Investigation of improvement in stability and power conversion efficiency of organic solar cells fabricated by incorporating carbon nanostructures in device architecture

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Abstract
Carbon nanotubes (CNTs) along with reduced graphene oxide (RGO) are synthesized using modest methods and their composites with the polymers PEDOT:PSS and P3HT are prepared using an easy solution method. An attractive improvement in the composites’ physical properties with wt% increase of the filler material is observed, encouraging their applications in the fabrication of organic solar cells (OSCs). Using the composites in appropriate layers of the device architecture, OSCs have been fabricated by spin coating, and the incorporation of filler CNTs and RGO has been observed to result in considerable improvement in the power conversion efficiency (PCE) of all OSCs. To study the stability of the devices, the electrical properties of the OSCs have been periodically investigated in two different environments to understand the impact of both intrinsic and extrinsic degradation. The incorporation of filler carbon nanomaterials has been noticed to be successful in significantly prolonging the stability of the OSCs while maintaining the augmentation in PCE. For the best performing devices, the incorporation of CNTs and RGO has enhanced the PCE by 12.52% and 13.21% and improved the device lifetime by 37.31% and 43.23%, respectively, compared to the reference device. The results discussed in this report are greatly promising for the large scale consideration of a pioneering role of organic materials in numerous optoelectronic devices from a new and innovative perception assisted by the application of carbon-based nanomaterials.

1. Introduction

Humanity is now facing the grievous impact of energy deficiency which is going to become a critical threat if the quest for superior methods to employ renewable energy is not efficiently intensified. In this context, being extremely abundant, economically accessible, sustainable, and nondestructive, solar energy stands with its comparatively unparalleled advantages as the best preference compared to all the other available options of energy resources. Among the various promising photovoltaic technologies, the third generation-belonging organic solar cells (OSCs) have acquired a flourishing interest of the scientific research community because they are non-toxic, inexpensive, flexible, light weighted, and practically applicable by being fabricated through simple techniques devouring less energy, hence showing a great potential for developing an ecologically benign energy technology [1,2]. However, owing to their comparatively lower power conversion efficiency (PCE) than the other generations of photovoltaic technologies, and even more importantly, due to the material degradation that results in their limited stability, the OSCs are still unable to acquire a reverent position among their competitors to rule the global markets through a solid commercial establishment [3–6].

The factors which decide the worth of a photovoltaic technology are the PCE, lifetime, and the total cost of the device construction and preservation, which in turn depend on the cell architecture, nature of device...
materials, and the environmental conditions under which the device is performing. Among the simplest configurations adopted for the fabrication of OSCs, perhaps the best approach is the bulk heterojunction (BHJ) concept, which involves an intimate mixture of donor and acceptor materials that not only facilitates multiplicity of domains with large surface area of donor/acceptor interfaces for significant dissociation of charge carriers, but also removes the requirement of long diffusion lengths for the excitons [7–9]. However, the efficiency of such BHJ OSC is severely restricted by factors such as necessity of lot of energy for the dissociation of strongly bound Frenkel excitons, declination of lifetime of charge carriers due to recombinations, defects in active layer, discontinuous pathways, remote domains, presence of charge carrier traps, and limited charge mobility owing to the hopping transport mechanism. Moreover, the intrinsic degradation due to inter diffusion and decomposition of OSC materials, along with the extrinsic degradation due to the reactions caused by atmospheric oxygen, water, and also illumination, all occurring at different rates and at different locations of the device also contribute to the serious deterioration of the OSC performance and stability [10–12]. Hence, to advance the performance of the OSCs, the device architecture needs to be modified in order to prevent the recombination of charge carriers by providing continuous pathways for their active participation to enhance the device performance, and to slow down the rate of material degradation for providing better stability to the device.

The prominent applications of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as charge transport layer and, poly[3-hexylthiophene-2,5-diyl] (P3HT) in the active layer for the fabrication of BHJ OSCs have already been well reported [13, 14]. PEDOT:PSS is a conducting polymer with highly notable physical properties like smooth surface morphology, low cost, solution processability, transparency, light weight, high work function, electrochemical stability etc supporting for its applications in electrode layer. Though PEDOT:PSS films are generally used as hole transporting layer (HTL) in OSCs, they suffer due to their extreme hygroscopic nature and acidity, along with a substantial compromise in their conductivity due to the presence of PSS counter anion which is nonconductive in nature [15, 16]. On the other hand, P3HT is a p-type semiconducting polymer of substantial interest owing to its attractive physical properties like high absorption in visible range, greatly delocalized system of π-electrons along the conjugated backbone and remarkable solubility in organic solvents [17–19]. However, in OSCs fabricated using the P3HT, a significant amount of free energy is lost for the exciton dissociation into separate charge carriers. Many other aspects like structural traps, remote domains, and disjointed pathways in the active layer also play a significant role resulting in inefficient charge transport and cause a lower device PCE. In this regard, owing to their extraordinary electrical mobility, outstanding conductivity, ballistic charge transportation ability, anisotropy, chemical and thermal stability, low reflectance, high mechanical strength and extremely large specific surface area, carbon nanostructures like carbon nanotubes (CNTs) and graphene can be considered as the best and most preferable choices for the purpose of incorporation in both charge transport layer and active layer to enhance the output as well as lifetime of the OSCs [20–23].

Fischer et al have discussed about the improvement in the output of flexible organic photodiode due to the electrode application of CNTs/PEDOT:PSS composite [24]. Park et al have discussed the dependence of electrical properties of CNTs/PEDOT:PSS composites on the amount of CNTs in their report [25]. On the other hand, Lee et al have described how counter electrodes of graphene dots/PEDOT:PSS composites have enhanced the PCE of Pt free solar cells [26], while the improvement in physical properties of PEDOT:PSS due to graphene incorporation was reported by Soltani-kordshuli et al [27]. The significant applications of CNTs/PEDOT:PSS and graphene/PEDOT:PSS composites in various optoelectronic devices can be found in many other reports [28–37]. To consider the applications of carbon nanostructures in the device active layer, Singh et al have shown enhancement of PCE from 1.33% to 2.71% by incorporation of CNTs in P3HT:PCBM OSC [38]. Jun et al have achieved impressive 4.39% PCE of solar cell through CNTs incorporation [39]. Liu et al have reported 1.1% PCE of a P3HT/graphene based OSC [40]. Yu et al have discoursed an escalation in the PCE of P3HT/graphene blend based OSC [41]. Robaeyts et al have demonstrated an improvement in PCE form 2.79% to 3.17% of P3HT:PCBM BHJ OSC by graphene addition [42]. Many other articles can be found that have remarkably reviewed the applications of carbon nanostructures by discussing various methods for their incorporation to not only enhance the physical properties of conducting polymers, but also to improve the performance of optoelectronic devices [43–51]. Literature discussing various mechanisms of solar cells and applications of materials to improve their performance can also be found to further enhance the knowledge in corresponding field [52–58].

However, to the best knowledge of the authors, a prominent discussion on significant applications of carbon nanostructures to improve the stability of OSCs along with a brief study on the impact of degradation in different environmental conditions are yet to be satisfactorily reported. A knowledge of feasible techniques for the optimization of the OSC fabrication to achieve better efficiency and longevity is extremely crucial to fill the emptiness in the documentation of various mechanisms governing the performance of the devices. In this background, this report not only aims in discussing the application of
reduced graphene oxide (RGO) and CNTs in improving the performance of OSCs, but also focuses on the efforts in contending against the deterioration of device stability due to intrinsic as well as additional extrinsic degradation, by subjecting the devices to dark vacuum (DV) and to open atmosphere (OA). The results briefed in this article can significantly help to construct a commercial stage for the establishment and persistence of OSCs among the well reputed generations of different photovoltaic technologies. This article also offers assistance in the development of other emerging organic optoelectronic energy systems to enable their smart and promisingly effective future applications in multidisciplinary energy sectors.

2. Materials and methods

Graphite powder (particle size <50 µm), Conc. H_2SO_4, KMnO_4, NaNO_3, H_2O_2, hydrazine hydrate, Ferrocene, Toluene, Conc. HCl, regioregular P3HT, PCBM, PEDOT:PSS (1.3 wt% in H_2O), TiO_2, and 1,2-dichlorobenzene of analytical grade have been procured commercially and used as received.

The synthesis methods of CNTs and RGO, along with the procedure followed to prepare the composites of CNTs/PEDOT:PSS and RGO/PEDOT:PSS have been already discussed in our previous report [59].

2.1. Preparation of CNTs/P3HT and RGO/P3HT composites

P3HT is mixed in 1,2-dichlorobenzene and stirred in darkness for 3 h. A separate homogenous mixture of CNTs in 1,2-dichlorobenzene has been obtained via sonication for 1 h. The CNTs/P3HT composites named CP1, CP2, CP3, CP4, and CP5 have been then prepared by mixing the CNTs dispersion with a fixed amount of P3HT solution such that the amount of CNTs present has been 1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt% of P3HT in the composite, respectively. The RGO/P3HT composites named RP1, RP2, RP3, RP4, and RP5 composites have been prepared by following the same procedure in which, RGO has been used instead of CNTs. All the composites have been then stirred for 3 h more in darkness and then sonicated for 1 h.

2.2. Fabrication of solar cells

To investigate about the effects of wt% of CNTs and RGO filler in the composite on the performance of the devices under different conditions of degradation, modest designs have been considered (as given in figure 1) to manufacture the conventional BHJ OSCs. Designs showed in figures 1(a) and (b) have been considered for learning the impact of incorporation of filler carbon materials in the charge transport layer, while designs showed in figures 1(c) and (d) have been adopted for studying the role played by CNTs and RGO in the device active layer to decide the performance of OSCs. The performance of all the OSCs has been checked using a solar simulator (which has been fitted with AM 1.5 G filter) providing 100 mW cm^{-2} irradiance. The fill factor (FF) and PCE (η) have been calculated respectively using the formulae FF = \frac{P_{max}}{P_{sc}} and \eta = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}} , where ‘P_{max}’ is the maximum power obtained, ‘I_{sc}’ is the short-circuit current density, ‘V_{oc}’ is the open-circuit voltage, and ‘P_{in}’ is the power input.

However, the improvement in the PCE alone is not sufficient to encourage the application of CNTs and RGO for the commercialization of OSCs and it is highly necessary to know how the incorporation of CNTs or RGO can be profitable in prolonging the lifetime of the OSCs devices against the intrinsic and extrinsic degradation conditions. Hence, the OSCs have been kept in DV and exposed to OA, and their electrical properties have been examined at room temperature once after every 6 h until they failed to give any output.

The deposition of HTL has been done by spin-coating PEDOT:PSS on the ITO coated glass substrate followed by annealing at 110 °C for 10 min. The same process had been followed to deposit the CNTs/PEDOT:PSS or RGO/PEDOT:PSS composites as the HTL, replacing PEDOT:PSS. To prepare the P3HT:PCBM blend active layer material, P3HT and PCBM (in 5:4 ratio) have been mixed with 1,2-dichlorobenzene and stirred in darkness for 24 h. The active layer material has been spin coated on the top of the HTL and dried, at 110 °C for 10 min. Following the same process, CNTs/P3HT and RGO/P3HT composites based OSCs have been fabricated, just by replacing P3HT with the composites CP1, CP2, CP3, CP4, CP5, RP1, RP2, RP3, RP4 and RP5. TiO_2 had been dispersed in deionized water by sonicating it for 1 h, and then it had been spin coated on the active layer and then dried at 110 °C for 10 min to serve as the electron transport layer (ETL). Deposition of Aluminum as the top electrode by thermal evaporation had finalized the device fabrication. The reference OSC showed in figure 1(a) is named as PP, the reference OSC showed in figure 1(c) is named as P3HT, and all the other composites based OSCs have been named according to the name of the composite material used for their fabrication. ETL has not been included in designs showed in figures 1(a) and (b) since the aim was to only investigate the effects of incorporation of CNTs or RGO in the HTL on the performance and the stability of the devices.
3. Results and discussion

The physical properties of CNTs, RGO, and the composites of CNTs/PEDOT:PSS and RGO/PEDOT:PSS have been discussed in our previous report [59].

3.1. Properties of CNTs/P3HT and RGO/P3HT composites

The XRD patterns of pristine P3HT and all the composites have been shown in figure 2. The characteristic peak that can be seen at around 5.66° for pristine P3HT as well as for the composite materials had resulted due to the Bragg reflection from P3HT crystallites with a-axis orientation and it represents the polymer lamellae in the (100) plane consistent to the in-plane interchain distance between the thiophene rings [60]. This characteristic peak becomes significantly noticeable due to the solvent evaporation of spin-coated thin film that allows the self-organization of P3HT and formation of polycrystalline domains and resulting in an interchain stacking. On the other hand, the (002) indexed characteristic peaks observed at around 26.8° correspond to the graphitic signature and they indicate the presence of the incorporated carbon nanostructures in the composite materials. The favorable edge-on P3HT lamellae orientation allows significant dispersion of both CNTs and RGO sheets in the P3HT, resulting in productive addition of filler materials in the polymer matrix. The non-covalent p-p stacking interaction between the P3HT backbone and the surface of the filler carbon nanomaterials causes the regioregular P3HT to form a crystalline monolayer which covers over RGO sheets and CNTs, and as the polymer wraps around them, the incorporated carbon materials modify P3HT self-assembly in their neighborhood resulting in further improvement of the crystallization.

The optical properties of a polymer depend on several aspects like its regioregularity, the degree of π-electrons delocalization, and electronic conjugation. Also, it is well known that in conjugated polymers, the absorption maximum that corresponds to the energy of the π-π* transition is directly affected by the extent of the conjugation. From the UV–visible spectra of P3HT, CNTs/P3HT, and RGO/P3HT composites shown in figure 3, we can see that the absorbance increases as the wt% of filler CNTs and RGO in the composites increases, which can be attributed to the non-covalent interaction between the polymer and filler carbon materials. The observed enhancement of absorbance can also be ascribed to the fine dispersion of CNTs and RGO sheets in the P3HT matrix which separates the agglomerated polymer chains, hence resulting in reduction in the degree of chain twists. For pristine P3HT, the maximum absorbance had been noticed at around 462 nm corresponding to the intra-chain π-π* transitions and intra-molecular ordering of electrons indicating the regioregular nature of the polymer, while the lamellar arrangement of its chains are responsible for the subsequent shoulder which can be seen at around 600 nm. A small additional rise of absorbance in the range 250 nm to 300 nm had been found in the UV–visible spectra of the composites, which can be observed getting stronger as the wt% of the filler material increases. A minor red-shift was noticed in the maximum absorbance wavelength with respect to the increase in the wt% of filler materials.
and it has been shown in the insets of corresponding figures. This shift has been primarily ascribed to the delocalization of electrons along the interconnected P3HT chains, prompted by the presence of filler carbon materials. The $\pi-\pi$ interactions between the benzene rings of filler carbon materials and the thiophene rings of P3HT, along with the CH-$\pi$ interactions initiating from the sections of the pendent polymer hexyl groups that are in the close proximity to the graphitic walls are mainly responsible for the observed red-shift of the absorption maxima \[61\]. On the other hand, unwinding of P3HT chains at the edge defects and surface imperfections of both CNTs and RGO sheets can result in a possible decrement in the torsional disorder of the polymer chains, and the increment in system conjugation \[62\].

The cyclic voltammetry data given for pristine P3HT, along with CNTs/P3HT and RGO/P3HT composites in figures 4(a) and (d) suggests that there has been a slight change in the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) levels of the composites with increment in the wt% of filler carbon nanomaterials in P3HT. The incorporation of CNTs and RGO changes the effective surface area available for the passage of charge carriers in the composites, and this is evident from the change observed in current corresponding to oxidation and reduction peaks. Figures 4(b) and (e) display the variation of oxidation potential and reduction potential with increase in wt% of incorporated carbon nanostructures in P3HT. To determine the values (in eV) of energy levels of LUMO and HOMO of the materials, the formulae $E_{\text{LUMO}} = - (E_{\text{red}} + 4.4)$ and $E_{\text{HOMO}} = - (E_{\text{ox}} + 4.4)$ have been used \[63\]. The bandgap for the materials has been calculated from the difference between their corresponding HOMO and LUMO energy levels, and the variation of bandgap of the materials with the increasing wt% of filler carbon nanomaterials has been shown in figures 4(c) and (f). In case of CNTs/P3HT composites, the direct communication of the chemically attached P3HT chains with the $\pi$-electrons density facilitating electron delocalization at the surface of CNTs is responsible for the perceived reduction of bandgap with increasing wt% of CNTs in P3HT. On the other hand, in case of RGO/P3HT composites, the extensive electron
Figure 4. (a) Cyclic voltammetry data, (b) Variation of oxidation and reduction potentials, and (c) variation of bandgap of pristine P3HT and CNTs/P3HT composites, (d) cyclic voltammetry data, (e) variation of oxidation and reduction potentials, and (f) variation of bandgap of pristine P3HT and RGO/P3HT composites.

Table 1. Initial values of parameters of reference PP OSC, CNTs/PEDOT:PSS composites and RGO/PEDOT:PSS composites based OSCs measured at room temperature.

| Device name | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (mV) | FF (%) | PCE (%) | Device name | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (mV) | FF (%) | PCE (%) |
|-------------|----------------------|--------------|--------|---------|-------------|----------------------|--------------|--------|---------|
| PP          | 10.661               | 654.93       | 52.737 | 3.682   | PP          | 10.661               | 654.93       | 52.737 | 3.682   |
| CPP1        | 10.679               | 655.115      | 52.828 | 3.696   | RPP1        | 10.681               | 655.299      | 52.829 | 3.698   |
| CPP2        | 10.708               | 655.144      | 52.853 | 3.708   | RPP2        | 10.701               | 655.395      | 52.89   | 3.71    |
| CPP3        | 10.752               | 655.712      | 52.887 | 3.729   | RPP3        | 10.744               | 655.822      | 52.906 | 3.728   |
| CPP4        | 10.786               | 656.035      | 52.86  | 3.74    | RPP4        | 10.769               | 655.999      | 52.89   | 3.736   |
| CPP5        | 10.829               | 656.21       | 52.837 | 3.755   | RPP5        | 10.798               | 656.055      | 52.834 | 3.743   |

Delocalization due to the charge transfer interaction of graphitic basal plane of RGO with the aromatic rings and end-anchored chains of the P3HT polymer causes the declination of bandgap. The decreasing trend in the bandgap of the composites is in healthy agreement with their respective UV–visible spectroscopic patterns given in figure 3, representing augmentation in the conjugation length due to the incorporation of CNTs and RGO.

3.2. Investigation of CNTs/PEDOT:PSS and RGO/PEDOT:PSS composites based OSCs

In figures 5(a) and (c), the variation of current density ($J$) with applied voltage ($V$) at room temperature for all the CNTs/PEDOT:PSS and RGO/PEDOT:PSS based OSCs can be noticed demonstrating the effects of incorporation of filler CNTs and RGO on the electrical properties of the devices, while the inset figures are given to evidently reveal the device performances at both short-circuit and open-circuit conditions. The variation of the electrical parameters with the wt% of filler carbon material is given in figures 5(b) and (d). The magnitudes of all device parameters obtained are given in table 1. It is clear from the data that the magnitude of all device parameters increases in correlation with the increase in the wt% of filler carbon material. Though an ohmic contact has been established due to the high work function of PEDOT:PSS, which enables a smooth transport of holes to the electrode from device active layer, the further observed enhancement in the values of device parameters can be attributed to the incorporation of filler carbon nanomaterials in the device HTL. The presence of CNTs or RGO results in an additional advantage by creating multiple conductive paths and gives rise to better performance of the OSCs through ensured synergistic effects with increase in wt% of FLECEG in PEDOT:PSS.

The overall performance enhancement of the devices can hence be attributed to the high mobility of filler materials resulting in considerable charge transport, and formation of interconnecting conductive percolation network by which, different domains of the active layer materials are linked to the electrodes via the bridging carbon nanostructures. However, since it is necessary to check which among CNTs and RGO are helping better for the improvement of device performance, the $J_{sc}$, $V_{oc}$, and PCE of all the devices have been
mutually compared in figure 6. In terms of $J_{sc}$ and PCE, it can be clearly observed that the OSCs fabricated using CNTs/PEDOT:PSS composites demonstrated better performance than those prepared using RGO/PEDOT:PSS composites. This can be attributed to the presence of residual functional groups in RGO that are left due to the inadequate reduction, which results in low conductivity of RGO.

The devices PP, CPP3, RPP3, CPP5, and RPP5 have been kept in DV and all the values of their device parameters attained from periodical measurements are given in ST-1 (supplementary data(https://stacks.iop.org/JPMATER/3/045004/mmedia)). From the given data, though it is evident that the PCE of all devices is declining with time, it can be noticed for devices fabricated using the composites that the rate of degradation is comparatively slower. To study the variation of stability of the OSCs under extrinsic degradation conditions, three of the selected OSCs (PP, CPP5, and RPP5) have been fabricated again and exposed to OA, and the corresponding values of device parameters obtained are given in ST-2 (supplementary data). As predicted, the extrinsic degradation caused even serious declination in the magnitudes all the device parameters with time. Also, the trend of enhancement in the magnitudes of parameters of composites based OSCs compared to the reference PP OSC device has been noticed to be consistently sustained for the OSCs (as long as they worked) due to the presence of filler carbon nanomaterials in the HTL.

The time taken for the PCE to drop to different percentages of its initial value for the OSCs under both degradation conditions has been interpolated, and the data has been given in ST-3 (supplementary information). Figure 7 compares the stability of the devices in both conditions from which it can be seen that OSCs fabricated using the composites have lasted longer by taking more time to degrade compared to the reference PP OSC. From the figure, it can be noticed that the value of $T_x$ (which is the time taken by the OSC PCE to decrease to x% of its initial value) has been more for the composites based devices compared to the reference PP OSC, which indicates that the incorporation of CNTs and RGO has been helpful throughout the lifetime of OSC to endure against the degradation effects. As a remarkable outcome, in OA, compared to the reference device, the CPP5 OSC has achieved 7.35% more lifetime while the RPP5 OSC demonstrated 5.48% more stability hence indicating the prominence of filler incorporation in device HTL.
3.3. Investigation of CNTs/P3HT and RGO/P3HT composites based OSCs

In figures 8(a) and (c), the variation of current density ($J$) with applied voltage ($V$) has been shown for all the CNTs/P3HT and RGO/P3HT composites based OSCs at room temperature signifying the effects of incorporation of filler carbon nanomaterials on the electrical properties of devices, while the inset figures are given for the evident demonstration of the device performances at both short-circuit and open-circuit conditions. The values of device parameters obtained for all OSCs are given in table 2, while they have been compared in figures 8(b) and (d) from which, the improvement in $J_{sc}$, $V_{oc}$ and PCE with increase in wt% of filler carbon nanomaterial in P3HT can be observed. The observed improvement in the performance of all OSCs fabricated using the composites suggests that the monomolecular recombination at short-circuit situation and the bimolecular recombination at open-circuit condition are successfully and considerably
Table 2. Initial values of parameters of reference P3HT OSC, CNTs/P3HT composites and RGO/P3HT composites based OSCs measured at room temperature.

| Device name | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (mV) | FF (%) | PCE (%) | Device name | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (mV) | FF (%) | PCE (%) |
|------------|----------------------|---------------|--------|---------|------------|----------------------|---------------|--------|---------|
| P3HT       | 11.399               | 664.144       | 57.132 | 4.325   | P3HT       | 11.399               | 664.144       | 57.132 | 4.325   |
| CP1        | 11.475               | 664.74        | 57.406 | 4.379   | RP1        | 11.413               | 664.558       | 58.248 | 4.418   |
| CP2        | 11.543               | 664.789       | 58.509 | 4.49    | RP2        | 11.474               | 664.137       | 59.348 | 4.523   |
| CP3        | 11.588               | 666.052       | 58.807 | 4.539   | RP3        | 11.527               | 665.873       | 59.457 | 4.564   |
| CP4        | 11.752               | 667.117       | 60.819 | 4.768   | RP4        | 11.599               | 667.018       | 61.749 | 4.777   |
| CP5        | 11.807               | 668.257       | 61.598 | 4.86    | RP5        | 11.721               | 667.985       | 62.487 | 4.892   |

Figure 8. (a) and (c) Variation of $J$ with $V$, and (b) and (d) Variation of $J_{sc}$, $V_{oc}$, and PCE for all CNTs/P3HT and RGO/P3HT composites based devices as % of their values corresponding to reference P3HT OSC as measured at room temperature.

suppressed due to the presence of CNTs or RGO in the active layer. From the curves seen in figures 8(a) and (c) it can be clearly perceived that the FF has expressively improved with increase in the filler wt%, which can be attributed to the dramatically modified optoelectronic properties of P3HT due to the incorporation of CNTs or RGO.

In OSCs, the absence of highly organized chains in the polymer materials may lead to the exciton recombination, and the defects existing can slow down the charge carrier transport, resulting in low PCE. However, the carbon nanostructures incorporated in the active layer not only increase the effective interfacial area facilitating better dissociation as well as extraction of excitons, but also act as conductive bridges providing smooth pathway for improved transport of photo-generated charge carriers through the interfaces of active layer and charge transport layer. The presence of CNTs and RGO also enables an ultrafast charge transfer process occurring in a time period that is much less than the lifetime of the singlet exciton, and provides more uninterrupted paths for the passage of charge carriers, hence enhancing the electrical output of the OSCs. In addition, the incorporated filler materials, due to their high electrical conductivity, help in both diffusion as well as drift of charge carriers, which decreases the recombination of charge carriers occurring at the hetero-interface. The OSCs are also benefited due to the presence of CNTs and RGO which facilitate in avoiding the trapping of charge carriers near the electrodes arising due to the imbalance between hole mobility of P3HT and electron mobility of PCBM resulting in a significant enhancement of device FF.
To understand the presence of which among CNTs and RGO in the active layer is more effective towards enhancing the output of the OSCs, the device parameters of all OSCs have been compared in figure 9. It can be clearly seen that CNTs have been more beneficiary compared to RGO in terms of enhancement in the device $J_{sc}$ and PCE, while the incorporation of RGO in the active layer had been noticed to comparatively more significant in improving device $V_{oc}$ than CNTs incorporation. CNTs show ballistic charge transport property owing to the high conductivity along their axis, and their extremely high aspect ratio, and hence the manifestation of CNTs in the active layer reduces the path impedance and increases the number of charge carriers passing towards the electrodes, and result in non-radiative energy transfer of singlet excitons from the photo-excited P3HT to the CNTs [20]. Multiple polymer–nanotube junctions are formed and a network of internally connected percolation pathways is created due to the addition of CNTs inside the active layer allowing for not only the dissociation, but also the significant transport of charge carriers. The conducting mesh-like network (comparable to a nest) throughout the polymer matrix bridges multiple crystalline grain boundaries and enables the charge carriers to rapidly travel across, hence improving the $J_{sc}$. On the other hand, the direct transfer of electrons from P3HT to RGO along with the giant carrier mobility of graphene is an advantage resulting in an improvement of conductivity leading to enhanced $J_{sc}$ of the OSCs. The increment in $J_{sc}$ can also be credited to the strong interaction of $\pi$-electrons on the conjugated plane of RGO and the conjugated skeleton of the polymer, which reinforces the transfer integrals and improves the charge transfer rate [42]. Also, since the graphene work function lies in between the energy levels of HOMO and LUMO of P3HT, RGO can play the role of acceptor of electrons, resulting in improved separation as well as transfer of electrons from P3HT to the RGO, hence additionally contributing to the improvement in the performance of the OSCs. Also, since it is well known that the difference in the levels of LUMO and HOMO of the donor material has a role to decide the $V_{oc}$ of the OSCs, the evident modification of bandgap of the composite material due to the variation of wt% CNTs and RGO in P3HT also explains the improvement in the PCE of OSCs fabricated using those composites in the active layer.

To understand how CNTs and RGO in the active layer significantly oppose intrinsic degradation and assist in prolonging the stability of the OSCs, all the OSCs have been kept in darkness under vacuum and their performances have been investigated through periodical measurements of device parameters in every 6 h at room temperature until they have failed to give any output. The values of all the device parameters
obtained corresponding to all the OSCs measured at room temperature in different time periods have been given in ST-4 (supplementary material). At any particular time, the devices fabricated using the carbon nanostructures based composites can be seen giving better output with higher magnitudes of device parameters as compared to the reference P3HT device. However, for any particular device, all the values of $J_{sc}$, $V_{oc}$ and FF can be seen to be declining as the time progresses, together resulting in a reduced PCE value. This is due to the molecular isolation in the active layer and large scale phase separation in the materials along with an interfacial reordering, all of which together have hindered the charge extraction and gradually reduced the number of charge carriers created. The observed declination in electrical properties with time can also be attributed to the disturbance in polymer backbone ordering due to chain scissions that disrupt the π–π-conjugation in the active layer, hence deteriorating the charge transport [64]. However, from the values of device parameters resulted, it is clear that the incorporation of CNTs as well as RGO have been fruitful in upholding the comparative enhancement of device output.

Even though the incorporation of carbon nanostructures has been observed to be productive in contending against intrinsic degradation, for practical and commercial purposes, the devices need to be tested in an even more challenging scenario presented by the severe influence of extrinsic degradation. Hence, to investigate the impact of extrinsic degradation on the stability of the devices, five of the selected OSCs (that are P3HT, CP3, RP3, CP5 and RP5 OSCs) have been manufactured again and kept wide-open to the outer atmosphere. The output values of the devices have been measured at room temperature periodically (after every 6 h) until their failure, and the corresponding magnitudes of the device parameters obtained are given in ST-5 (supplementary information). The declination in the magnitudes of device parameters had been observed to be accelerated due to extrinsic degradation caused by many major contributing reasons among which, the most important are the atmospheric oxygen and moisture. When exposed to the open air, the conjugation in P3HT gets damaged due to photosensitization, while its hexyl side chains decompose and suffer with scissions hence weakening the absorption properties of P3HT. The intercalated oxygen results in declined mobility of PCBM and escalates the quantity of charge trapping centers throughout the active layer which in turn decreases the output from the OSCs. On the other hand, the absorption of moisture from the atmosphere corrodes the top Aluminum electrode and the water gets diffused through the device layers down to the hydrophilic PEDOT:PSS resulting in formation of random insulating regions throughout the HTL, hence causing a decrease in the values of both $J_{sc}$ and FF [10]. The irradiation further intensifies the device degradation by supporting the diffusion of atmospheric components into the OSCs and results in even more reduction in the device PCE as well as lifetime. However, the incorporation of filler carbon nanomaterials can greatly assist to overcome these problems by being significantly resistent towards chemical reactions and preventing diffusion of atmospheric components into the device layers. CNTs and RGO can also modify the optical field and reduce the charge trapping by creating the interconnected conducting system throughout the active layer, which results in a comparatively enhanced performance. The filler carbon nanomaterials can also significantly adhere with the polymer enabling a high degree of charge transport and can physically quench the oxidization, ensuring the longevity of the OSCs.

To concurrently compare the impact of both intrinsic and extrinsic degradation processes on the output of the OSCs, the time taken for the PCE to drop to different percentages of its initial value for the OSCs (both when they had been kept in DV, and when they had been exposed to the OA) has been interpolated, and the data has been given in ST-6, ST-7 and ST-8 (supplementary information) and the variations have been shown in figure 10. It can be observed that under any condition, the degradation rate is comparatively lower for the OSCs fabricated using composites containing higher carbon nanomaterial concentration. Compared to the reference P3HT OSC, in DV, the best performing CNTs based device (i.e. CP5 OSC) had been observed to achieve 16.9% more stability while the best performing RGO based device (i.e. RP5 OSC) has showed 16.73% more lifetime. On the other hand, when exposed to OA, compared to P3HT OSC, CP5 OSC and RP5 OSC have demonstrated a considerable 37.31% and 43.23% higher stability respectively. Hence, though the impact of degradation has extremely declined the output of the OSCs, it can be appealed that the addition of a substantial quantity of carbon nanomaterials in the active layer not only assists in augmenting the PCE of the OSCs, but also extends the lifetime of the OSCs by improving their longevity, and the obtained results further strengthen the need for incorporation of carbon nanostructures to prolong the device endurance with sustained efficiency.

There can be many other reasons contributing to the degradation mechanisms in OSCs and many of them have been already reported by various groups that have researched on various organic materials and organic optoelectronic devices [65–69]. The list of noteworthy reasons includes clustering of the active layer materials due to spatial reorganization, photo-dimerization of PCBM, free-radical reaction due to photo-oxidation which breaks the macromolecular backbone of the polymer that in turn results in bleaching, destruction of photoactive layer morphology due to the aggregates of PCBM formed under the illumination, delamination and swelling of OSC layers by diffusion of oxygen and water etc.
PCE of magnitude better than that mentioned in this paper has already been accomplished in the field of organic photovoltaic technology by many researchers who have used complex device designs and costly fabrication techniques. However, this report adopted a simple device configuration with modest, cost effective, and environmental friendly procedure for material synthesis and device fabrication methodology, as our focus concerned about understanding the role of filler carbon materials in improving the device efficiency and stability, and as reported, encouraging outcomes have been achieved. By following similar experimental methods reported in this article, various other composite materials can be prepared by considering different combinations of many available conducting polymers and filler materials, since the results discussed in this report are useful in the development of sustainable energy conversion and energy storage systems based on organic materials. Even this research can be further extended by trying with more wt% of CNTs and RGO in the polymers to prepare composites that can serve in further improving the performance of numerous optoelectronic devices where degradation remains as a major problem. Organic photovoltaics have an undeniably dependable potential to diversify the energy technology, and we hope that this article can motivate global scientific communities for their further active contribution through multidisciplinary research in energy sector for achieving a successful and commercial establishment of OSCs to create a healthy, sustainable and environmentally benevolent future for mankind.

4. Conclusions

Following a simple solution method, composites of CNTs and RGO with PEDOT:PSS and P3HT have been prepared, and it has been observed that with increase in wt% of filler material, the physical properties of the composites have been enhanced, promising their applications in OSCs. Conventional BHJ OSCs have been fabricated by spin coating, using CNTs/PEDOT:PSS and RGO/PEDOT:PSS composites as HTL and CNTs/P3HT and RGO/P3HT composites in the active layer. The device parameters of the OSCs have been periodically measured at room temperature under DV and in OA and have been compared with those of corresponding reference devices. Improvement in the performance of all the OSCs has been noticed due to the filler incorporation, and the PCE as well as stability of the devices have been perceived to be significantly enhanced with increasing wt% of CNTs and RGO in the composites. Considering the case of incorporation

Figure 10. Comparison of stability of (a) all CNTs/P3HT and (b) RGO/P3HT composites based OSCs kept in DV, and (b) CP3, RP3, CP5 and RP5 OSCs exposed to OA with respect to reference P3HT OSC.
of filler carbon materials in the HTL, compared to the reference PP OSC, the best performing CNTs/PEDOT:PSS based OSC has achieved 7.35% improvement in stability (in OA), while the same for the best performing RGO/PEDOT:PSS OSC is found to be 5.48%. On the other hand, for the situation when the carbon nanostructures have been incorporated in the active layer, compared to the reference P3HT OSC, the best performing CNTs/P3HT based device attained 12.52% more PCE and 37.31% more stability (in OA) while the best performing RGO/P3HT based OSC demonstrated 13.21% enhancement in PCE and its lifetime (in OA) has been prolonged by 43.23%. These results undoubtedly reveal the importance of incorporating CNTs and RGO for augmented device performance and stability, encouraging their further applications in the progress of various organic optoelectronic devices to serve for the global and social sustenance.

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Conflict of interest

The authors declare no actual or potential conflict of interest including any financial and personal relationships with other people or organizations.

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