

Polymer Solar Cells Synthesized with Copper Oxide Nanoparticles

Nidal H. Abu-Zahra, Aruna P. Wanninayake

Abstract— Copper Oxide (CuO) is a p-type semiconductor with a band gap energy of 1.5 eV, this is close to the ideal energy gap of 1.4 eV required for solar cells to allow good solar spectral absorption. The inherent electrical characteristics of CuO nanoparticles make them attractive candidates for improving the performance of polymer solar cells when incorporated into the active polymer layer. The UV-visible absorption spectra and external quantum efficiency of P3HT/PC70BM solar cells containing different weight percentages of CuO nanoparticles showed a clear enhancement in the photo absorption of the active layer, this increased the power conversion efficiency of the solar cells by 24% in comparison to the reference cell. The short circuit current of the reference cell was found to be 5.234 mA/cm² and it seemed to increase to 6.484 mA/cm² in cells containing 0.6 mg of CuO NPs; in addition the fill factor increased from 61.15% to 68.0%, showing an enhancement of 11.2%. These observations suggest that the optimum concentration of CuO nanoparticles was 0.6 mg in the active layer. These significant findings can be applied to design high-efficiency polymer solar cells containing inorganic nanoparticles.

Keywords— Copper Oxide nanoparticle; UV-visible spectroscopy; Polymer Solar Cells; P3HT/PCBM.

I. INTRODUCTION

EXTRACTING photovoltaic (PV) energy from sun light is one of the most promising ways to tackle today's energy crisis. Semiconducting polymers facilitate the fabrication of Organic Photovoltaic (OPV) cells due to their light weight, design flexibility, and low manufacturing costs [1-4]. Ma et al [5] reported that the active layer of blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C71-butyric acid methyl ester (PCBM) polymer solar cells (PSCs) have a power conversion efficiency (PCE) of up to 5% due to their thermal stability and high electron mobility [6,7]. To achieve high power conversion efficiency, the open circuit voltage (Voc) and short circuit current (Jsc) should be improved. The Voc and Jsc mainly depend on the optimum morphology of the polymer film as it describes the energy level, band gap and the hole mobility of the conjugated polymer.

The optimum morphology of P3HT/PCBM films describes two main features: 1) the molecular ordering within the donor or acceptor phase, which affects the photon absorption and

carrier mobility; and 2) scale of phase separation between the donor and the acceptor, which can directly influence the exciton dissociation and charge transport and/or collection processes. The aforementioned factors are crucial for solar cells with high performance efficiency [8-12]. Compared to inorganic solar cells, PSCs usually have insufficient light absorption due to the thin active layer which is restricted by the short exciton diffusion length and low carrier mobility. Efficient conversion of solar energy requires the compounds to absorb strongly in the visible region of the spectrum [13]. Incorporation of inorganic nano particles like CuO nanoparticles can help overcome these drawbacks and improve the power conversion efficiency.

One of the key factors attributed to insufficient photo absorption is the thickness of the photoactive layer in typical PSCs; increasing the thickness of the active layer can improve solar light absorption [14]. However, the maximum thickness is limited to approximately 100 nm, which means that it cannot absorb all of the incident photons, due to the low mobility of organic materials and the high degree of charge recombination. Also the absorption range of single organic materials is usually narrow [15, 16]. An effective approach to resolve this issue is the use of nanoparticles in PSCs appropriately.

A great deal of research has been done on the incorporation of inorganic nanoparticles (INPs) in solar cells. INPs such as ZnO, TiO₂, or CdSe have been used as electron acceptors [17, 18] and Au, Ag, or CdSe [19, 20] have been used in conjugated polymer films as light-harvesting absorbers, or light-scattering centres'. Liu et al. [21] have reported that the PCE of SiNW/organic hybrid solar cells was in the range of 2.47% to 3.23% with an enhancement of up to 30%. This improvement was due to the incorporation of inorganic materials, which have high carrier mobility with an ability to reduce reflection, and trap light more efficiently which results in strong photo absorption. It has also been found that the use of CdSe and TiO₂ nanocrystals as electron acceptors, can improve the PCE by over 2% [22, 23]. Since semiconducting polymers have short exciton diffusion length (less than 10 nm), only excitons generated within 10–20 nm distance from the donor/acceptor interface can diffuse in the interface and dissociate into free carriers [24, 25].

The oxides of transition metals are an important class of semiconductors having applications in multiple technical fields like solar energy transformation. Wu et al. [26] reported that PSCs with transition metal oxide, ZnO, have achieved

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efficiencies of 3.26% and the PSCs investigated by P.S. Mbule et al. [27] have reached a PCE of 2.37% with ZnO incorporated into the electron extraction buffer layer. Solar cells with Ag-SiO₂ core-shell INPs in the active layer have shown 15.11% enhancement of PCE [28], while an active layer which incorporated spectrally tuned gold/silica (Au/SiO₂) nanospheres has led to a 9.1% increase in PCE [29].

Among transition metal oxides, copper oxide nanoparticles (CuO NPs) are of special interest as they are of low cost, non-toxic, and have high optical absorption capabilities. This study demonstrates the enhancement of power conversion efficiency and the current voltage (JV) characteristics of P3HT/PC70BM bulk heterojunction solar cells by incorporating copper oxide nanoparticles (CuO NPs) in the active layer. Copper Oxide (CuO) is a p-type semiconductor which has a band gap energy of 1.5 eV and this value is close to the ideal energy gap of 1.4 eV required for solar cells to allow good solar spectral absorption [30-32]. The effect of adding CuO NPs to P3HT/PC70BM on the performance is comparatively studied by UV absorption, External Quantum Efficiency (EQE) and solar simulation.

II. EXPERIMENTAL METHOD

A series of P3HT/PC70BM PSCs with different amounts of CuO nanoparticles were prepared and analyzed under the same operating conditions. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) 1.3 wt% dispersion in H₂O, conductive grade was purchased from Sigma-Aldrich and diluted by adding equal volume of H₂O. Regioregular P3HT Rieke 'E' was purchased from Rieke Metals, Inc., and used as received. PC70BM was purchased from SES Research Inc. and used as received. ITO coated glass slides measuring 25 x 75 x 1.1 mm (10 Ohm/sq., and ITO thickness 20-100nm) were purchased from nanocs.com. CuO NPs in the size range of 10~30 nm was purchased from nanocs.com. Ultra high purity, oxygen free nitrogen gas was purchased from Airgas. Aluminum wire of 0.15mm diameter was purchased from Ted Pella, Inc.

Polymer solar cells containing CuO nanoparticles were fabricated in a clean room inside a glove box in an inert atmosphere using nitrogen gas. The P3HT/PCBM/ CuO NPs hybrid solution was prepared in a two-step process. The first step was to obtain the P3HT/PC70BM blend by dissolving 10 mg of regioregular P3HT and 10 mg of PC70BM in 2 mL chlorobenzene. The mixture was stirred at 50°C for 12 hours. The second step is the incorporation of CuO NPs into the blend by dispersing CuO NPs in 2ml of chlorobenzene and adding it to the P3HT/PCBM blend in weights leading to the final weight ratios (P3HT/PCBM/CuO-NPs) of 10:10:0.2; 10:10:0.4; 10:10:0.6; 10:10:0.8; and 10:10:1 mg; respectively.

A schematic illustration of the structure of the photovoltaic devices which are fabricated for this study is shown in Fig. 1. The devices were fabricated in a glove box in nitrogen atmosphere by depositing layers of the materials on a 1 mm glass substrate. The transparent electrode ITO (Merck) was ultrasonically cleaned using a series of solvents like

ammonia/hydrogen peroxide/deionized water mixture, methanol, and isopropyl alcohol. The PEDOT/PSS layer with a thickness of 40 nm was spin coated at 4000 rpm on the substrate and then baked at 120 °C for 15 minutes. This serves as a thin hole-transport layer. Once the sample cooled to room temperature, the hybrid solution containing P3HT/PC70BM/CuO NPs was deposited by spin-coating at 800 rpm for one minute, which leads to a film thickness of about 100-150 nm. The purpose of this layer is to serve as the active layer. The upper cathode layer with a thickness of approximately 100nm was formed by thermally evaporating Aluminum under high vacuum. The final device had an area of 0.15 cm².

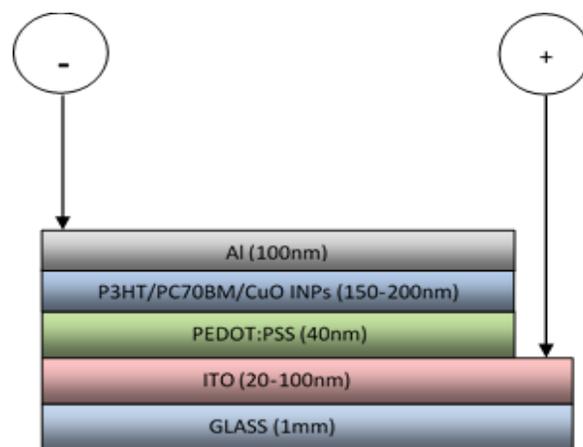


Fig. 1 Schematic illustration of the structure of a polymer solar cell

Six devices of each CuO NP composition were characterized under ambient conditions. The samples were placed under a UV solar simulator lamp (xenon lamp, Oriel Instruments) that was equipped with AM 1.5G filter. The output intensity of the lamp was adjusted to 100 mW/cm² using a silicon photodiode (LI-200 pyronometer). The current density-voltage (J-V) measurements were carried out using a source meter (Keithley 2400). The photovoltaic parameters, open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) were measured in devices with and without CuO NPs that were made under the same conditions.

The external quantum efficiency (EQE) was measured by placing a quantum efficiency measurement kit (Newport, serial number 425) inside the solar simulator. A 300W Xenon arc lamp was used as a light source with a Merlin monochromator to provide throughput to the cells under test. The software supplied with the kit generates an EQE spectrum against a broad wavelength, the peak value of the spectrum is considered in the discussion.

The optical properties of all the solar cells including the reference cell which did not contain any CuO NPs were determined using a UV-Vis spectrophotometer (PerkinElmer LAMBDA 650 spectrophotometer). The surface structures of the solar cell and the distribution of CuO NPs were analyzed using a scanning electron microscope with an energy dispersive X-ray detector (FEG-SEM Hitachi S-4800).

III. RESULTS AND DISCUSSION

A SEM micrograph of the fabricated solar cell showing the spin coated PEDOT: PSS and the CuO NPs/P3HT: PCBM layers is shown in Fig. 2a. A thin layer (40 nm) of PEDOT: PSS layer is required to facilitate the transfer of the carriers to the ITO anode. The thickness of the P3HT/PCBM active layer was restricted to 100 -150 nm to avoid the recombination of charges. The CuO NPs are dispersed in the P3HT/PCBM active layer which contains the crystalline P3HT and amorphous PCBM domains as shown in Fig. 2b.

A schematic energy level diagram of the P3HT/CuO/PCBM active layer is shown in Figure 2c. The band structure of P3HT and PCBM [33] makes them an ideal donor and acceptor pair. In comparison to P3HT, the energy levels of the conduction and valence bands of CuO [34] and the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of PCBM are such that CuO and PCBM can form a semiconductor heterojunction; which makes them a suitable donor and acceptor pair. The electrons generated can thus transfer from the conduction band of the CuO to the PCBM and the separated holes can in turn transfer from the valence band of the CuO to the ITO side. When compared to a Si semiconductor, which has an indirect transition band structure, CuO has a direct transition band gap which leads to greater optical absorption. Therefore, copper oxide nanoparticles can potentially provide efficient charge injection at the active layer, thus enhancing the power conversion efficiency of the solar cell.

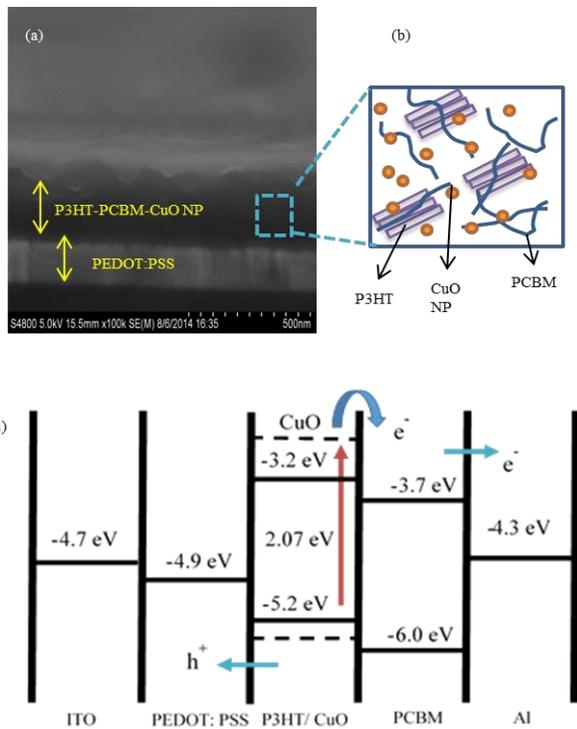


Fig. 2 (a) SEM image of the polymer solar cell (b) Schematic of the P3HT/PCBM active layer containing CuO NPs (c) Schematic band structure of the P3HT/PCBM/CuO NP active layer [33, 34]

The current density – voltage (J-V) characteristics of the hybrid solar cells containing CuO NPs are compared to the reference cell in Table I. It can be seen that the performance of the devices containing CuO NPs is improved in comparison to the reference devices. This can be attributed to the enhanced light absorption of the polymer films incorporated with CuO NPs. The short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor ($FF = J_m \cdot V_m / J_{sc} \cdot V_{oc}$), and power conversion efficiency (PCE) (η) of all the cells are listed in Table 1. According to the J-V characteristics of the devices, the short circuit current of the reference cell was found to be 5.234 mA/cm² and it seemed to increase to 6.484 mA/cm² in cells containing 0.6 mg of CuO NPs which accounts for a 24.2% increase. The current gain improves the power conversion efficiency (PCE) from 2.106% to 2.963%; in addition the FF increases from 61.15% to 68.0% which accounts for an 11.2% enhancement in the solar cell. The linear increase in the FF with the concentration of CuO NPs indicates higher mobility of charges due to the CuO nanoparticles induced into the PCBM polymer clusters [35].

TABLE I
PARAMETERS OF P3HT/PCBM/CUO-NP HYBRID SOLAR CELLS

CuO NPs (mg)	J_{sc} (A/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
0	5.234	0.658	61.15	2.106
0.2	5.726	0.675	66.52	2.571
0.4	5.993	0.670	66.21	2.632
0.6	6.484	0.673	68.00	2.963
0.8	6.320	0.668	68.50	2.895
1.0	6.122	0.674	66.84	2.758

The PCE, which is defined as a ratio of the product of the V_{oc} , J_{sc} and FF to the total incident power density values of the solar cells incorporated with different amounts of NPs are shown in Fig. 3. The PCE of the solar cells seem to increase drastically as the amount of CuO NPs are increased in the active layer up to 0.6 mg and then drop slightly as the amount of CuO NPs are increased further.

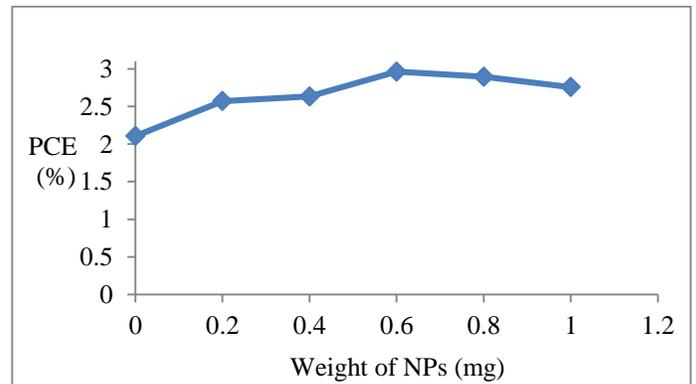


Fig. 3 Power conversion efficiency of hybrid solar cells

A similar behavior is observed in the V_{oc} and J_{sc} of the

cells, this may indicate some hindrance to the optical absorption in the active layer either due to the increasing thickness as the amount of CuO NPs is increased or due to the agglomeration of the CuO NPs in the active layer at higher concentrations. Fig. 4 shows the EDX mapping of elemental copper in the active layer of the solar cells, which illustrates the distribution of CuO NPs in the active layer. Higher agglomeration can be seen in 5d and 5e, which correspond to the cells containing 0.8 and 1 mg of CuO NPs; respectively.

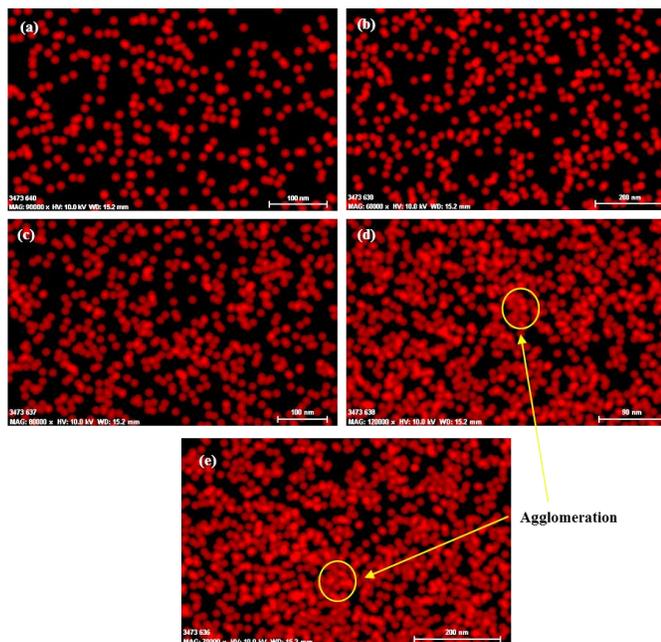


Fig. 4 EDX mapping showing the distribution of elemental copper in the P3HT/PCBM active layer of PSCs containing: (a) 0.2 mg, (b) 0.4 mg, (c) 0.6 mg, (d) 0.8 mg and (e) 1 mg CuO NPs

External quantum efficiency (EQE) is generally defined as the ratio of the number of charge carriers collected by the solar cell to the number of photons shining on the solar cell from outside sources. Fig. 5, shows that the EQE of the hybrid solar cells increases as the amount of CuO NPs increases. The highest EQE of 62.13% was recorded in the cells containing 1.0 mg of CuO NPs, while the reference cell showed the lowest EQE of 42.2%. It is evident that the EQE of the devices containing CuO NPs increases over a broad wavelength ranging from 350 to 640 nm.

The improvement of EQE can be attributed to the increased hole and electron polaron mobilities, charge collection at the electrodes, and photon absorption. It is clear that, other than the conventional transporting route through PCBM clusters, the distinctive network with dense PCBM molecules formed by the dispersion of CuO provides an additional pathway of charge carriers transporting towards the electrode. The separated free electrons from excitons generated in P3HT phases in the bulk device can only be transported through interconnected PCBM clusters. However, the free electrons in the device with INPs have excellent transport routes within the nanoparticle-tuned nanostructure through multiple pathways; 1) through the conventional interconnected PCBM clusters 2)

the INP-clusters 3) the INP-containing network in the PCBM/P3HT amorphous domain. As a result, the electron mobility is enhanced leading to the significantly improved device performance and EQE [36]. The spectra also show clear evidence of the response in the region where only the nanoparticles absorb, beyond the absorption region of the polymer, indicating hole transfer from nanoparticles to polymer as was also claimed by Fujimoto et al [34].

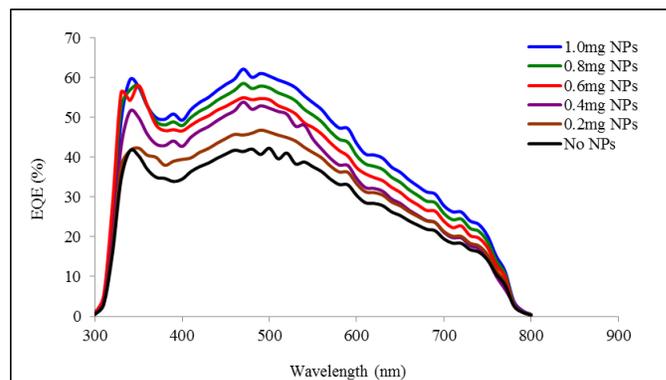


Fig. 5 External quantum efficiency of hybrid solar cells

The results from EQE concur with the results obtained from UV-Vis absorption. The optical absorption spectrum from the UV-Vis spectrometer is shown in Fig. 6. It is clear that the absorption of P3HT:PC70BM cells in the range of 420 nm to 550 nm are enhanced after incorporating CuO NPs in the active layer. Further increase in the amount of CuO NPs improved the absorption from 0.37 to 0.94. This indicates that higher amounts of CuO NPs lead to more absorption and higher EQE of the cell; i.e. higher electron mobility, photo generated carrier injections and better J-V characteristics. It is clear from EQE spectra and UV-vis absorption spectra that CuO NPs show drastic improvement in comparison to the reference cells.

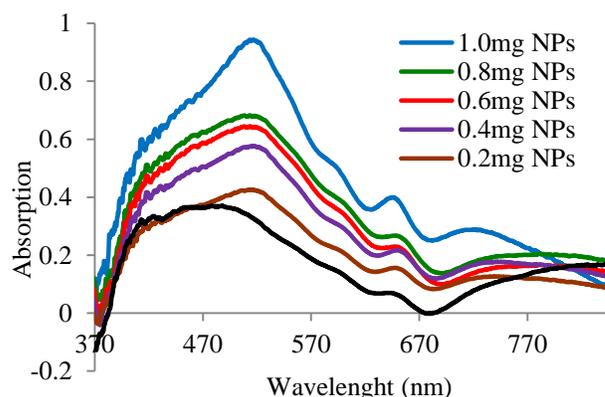


Fig. 6 Optical absorption spectra of hybrid solar cell

The short circuit current, J_{sc} is directly proportional to the EQE, and can be determined theoretically using the following equation [37]:

$$J_{sc} = \frac{q}{hc} \int_{\lambda_{min}}^{\lambda_{max}} EQE P_{in}(\lambda) \lambda d\lambda \quad (1)$$

Where q is the charge of the carriers/electrons, P_{in} is the incident input power, h is the reduced Planck constant, c is the velocity of light and λ is the wavelength.

The λ_{min} and λ_{max} values correspond to the starting wavelength (300 nm) and the wavelength at EQE_{max} in the EQE spectrum. The maximum EQE values are found to increase with increasing the amount of CuO NPs in the active layer, and based on the above equation, one would expect J_{sc} to increase accordingly. However, since the maximum EQE occurs at different wavelengths (λ_{max}), the relationship between J_{sc} and EQE is nonlinear, as shown in Table 2. The theoretical values of J_{sc} , are calculated using the EQE values at λ_{max} , which seem to follow the same trend as the experimental values, show that the cells with 0.6 mg of CuO NPs exhibit the highest J_{sc} value.

TABLE II
COMPARISON OF THEORETICAL AND EXPERIMENTAL SHORT CIRCUIT CURRENT (J_{sc}) VALUES WITH RESPECT TO THE EQE OF THE PSCS

CuO NPs Q(mg)	λ_{max} (nm)	EQE (%)	J_{sc} (A/cm ²)	
			Experimental	Theoretical
0	490	42.2	5.234	3.860
0.2	490	46.8	5.726	4.281
0.4	470	53.8	5.993	3.940
0.6	500	54.7	6.484	5.544
0.8	470	58.5	6.320	4.284
1.0	470	62.1	6.122	4.548

The short circuit current (J_{sc}) and open circuit voltage (V_{oc}) values of the solar cells measured experimentally, with respect to the weight of CuO NPs are presented in Fig. 7. The improvement of J_{sc} can be attributed to the enhancement of light absorption as the amount of CuO NPs increases. Higher absorption of light will introduce more photo generated carriers and lead to improved current density [38]. The addition of CuO NPs has not significantly changed the value of the open circuit voltage (V_{oc}) for the PSC probably because CuO NPs do not change the active layer P3HT conjugation length. As a result, the HOMO energy level of P3HT remains unchanged. Therefore, V_{oc} may have not contributed to the enhancement of PCE of CuO NPs incorporated solar cells.

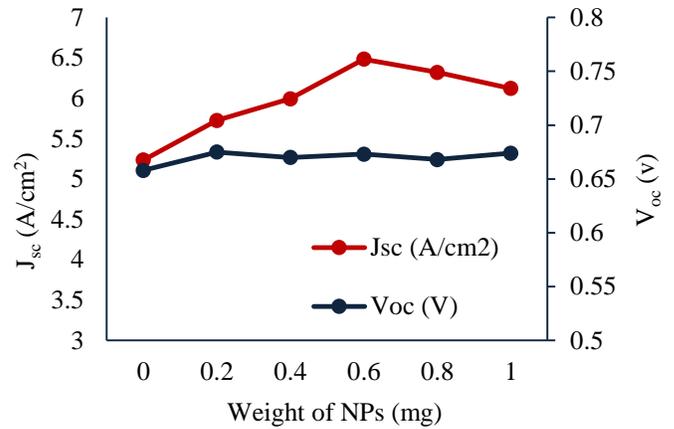


Fig. 7 J_{sc} and V_{oc} of P3HT/PCBM/CuO-NPs hybrid solar cells

The V_{oc} is also controlled by the energetic relationship between the donor and the acceptor. The energy difference between the HOMO of the donor and the LUMO of the acceptor is known to most closely and linearly correlate with the V_{oc} [39]. Therefore, controlling the energy levels is important to increase the power conversion efficiency [40, 41].

IV. CONCLUSIONS

P3HT is one of the most commonly used donor polymers in organic solar cells, and PCBM is currently considered to be an ideal acceptor material. CuO has a direct transition band structure and 1.5 eV band gap energy, which is more suitable for optical absorption. In this work, CuO NPs were added to P3HT/PC70BM polymer blends to improve the photo absorption of the P3HT layer and to enhance the P3HT/PC70BM exciton generation rate. The EQE of these cells increased due to enhanced hole and electron polaron mobility, carrier collection, and photo absorption with CuO NPs. Higher absorption introduces more photo generated carrier injections and leads to improving the donor level of P3HT; which increases the short circuit current (J_{sc}) in the solar cells. However, the open circuit voltage V_{oc} of solar cells containing CuO NPs does not seem to change significantly.

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