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ABSTRACT
Solution processed hole transport layer based on graphene oxide (GO) and molybdenum oxide (MoO₃) composite in bulk heterojunction organic solar cell (OSC) devices offer low cost, improved performance compared to conventional organic solar cells. Here, we have made a study comparing the power conversion efficiency (PCE) of this composite to the pristine GO and MoO₃ as a hole transport layer in the organic photovoltaics. The devices with the composite shows optimized performance with PCE of ∼ 5.1%, while the pristine GO and MoO₃ display 1.59% and 2.5%, respectively. These differences are attributed to the lower short circuit current (J_{sc}) and thereby lower fill factor (FF) with respect to the GO and MoO₃. Nevertheless, the composite based devices exhibits improved optical absorption and photoluminescence quenching as compared to pristine interface layer. This study intends to highlight efficient modulation of the interface barrier of hole transport layer which allow us to give faster transport and extraction of the charge carrier efficiently at the electrodes.

INTRODUCTION
Organic photovoltaics (OPVs) have attracted attention due to their low cost, easy synthetic processes and roll to roll fabrication techniques. The power conversion efficiency of OPVs for single junction is as high as 14% and for tandem solar cells it is ~17.3%, respectively. The performance of the device depends on several factors such as the photoactive materials, device architecture, morphology formed between donor and acceptor materials and interfacial layers (IFs). Several theoretical studies have been carried out for understanding and improving the performance of OSCs. The hole transporting layer (HTL) and electron transporting layer (ETL) are utilized in the device architecture to optimize the energy level tuning at the electrode/active layer interface for better extraction of charge carriers. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is considered as the ideal HTL in the conventional device structure of OPVs due to its matching work function with many photoactive materials. However, the hygroscopic and acidic nature causes the degradation in the devices, thus limiting its uses. Numerous efforts are being done to develop new ILs utilizing transition metal oxides with high work function and good stability.
The solution processable molybdenum oxide (MoO$_{3-x}$) is a promising material due to its high conductivity, mobility, work function and better stability. MoO$_{3-x}$ and hydrogen molybdenum bronzes have been reported as good HTLs for OPVs respectively. However, thermal annealing up to 190 °C is required for these HTLs, is not feasible for flexible substrates. Alternatively, MoO$_{3-x}$ could be relevant for the hole extraction as the barrier for hole at the ITO/HTL interface is lower due to its high work function. Molybdenum disulphide (MoS$_2$) and exfoliated MoO$_2$ nanosheets are also reported as an efficient HTLs in OPVs. The oxygen vacancies in the MoO$_3$ nanosheets provides enhanced electronic properties due to its high charge carrier mobility of ~1100 cm$^2$ V$^{-1}$ s$^{-1}$.

The two-dimensional nanomaterials which includes graphene oxide (GO) and reduced graphene oxide (rGO) have also been reported as HTLs in OPVs. The mechanical robustness, flexibility and tuneable chemical, electrical and optical properties make their effective use in OPVs. The nanoscale domains of the sp$^2$ hybridized carbon which are interrupted by the lattice defects and sp$^3$ functionalized oxygen containing groups proves its versatility in various applications.  

Due to this structure, GOs are used for the chemical interfacing and the covalent attachment of different functional moieties for its variable applications in sensing, drug delivery and development of composite materials apart from the most discussed OPVs. Although, the pristine GOs are electrically insulating but the reduced GOs (by removing the oxygen containing functional groups) is reported as the conducting material with 3112 S/cm as its reported conductivity. Also, GO is optically transparent and possess fluorescent behaviour.

Keeping in mind the potential of pristine GO and MoO$_2$ as the HTL in OPVs, the combination as a composite of these materials has been utilised in these investigations which provide enhanced optical and electrical properties. Therefore, the detailed understanding of how the GO-MoO$_2$ composite improves the charge collection by better interaction between HTL and active layer interface is discussed. Herein, we report the solution processable GO-MoO$_2$ composite for PCDTBT:PC$_{70}$BM based solar cells. The systematic study of the composite layer by comparing with the pristine materials as HTL in the device will provide an insight into the further improvement of this class of HTLs and its functionality as well as improving further the performance of OSCs.

**EXPERIMENTAL METHODS**

**Materials**

All the chemicals used in the synthesis have been purchased from commercial sources and were used as received without any further purification. Poly [N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’ benzothiazidazole)] (PCDTBT) and [6,6]-Phenyl-C$_71$-butyric acid methyl ester (PC$_{71}$BM) were purchased from 1-AMmonium. Molybdenum molybdate tetra hydrate [(NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O] and graphite flakes were obtained from Sigma Aldrich.

**Methods**

**Preparation of graphene oxide (GO)**

The graphene oxide (GO) is prepared according to modified Hummers method. In the synthesis 1 g graphite powder is added into 100 ml conc. H$_2$SO$_4$ and H$_3$PO$_4$ (90:10 ml) solution and stirred for uniform dispersion. Then, 3 g of KMnO$_4$ has been slowly added to above solution maintaining the temperature below 20 °C using an ice bath. This solution is then kept at 40 °C for 2 hr. 100 ml distilled water has been slowly added to this solution under continuous stirring maintaining temperature below 90 °C. Subsequently, 120 ml of water and 15 ml H$_2$O$_2$ (30%) have been simultaneously added under stirring for the reduction of permanganate and manganese dioxide. This changes the brownish color of solution to greenish-yellow. The solution is then filtered and washed with 1:10 HCl (aq). The residue is dried to obtain the powder and dispersed in 200 ml distilled water for 15 days dialysis to remove metallic species, changing the water twice in a run. The dialyzed solution has been diluted to 400 ml and stirred overnight for uniform mixing. The solution is sonicated for 10 min to exfoliate the graphite oxide layers. The graphite which was not exfoliated has been removed through centrifugation at 3000 rpm for 40 min and exfoliated graphite oxide received as supernatant is called as graphene oxide (GO). GO solution with the concentration of 1mg/ml with NMP solvent is stirred for 2 hr and then sonicated for 5 hr constantly. After successful dispersion of GO into NMP it is then centrifuged at 5000 rpm for 5 minutes and unruffled supernatant as GO solution is used further.

**Preparation of MoO$_2$ solution**

The concentration of moly solution (s-MoOx) is done by adding 40 mg of ammonium molybdate tetra hydrate [(NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O] in 1 ml of distilled water with continuous stirring at 80 °C for 1 hr.

**Preparation of GO: MoO$_2$ nanocomposite**

The composite of GO:MoO$_2$ is prepared by mixing GO and MoO$_2$ solution in the ratio of 1:1 and stirred for 2 hr followed by ~5 h of continuous sonication. The as-prepared mixture solution was used after 24 hrs of stabilization.

**Characterization**

The absorption and transmittance spectra were measured on Shimadzu 2401 PC. The Raman spectra was measured on a HORIBA T64000 with 514 nm laser source. X-ray diffraction (XRD) was recorded by using Reaku X-ray diffractometer equipped with CuKa (1.54Å). AFM images were obtained by using Nano First-3100 in a tapping mode. TEM images were obtained from FEI-Tecnai F30 G2 STWIN (300kV FEG). The X-ray photoemission spectroscopy (XPS) measurements were performed by using an Omicron μ-metal ultra-high vacuum (UHV) system equipped with a monochromatic Al K$_\alpha$ X-ray source (hv=1486.7 eV) and a multi-channeltron hemispherical electron energy analyzer (EA 125). The photoemission measurements were performed inside the analysis chamber under a base vacuum of ~5.0 × 10$^{-11}$ mbar at room temperature. The samples were mounted on Indium paste to make the electrical contact between the sample and Omicron sample plate. We have also used charge neutralizer (CN10) for MoO$_2$ sample to neutralize the positive potential created by the photo-excited electron leaving from the sample surface. As MoO$_2$ sample exhibits insulating behavior this procedure helped us to avoid any significant charging. Other two samples do not show any charging behavior. The C 1s core levels were measured throughout the experiment particularly before and after each
core level spectra to guide any charging behavior during XPS measurements. The binding energy of all the spectra was corrected by using the value of 284.6 eV for the C 1s core levels. The work function of all HTL have been measured using Kelvin probe incorporated with an atomic force microscope (AFM) system (NT-MDT Solver Pro).

**Device fabrication**

Conventional Organic BHJ solar cells were fabricated on pre-cleaned ITO coated glass substrates with a sheet resistance $\sim 16 \Omega \text{ cm}^{-1}$. Each ITO coated sample used for device fabrication were first scrubbed manually with a solution of soap and de-ionized water followed by ultrasonic treatment in acetone, and isopropanol (IPA), each for 15 minutes to remove any organic impurity. Afterwards the cleaned substrates were dried in vacuum oven at 140 $^\circ C$ for 10 minutes in ambient conditions, followed by oxygen plasma treatment for 20 minutes prior to depositing any films. The substrates were then first spin-coated with three types of hole transporting layer (HTLs) on the top of the ITO film. The 2 nm of graphene oxide film in a solution of NMP spin cast at 3500 rpm for 50 s, a 8nm thick film from a solution of MoO$_3$ is spin coated at 3500rpm for 50 s and a 10 nm thick layer of nanocomposite of graphene oxide and Moly oxide (GO:MoO$_3$) was fabricated by spin coating. After being baked in air at 150 $^\circ C$ for 10 min, the substrates were then transferred inside a nitrogen glove box for the spin coating of active layer. The uniform thin film consisting of PCDTBT:PC$_{71}$BM based blend fabricated by spin-coating in a solution of ODCB at 1000 rpm for 30 s, followed by thermal annealing at 80 $^\circ C$ for 10 min leads to formation of uniform nano morphology. Finally, a 120 nm Al layer is thermally evaporated through a shadow mask as a cathode under the vacuum conditions of $2 \times 10^{-6}$ Torr with a defined active area of 4 mm$^2$.

**J-V characterization**

The measurements for power conversion efficiency (PCE) values were performed by current density-voltage ($J-V$) curves which were determined using a computer controlled Keithley 2420 source unit under AM 1.5G illumination at 100 mW cm$^{-2}$ by a solar simulator. The incident light was adjusted by using a pyranometer.

**RESULTS AND DISCUSSION**

The molecular structures of PCDTBT and PC$_{71}$BM as donor and acceptor materials used in our study and a simple schematic representation of the developed composite as HTL are shown in Figure 1. The preparation of GO, MoO$_3$ nanosheets and the composite is shown in experimental methods. The GO:MoO$_3$ composite has the characteristics of both the pristine GO and MoO$_3$. This can be indicated by the detailed investigation of its structural and morphological analysis of the composite and compared to that of the pristine GO and MoO$_3$.

**Analysis of composite and pristine materials**

To examine the structural difference in the composite, we recorded the Raman spectra for pristine GO, MoO$_3$ and GO:MoO$_3$.
composite, respectively as shown in Figure 2. In general, Raman spectra of graphite exhibits a band at 1580 cm$^{-1}$ named as “G band” and other band at 1350 cm$^{-1}$ names as “D band”. The peak at 1600 cm$^{-1}$ and 1357 cm$^{-1}$ corresponds to the G band and D band of the GO. The former is due to the first order scattering of E$_{2g}$ mode and shifted towards higher wavenumber which is due to the oxygenation of graphite. The D band in GO is broadened which was due to the reduction in size of in-plane sp$^2$ domains by the creation of defects, vacancies and distortions of the sp$^2$ domains after complete oxidation.\textsuperscript{39,40} These peaks for GO are now well confirmed by Mativesky’s group.\textsuperscript{41} The prominent peak at 159 cm$^{-1}$ originates due to the translation of rigid chains, the peak at 281 cm$^{-1}$ is due to the wagging modes of terminal oxygen atoms, peak at 662 cm$^{-1}$ is due to the asymmetric stretching of the Mo-O-Mo bridge, the 816 cm$^{-1}$ of pristine MoO$_3$ for (002) and (100), respectively. Similarly the diffraction pattern gen atoms.

These prominent peaks of pristine GO and MoO$_3$ composite confirms the composite formation with both the structures.

Then, we analyzed the XRD spectra of pristine GO, pristine MoO$_3$ and GO:MoO$_3$ composite as shown in Figure 3. The diffraction peaks for pristine GO is observed for 2$\theta$ value at 10.5 and 41.9 for (002) and (100), respectively. Similarly the diffraction pattern of pristine MoO$_3$ exhibited at 2$\theta$ values of 12.8, 23.4, 25.7, 27.45, 33.7, 35.5, 39.5, 46.2, 49.3, 52.5, 58.9, 64.6, and 67.8, for (020), (110), (040), (021), (131), (111), (150), (002), (230), (211), (081), (062), and (270) planes of orthorhombic phase. These all peaks are matched well with the GO:MoO$_3$ composite which has the characteristic of both the pristine materials. XPS measurements of GO:MoO$_3$ composite was conducted to elucidate oxidation states of molybdenum and compared with that of the pristine MoO$_3$ sample. The Mo 3d core level spectrum carries a substantial amount of physics involved in the properties of these materials. In order to investigate the oxidation state of molybdenum, we have fitted by Gaussian–Lorentzian curves to the peaks of Mo 3d core-level region, which are shown in Figure 4a. A Shirley background has been subtracted from the experimental data. The spectrum from MoO$_3$ sample consists of three pair of peaks which corresponds to the presence of three different oxidation states of molybdenum in the sample. One major pair of peaks corresponds to Mo$^{6+}$, while the two minor pair of lines provides the evidence for the presence of Mo$^{5+}$ and Mo$^{4+}$ states. Except the energy position and area, the width, line shapes and branching ratio of Mo$^{4+}$, Mo$^{5+}$, and Mo$^{6+}$ pair of peaks were kept same. The two minor pair of peaks at 229.3 and 232.5 eV corresponds to the Mo$^{4+}$ 3d$_{3/2}$ and Mo$^{5+}$ 3d$_{3/2}$, and 231.4 and 234.7 eV corresponding to Mo$^{5+}$ 3d$_{3/2}$ and Mo$^{5+}$ 3d$_{5/2}$, respectively. The one major pair peaks at 233.3 and 236.6 eV belongs to Mo$^{6+}$ 3d$_{3/2}$ and Mo$^{6+}$ 3d$_{5/2}$, respectively. The relative contents of Mo$^{6+}$, Mo$^{5+}$ and Mo$^{4+}$ oxidation states of molybdenum are around 13, 34 and 52%, respectively. This confirms the presence of oxygen vacancies in the MoO$_3$ sample. However, only one oxidation state of molybdenum in the composite sample was observed, which is fitted by using Gaussian–Lorentzian line shapes with one pair of 3d components. The binding energy peaks at 233.3 and 236.6 eV corresponds to Mo$^{6+}$ 3d$_{3/2}$ and Mo$^{5+}$ 3d$_{5/2}$, respectively. Thus, this sample has very less number of oxygen vacancies, which indicates that less number of dangling bond exits in the composite. The composite exhibits inert properties with Mo$^{5+}$ states and are thus having less number of charge trap states. The improved charge extraction capability in the HTL in composite sample was observed as MoO$_3$ in composite has negligible oxygen vacancies in the lattice.

Figure 2 shows the Raman spectra of all three samples. Intensities of all the spectra are normalized and shifted along y axis for clarity. The position of the valence band maxima is calculated to be 0.95 and 0.25 eV below Fermi level for MoO$_3$ and composite samples, respectively, indicating p-type conductivity of
the MoO₃ sample. While the GO sample shows finite intensity at the Fermi-level, depicting conducting nature of this sample.

To confirm the morphology of the GO:MoO₃ composite, we recorded the transmission electron microscopy (TEM) images as shown in Figure 5. The clear distinct images of both GO and MoO₃ from composite can be observed and look similar to those reported earlier in the literatures, confirming the formation of composite.

The morphological study of different HTL layers was investigated with Atomic force microscopy (AFM) images as shown in Figure 6. Clearly, the morphology of the GO:MoO₃ composite used as HTL layer is homogeneous and smooth with the root mean square (rms) roughness value of ~1.7 nm. The composite as the HTL layer helps in the planarization of the surface of the active layer. It is clearly established that the roughness of the composite layer is improved as compared to that of the individual layers of GO and MoO₃. The measured rms roughness of GO and MoO₃ is found to be ~1.8 and ~0.618 nm, respectively. Thus the AFM images have shown that the morphology with composite as HTL layer is better compared with the pristine GO and MoO₃. This will be well correlated with the photovoltaic parameters.

**Photovoltaic characterization**

Figure 7a and 7b show the illuminated current density-voltage plots and corresponding band alignment diagram for the fabricated PCDTBT:PC₇₀BM bulk heterojunction devices with pristine GO (-5.09 eV), pristine MoO₃ (-5.2 eV) and GO:MoO₃ (-5.3 eV) composite as HTL, respectively which are similar to the reported values. The photovoltaic parameters obtained from the devices are summarized in Table I which indicate that by introducing GO:MoO₃ composite as the interfacial layer it significantly increases the device efficiency compared to pristine GO and MoO₃ due to improvement in work function and smoothness. The improvement in the work function causes proper alignment between HOMO (highest occupied molecular orbital) of donor and the HTL layer (marked in red in Figure 7b) influencing better hole transport. The composite layer as HTL exhibited enhanced device performance of 4.11% with short circuit current density ($J_{SC}$) of 14.71 mA cm⁻², an open circuit voltage ($V_{OC}$) of 0.63 V and a fill factor (FF) of 44.00% compared to the pristine GO which yields PCE of ~1.59% with $J_{SC}$, $V_{OC}$ and FF of ~8.86 mA cm⁻², ~0.52 V and ~34.40% respectively and the pristine MoO₃ which yields PCE of ~2.58% with $J_{SC}$, $V_{OC}$ and FF of ~10.48 mA cm⁻², ~0.65 V and ~37.80% respectively. This enhanced performance is attributed to the lowest gap between HOMO level of PCDTBT (-5.45 eV) and composite work function (-5.3 eV) which increase the probability of collection of charges at ITO ultimately improved $J_{SC}$ and FF. The fabricated device with GO as a HTL shows poor performance; primarily as a result of low $J_{SC}$ and $V_{OC}$. The MoO₃ demonstrates slightly improved performance over the GO layer as the $J_{SC}$ and $V_{OC}$ of the MoO₃ device is higher with the improved FF. Further improvement in the device performance has been noticed with the significance improvement in $J_{SC}$ and FF when we used the GO:MoO₃ composite as a HTL. The higher FF observed here could be due to improved charge extraction, probably as a result of suitable interface barrier modulation and the better interface morphology as revealed by the AFM images. This establishes that the use of GO:MoO₃ composite as a HTL layer...
as compared to the pristine GO and MoO$_3$ for improving the efficiency of the device dominantly through improvements in $J_{SC}$ and FF, which is reflected in the improved PCE of fabricated devices. It is supported by poor shunt resistance ($R_{SH}$) and highest series resistance ($R_S$) for MoO$_3$ as compared to GO:MoO$_3$ composite. This in turn also results in better charge collection for the composite HTL. All these parameters are presented in Table I.

To give further evidence that GO:MoO$_3$ composite work as better HTL, we analyzed the dependence of leakage current density ($I_{leakage}$) on $R_{SH}$ and $R_S$ for all HTLs as given by,

$$I_{leakage} = \frac{V - (JR_S)}{R_{SH}}$$ \hspace{1cm} (1)

Here, for our devices, $R_S$ is calculated from the inverse slope of the dark current around $J$ (0 mWcm$^{-2}$, 0.8 V) and $R_{SH}$ is derived from the inverse slope around $J$ (0 mWcm$^{-2}$, 0 V). From Figure 7c, it is observed that the highest leakage current is seen for GO followed by MoO$_3$ and GO:MoO$_3$ composite (indicated by the direction of arrow). This is due to lowest $R_{SH}$ in the same order giving the evidence that GO is not the proper HTL for this system. Further, the large value of $R_S$ for MoO$_3$ suggests higher $J^2R_S$ loss which affects the performance of fabricated solar cell using MoO$_3$ as HTL. The variation in the leakage current density is affected by many parameters such as cleaning of substrates, thickness of each layer, types of transport layer and deposition techniques. In our case, pristine GO/MoO$_3$ have different degree of diffusion with respect

![FIG. 6](image-url) Atomic force microscopic (AFM) images of (a) Pristine GO, (b) pristine MoO$_3$ and (c) GO:MoO$_3$ composite thin films spin coated at 3500 rpm on ITO substrates.

![FIG. 7](image-url) (a) J-V characteristics of PCDTBT: PC$_{71}$BM photovoltaic devices with different HTLs, (b) Band diagram of conventional device architecture with their corresponding values of work function measured from Kelvin probe experiment and (c) Plot of leakage current density with corresponding voltage.
TABLE I. Summary of Photovoltaic parameters for fabricated OPVs. Here, $R_S$ and $R_{SH}$ calculated for light J-V curves.

| HTL         | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF (%) | PCE (%) | $R_S$ (Ω cm$^{-2}$) | $R_{SH}$ (Ω cm$^{-2}$) |
|-------------|-----------------------|--------------|--------|---------|---------------------|------------------------|
| GO          | 8.86                  | 0.52         | 34.40  | 1.59    | 16.92               | 91.74                  |
| MoO$_3$     | 10.48                 | 0.65         | 37.80  | 2.58    | 37.55               | 292.39                 |
| GO:MoO$_3^a$| 14.0±1.5             | 0.64±0.2     | 43.4±1.8 | 4.0±1.8 | 16.4±2.2           | 315±25                 |

$^a$represents data for five devices.

To composite film of GO:MoO$_3$ which plays a crucial role in the charge transport from active layer to respective electrodes and hence in the improvement of device parameters. This discussion provide strong evidence that fewer leakage current pathways are generated and fewer interfacial traps suppresses carrier recombination in the composite interlayer, accounting for the enhancement in the FF (see Table I).

To gain additional insight into the improved performance of PCDTBT:PC$_{71}$BM photovoltaic devices with GO:MoO$_3$ composite as the HTL, we optimized the fabricated devices by systematic variation in the spin coating frequency as shown by the dark and light J-V curves in Figure 8a and 8b. Table II shows the photovoltaic performance parameters for PCDTBT:PC$_{71}$BM devices with composite as HTL at different spin frequency of 3500, 4000, 4500 and 5000 rpm. It can be observed that the highest PCE obtained at 4500 rpm with best $J_{SC}$ and $V_{OC}$ among the all. Also, we analyze that the thickness of HTL layer plays an important role on the resistive parameters. At lower spin rate (3500 rpm) and at highest spin rate (5000 rpm), the value of $R_S$ is very high and value of $R_{SH}$ is very low. Thus, apart from the losses within the active layer (geminate/non-geminate recombination) the poor charge collection at active layer/HTL also influences the reduced performance.

 Optical analysis

To further evaluate the function of GO:MoO$_3$ composite as HTL layer, we have measured the transmittance to determine the overall performance of organic solar cells (OSCs). From Figure 9a, it can be clearly observed that the composite shows broader transmittance range towards the UV region as compared with that of the pristine GO and MoO$_3$, indicating the absorbed photons by both PCBM and PCDTBT can generate charges which can be transferred by the respective HTL and ETL layers. The increase in the transmittance can substantially affects the photocurrent generated in the device. The PCE can be effectively increased with the increase in the transmittance. This is well correlated with the photovoltaic performance of PCDTBT:PC$_{71}$BM solar cells with composite as the HTL layer as explained in the above section.

**FIG. 8**. J-V characteristics of PCDTBT:PC$_{71}$BM photovoltaic devices with GO:MoO$_3$ composite as HTL at different spin frequency for (a) dark and (b) light.
the interface, the photoluminescence (PL) measurement was undertaken. Figure 10 depicts the PL spectra of PCDTBT:PC71BM with all the three HTLs. The quenching of PL in the composite film used as HTL layer was more pronounced compared to the GO and MoO3 pristine which indicates effective charge transfer from PCDTBT:PC71BM to the HTL films. Improvement in the quenching of PL represents absorption of higher photoinduced carriers which are converted into excitons. Thus, the PL quenching in the composite is in accordance with the device performance.

To get more insight into the interface charge recombination, we fitted J-V curves using equation 2 given by Neher et al.,

\[ J = J_0 \left\{ \exp \left( \frac{q(V - V_{OC})}{1 + a} k_BT \right) - 1 \right\} \] (2)

Where, \( J_0 \) is photogenerated current density, \( k_B \) represents Boltzmann constant, \( T \) represents temperature, \( q \) is the elementary charge and \( a \) is dimensionless recombination parameter defined as,

\[ a = \frac{J_0 L}{2k_B T \mu_{eff} N_i} \exp \left( - \frac{q V_{OC}}{2 k_B T} \right) \] (3)

Where, \( \mu_{eff} \) represents the effective carrier mobility of charge carriers, \( L \) represents the active layer thickness and \( N_i \) represents the intrinsic charge carrier density.

By knowing this value of \( a \), we can directly calculate charge collection probability \( P \) using following relation by Chauhan et al.,

\[ P = \frac{1}{1 + \left( \frac{2 V_{OC}}{V_L} \right)^2} \] (4)

This equation was derived using the relationship between \( a \) and \( \theta \) \[ \theta = \left( \frac{2 V_{OC}}{V_L} \right)^2 \] because \( \theta \) is the ratio of recombination (\( k_r \)) to extraction rate (\( k_e \)) and as per the charge carrier dissociation probability model given as \( P = k_e + k_r \).

Using Equation 2, all experimental J-V curves have been fitted for the particular value of \( a \) as shown in Figure 11a. An agreement was observed for all the J-V curves using all three HTLs. A decreased value of \( a \) is observed with the increased value of FF under the influence of decreasing recombination rate and change in recombination processes respectively. For the lower \( a \) value (8.6) of composite, the highest value of FF (44.13%) is achieved and for higher value of \( a \) (12.8) of GO, the lowest value of FF (34.4%) is obtained. This indicates that a comparatively higher FF can be maintained for composite due to higher charge collection probability (67.18%) as shown in Figure 11b (Calculated using Equation 4). This finding makes it possible to predict the effect of interface layer on FF which is directly explain the device performance.

Finally, the improvement in the hole transport property of composite is studied by measuring the hole mobility of the device. Hole-only devices with the device configuration of ITO/HTL/PCDTBT/HTL/Al were fabricated for measuring \( \mu_h \) from the J-V curves shown in Fig. 7a using space charge limited current (SCLC) method. The \( \mu_h \) value is calculated from the Mott–Gurney equation,

\[ J_{SCLC} = \frac{9}{8} e \varepsilon_0 \varepsilon_r \mu_h \left( \frac{V^2}{L^3} \right) \] (5)

where, \( J_{SCLC} \) represents current density, \( \varepsilon_r \) represents the relative dielectric constant of the blend (assuming 3.5), \( \varepsilon_0 \) is the permittivity of the free space (8.85 × 10⁻¹² CV⁻¹s⁻¹). The measured \( \mu_h \) values are

| Spin frequency (rpm) | JSC (mA/cm²) | VOC (V) | FF (%) | PCE (%) | Rs (Ω cm²) | Rsh (Ω cm²) |
|----------------------|--------------|---------|--------|---------|------------|------------|
| 3500                 | 14.71        | 0.63    | 44.13  | 4.11    | 16.64      | 325.70     |
| 4000                 | 13.65        | 0.66    | 49.44  | 4.52    | 3.99       | 492.60     |
| 4500                 | 16.16        | 0.66    | 47.11  | 5.10    | 4.30       | 555.50     |
| 5000                 | 9.78         | 0.68    | 21.95  | 1.47    | 164.50     | 120.79     |

FIG. 9. (a) Transmittance and (b) Absorption spectra of pristine GO, MoO3, and GO:MoO3 composite with the ITO/HTL/PCDTBT:PC71BM (~90 nm) bulk heterojunction.
listed in Figure 12. For the PCDTBT system, the calculated \( \mu_h \) value of composite based device is \( 3.2 \times 10^{-5} \, \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \), which is higher than those of GO based (\( 1.05 \times 10^{-5} \, \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \)) and MoO3 based devices (\( 1.9 \times 10^{-5} \, \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \)). The trend of the mobility curve is comparable with the reported article.\(^5\) The enhanced mobility in the composite device will facilitate the faster collection of holes at anode which will improve \( J_{SC} \). Hence, the enhanced \( J_{SC} \) has been attributed to the better mobility. The increase in current can be attributed to the better charge transport with improved FF and acceptable \( V_{OC} \) with the overall increase in efficiency of composite based OSCs.

CONCLUSION

In conclusion, the solution processed GO:MoO3 composite has been used as HTLs in OPVs and its performance is compared with pristine GO and MoO3. The structural, morphological and optical analysis of the synthesized composite is thoroughly characterized with the state-of-the-art techniques. The performance of pristine MoO3 is better than pristine GO HTL based solar cells. However, when we use GO and MoO3 as composite HTL, it forms a favourable energy level gradient with HOMO of PCDTBT for efficient and fast hole extraction and transport. Furthermore, it provides a better smoothness of the surface. The PCE in these devices improves from \(~1.5\) and \~2.58\% to \~5.1\% due to incorporation of the composite HTL. This has dominantly been attributed to the suitable modulation of the interface barrier at HTL and active layer which results in faster transport and extraction of the charge carriers at the electrode.
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There are no conflicts to declare.

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