

AN EXTENSIVE STUDY OF THE PHYSICAL PROPERTIES IN GRAPHENE OXIDE DOPED PEDOT: PSS HOLE TRANSPORT LAYERS

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ABSTRACT

Hole Transport Layers in Perovskite Based solar cells have been attracting increasing attention in recent years. Among the benefits they provide, such as being easily reproducible and affordable, they pose their own problems with device degradation, stability, and wettability. We probed the Graphene Oxide doped PEDOT: PSS (GO) / poly (3,4 ethylenedioxythiophene):poly(styrene sulfonate) composite for the application in 2D carbonaceous hole transport layers for perovskite solar cells. We discussed the advancement of the hole transport layer and described the effects of Graphene Oxide (dopant) on device transmission, surface wettability, and film quality. Findings included the decrease in transmission, decreased oxidation of the Perovskite, and increased surface wettability.

KEY TERMS: Active Layer, Dispersion, Hole Transport Layer, Graphene Oxide, Perovskite, Spectrometer

I. INTRODUCTION

Perovskite solar cells (PSCs) have gained increasing attention due to their low cost, decreased thickness, and high mechanical flexibilities.^[4] The active layer in our solar cell is methylammonium leadhalide ($\text{CH}_3\text{NH}_3\text{PbX}_3$) in place of silicon which is common in traditional solar cells. The specific type of PSC's we have produced use an inverted planar heterojunction (p-i-n) for the device structure. The integration of perovskite brings subpar cell performances in comparison to silicon-based cells. This can be accredited to the relatively novel research of the field. A method to improve the efficiency and stability in solution processable devices such as the following is by implementing a hole transport layer (HTL). HTL's reduce the differences in work functions between the anode and perovskite. This transparent layer can improve charge carrier mobility and reduce recombination of charges. PEDOT:PSS, a well-known p- type semiconductor used in this experiment poses a host of its own problems including moisture locking, poor surface dispersibility, and mediocre conductivity. A general problem faced during the deposition of HTL's is the formation of pinholes. The presence of pinholes presents a problem where an induced current will short circuit, rendering the device useless. It also decreases the current density and open circuit voltage leading to an overall decrease in the power conversion efficiency of the solar cell. The pinholes are formed as a result of poor wettability of PEDOT:PSS on ITO. These composite further limits the efficiency of the solar cell due to its hygroscopic nature and inability to block electrons.[1] The goal of maximizing the quantity of charges into the perovskite layer poses the use of dopants to heighten functions of PEDOT:PSS. Recently, consideration has been given to the stable aqueous dispersions of graphene oxide (GO) in addition to PEDOT:PSS to improve the HTL. This nanomaterial promises the ease of processability in water and a large surface area to increase conductivity. Suspensions of Graphene Oxide flakes have unique structures that account for a mixed presence of sp^2 and sp^3 hybridizations and high surface areas for electrical conductivity. The sp^2 hybridization can be credited for (GO)'s insulating properties, however, Graphene Oxide proves to bring superior conductivity than anticipated accredited to electron

hopping.[2] Delocalized electrons allow for carrying electric charges. The addition of GO improves stability, and partially removes the hygroscopic PSS dopant for PEDOT at the surface of the PEDOT:PSS, thus improving moisture resistance. GO has the potential to improve the wettability of PEDOT:PSS, resulting in better crystallinity and fewer pinholes. The use of thermoelectric polymers such as PEDOT:PSS pose a problem by displaying the lack in conductivity, reigning at $.2 \text{ S}\cdot\text{cm}^{-1}$.[3] Adding an organic dopant such as Graphene Oxide can raise the device conductivity and stability by preventing pinholes. By increasing the wettability of surface without the use of surfactants, a decrease in pinholes will be evident. In this project, we compare perovskite solar cells with and without the addition of Graphene Oxide by producing smooth films and analyzing the film quality.

II. METHODOLOGY

- 2.1. Graphene Oxide Flakes Define (Sigma-Aldrich, Germany) were purchased and broken down into a fine powder using a mortar and pestle. A 1 mg/ml dispersion of GO was created by filtering distilled water through a $.2\mu\text{m}$ pore filter and mixed with graphene oxide powder to create a 1mg/ml dispersion to form a light brown suspension. The solution then underwent an alternating cycle of being homogenized with a vortex and bath sonicator at 40 khz for 5 minutes each for a total of 2 hours to break the Graphene Oxide into finer colloids.
- 2.2. Indium-Tin-Oxide (ITO) coated glass substrates with sheet resistance of 65 ohms were cut into small squares with dimensions 2.5 cm x 2.5 cm using a glass cutter. $\frac{2}{3}$ of the slides were then taped free of air bubbles so ITO could not be etched in these respective areas. They were put in a petri dish containing HCl and Zinc powder which were used to etch $\frac{1}{3}$ of the slides of ITO, creating an opening for the circuit. The etched ITO slides were then cleaned twice with distilled water and sonicated in soapy water, distilled water, acetone, and IPA in for 30 minutes for each step. The slides were further treated with ultraviolet ozone (PDC-32G) for 20 minutes and later blasted with compressed nitrogen prior to spin coating.
- 2.3. PEDOT:PSS (AI 4083) of a 1.3 wt.% of PEDOT:PSS in water was used in the preparation of (GO)/PEDOT:PSS. PEDOT:PSS was filtered through a $.45\mu\text{m}$ pore filter before adding it to Graphene Oxide. The (GO)/PEDOT:PSS dispersion consisted of .1% of Graphene Oxide by weight. The two composites were mixed together using a vortex and then bath-sonicated for 2 hours.
- 2.4. The control cell with pristine PEDOT:PSS was obtained by spin coating the composite solution at 2000 rpm for 60 seconds [10] and annealing for 15 minutes on a hot plate at 120° Celsius. This was then set in a vacuum free of heat. The proceeding films were spin coated with (GO)/PEDOT:PSS at 5000 rpm for 45s and annealed for 20 minutes on a hot plate at 120° Celsius. The active layer was coated using the following procedures:[5] A 1.2 M solution of Lead Iodide (PbI_2) was created using Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO) in a 1:9 ratio respectively. The solution was later filtered through a $.45\mu\text{m}$ pore filter and left on hot plate for 10 hours at 60° Celsius. The Lead Iodide solution was spin coated on the PSC at 4000 rpm for 40 seconds. Later, a 0.42 M solution of Methylammonium Iodide (MAI) in IPA was made and vortexed. It was then spin coated on top of the Lead Iodide layer at 4000 rpm for 40 seconds and was then left on the hotplate for 10 minutes. For the Electron Transport Layer (ETL), Phenyl-C₆₁-Butyric Acid Methyl Ester (PCBM) and, Bathocuproine (BCP) were mixed in a 15% weight ratio to create 25mg/ml of solution using Dichlorobenzene. The solution was then spin coated on top of the active layer at 1250 rpm for 40 seconds and was then put on a hotplate for 10 minutes.

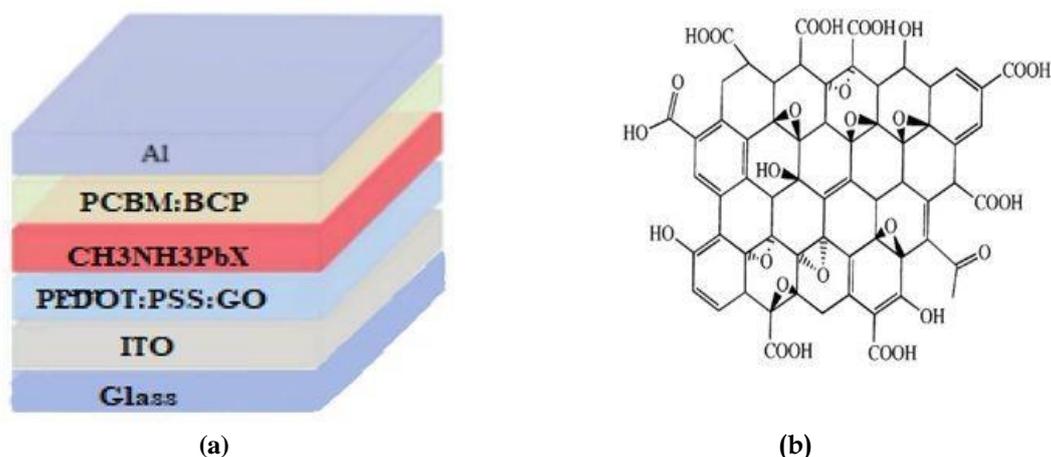


Fig.1 (a) Device structure; (b) Graphene Oxide. Figure 1a displays the full device and its constituent layers. Figure 1b shows the structure of Graphene Oxide, highlighting the functional groups and hybridizations

III. CHARACTERIZATION

A spectrometer (PERKIN ELMER UV/VIS/NIR) was used to obtain transmission data of PEDOT:PSS and (GO)/PEDOT:PSS from wavelengths of 300-1200 nm. The cells were examined under an optical microscope at 70x zoom to obtain high resolution images of pinholes and oxidation. Dispersibility was examined by reflecting light onto the respective coatings of PEDOT:PSS and its doped rendition.

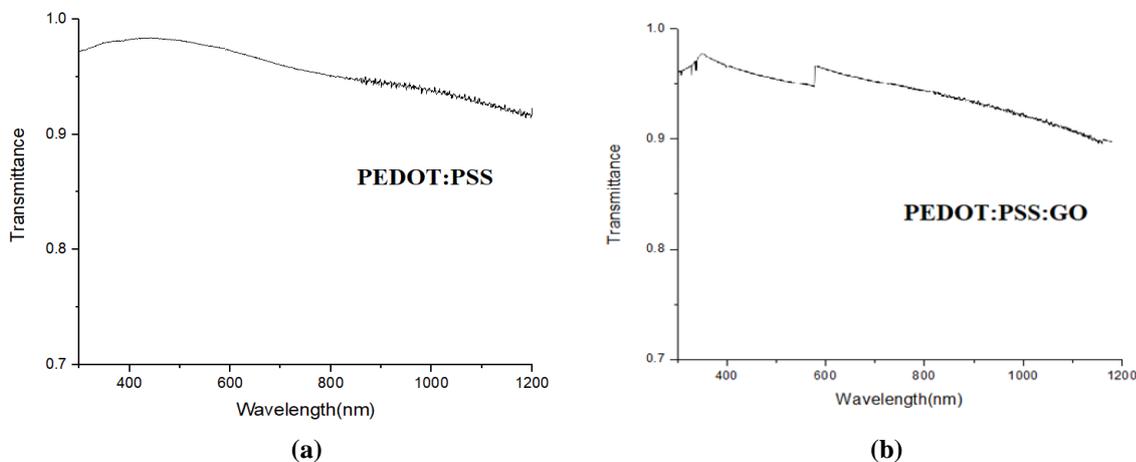


Fig. 2 (a) Transmission of pristine PEDOT:PSS; (b) Transmission of (GO)/PEDOT:PSS are taken over wavelengths from 300-1200 nm.

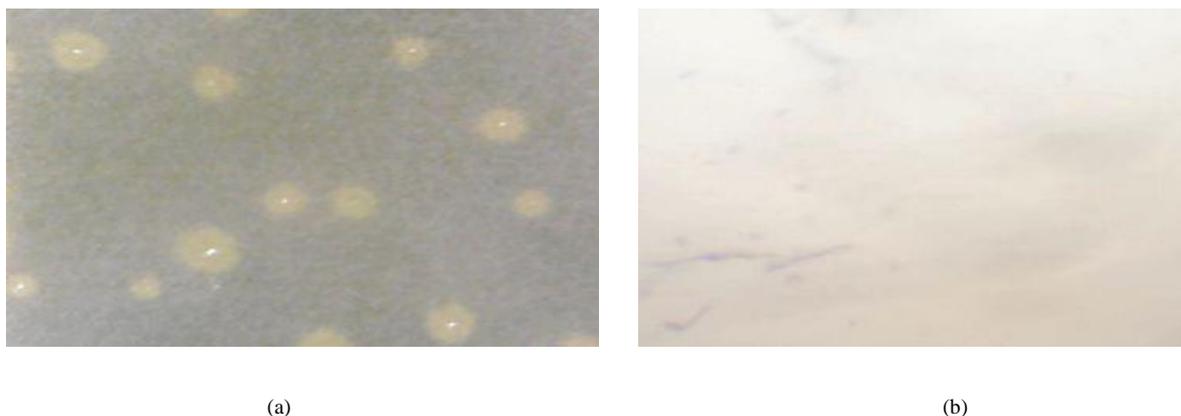


Fig. 3 (a) Optical Image of PEDOT:PSS; (b) Optical Image of (GO)/PEDOT:PSS. Pinholes are displayed by the yellow circles. Black streaks in Figure 3b are Graphene Oxide.

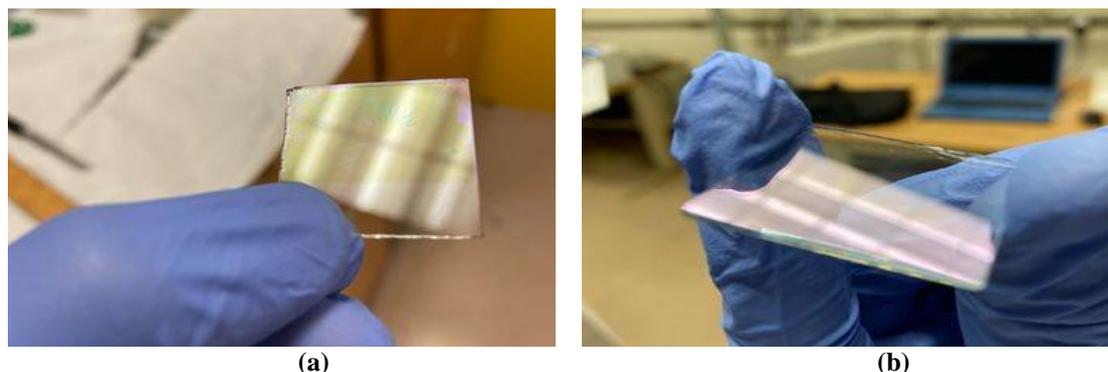


Fig. 4 (a) Image of pristine PEDOT:PSS; (b) Image of (GO)/PEDOT:PSS. Figure 4a displays spidering and an uneven coating of the solution highlighted by the edges.

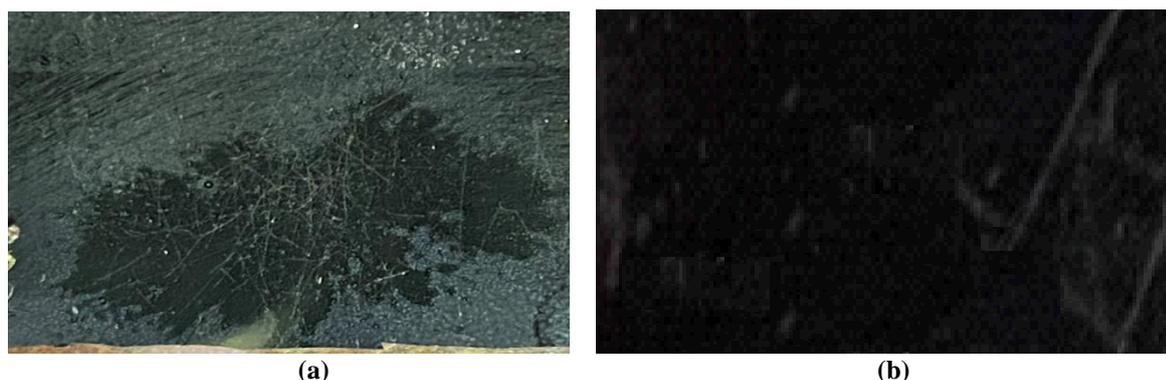


Fig. 5 (a) Optical Image of the perovskite in the pristine PEDOT:PSS cell. (b) Image of the Perovskite in the (GO)/PEDOT:PSS cell. Both cells have oxidation as shown above, a more degraded cell shows in Figure 5a. Images taken at 15x zoom.

IV. RESULTS / DISCUSSION

After spin coating all the respective layers of the cell, both cells had big differences in their physical aspects. After each hole transport layer was spin coated, the transmission for PEDOT:PSS was slightly higher than that of PEDOT:PSS doped with GO. Fig. 2b displays the steepening transmission of PEDOT:PSS doped with Graphene Oxide.

Pictures taken by an optical microscope at 70x zoom of PEDOT:PSS and (GO)/PEDOT:PSS as shown in Figure 3a indicate formed pinholes for the control cell with pristine PEDOT:PSS. The hole transport layer with Graphene Oxide indicates a lack in visible holes as seen in Figure 3b. Figure 4 depicts the ability of the respective solutions PEDOT:PSS and (GO)/PEDOT:PSS to disperse on ITO. Figure 4a shows spidering and improper wetting of the surface indicated by the edges lacking PEDOT:PSS. Figure 4b displays a surface free of defects. Severe oxidation of the active layer is shown in Figure 5a. Figure 5b displays a less severely oxidized active layer.

V. CONCLUSION

(GO)/PEDOT: PSS was used as the hole transport layer in this PSC to counter the drawbacks of pristine PEDOT:PSS. The addition of the Graphene Oxide dispersion decreased the overall solution transmission, indicated by Figure 2b due to Graphene Oxide colloids absorbing particles of light. An improvement was seen in the decrease in pinholes in the hole transport layer itself from scattered pinholes to none. This lack of pinholes is connected to the increased surface wettability of the solution, attributed to the modification of the PEDOT: PSS structure. This is due to the partial removal of PSS chains from PEDOT itself caused by the alcohol functional groups in Graphene Oxide. Slight screening changed the structure and increased the dispersibility of the solution. Degradation of the active layer was caused by the oxidation of the Perovskite. Graphene Oxide blocked most of the highly acidic PEDOT: PSS molecules from oxidizing the active layer.

Future considerations can be given to the use of sugar alcohols to further screen PSS chains from PEDOT and decrease the hygroscopic nature of PEDOT:PSS.

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