Nickel Oxide embedded with Polymer Electrolyte as Efficient Hole Transport Material for Perovskite Solar Cell

Monika Srivastava, Karan Surana, Pramod Kumar Singh and Ram Chandra Singh*

Abstract

The use of organic hole transport material (HTM) is usually quite expensive owing to its synthesis procedure and high purity requirement. Therefore, we have synthesized an inexpensive, inorganic HTM, nickel oxide (NiO) in the laboratory. The perovskite precursor *i.e.*, CH$_3$NH$_3$I was also synthesized in the laboratory and characterized for surface morphology and elemental analysis. Perovskite Solar Cell (PSC) was successfully prepared using NiO as the HTM with a supporting layer of polymer electrolyte. The fabricated sandwich structured PSC exhibited an open circuit voltage ($V_{oc}$) of 0.77 V, short circuit density ($J_{sc}$) of 18 mA/cm$^2$, and an effective photon conversion efficiency (PCE) of 5.13%.

Keywords: Perovskite; Polymer Electrolyte; Nickel Oxide; Perovskite Solar Cell; Hole Transport Material.

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1. Introduction

Perovskite Solar Cells (PSCs) based on methyl ammonium lead halide (CH$_3$NH$_3$PbX; X = halide) are one of the most promising candidates for efficient and cost-effective use of solar energy in the field of photovoltaics. The power conversion efficiency (PCE) has increased rapidly from 3.8% to ~24% in a span of only ten years. Among the initial reports by Kojima et al., they worked on two types of PSCs, viz., CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$BrI$_3$, and achieved a PCE of 3.8% and 6.5%, respectively.[1] These breakthroughs suggested that the coming years will advance the perovskite based solar cells to higher efficiency while retaining low cost and easy processability.[2] In another report, PCE of over 18% was obtained by replacing TiO$_2$ with SnO$_2$. It further stated that for large scale manufacturing, the planar electron selective layers are more suitable than the mesoporous one.[3] Another study suggested that the fabrication of very thin perovskite layer is crucial for high performance PSCs. PCE of 22.1% for smaller cells and 19.7% for 1 square centimetre cells were achieved.[4]

Perovskites have many useful properties like ease of processing, band tunability, and high absorption coefficient, which help in achieving better photovoltaic characteristics in PSCs. On the other hand, the hole transport material (HTM) also plays an important role as it is responsible for effective charge extraction and collection at the electrodes. Many studies have reported the use of organic HTMs like Spiro–MeOTAD, but it is neither cost effective nor viable for large scale production of solar cells.[5] There are a wide range of inorganic p–type semiconductors, which can play the role of HTM for effective fabrication of PSCs, such as CuSCN, Cu$_2$O, CuO, Cul or NiO$_x$. The use of CuSCN results in thermally stable PSCs, which retains an even better operational stability if GO (graphene oxide) is applied in between the CuSCN and Au contact. PSCs using Cul as HTM succeeded in achieving a PCE of 6.0% with stable photocurrent.[6,7] A CuO$_x$ hole transport layer (HTL) was used by Sun and group in an inverted planar heterojunction PSC, which resulted in a PCE of 17.1%, an open circuit voltage ($V_{oc}$) of 0.99 V, a short-circuit current density ($J_{sc}$) of 23.2 mA·cm$^{-2}$, and a fill factor (FF) of 74%. The use of Cu$_2$O resulted in a PCE of 13.35%, making it one of the most promising HTM in the field of photovoltaics.[8,9]

The fabrication of PSC with NiO, a p–type inorganic semiconductor, as the HTM has also been reported. It was observed that PSC with NiO as HTM not only showed good efficiency but it also helped in increasing the $V_{oc}$ to over 1 V.[10] NiO has good optical transparency, reduces electron leakage, and has suitable energy levels to possess a wide band gap, which makes it a promising candidate as HTM for PSC.[11,12] It also acts as an electron blocking layer, suppressing charge recombination, thereby facilitating better charge (hole) extraction in solar cells. Jeng et al. obtained the highest PCE of 15.2% using NiO$_x$, where the NiO$_x$ film was sputter coated...
over the perovskite layer. NiO has a favorable deep–lying Highest occupied molecular orbital (HOMO, valence band edge value) with work function between 5 and 5.6 eV. Regarding the effect of NiO on fluorine doped tin oxide (FTO), it was reported that being an inert material, NiO is non– corrosive towards FTO substrates. Initially, Snaith et al. used NiO layer as HTM and obtained a low PCE of <0.1%, which was due to improper contact between perovskite and NiO layer. An efficient inverted planar PSC was fabricated where NiO was used as the hole–collecting layer and irradiation with UV light helped increase its work function. Liu et al. had deposited CH$_3$NH$_3$PbI$_3$ onto NiO layer through spin–coating and fabricated a planar ITO/NiO/CH$_3$NH$_3$PbI$_3$/PCBM/BCP/Al (where ITO is Indium tin oxide, PCBM is Phenyl-C61-butyric acid methyl ester and BCP is Bathocuproine) device which exhibited an efficiency of 7.9%; however, when a mesoporous NiO layer was used, the efficiency increased to 9.51%. They also found that the Ultraviolet–Ozone (UVO) treatment was beneficial for the device. In another study, NiO(CH$_3$NH$_3$PbI$_3$) solar–cell device was used and the rough NiO film surface caused the formation of an intimate, large interfacial–area junction with the CH$_3$NH$_3$PbI$_3$ film, which dramatically improved the cell efficiency. These results in general portray that NiO is indeed a very promising functional HTL in PSCs. In the recent reports of PSCs with NiO as HTM, a record efficiency of 22.1% has been reported with a hybrid organic inorganic perovskite material. However, NiO is reactive towards perovskite under the effect of light, temperature and electrical stress, which is detrimental to the long–term stability of PSC. In another study, the CH$_3$NH$_3$PbI$_{3.5}$Cl$_{0.5}$ has been used with NiO HTM leading to the development of a highly stable interface maintaining 85% of the efficiency after 670 h. Alternatively, KI modified NiO was used as HTM in inverted PSCs, which improved the photovoltaic parameters by increasing the FF to 0.814. Another research work represented a comparative study of PSCs between PEDOT:PSS and Cu doped NiO as HTM. The results showed that in addition to enhanced photovoltaic performance, the latter also showed slower degradation.

In the present work, we report the synthesis of perovskite (CH$_3$NH$_3$PbI$_3$) material in room ambient condition. The synthesis of NiO was carried out using a simple sol–gel method. The prepared materials were further characterized for UV–Vis absorption, x–ray diffraction (XRD), energy dispersive x–ray (EDX), and scanning electron microscopy (SEM) studies. The prepared sandwich structured PSC with a supporting layer of polymer electrolyte resulted in $V_{oc}$ of 0.77 V, $J_{sc}$ of 18 mA·cm$^{-2}$, and PCE of 5.13% in room ambient condition.

2. Experimental section
The materials used for synthesis are given in supplementary information.

2.1 Preparation of methyl ammonium iodide (MAI)
The perovskite precursor, methyl ammonium iodide (CH$_3$NH$_3$I), was synthesized by mixing 27.86 mL of methylamine (CH$_3$NH$_2$) and 30 mL of HI in a round bottom flask kept under ice–bath treatment at 0 °C for 2 h. The obtained product was kept in a laboratory oven at 60 °C for 24 h, which resulted in a light–yellow colored precipitate. The precipitate was then washed thoroughly with diethyl ether resulting in whitish crystals. Further, the precipitate was kept at 100 °C in vacuum oven for 24 h to obtain dried powder. For the synthesis of CH$_3$NH$_3$PbI$_3$ solution, the prepared CH$_3$NH$_3$I powder was mixed with PbI$_2$ in 2 mL of DMF in equal ratio. The solution was stirred continuously for approximately 6 h at 60 °C which resulted in the formation of methyl ammonium lead iodide (CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$) perovskite solution.

2.2 Synthesis of NiO
NiO powder was prepared by mixing 1.5 g of NiCl$_2$·6H$_2$O with 70 mL ethanol under continuous stirring. In another beaker, 0.5 g NaOH was dissolved in 100 mL ethanol. Both the solutions were continuously stirred for approximately 2 h, which resulted in the formation of a light–green colored gel. The gel was kept undisturbed for three hours following which it was filtered and washed with double distilled (DD) water and ethanol, leaving behind light–green colored precipitate. The precipitate was dried in an oven at 100 °C for 2 h, which resulted in the formation of fine green powder as shown in the supplementary information (Fig. S1).

2.3 Preparation of Polymer Electrolyte
The polymer electrolyte solution consisting of PEO (Polyethylene Oxide) with 10% KI and 1% I$_2$ was prepared in 20 mL acetonitrile as reported in previous literature. In a typical process, the solution was kept on a magnetic stirrer for few days to allow uniform mixing and sufficient evaporation of solvent. The obtained quasi-solid electrolyte was used in the sandwich structured perovskite solar cell.

2.4 Fabrication of the Perovskite Solar Cells
The preparation of working and counter electrodes is crucial, as they are responsible for proper functioning of the solar cell. Firstly, the FTO glasses were sonicated thoroughly in DD water followed by acetone. For the preparation of the working electrode (WE), blocking layer (BL) was spin–coated at ~1000 rpm for 60 s and then kept for calcination at 500 °C for 30 min in a furnace. The thickness of the TiO$_2$ film was optimised by using two layers of scotch adhesive tapes. The TiO$_2$ paste was spread by doctor blade method on the BL coated FTO and calcined at 500 °C for 30 min resulting in TiO$_2$ film of thickness ~10 µm. The counter electrode (CE) was prepared by spin–coating of H$_2$PcCl$_6$ solution on an FTO glass followed by calcination at 500 °C for 30 min.

The prepared perovskite solution was spin–coated on the TiO$_2$ layer followed by heating at 70 °C for 30 min on a hot plate. For the preparation of HTM, 0.72 g of green colored
NiO powder was mixed with 2 mL of 6% HCl and subjected to constant stirring at 90 °C for 10 min.\textsuperscript{[30]} After spin coating at a speed of ~1500 rpm for 60 s the substrate was heated at 100 °C for 10 min.\textsuperscript{[31,32]} A thin layer of PEO polymer electrolyte was coated over the NiO film. The Pt CE was finally sandwiched over the electrolyte coated WE. The final architecture of the prepared PSC was FTO/BL/TiO\textsubscript{2}/Perovskite/NiO/PEO/Pt/FTO.

3. Results and discussion
The details of characterization techniques used is given in supplementary information.

3.1 Scanning Electron Microscopy (SEM)
Fig. 1 demonstrates the SEM image of MAPbI\textsubscript{3} film, which depicts islands of well–defined flowery rod like structures illustrating the crystalline nature of the sample. The rod shaped structures of MAPbI\textsubscript{3} are favourable for efficient charge transfer applications and act as better light harvesters as these rods not only absorb a portion of the wave incident directly on it but also the surrounding ones.\textsuperscript{[33-35]} On further magnification, it is observed that these rods have porous surface, which allows the HTM solution to properly seep into the perovskite layer, thus creating better interface for charge transfer through the HTM.

Fig. 2 illustrates the surface morphology of NiO, whereby the presence of non-uniform particles of different sizes can be observed (Fig. 2(a)). Further magnification (Figs. 2(b) and (c)) reveals the agglomeration of particles with distinctly visible cracks. The agglomeration of particles tends to the formation of granules, which possess challenge in the uniform deposition of the NiO solution on the perovskite layer. Consequently, this affects the formation of proper interface between perovskite and NiO.

3.2 Atomic Force Microscopy (AFM)
The subsequent layers of the WE may have varying surface roughness as well as porosity. The surface roughness of any layer is determined by the \( R_{\text{rms}} \) value, i.e., root mean square value of roughness. \( R_{\text{rms}} \) is obtained by the standard deviation of data from AFM images. The formula for \( R_{\text{rms}} \) is given by,

\[
R_{\text{rms}} = \sqrt{\frac{1}{N-1} \sum_{n=1}^{N} (z_n - \bar{z})^2}
\]

where, \( z_n \) is the height of the \( n \)th AFM data and \( \bar{z} \) represents the mean value of \( z_n \) of the AFM images, while \( N \) represents the number of AFM data. In this study, all the measurements have been performed over films coated on FTO substrate.

Figs. 3 and 4 represents the 3D AFM images of FTO coated with TiO\textsubscript{2} and FTO coated with TiO\textsubscript{2}/perovskite layer, respectively. Figs. 3(a) and 3(b) shows wide range of high intensity peaks and also the highly porous nature of the TiO\textsubscript{2} layer. When MAPbI\textsubscript{3} layer is spin coated on TiO\textsubscript{2} (Fig. 4), the surface roughness decreases from 13.9 nm to 10.7 nm, which suggests the proper coverage of perovskite material over the TiO\textsubscript{2} surface. A reduction in the high intensity peaks is also seen in Fig. 4. Further, the pores (black regions) in TiO\textsubscript{2} (Fig. 3b) almost vanished upon perovskite coating (Fig. 4b). Thus, the study of variation in the surface morphology of TiO\textsubscript{2} and the perovskite layer in terms of roughness also concludes that perovskite is properly adsorbed on to the TiO\textsubscript{2} layer.
3.3 Energy Dispersive X–Ray (EDX)

The EDX microanalysis technique determines the elemental composition of a compound by electron microscopy based on the generation of characteristic x–ray. As a result, it also helps to analyze the purity of a synthesized sample or compound. The elemental analysis of the synthesized perovskite is depicted in Fig. S2 (supplementary information), which clearly shows the absence of any foreign elements, thereby affirming the purity of the prepared material. The atomic weight percentage of the elements is given in the Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>At. No.</th>
<th>Series</th>
<th>Norm. C [wt.%]</th>
<th>Atom. C [at%]</th>
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<tbody>
<tr>
<td>Pb</td>
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<td>M-series</td>
<td>53.77</td>
<td>33.32</td>
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<tr>
<td>I</td>
<td>53</td>
<td>L-series</td>
<td>44.06</td>
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<tr>
<td>C</td>
<td>6</td>
<td>K-series</td>
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<tr>
<td>N</td>
<td>7</td>
<td>K-series</td>
<td>0.67</td>
<td>6.18</td>
</tr>
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</table>

Fig. S3 (supplementary information) shows the presence of elements Nickel (Ni) and oxygen (O) with the atomic weight percent as given in the Table 2. This confirms that the sol–gel method used for the preparation of NiO is effective. A small percentage of impurity in the form of Carbon is also present, which could have appeared during sample loading.

3.4. X-ray Diffraction (XRD) Studies

The obtained XRD pattern of MAPbI₃ is depicted in Fig. 5. The crystallite size was calculated by using Debye-Scherrer’s formula, which is given by the following equation.

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

where k is an empirical constant equal to 0.9, \( \lambda \) is the wavelength of x–ray source = 1.5405 Å, \( \beta \) is the full width at half maximum (FWHM) of the diffraction peak, and \( \theta \) is the angular position of the peak. The calculated crystallite size from the XRD pattern is 45.82 nm, which indicates the formation of MAPbI₃ nanoparticles. The XRD pattern of the perovskite material shows peaks at 13.26°, 20.56°, 29.03°, 32.45°, 39.25°, 41.02°, and 52.91° which is in close agreement with the peaks reported earlier.\(^{[36]}\) The 2\( \theta \) values correspond to (100), (110), (200), (210), (310), (330), and (004), respectively, which is indicative of cubic structured MAPbI₃. However, it also suggests the phase transition of perovskite material from...
Fig. 4 3D AFM image of perovskite layer at an average width of (a) 1 µm and (b) 5 µm.

The XRD pattern of MAPbI₃ will have a tetragonal to cubic crystal structure which occurs at a temperature of ~ 67 °C. The hump from 20° to 35° along with the unmarked peaks are attributed to the presence of amorphous SiO₂ (glass slide).

The XRD pattern of powdered NiO is presented in Fig. 6. As observed, the three major peaks are observed at 2θ = 38°, 43°, and 62° which is in good agreement with the JCPDS data (JCPDS card No. 22–1189). The corresponding miller indices for the aforementioned peaks are (111), (200), and (220), respectively. The obtained pattern is further indicative of the crystalline nature of the HTM.

3.5 SEM analysis of PSC
Fig. 7(a) represents the porous TiO₂ coating on FTO. Owing to the mesoporous nature of TiO₂, the pores are not visible in the SEM image. From Fig. 7(b) it is clear that the surface morphology changes upon spin coating of perovskite onto TiO₂. Tiny island type structures of perovskite can be seen in the image, which resembles the SEM image of only perovskite material (Fig. 1) thereby further confirming that perovskite has covered the TiO₂ in entirety. The rod type structure formation should help in better trapping of photons as well as facilitate efficient charge transfer. The perovskite layer is followed by drop–casting the NiO solution. From the SEM analysis of the NiO layer (Fig. 7(c)) it is clear that it consists of highly aggregated spherical particles, which offers better surface area. Further, it can be observed that NiO covers the perovskite layer perfectly with minute cracks.
The cross-sectional view of the WE of the fabricated PSC is shown in Fig. 8. This image represents the successful fabrication of different layers of PSC, i.e., TiO₂ which acts as electron transport layer (ETL), perovskite as the sensitizer and NiO playing the role of HTL, thus achieving a well-formed hetero-junction structure of PSC. However, it should be noted that apart from the TiO₂ layer, the thickness of perovskite and NiO are much greater than the optimum one. For instance, the reported ideal thickness for perovskite layer is 200 – 400 nm and that of the HTL is < 180 nm. Since, no sophisticated tools were used, controlling the thickness of sensitizer and NiO deposition was not possible.

3.6 Photovoltaic performance
The obtained characteristic of the PSC with an active area of 0.40 cm² is shown in Fig. 9. An above average V_{oc} of 0.77 V was obtained with a decently high J_{sc} of 18 mA/cm². However, the J–V curve did not have the ideal rectangular shape, hence a low FF of 0.37 was obtained. The low value of FF indicates non-uniform formation of the different semi-conductor layers, high interface impedance (as observed in impedance curve, Fig. 11), and recombination losses. The non-uniform formation of the functional layers is attributed to the use of spin-coating technique, which although being cost-effective but probably not suitable for PSC. The calculated PCE in room ambient condition was 5.13%.

The absorption of photons in the active layer of perovskite leads to the generation of electron hole pair. The excited electrons move to the conduction band (CB) of TiO₂ leaving behind hole in the valence band (VB) of the perovskite. The fermi level of TiO₂ increases as the excited electrons from CB of MAPbI₃ moves to the CB of TiO₂ while hole moves towards the VB of NiO (HTM), which is a wideband gap material. The CB of NiO lies at approximately -2.2 eV, which is much higher than the CB of MAPbI₃, i.e., -3.9 eV. Therefore, the injection of electrons from CB of MAPbI₃ into CB of NiO is not energetically favorable, which suggests that HTM also acts as an electron blocking layer. The addition of polymer electrolyte after the HTM layer improves the contact between the sandwiched electrodes, thereby helping in efficient charge transfer through the redox couple (I₃⁻/I⁻). The redox couple acts as a shuttle to carry the electrons, thus regenerating the HTM as well as the perovskite sensitizer. The schematic diagram of the entire process with energy band levels as given in literature, is shown in Fig. 10.

As evident from the previous results, the use of only polymer electrolyte leads to poor efficiency (0.9%). However with the addition of NiO as HTM between the electrolyte and perovskite, the characteristics improves drastically. This is evident from the rise in efficiency to 5.13% from 0.9%.

3.7 Impedance Spectroscopy
The obtained impedance graph was subjected to curve fitting (Fig. 11) where R_s is the series resistance comprising of the
wires, FTOs and clips; $R_t$ is the resistance at the junction between WE (blocking layer to dye) and electrolyte while $R_e$ is the resistance at the junction between electrolyte and CE.\(^{[46]}\)

The equivalent circuit is shown in the inset of Fig. 11.

The inset of Fig. 11 also presents the expanded initial region of impedance where the initial high frequency impedance is shifted from zero. This shift of 18 $\Omega$ accounts for the value of $R_e$. The first partially formed semi-circle gives the value of $R_e$ which stands at 24.36 $\Omega$. The low value of junction resistance between electrolyte and CE suggests smooth interface between the two. The value of $R_t$ is rather high, 2211.26 $\Omega$ which is expected owing to the use of the polymer electrolyte.\(^{[46,47]}\) Nevertheless, the well-formed impedance pattern of the PSC shows proper junction formation and smooth charge transfer between the individual components.

4. Conclusions

The present work was focused on the fabrication of PSC in a sandwich configuration using NiO as HTM embedded with polymer electrolyte in room ambient condition. The rod type structured perovskite enabled efficient trapping of photons and generated decent photo-current. The NiO well served its role of being an efficient inorganic HTM by transporting the holes to the CE via the polymer electrolyte while also suppressing the electron recombination. The simple sandwich architecture of the PSC led to a $V_{oc}$ of 0.77 V, a $J_{sc}$ of 18 mA/cm$^2$ with an overall PCE of 5.13%. However, the obtained efficiency is low as compared to the ones mentioned in literature, which is chiefly attributed to the preparation of PSC at room ambient conditions, use of polymer electrolyte, and the utilization of low-cost techniques, such as spin-coating and doctor blading. The fabrication of PSC in laboratory ambient conditions reflects upon its low cost and its easily processable nature. The low value of FF suggests modification in the architecture of the PSC, possibly in the context of a suitable polymer electrolyte which would also help in lowering the junction resistance, thereby improving the overall photovoltaic characteristics. The study of PSC using only NiO and other HTMs are underway.

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Conflict of interest
There are no conflicts to declare.

Supporting information
Applicable.

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