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Efficient and stable polymer solar cells prepared using plasmonic graphene oxides as anode buffers

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Abstract

Gold nanoparticle-decorated graphene oxides (AuNP-GOs) have been incorporated into inverted organic photovoltaic devices (OPVs) as anode interlayers. The OPVs fabricated with AuNP-GOs exhibited significant improvement in both the short-circuit current and fill factor compared to a reference device fabricated with neat GOs. We attribute the improvement in the efficiency of the device to the plasmonic effects of the AuNP-GO nanocomposites, which induced local enhancement of the electromagnetic field. More importantly, the inverted OPVs also exhibited better reliability after the use of AuNP-GO nanocomposites.

Keywords: polymer, solar cells, nanoparticle, graphene oxide, plasmonic

(Some figures may appear in colour only in the online journal)

1. Introduction

Organic photovoltaic devices (OPVs) possess many advantageous properties, including light weight, mechanical flexibility, short energy pay-back time, and low fabrication costs [1–5]. They have been regarded as promising candidates for use in next-generation renewable energy sources. At present, OPVs based on donor-acceptor heterogeneous polymer blends have achieved a power conversion efficiency (PCE) of approximately 10% based on a single-junction structure [4]. Nevertheless, much effort is still being focused towards further improving the efficiency of the device to realize industrialization. The inferior lifetime of the device is also a source of concern.

Currently, the internal quantum efficiency of OPVs, which is closely relative to the efficiencies of charge separation and transportation, has approached almost 100% [5]. Therefore, absorption efficiency remains one of the major limitations toward even higher efficiencies. Although thicker active layers are allowed in some special cases, e.g. nanowire-based active layers [6] or the use of particular additives [7], attempts to use thicker photactive layers for increasing the absorption efficiency, however, inevitably increased the series resistance and the possibility of charge recombination. Consequently, many light trapping strategies, including the use of folded device architecture [8] and the incorporation of optical spacers [9] and photonic crystals, have been proposed for achieving higher absorption efficiencies using thin films with a limited thickness [10]. Among these light trapping techniques, the exploitation of surface plasmon resonance (SPR) effects has been considered recently as an effective means for improving the absorption efficiencies [10–20]. Metal nanostructures, which can effectively trigger SPR, have been introduced into the devices. However, the issue of stability is rarely addressed [18, 19].

The contact property of the interfaces between the active layer and electrodes is another important factor that affects the performance of OPVs. For instance, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is commonly used as an anode interfacial layer to reduce the contact
resistance and to enhance the charge collection efficiency. However, its highly acidic nature often corrodes the indium tin oxide (ITO) electrodes, and the hygroscopic properties also bring moisture into the devices, leading to device failure and degradation [21]. More recently, graphene oxides (GOs) have been reported as one of the promising alternatives to PEDOT:PSS, which function very well as anode buffers of OPVs [22–24]. Its reduced form, reduced GOs (rGOs), has been also employed to improve device stability [23]. Because GOs contain a range of reactive oxygen functional groups, they have been considered as promising nanoscale building blocks for tailoring the material functionalities for OPVs [20, 25].

However, the inverted structure usually eliminates the use of low-work-function metals, which are sensitive to oxygen and moisture in the air, and the upper polymer layers naturally behave as protection layers. Therefore, inverted OPVs usually exhibit prolonged device lifetimes [18, 26–28]. In this study, we fabricated inverted OPVs using nanoscale GO interlayers containing gold nanoparticles (Au NPs), which were able to induce localized surface plasmon resonance (LSPR) for increasing light harvesting ability. Moreover, we found that device reliability could be further improved using such nanoscale interlayers.

2. Experimental details

The inverted OPVs were fabricated on patterned ITO glass substrates; the device structure is illustrated in figure 1(a). Solution-processed zinc oxide nanoparticles were dissolved in ethyl glycol/isopropanol mixed solvent, and the resulting solution was spin-coated on the ITO substrates [29]. The ZnO thin films were annealed at 140 °C for 1 h. The photoactive layer, a blend of poly(3-hexylthiophene) (P3HT) and 1-(3-methoxy-carbonyl)propyl-1-phenyl[6,6]methanofullerene (PCBM) at a weight ratio of 1:1, was spin-coated from a solution of 1,2-dichlorobenzene on the ZnO layer. The polymer films were subject to solvent annealing for 2 h in a Petri dish [30]. For the preparation of the anode buffer layers, the AuNP-GO nanocomposites were first synthesized using the procedures described previously; glycine was used as the reducing agent.
Under the mild reduction condition, the GOs were only slightly reduced and the chemical structure was hardly changed [32]. Figure 1(b) shows the transmission electron microscopy (TEM) images of the AuNP-GO nanocomposites. We clearly observed that the AuNPs anchored to the GO surfaces. The average particle size was ca. 8 nm [32]. The distribution of the AuNPs was also displayed in figure 1(c). The GO or AuNP-GO was dispersed in a solvent mixture consisting of water, 2-ethoxyethanol and butyl alcohol at a volume ratio of 1:1:2; the concentration was ca. 0.2 mg mL\(^{-1}\). The solution was spin-coated onto the P3HT:PCBM layers at a spin rate of 4000 rpm. The devices were encapsulated by cover glasses and sealed with UV-cured epoxy in a N\(_2\)-filled glovebox before characterization. All the measurements were performed in air. The electrical characteristics of the OPVs were measured using a Keithley 2400 source-measure unit. The photocurrent densities were acquired while the devices were illuminated with a 150 W Thermal Oriel solar simulator. The light intensity was calibrated using a standard Si photodiode equipped with a KG-5 filter (Hamamatsu, Inc.). The external quantum efficiency (EQE) spectra were obtained using an Enli Technology measurement system. The absorption spectra were recorded using a Perkin–Elmer Lambda 650 ultraviolet/visible/near infrared spectrometer.

3. Results and discussion

Figure 2(a) displays the current density-voltage (J-V) characteristics of the OPVs prepared with different numbers of spin-coating process of GOs. (b) J-V characteristics, recorded under illumination (100 mW cm\(^{-2}\), AM 1.5G), of the inverted OPVs prepared with different times of spin-coating process of GOs. (b) J-V characteristics, recorded under illumination (100 mW cm\(^{-2}\), AM 1.5G), of the inverted OPVs before and after the incorporation of Au NPs.

The AuNP-GO nanocomposite was also spin-coated onto the active layer four times to introduce the SP effects. As displayed in figure 2(b), after decorating the GO surfaces with the Au NPs, the values of \(V_{oc}\) remained unchanged (0.59 V), suggesting that the anode interface was hardly affected. The values of \(J_{sc}\) and \(FF\), however, were increased to 10.05 mA cm\(^{-2}\) and 0.61, respectively, yielding an improved PCE of 3.60%. During the fabrication of the devices, we have found that the NP density is an important factor affecting the performance of the device [12–14]. We have prepared the buffer layers containing various concentrations of NPs though altering the weight ratio of AuNP-GO and GO. The optimized AuNP-GO:GO weight ratio was 2:3 in the solvent mixture. Unfortunately, the exact NP density was difficult to obtain.
because of the rough surface of the P3HT:PCBM thin films. As shown in figure 3(a), the root-mean-square (RMS) roughness of the P3HT:PCBM film was 15 nm. After the GO films were deposited, the RMS roughness was increased to 18 nm (figure 3(b)). After the AuNP-GO nanocomposite was deposited (figure 3(c)), it was further increased to 25 nm. Because the thin film roughness was even larger than the dimension of Au NPs, we spin-coated the AuNP-GO:GO

<table>
<thead>
<tr>
<th>Number of spin-coating</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>GO thickness (nm)</th>
<th>$R_s$ ($\Omega$ cm$^{-2}$)</th>
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<tr>
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<tr>
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<td>8.1</td>
<td>2.3</td>
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</table>

Figure 3. AFM images (5×5 μm$^2$) of the P3HT:PCBM active layers prepared under different conditions: (a) as prepared; (b) after covered with GO films; (c) after covered with AuNP-GO films. (d) AFM image of the AuNP-GO composite deposited on a SiO$_2$/Si substrate.
blends on flat Si substrates using the same conditions to evaluate the thickness of the GO layers. The obtained thicknesses are listed in Table 1. Further, from Figure 3(d), we can also roughly estimate that the NP density was ca. 2 μm\(^{-2}\), which is close to values of our previous reports [19].

To explore the mechanism responsible for the improvement of the device, we measured the external quantum efficiency (EQE) spectra of the devices before and after the use of Au NPs (Figure 4(a)). We found that the efficiencies were increased after incorporating the Au NPs. The results were consistent with the J–V characteristics as displayed in Figure 2(b). The curve of the increase in EQE (ΔEQE) after the decoration of Au NPs is also displayed in Figure 4(b). The spectrum indicated that the EQE values increased within the wavelength range from 350 to 600 nm. The spectral regime is similar to the extinction range of the AuNP-GO nanocomposites as shown in Figure 1(d), in which a plasmonic peak near ca. 560 nm was observed. The spectral similarity suggests that excitation of LSPR did improve the efficiencies. To further support the beneficial effect of Au NPs, we also measured the absorption spectra of the two samples: ITO/ZnO/P3HT:PCBM/GO and ITO/ZnO/P3HT:PCBM/AuNP-GO; the absorption difference between the two devices was then plotted in Figure 4(b). We observed that the absorption was increased in the spectral range from 350 to 600 nm. Such spectral range is even closer to that of ΔEQE. Note that the absorption spectrum displayed in Figure 1(d) was obtained from the dispersion of nanocomposites in water. Therefore, their plasmonic properties in the devices might be different because the resonance peak of the NPs strongly depends on the surrounding medium [34, 35]. On the other hand, the differential absorption spectrum obtained herein should more closely reflect the true plasmonic behavior of the AuNP-GO nanocomposites. Therefore, Figure 4(b) suggests that the incorporation of Au NPs improved the absorption efficiencies of the inverted OPVs.

Device reliability is another critical concern for the successful commercialization of OPV technology in the future. Previous studies reveal that the OPVs prepared with graphene derivatives, such as reduced GOs, exhibited a much longer lifetime compared with the cells fabricated with PEDOT:PSS [23, 24]. In this work, we found that the device prepared with GO derivatives exhibited higher device stability. The normalized photocurrent, as a function of the exposure time to AM 1.5G solar irradiation, of the inverted OPVs prepared with various anode buffer layers is plotted in Figure 5(a). The
photocurrent of the device fabricated with PEDOT:PSS decayed by more than 5% after continuous operation for 2 h. The degree of the photocurrent decay, however, was less than 3% for the devices prepared with GO derivatives. For the device containing Au NPs, the photocurrent was almost unchanged within 40 min. Figure 5(b) further compares the ‘storage stability’ of these devices. All the OPVs were first encapsulated in the N2 glovebox and stored under ambient conditions; the test protocols were qualified as an ISO-D-1 experiment [36, 37]. From the results shown in figure 5(b), we can see that the device prepared with PEDOT:PSS degraded more rapidly, presumably because of its acidic and hygroscopic properties. We also observed that the device containing Au NPs exhibited slightly better stability than that of the device prepared with neat GOs. We suspect that the NPs might quench the triplets, thus inhibiting photooxidation processes within the OPVs [38]. In short, the results of the reliability test further reveal that the GO derivatives are more stable anode buffer layers than PEDOT:PSS.

4. Conclusion

In conclusion, we have improved the performance of inverted OPVs through introducing Au nanoparticle-decorated GOs as the anode buffer layer. The primary origin of the improvement of the device can be attributed to the local field enhancement induced by the LSPR. More importantly, as the inverted devices are usually more stable than the conventional ones, we have also shown that the plasmonic-enhanced OPVs exhibited better reliability.

Acknowledgments

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