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Interfacial improvement of hole transporting layer using graphene quantum dots for efficiency enhancement of organic photovoltaics

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Abstract

Graphene quantum dots (GQDs)/PEDOT:PSS films exhibit the improved interfacial contact with substrate encouraging better charger transport in organic photovoltaics (OPVs). The GQDs/PEDOT:PSS films were successfully prepared by mixing of GQDs and PEDOT:PSS under sonication. The mixtures were deposited on SnO_2:F (FTO) substrate using a convective deposition system and characterized. Optical transmittance of the GQDs/PEDOT:PSS films reveals higher average value than that of the PEDOT:PSS films. Surface contact angles display similar decreasing trends for all films. For OPVs fabrication, GQDs/PEDOT:PSS films were used as a hole transporting layer in the OPV device. Power conversion efficiency (PCE) is enhanced to the maximum value of 1.71% for the GQDs/PEDOT:PSS film-based in comparison to the PEDOT:PSS film-based (1.14%). The enhancement is dominating correlation to the improved short-circuit current density and fill factor due to the high transmittance and the improved interfacial contact, respectively. GQDs are not only improving interfacial contact on the FTO substrate but also full-filling coverage over the substrate. Therefore, GQDs are demonstrated as a potential additive material for PCE enhancement of OPVs.

Keywords: Graphene quantum dots, interfacial contact, organic photovoltaics, convective deposition, hole transporting layer
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1. Introduction

Interfacial defect in thin-film based devices is a majoring concern because it directly involves charge carrier transport. The charge carrier transport behavior between interfacial contacts can affect device performance. Organic photovoltaics (OPVs) is one of thin-film based device that has the interfacial defect problem because it consists of multi-layer thin films that easy causes defect between layered interface which affecting the loss of carrier transport efficiency. To solve the problem, interfacial contact between each layer should be improved for better device performance. The addition of proper additives is considered as a facile method for modifying the electronic property of materials. Graphene quantum dots (GQDs) are interestingly investigated for a decade due to unique properties such as good conductivity, high transparency, low heat capacity [1]. It is demonstrated an efficient material for improving several devices such as UV detector, optoelectronic devices, and solar cells [2,3]. Especial to solar cell application, Sharma et. al. [4] demonstrate a theoretical effect of adatoms (nitrogen, boron, and phosphorus) on COOH edge-functionalized GQDs materials for applying in quantum dot solar cells (QDSCs). The improvement of power conversion efficiency (PCE) is found after doping due to the change of electrical and optical properties. The decrease in energy band gap (E_g) and stronger absorption are observed at the same time. The absorption peak shifts to larger wavelength correlating to lower E_g. These changes beneficial result in the raise of short-circuit current density (J_{sc}) which final result a PCE enhancement of the QDSCs. Kim

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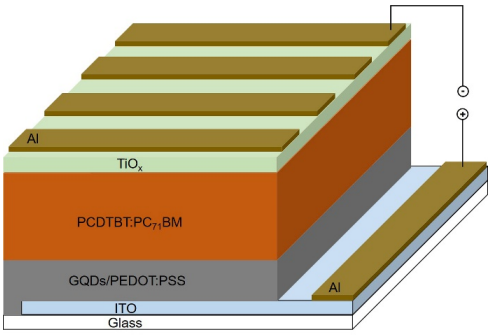

Figure 1: Schematic structure of OPVs.

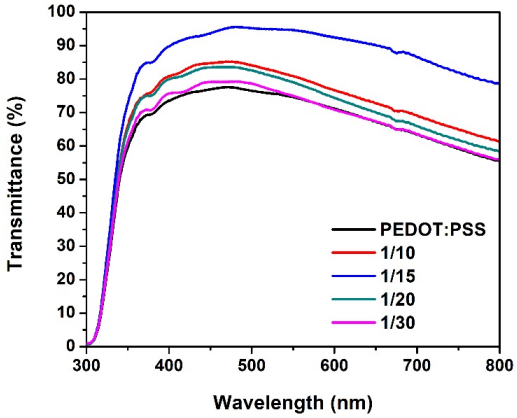

Figure 2: Transmittance spectra of PEDOT: PSS films and GQDs/PEDOT: PSS films at different volumetric ratios.

et. al. [1] present the development of dye-sensitized solar cells (DSSCs) by incorporating GQDs into TiO_2 photoelectrode for DSSC application. They found that low GQDs size around 5 nm shows a potential to enhance *PCE* of DSSC device in comparison to larger GQD size (10 nm). The enhancement is examined and revealed the correlation to high incident-photon-to-current conversion efficiency (IPCE). This effect is described that small quantum size offers unique electron energy for generating numerous electrons, which results in high J_{sc} and *PCE*. Moreover, several effective parameters are changed including low recombination, enhanced electron transport, and increased light scattering. The improved IPCE of DSSCs is occurred due to GQDs incorporation which is agreed to a report of Kumar et. al. [5]. They incorporated GQDs with TiO_2 and prepared as photoelectrode for fabricating flexible DSSCs. *PCE* of 5.48% is observed for the GQDs-TiO_2 photoelectrode based DSSCs with J_{sc} and open-circuit voltage (V_{oc}) of 11.54 mA/cm^2 and 0.73 V, respectively. The role of GQDs for increasing charge extraction and reducing recombination is successfully examined. Majumder et. al. [6] modified ZnO photoelectrode using sulfur and nitrogen co-doped GQDs (SNGQDs). The modified photoelectrode affects in high IPCE around 92%. This phenomenon leads the high J_{sc} and V_{oc} which is resulting in higher *PCE* compared with conventional ZnO photoelectrode. Additional to the internal charge mechanism, they found that charge transfer is improved due to the high conductivity of GQDs. In other words, it could interpret that recombination is also reduced due to fast charge carrier separation upon GQDs incorporation. Shin et. al. [7] shows an improved *PCE* of perovskite solar cells (PSCs) after modifying with GQDs. The modification is performed by doping GQDs in phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$) for applying as an electron transport layer (ETL). The modified ETL explores the improvement in conductivity and optical transmittance. Moreover, charge recombination behavior between ETL and perovskite of PSC is reduced. These effects result in *PCE* enhancement. Not only ETL application, but hole transporting layer (HTL) is also modified by GQDs according to a report of Kang et. al. [3]. They modified poly (3,4-ethylenedioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS) by mixing with nitrogen- and oxygen-doped GQDs (NO-GQDs) for PSC application. *PCE* enhancement has appeared in comparison to pure PEDOT:PSS based PSCs. The occurrence is due to high crystallinity and good electrical properties of NO-GQDs for facilitating internal electrical mechanisms. It should be noted that high quantum yield is also found for the NO-GQDs implying well structural confinement for electrical and optical properties. Due to the successful application of GQDs in several solar cells and the unique property, thus it is a good interesting candidate material that should be considered as a potential functional material for modifying HTL in OPVs.

In this work. GQDs and PEDOT:PSS are mixed and prepared as GQDs/PEDOT:PSS composite films for using as HTL in OPV device. Due to the excellent conductivity and the low dimension of GQDs, it is expected to improve the charge carrier transport and interfacial contact [8]. Thus, incorporation of GQDs could enhance *PCE* of OPVs.

2. Experimental

0.1 M GQD solution was prepared following to a previous report [9]. Briefly, carbon source was performed from citric acid. The citric acid precursor was prepared by dissolving citric acid monohydrate powder in ethanol and carbonized at 250 °C to form as GQDs. The GQDs was mixed with PEDOT:PSS solution under sonication. Volumetric mixtures of GQDs/PEDOT:PSS were varied as 1/10, 1/15, 1/20 and 1/30. Before the HTL deposition, SnO_2:F (FTO) substrate was patterned and then sequentially cleaned with alconox, distilled water, and isopropanol for 30 min each using sonication and dried with N_2 gun, following by surface treatment with oxygen plasma.

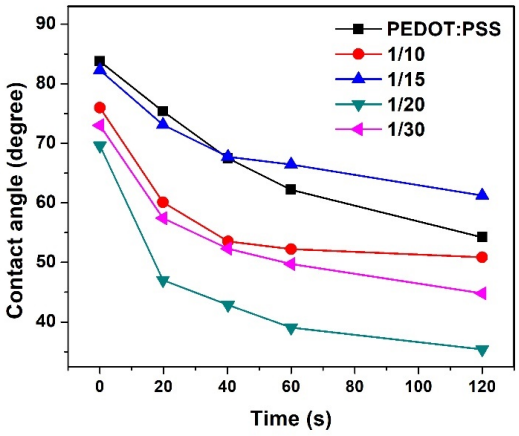

Figure 3: Contact angle of PEDOT:PSS films and GQDs/PEDOT:PSS films at different volumetric ratios.

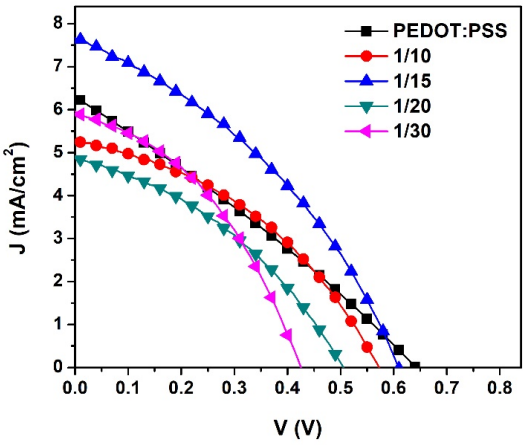

Figure 4: J-V characteristic curves of OPVs fabricated with PEDOT:PSS films and GQDs/PEDOT:PSS films at different volumetric ratios.

Then, a portion of the mixtures (20 μL) were deposited on the FTO substrate using a convective deposition system [10], following by heating at 120 °C for 30 min to form GQDs/PEDOT:PSS films. The films were characterized using several techniques. Optical transmittance was measured using ultraviolet-visible (UV-Vis) spectroscopy. Contact angle was examined using a contact angle measurement system. Functional group was examined using Fourier-transform infrared spectroscopy (FTIR). Cross-sectional image was observed using scanning electron microscopy (SEM). For OPV fabrication, the GQDs/PEDOT:PSS films were used as HTL and it was sequentially deposited by other layers according to previous reports [11]. Brief description, active layer was prepared by mixing of poly [N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and $PC_{71}BM$ and convectively coated on the HTL. Then, the TiO_x solution was coated over the active layer and heated. Finally, the aluminum films were deposited to cover the TiO_x layer using thermal evaporation. After the fabrication, the complete OPV as illustrated in Fig. 1 was moved to measure photovoltaic characteristics under standard irradiation of 100 mW/cm^2 from a solar simulator.

3. Results and Discussion

Optical transmittance spectra of all films are measured as shown in Fig. 2, and average transmittance in the visible region is listed in Table 1. The average transmittance of the GQDs/PEDOT:PSS films reveals higher values than that of the PEDOT:PSS films. The phenomena might be a result of smooth surface formation [12, 13] which could be caused by GQDs assistance. GQDs have a lower dimension that can reduce the thickness and maintain the optoelectronic property of the GQDs/PEDOT:PSS films at the same time. The initial contact angle of GQDs/PEDOT:PSS films show lower values than the PEDOT:PSS films (can see in Table 1) indicating a little hydrophilic surface improvement. However, decreasing trends of contact angle show similarity between the PEDOT:PSS films and the GQDs/PEDOT:PSS films as shown in Fig. 3, indicating the slow spreading of the mixing solution on substrates.

All prepared films were then transferred to use as HTL for OPV fabrication, current density (J) versus voltage (V) curves were measured as shown in Fig. 4. Photovoltaic parameters were calculated using Eq. (1) – (2) [14, 15] as listed in Table 2.

$$PCE = \frac{J_{sc}V_{oc}FF}{P_{in}} \quad (1)$$

$$FF = \frac{J_{max}V_{max}}{J_{sc}V_{oc}} \quad (2)$$

where FF is fill factor, P_{in} is a power of incident simulated sunlight, J_{max} and V_{max} are current density and voltage at the maximum power point, respectively. There are varieties in PCE values and maximum PCE is observed for the GQDs/PEDOT:PSS ratio of 1/15. The maximum PCE is enhanced to be 1.71% (50% increase) in comparison to the conventional device (device fabricated with PEDOT:PSS) of 1.14%. Thus, the GQDs/PEDOT:PSS ratio of 1/15 is considered as an optimal condition for OPV application in this case. The PCE enhancement dominating correlates to the increase of J_{sc} and FF. The increased J_{sc} is due to higher electron-hole pair generation corresponding to the highest transmittance. The improved FF is caused by excellent charge carrier transport through external load due to better interfacial contact between FTO substrate and GQDs/PEDOT:PSS films. To investigate the interfacial contact on the substrate, cross-sectional

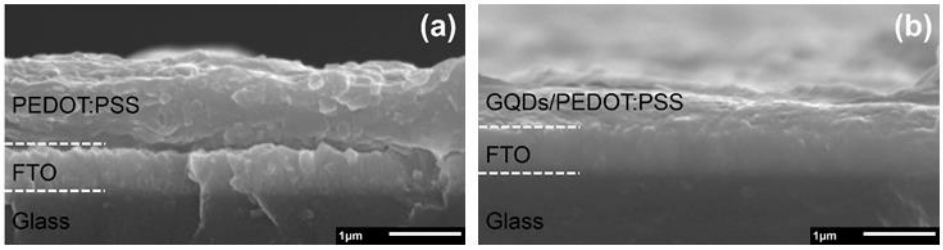

Figure 5: Cross-sectional image of (a) PEDOT:PSS films and (b) GQDs/PEDOT:PSS films.

images of PEDOT:PSS films and GQDs/PEDOT:PSS films at the ratio of 1/15 are observed as shown in Fig. 5. It is found that discontinuation of interfacial contact between substrate and PEDOT:PSS films are found, while better interfacial contact is observed in the case of GQDs/PEDOT:PSS films. Thus, it confirms that the addition of GQDs can improve interfacial contact on FTO substrate. Note that, the films form better coverage and smoother surface. The behavior could describe that GQDs likely act as seeds for distributing PEDOT:PSS on substrate. The appropriate distribution can avoid the accumulation of PEDOT:PSS molecules which resulting in high transmittance and good interfacial contact. The small size of GQDs is also believed that can penetrate to full-fill the void position for uniform film formation during the preparation. Additional to V_{oc}, it is believed that V_{oc} changes due to the change of injected electron density (I_{inj}) which involve J_{sc} as describing in the Eq. (3) [16].

$$V_{oc} = \frac{k_B T}{e} \ln\left(\frac{I_{inj}}{n_{cb} k_r c}\right) \tag{3}$$

where k_B is the Boltzmann constant, T is the absolute temperature, e is electron charge, n_{cb} is the electron density in the conduction band, k_r is the recombination rate, and c is the charge concentration.

In addition, FTIR of the PEDOT:PSS films and GQDs/PEDOT:PSS films were investigated to characterize functional groups as shown in Fig. 6. Appeared peak at 1556 cm^{-1} attributed to the asymmetric stretching of C = C bonds [17]. The peaks at 1216 cm^{-1} and 1124 cm^{-1} attributed to the stretching vibration of C-O-C bonds [18]. The observation of these peaks implies that interaction between GQDs and PEDOT:PSS has occurred. This interaction is believed as one factor that causing the better interfacial contact.

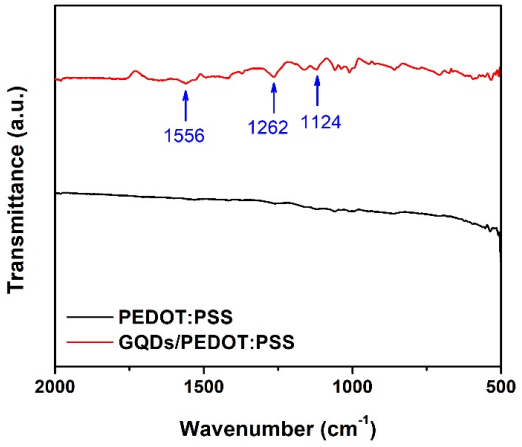

Figure 6: FTIR of PEDOT:PSS films and GQDs/PEDOT:PSS films.

4. Conclusion

GQDs/PEDOT:PSS films exhibit the improved interfacial contact with substrate encouraging better charger transport in OPVs. The GQDs/PEDOT:PSS was successfully prepared by mixing of GQDs and PEDOT:PSS under sonication. The mixtures were deposited on the FTO substrate using a convective deposition system and characterized. Optical transmittance of the GQDs/PEDOT:PSS films show higher than that of the PEDOT:PSS films. Surface contact angles reveal similar decreasing trends for all films. For OPVs fabrication, PCE is enhanced to the maximum value of 1.71% for the GQDs/PEDOT:PSS film-based in comparison to the PEDOT:PSS film-based (1.14%). The enhancement is dominating correlation to the improved J_{sc} and FF due to high transmittance and improved interfacial contact, respectively. GQDs are not only improving interfacial contact on the substrate but also full-filling coverage over the substrate. Therefore, GQDs can able be used as a potential additive material for PCE enhancement of OPVs or thin-film based device applications.

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References

[1] J. Kim, B. Lee, Y. J. Kim, S. W. Hwang, Enhancement of dye-sensitized solar cells efficiency using graphene quantum dots as

photoanode, Bulletin –Korean Chemical Society 40 (2019) 56 – 61.

[2] S. Dhar, T. Majumder, S. P. Mondal, Graphene quantum dot-sensitized ZnO nanorod/polymer Schottky junction UV detector with superior external quantum efficiency, detectivity, and responsivity, ACS Applied Materials & Interfaces 8 (2016) 31822 – 31831.

[3] G. S. Kang, S. Lee, J. S. Yeo, E. S. Choi, D. C. Lee, S. I. Na, H. I. Joh, Graphene quantum dots with nitrogen and oxygen derived from simultaneous reaction of solvent as exfoliant and dopant, Chemical Engineering Journal 372 (2019) 624 – 630.

[4] V. Sharma, P. K. Jha, Enhancement in power conversion efficiency of edge-functionalized graphene quantum dot through adatoms for solar cell applications, Solar Energy Materials and Solar Cells 200 (2019) 109908.

[5] D. K. Kumar, D. Suazo-Davila, D. García-Torres, N. P. Cook, A. Ivaturi, M. H. Hsu, A. A. Martí, C. R. Cabrera, B. Chen, N. Bennett, H. M. Upadhyaya, Low-temperature titania-graphene quantum dots paste for flexible dye-sensitised solar cell applications, Electrochim Acta 305 (2019) 278 – 284.

[6] T. Majumder, S. Dhar, P. Chakraborty, K. Debnath, S. P. Mondal, S, N Co-Doped Graphene Quantum Dots Decorated C-Doped ZnO Nanotaper Photoanodes for Solar Cells Applications, Nano 14 (2019) 1950012.

[7] D. H. Shin, J. M. Kim, S. H. Shin, S. H. Choi, Highly-flexible graphene transparent conductive electrode/perovskite solar cells with graphene quantum dots-doped PCBM electron transport layer, Dyes Pigments 170 (2019) 107630.

[8] A. Hasani, J. N. Gavgani, R. M. Pashaki, S. Baseghi, A. Salehi, D. Heo, S. Y. Kim, M. Mahyari, Poly(3,4 ethylenedioxythiophene): Poly(styrenesulfonate)/iron(III) porphyrin supported on S and N co-doped graphene quantum dots as a hole transport layer in polymer solar cells, Science of Advanced Materials 9 (2017) 1616 – 1625.

[9] P. Pimpang, R. Sumang, S. Choopun, Effect of concentration of citric acid on size and optical properties of fluorescence graphene quantum dots prepared by tuning carbonization degree, Chiang Mai Journal of Science 45 (2018) 2005 – 2014.

[10] A. Kaewprajak, P. Kumnorkaew, T. Sagawa, Influence of binary additives into the solvent for preparation of polymer and fullerene bulk heterojunction solar cells by convective deposition method, Organic Electronics 73 (2019) 18 – 25.

[11] S. Wiboonsak, K. Lohawet, B. A. T. Duong, P. Kumnorkaew, W. Koetniyom, Simple ITO surface treatments induced better performance for low cost organic solar cells, Chiang Mai Journal of Science 45 (2018) 2178 – 2189.

[12] D. P. Kepić, Z. M. Marković, S. P. Jovanović, D. B. Peruško, M. D. Budimir, I. D. Holclajtner-Antunović, V. B. Pavlović, B.M. Todorović Marković, Preparation of PEDOT:PSS thin films doped with graphene and graphene quantum dots, Synthetic Metals 198 (2014) 150 – 154.

[13] N. Boonyopakorn, H. Dinsakul, Effects of aluminium doping concentration on properties of AZO films prepared by RF magnetron sputtering technique, Journal of Thai Interdisciplinary Research 12 (2017) 12 – 17.

[14] S. Wongrerkdee, S. Moungsrijun, S. Sujinnapram, S. Krobthong, S. Choopun, Sulfuric acid treatment of ZnO photoelectrode for photovoltaic improvement in dye-sensitized solar cell, Journal of Physics: Conference Series 1144 (2018) 012164.

[15] F. E. Cherif, M. Hamza, H. Sammouda, High irradiance performance of cesium-formamidinium-based mixed-halide perovskite for concentrator photovoltaics under various operating conditions, Journal of Physics and Chemistry of Solids 135 (2019) 109093.

[16] S. Wongrerkdee, S. Moungsrijun, S. Sujinnapram, S. Krobthong, S. Choopun, Linkage modification of a zinc oxide photoelectrode prepared with polyethylene glycol for electron transport improvement in dye-sensitized solar cells, Bulletin of Materials Science 42 (2019) 91.

[17] J. Liu, J. Xu, Y. Chen, W. Sun, X. Zhou, J. Ke, Synthesis and electrochemical performance of a PEDOT:PSS@Ge composite as the anode materials for lithium-ion batteries, International Journal of Electrochemical Science 14 (2019) 359 – 370.

[18] W. Zhang, Y. Liu, X. Meng, T. Ding, Y. Xu, H. Xu, Y. Ren, B. Liu, J. Huang, J. Yang, X. Fang, Graphenol defects induced blue emission nhancement in chemically reduced graphene quantum dots, Physical Chemistry Chemical Physics 17 (2015) 22361 – 22366.