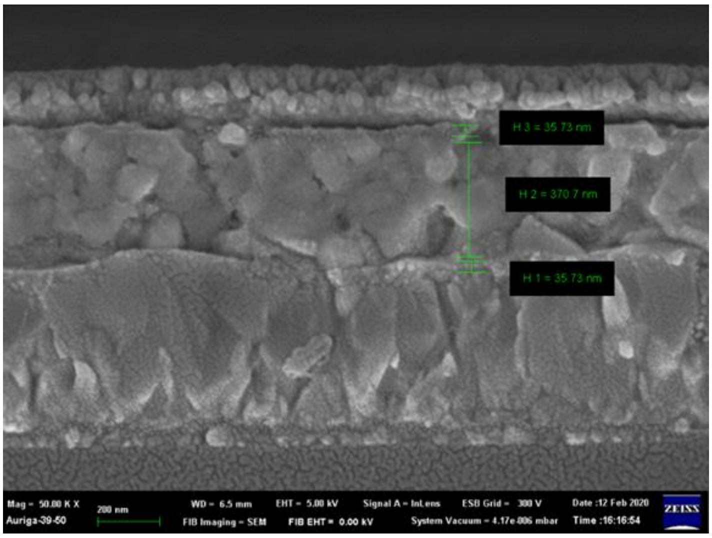


Figure 3. Cross-sectional SEM images of typical PSCs fabricated in this study.

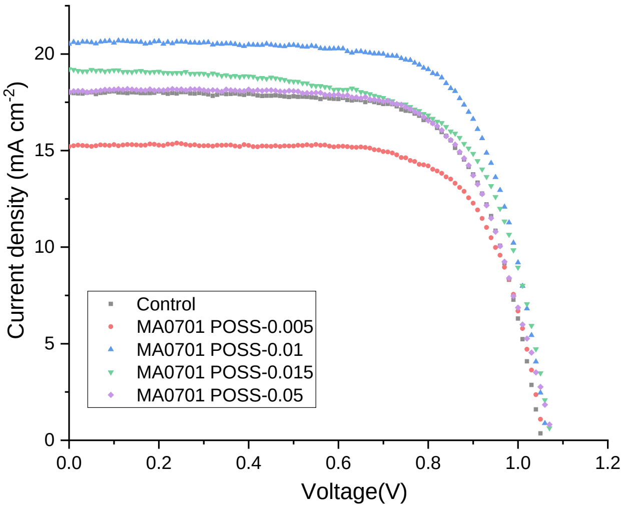


Figure 4. Photocurrent-voltage curves of PSCs fabricated with various POSS concentrations.

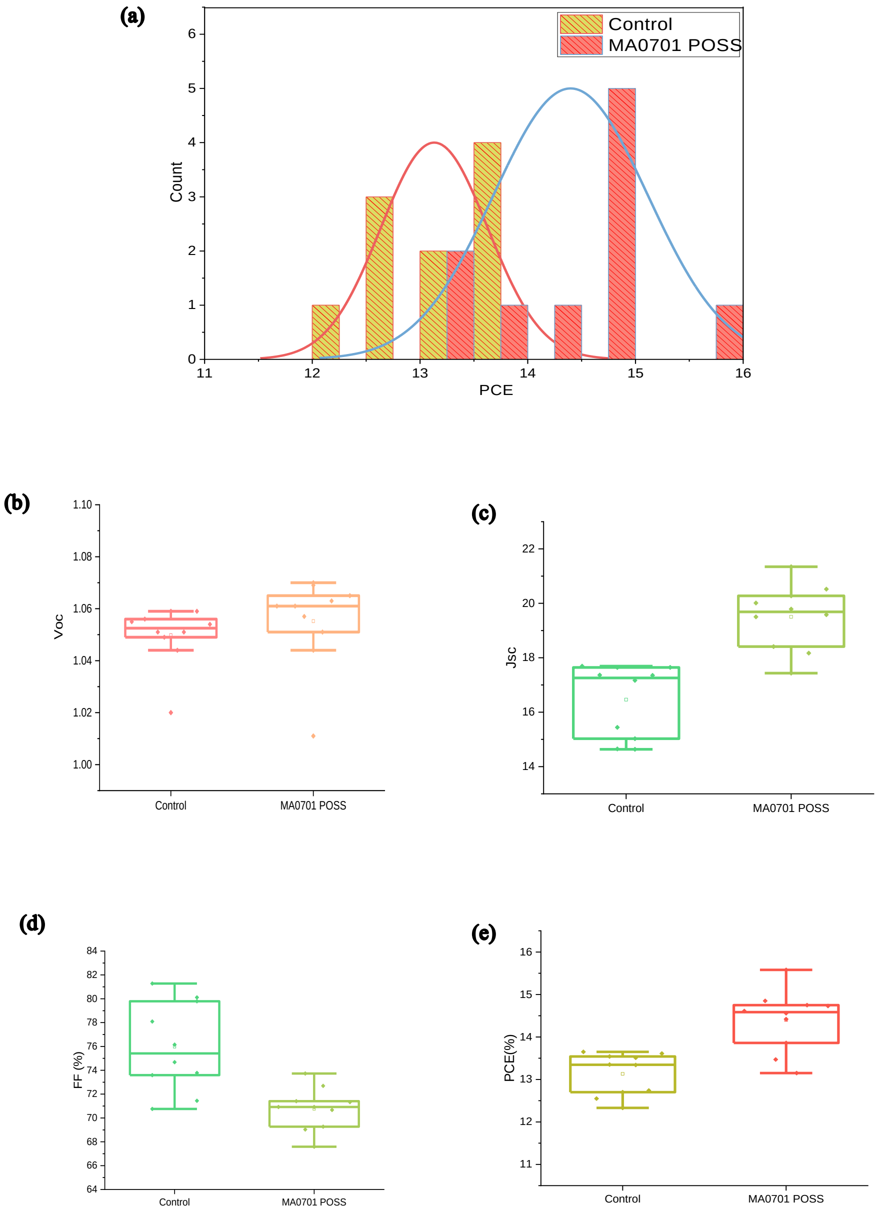


Figure 5. Variations of PCE distribution (**a**), V_{OC} (**b**), J_{SC} (**c**), FF (**d**), and average PCE (**e**) of PSCs fabricated with/without the POSS layer.

Table 1. Photovoltaic characteristics of PSCs fabricated with various POSS concentrations.

Sample	Voc [volt]	Jsc [mA cm^{-2}]	FF [%]	Average PCE [%]〔Best〕
Control	1.053	18.004	70.18	12.55±0.49〔13.30〕
POSS-0.005	1.048	18.391	73.78	12.64±1.23〔14.14〕
POSS-0.01	1.065	20.521	71.33	14.75±0.71〔15.58〕
POSS-0.015	1.074	19.222	66.16	12.85±0.35〔13.66〕
POSS-0.05	1.056	15.206	71.60	10.91±0.62〔11.50〕

4. Discussion

The XRD patterns of the perovskite layers over the POSS layer with various amount exhibited two peaks at 14.1° and 28.4° (Figure 1a), corresponding to planes (110) and (220), respectively, of the perovskite structure of $MAPbI_3$. No peak near 12.7°, attributed to PbI_2, was found on the curves. This result implies that POSS incorporation neither hinders the formation of crystal nor results in PbI_2 separated out from $MAPbI_3$. Particularly, the peak responding to plane (110) for POSS-0.01 and the UV-Vis absorbance (Figure 1b) are higher than others, indicating that crystallinity is better.

Figure 2 that there are a few tiny voids on the surface of the pristine perovskite layer. When the ultra-thin POSS passivation layer is introduced, the defects is reduced and reaches to the minimum at 0.01 mg/mL POSS, implying that the coverage of the perovskite layer is more complete. When the POSS is 0.005 mg/mL, the film becomes relatively uneven. However, the voids also increase when the POSS is 0.05 mg/mL. We inferred that too much or too little POSS amount may have a negative impact on the perovskite layer.

Figure 3 shows the cross-sectional image for typical PSCs with the POSS passivation layer in this study. The POSS-0.01 displays the highest PCE (Figure 4 and Table 1). The efficiency increases from 13.30 to 15.58% due to the POSS passivation layer. The current density increases from 18.0 to 20.5 mA/cm^2, increased by 13%. Figure 5 reveals that the pristine efficiency and current density are about 11~13% and 15~18 mA/cm^2, respectively, without POSS passivation. The POSS passivation increases PCE and J_{SC} to 13~15% and 18~20 mA/cm^2, respectively. However, the POSS passivation doesn’t change significantly the fill factor and V_{OC}.

Author Contributions: B.-T.L. conceptualized the work, designed the experiments, and wrote the manuscript. H.-R.L. conducted the fabrication and measurement of the cells.

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Conflicts of Interest: The authors declare no conflict of interest.

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