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0-dimensional Carbon Dot as Efficient Cathode Interfacial Layers for Organic Photovoltaics Providing Power Conversion Efficiencies up to 9.5%

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Abstract

In this study, we found that interfacial layers (IFLs) based on carbon dots(C-dots) with carboxylic groups, for the first time, were used as an efficient interfacial modification layer on the ZnO interlayers, greatly improving the device performance. The C-dots modifying showed decreased work function and smoothed surface of metal oxides, facilitating the enhancement of charge extraction efficiency and the decrease of recombination losses for the cathode. As a result, by incorporating ZnO/C-dots as the interlayers, Notably, a maximum PCE of up to 9.55 % was achieved with the ZnO/C-dots as the interlayers and PTB7-Th:$PC_{71}BM$ as the active layer .

1. Introduction

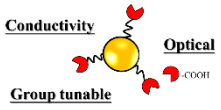
Polymer solar cells (PSCs) based on conjugated polymers and fullerene composites have been developed rapidly during the past decades because of their various advantages, such as low-cost processing and suit ability to industrial manufacturing of large-area and flexible devices. Particularly, invert polymer solar cells (i-PSCs) as the counterpart of the conventional polymer solar cells (c-PSCs) show major advantages of increased stability as well as enhanced device performance. The rapid advance of power conversion efficiency (PCE) benefits from the development of novel materials with improved photovoltaic properties, optimizing fabrication processing such as implementing smart architectures, controlling morphology, and inserting of inter layers to modify electrode.As for the cathode inter layer used in i-PSCs, zinc oxide (ZnO) is promising candidates due to their high electron mobility, excellent optical transparency and solution process. However there is a mismatch between conduction band energy level of ZnO and LUMO level of PC71BM . Moreover, as typical inorganic materials, ZnO has poor interfacial contact with active layers, which may lead to large series resistance (R_s), weak electronic coupling and severe back charge recombination.

In this study an effective approach to solve this problem is to modify the metal oxide surface with an organic layer, we demonstrate that water-soluble carbon dots (C-dots) with carboxylic groups can be used as excellent interface modifier materials for the first time atop metal oxide interlayers to greatly enhance the performance of (i-PSCs). Our purposed C-dots modification atop the ZnO interlayer could overcome the above-mentioned limitation of the existing polyelectrolyte-based modifier including the insulating nature and the lack of utilization of the incident light owing to the good electrical conductivity and luminescent down-shifting effect associated with the C-dots, while the luminescent down-shifting effect of C-dots could increase the light conversion of near ultraviolet and blue-violet portions of sunlight. More importantly, the C-dots modification can result in decreased work function and smoothed surface of the metal oxides, thus enhancing charge extraction efficiency and reducing recombination losses for the cathode. As expected, by incorporating ZnO/C-dots as the interlayers, our designed inverted polymer solar cells with PTB7-Th:PC71BM as the active layer obtained over 10% enhancement(relative to the devices with pure ZnO, from 8.62% to 9.55 %). Notably, a maximum PCE of up to 9.5% was achieved with the ZnO/C-dots as the interlayers and polymer poly[[2,6`-4,8-di(5-ethylhexylphenyl)benzo[1,2-b;3,3-b]dithio-phene] [3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] PTB7-Th:$PC_{70}BM$ as the active layer ,and our PCE outperforms all previously reported PSCs using carbon materials as additives in the active layer or the interface materials and is also higher than those of many previously reported bulk-heterojunction(BHJ) solar cells using the organic polymer modifier.

2. Results and discussion

Devices fabrication

ITO glass substrates were patterned lithographically, washed, and dried (140 °C, 10 min), and further cleaned with O_2 plasma for 5 min. The zinc oxide (ZnO) layer (50 nm) spin-coating (3000 rpm) in air and then the samples were dried(100 °C, 10 min) inside a glovebox. After cooling, the C-dots was spin-coated on the surface of the ZnO at (3000rpm/2000rpm/1000rpm) for 30s .Active layer solution of PTB7-Th and PC71BM (1:1.5) was stirred in chlorobenzene (CB) overnight, and then spin-coated (600−1000 rpm, 30 s) onto the ZnO layer (with or without IFLs). All devices were completed by depositing layers of MoO3 (5 nm) and Ag(100 nm) at pressures below 10−6 Torr.



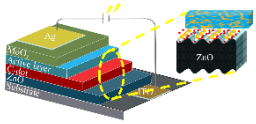


Fig. 1 Schematic of the inverted polymer solar cell modified with a C-dots layer.

Analysis

By modifying ZnO with C-dots, the root means quare(RMS) roughness reduced from 6.48nm(ZnO) to 4.75nm(ZnO/C-dots).

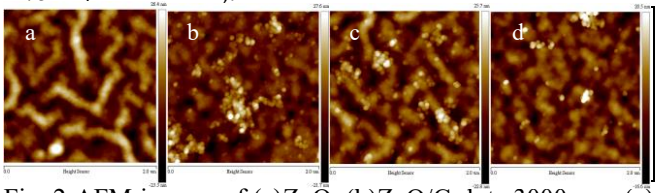


Fig. 2 AFM images of (a)ZnO, (b)ZnO/C-dots-3000rpm, (c) ZnO/C-dots-2000rpm,(d) ZnO/C-dots-1000rpm.

We obtained the γtotal of the ZnOs from their contact angles formed with distilled H2O and diiodomethane (CH2I2, DIM) as probe liquids. Table 1 lists the dispersive (γdispersive) and polar (γpolar) components and γtotal of the films of ZnO and of ZnO with various modified layers. The γtotal of ascast films of ZnO, ZnO/C-dots were 69.2 and 80.5 mN m−1, respectively. Next, ultraviolet photo-electron spectroscopy(UPS) was used to probe the electronic properties of the cathodes including ZnO, ZnO/C-dots, modified ITO. The C-dots made a Vacuum level shift of about 0.8eV(Fig. 2(e)), resulting in a significant decrease in the WF of ZnO. Moreover,the decreased WF value of C-dots modified ZnO allowsfor the formation of ohmic contacts with PC71BM acceptor and thus results in the increase of the built-in field, which is advantageous for enhancing charge extraction efficiency and reducing recombination losses .

ETL	θ water [deg]	θ DIM [deg]	γpolar [mN m−1]	γdispersive [mN m−1]	γtotal [mN m−1]
ZnO	38.05	37.17	27.8	41.43	69.29
ZnO/ C-dot	13.04	31.69	36.81	43.75	80.57

Table 1. Contact Angle (θ) and Surface Energy Data for ZnO Films.

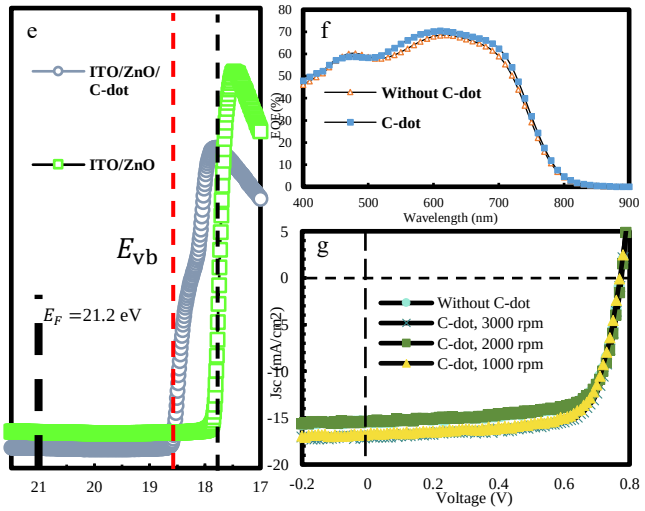


Fig. 2 (e) The UPS spectra of the film samples (Glass/ITO/ZnO) with various interlayers. (f) The EQE spectra of the inverted polymer solar cells(Glass/ITO/interlayer/PTB7-Th:PC71BM/MoO3/Ag) with corresponding interlayers. (g) J-V characteristics of the inverted polymer solar cells(Glass/ITO/interlayer/PTB7-Th:PC71BM/MoO3/Ag)

Interlayer	V_{OC}	J_{SC}	FF	PCE
ZnO	15.39	0.77	72.7	8.62
ZnO/C-dots 3000rpm	17.02	0.77	72.8	9.55
ZnO/C-dots 2000rpm	15.85	0.76	72.5	8.84
ZnO/C-dots 1000rpm	16.64	0.77	70.7	9.05

Table 2.Summary of electrical parameters for the inverted-polymer solar cells with corresponding interlayers and active layers.(Glass/ITO/interlayer/ PTB7-Th:PC71BM /MoO3/Ag.)

3. Conclusions

We have prepared three C-dots of different rotating speed and used them as cathode-modified layers for OPV applications.Through AFM ,UPS and contact angle analyses, we observed decreases in the surface roughness and surface energy for the IFL-modified ZnO films. We found that the bulk morphologies of PTB7−Th and PC71BM based blend films were different when incorporating the various IFLs. The PCE of the ZnO/C-dots,3000 rpm/PTB7-Th: PC71BM (9.5%) was significantly higher than that of the ZnO/ /PTB7-Th: PC71BM device (8.6%), the result of a remarkable increase in the value of Jsc. We attribute the higher values of Jsc for the ZnO/C-dots,3000 rpm/PTB7-Th: PC71BM device to its smaller degrees of phase segregation (AFM morphology) and related higher degrees of mixing between PTB7-Th and PC71BM, thereby improving the charge separation and efficiency of electron extraction. Facile control over the surface properties of ZnO layers and, hence, the morphologies and carrier transport properties of BHJs should facilitate the engineering of OPV devices.

References

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