

Highly Efficient Polymer-Based Optoelectronic Devices Using PEDOT:PSS and a GO Composite Layer as a Hole Transport Layer

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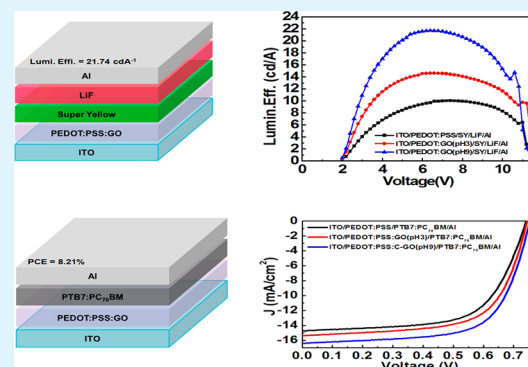
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Supporting Information

ABSTRACT: We demonstrate highly efficient polymer light-emitting diodes (PLEDs), as well as polymer solar cells (PSCs), using a solution-processable poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS):graphene oxide (GO) (PEDOT:GO) composite layer as hole transport layers (HTLs). The PEDOT:GO composite HTL layer shows enhanced charge carrier transport due to improved conductivity by benzoid–quinoid transitions with a well-matched work function between GO (4.89 eV) and PEDOT:PSS (4.95 eV). Moreover, it reduces remarkably exciton quenching and suppresses recombinations that bring higher charge extraction in PSCs and increases the recombinations of holes and electrons within the active layer by the blocking behavior of the electrons from a fluorescent semiconductor due to the existence of GO with large bandgap (~3.6 eV) in the PEDOT:GO composite layer, therefore leading to an enhancement of device efficiency in PLEDs and PSCs. The optimized PLEDs and PSCs with a PEDOT:GO composite HTL layer shows the maximum luminous efficiency of 21.74 cd/A (at 6.4 V) for PLEDs, as well as the power conversion efficiency of 8.21% for PSCs, which were improved by ~220 and 12%, respectively, compared to reference PLEDs and PSCs with a PEDOT:PSS layer.

KEYWORDS: PEDOT:PSS, graphene oxide (GO), polymer solar cells (PSCs), polymer light-emitting diodes (PLEDs)



INTRODUCTION

Polymer-based optoelectronic devices such as polymer solar cells (PSCs) and polymer light-emitting diodes (PLEDs) have attracted significant interest, because of their low-cost and solution-based fabrication process, as well as roll-to-roll processing for flexible device applications.^{1–6} Although the efficiency and stability of PLEDs and PSCs have both seen significant progress, further improvement is still required for their commercial application.

Charge injection/transport layers of PLEDs and PSCs are usually utilized to reduce the contact barrier between the cathode (or anode) and the lowest unoccupied molecular orbital (LUMO) (or the highest occupied molecular orbital (HOMO)) of an active layer, leading to improved charge carrier mobility and reduced contact resistance, as well as balanced charge transport via the blocking of majority carriers to maximize recombinations of charges in PLEDs or to suppress recombinations to maximize the extraction of charges toward electrodes in PSCs for higher device performance and greater efficiency.^{7,8}

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Figure 1b) is typically utilized as a hole transport layer (HTL) in organic optoelectronic devices, because it reduces the energy barrier between the HOMO of the active layer and the work function of the ITO electrode and smoothens the ITO surface after spin coating.^{9–13} However, the strong acidic PEDOT:PSS solution can make the ITO electrode corroded, which will eventually reduce device performance and stability after long-term operation.^{14,15} In addition, the radiative excitons quenching generally happens at the interface between the PEDOT:PSS and the emission layer, leading to a decrease of the efficiency of PLEDs.¹⁶ Therefore, many groups have attempted to find alternatives to PEDOT:PSS by introducing a few nanosized interlayers between ITO and the active layer^{17–22} or with a *p*-type metal oxide such as MoO₃,^{23,24} NiO,^{25,26} or WO₃,^{27,28} among others, to solve the problems associated with PEDOT:PSS,

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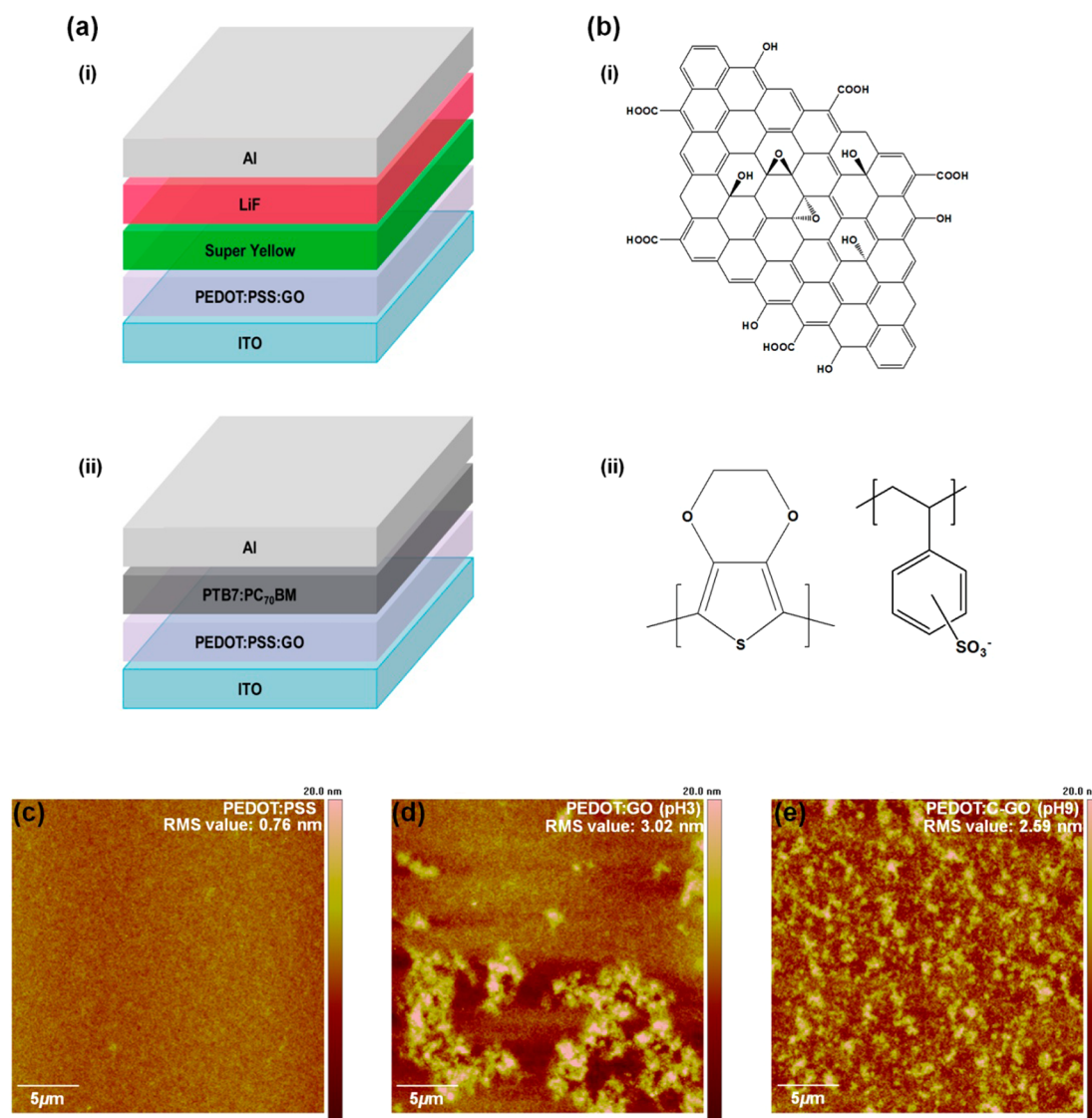


Figure 1. (a) Device structure of both (i) PLEDs and (ii) PSCs with the PEDOT:PSS/GO composite layer and (b) the chemical structure of the (i) GO and (ii) PEDOT:PSS. AFM images and RMS value of (c) PEDOT:PSS layer, (d) PEDOT:GO (pH 3) composite layer, and (e) PEDOT:C-GO (pH 9) composite layer. The acronym C means the prepared GO solution was centrifuged to get well-dispersed morphology of PEDOT:C-GO (pH 9).

with regard to device stability and efficiency. Moreover, a thin layer of graphene oxide (GO) (Figure 1b) has been suggested as an alternative to PEDOT:PSS as a HTL in PLEDs and PSCs.^{29,30} The efficiency values of PSCs with a GO layer are comparable to those of PSCs with a PEDOT:PSS layer, and the luminous efficiency values of PLEDs with a GO layer are more than two times higher than those with a PEDOT:PSS layer. On the other hand, GO has several drawbacks, including insulating properties, which means that Ohmic contact is difficult to achieve. Moreover, there is some difficulty with the full coverage coating of GO at a time. Therefore, a GO and PEDOT:PSS gel was demonstrated as an interconnect layer for the simple fabrication of solution-processable organic tandem solar cells through the properties of the adhesive after mixing of the GO and the PEDOT:PSS. In addition, the GO and PEDOT:PSS gel film showed higher electric conductivity than that of pure PEDOT:PSS due to the chain conformation of the benzoid–quinoid transition and morphology.³¹ Surface doping of the P3HT polymer by the coating of a thin layer of GO on

the conjugated polymer was also reported for improved electric conductivity, leading to enhanced PSC efficiency.³²

Here, we report the enhanced efficiency of both PLEDs and PSCs, using a solution-processable PEDOT:PSS and GO composite (PEDOT:GO composite) layer as a HTL. The PEDOT:GO composite layer enhances the charge carrier transport at the anode due to the improved conductivity by benzoid–quinoid transitions with a well-matched work function between the PEDOT:PSS (4.95 eV) and the GO (4.89 eV) and the blocking behavior of the electrons from the cathode due to the large bandgap (~ 3.6 eV) of GO.^{29,30} Moreover, it reduces the radiative exciton quenching between the emissive poly(phenylvinylene):Super Yellow (SY, Merck Co.) layer and the PEDOT:GO composite layer in PLEDs, therefore leading to an enhancement of device efficiency in PLEDs. In PSCs, recombinations are suppressed between the PEDOT:GO composite layer and the active layer, and the extraction of charges toward anodes is maximized through the use of the PEDOT:GO composite layer in PSCs.

■ EXPERIMENTAL SECTION

Preparation of GO. Graphite oxide (GO) was fabricated from natural graphite (Alfa Aesar, 99.999% purity, -200 mesh) by a modified Hummers method.⁴⁴ The detailed preparing procedure of GO powder is shown in ref 45. The resulting mixture was precipitated and freeze-dried to obtain the GO powder shown in Figure S1a in the Supporting Information. The resulting GO powder was further oxidized in the same manner for 5 h. Next, GO was exfoliated into GO nanosheets in deionized water (200 mg/L) by bath sonication for 1 h. The functionality of the GO nanosheets were confirmed by X-ray photoelectron spectroscopy (Model ESCALAB 250 (VG Scientific) spectrometer) and by Fourier transform infrared spectroscopy (Model BioRad 4200UP), as shown in Figures S1e and S1f in the Supporting Information.

Preparation of the PEDOT:PSS and GO Mixture Solution. The prepared GO solution was centrifuged at 4500 rpm for 15 min to separate any large GO nanosheets, after which 0.1 M of NaOH solution was slowly added to the solution of centrifuged GO until a pH value of 9 was reached.⁴⁶ Next, the PEDOT:PSS solution was directly mixed with a modulated GO solution. The composite solution was used after stabilization lasting one day.

Atomic Force Microscopy (AFM) Characterization. The surface morphologies of pure PEDOT:PSS/Si and several types of PEDOT:GO composite/Si samples were measured using a Multimode V AFM instrument (Veeco, USA).

Raman Spectroscopy Characterization. The Raman spectra of the PEDOT:GO composite and of the PEDOT:PSS layers were measured using a spectrophotometer (alpha300R, WITec, Inc.) with a helium neon laser wavelength of 532 nm.

Device Fabrication and Characterization. PLEDs and PSCs were prepared on an ITO anode, which was washed by a consecutive ultrasonic treatment in acetone and isopropyl alcohol (IPA). A PEDOT:PSS/GO (1:0.5 v/v) mixture solution was spin-coated at 5000 rpm for 45 s after an oxygen plasma treatment to enhance the wettability of the ITO substrates. The layer was annealed at 145 °C for 15 min.

For the fabrication of PLEDs, an SY solution dispersed in chlorobenzene (0.72 wt %) was spin-coated at 2000 rpm for 45 s onto PEDOT:PSS and PEDOT:GO composite layers.

For the fabrication of PSCs, a PTB7:PC₇₁BM (1:1.5 wt %) in chlorobenzene/1,8-diiodooctane mixed solvent (97:3 vol %) with an overall concentration of 25 mg/mL was spin-coated at 1000 rpm for 60 s onto a PEDOT:PSS or a PEDOT:GO composite layer.

Device Characterization. The PLEDs measurement was carried out using a source measurement unit (Keithley 2400, Keithley Co.) and a spectroradiometer (Model CS-2000, Minolta Co.).²⁴ The power conversion efficiencies of the PSCs were measured using an Iviumstat source meter (Ivium Technologies Co.) under an AM 1.5G spectrum from a solar simulator (1000 W m⁻²; Model PEC-L01, Peccell Technologies Co.).⁴⁷ IPCE values were obtained using a PV measurement system with monochromatic light from a xenon lamp under ambient conditions.⁴⁸

Time-Related Single Photon Counting (TCSPC) Characterization. The exciton lifetimes of the PEDOT:PSS and several conditions of PEDOT:PSS:GO composite layers were measured by the time-related single photon counting (TCSPC) technique. The details are shown in the literature.²⁴

■ RESULT AND DISCUSSION

Figures 1a and 1b describe the device structure of PLEDs and PSCs, using the PEDOT:GO composite layer as a HTL and the chemical structures of GO and PEDOT:PSS (AI 4083, Clevios Co.), respectively. Our polymer-based optoelectronic devices were fabricated by the consecutive coating of the PEDOT:GO composite, poly(phenylvinylene):Super Yellow (SY, Merck Co., $M_w = 950\,000\text{ g mol}^{-1}$) (100 nm) as an luminescent layer for the PLEDs and poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-

ethylhexyl)carbonyl] thieno[3,4-b]thiophenediyl]] (PTB7, 1-material Co.) and a [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM, EM Index Co.) blend as an active layer for the PSCs, LiF (1 nm), and Al (100 nm) cathode on ITO (150 nm) anode. The fabrications of PLEDs and PSCs are described in details in the Experimental Section. The PEDOT:GO composite layers were prepared by a spin-casting procedure of a mixture of the PEDOT:PSS solution and GO dispersion in water. GO nanosheets were fabricated by chemical exfoliation of graphite powder using the Hummers method. The oxidation of graphite disrupts the sp² network, and epoxy and hydroxyl groups are introduced in the basal plane, while carbonyl or carboxylic acid groups are incorporated in the edge sites. In this study, in order to retain high functionality even at the edge of the small GO nanosheets, graphite powder was oxidized two times for 3 h and 5 h (see Figure S1 in the Supporting Information). In each oxidation step, we can reduce the size of GO nanosheets as well as functionalize the graphene edge with more carboxylic acid groups that can interact with PEDOT. Although we can control the GO size during the exfoliation of graphite oxide by sonication, the number of carboxylic acid groups in the GO nanosheets can be limited. The details pertaining to the preparation of the GO mixture solution are shown in the Experimental Section. The GO nanosheet consisted of a dominant region—in this case, an unoxidized graphitic region—and a region heavily oxidized by functional groups, i.e., epoxy, carbonyl, and hydroxyl groups, and both the functional groups and the sp² conjugation of GO bring about hydrogen bonding and π - π stacking.³³ The PEDOT:GO composite layer without any treatment of the GO is expected to be well-dispersed, because of the use of similar hydrophilic solvents. However, the PEDOT:GO composite layer without centrifugation of the functionalized GO showed a significantly aggregated morphology (Figure 1d) with a root-mean-square (RMS) roughness value that had increased to 3.02, whereas the pure PEDOT:PSS film showed a flat surface (Figure 1c) with a small RMS roughness value of 0.76 nm, as measured by atomic force microscopy (AFM). In fact, it is well-known that the aggregation of GO flakes is easily seen at pH 3 in such a solution by hydrogen bonding³⁴ and adjusting the pH after centrifugation is one way to disperse the GO flakes in the solution.³⁵ Therefore, the GO solution was adjusted to pH 9 after centrifugation at 4500 rpm for 10 min in an effort to reduce the aggregation of the GO in the solution. Next, the modulated GO solution was mixed with the PEDOT:PSS solution. As a result, the number of aggregated sites decreased significantly with a smaller RMS roughness value of 2.59 nm, as shown in Figure 1e.

The electrical conductivity of both the PEDOT:PSS films and the well-dispersed PEDOT:GO composite layer was observed by four-point probe measurements (Model CMT-SR2000N, AIT Co.) to confirm the enhanced electric conductivity of the well-dispersed PEDOT:GO composite film by the interaction between the PEDOT chain and the GO, as shown in Figure S2b in the Supporting Information.^{36,37} The PEDOT:PSS layer used showed a very low conductivity value of 0.0044 S/cm, whereas the well-dispersed PEDOT:GO composite layer showed a greatly increased value of 0.013 S/cm, as shown in Table S1 in the Supporting Information. The conformational structure change of the PEDOT polymer from a benzoid structure to a quinoid structure was confirmed by the Raman spectra of the C _{α} -C _{β} stretching in the thiophene ring of the Raman shift of 1400–1500 cm⁻¹. The peak stiffness ranging

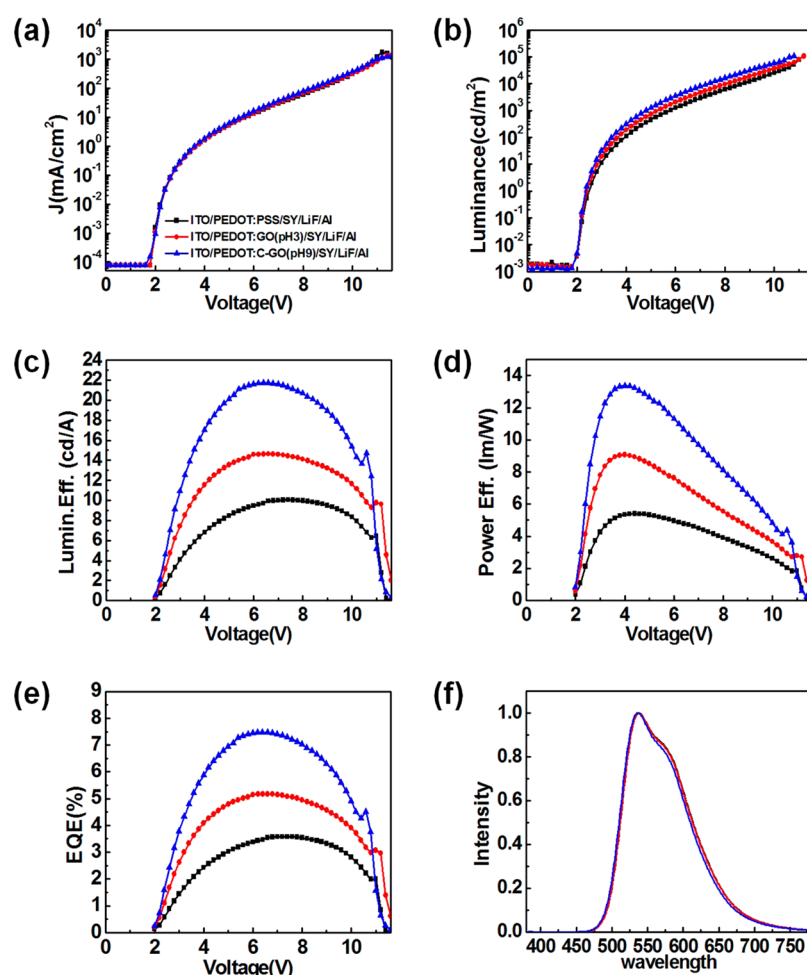


Figure 2. PLEDs light-emitting characterization with the well-dispersed PEDOT:GO composite, the aggregated PEDOT:GO composite, and the PEDOT:PSS presented in terms of (a) current density vs applied voltage (J - V), (b) luminance vs the applied voltage (L - V), (c) luminous efficiency vs the applied voltage (LE - V), (d) power efficiency vs the applied voltage (PE - V), (e) external quantum efficiency vs the applied voltage (EQE - V) curves for various hole transport layer, and (f) electroluminescence (EL) spectrum of PLEDs.

Table 1. Summarized Device Performances of PLEDs with the Well-Dispersed PEDOT:GO Composite, the Aggregated PEDOT:GO Composite, and the PEDOT:PSS Hole Transport Layers

devices configuration	L_{\max} [cd/m^2] @ bias	LE_{\max} [cd/A] @ bias	PE_{\max} [lm/W] @ bias	EQE_{\max} [%] @ bias	turn-on voltage [V]
ITO/PEDOT:PSS/SY/LiF/Al	77100 (11.0 V)	10.04 (7.4 V)	5.41 (4.4 V)	3.58 (7.2 V)	2.0
ITO/PEDOT:GO(pH 3)/SY/LiF/Al	105300 (11.2 V)	14.63 (6.6 V)	9.06 (4.0 V)	5.17 (6.6 V)	2.0
ITO/PEDOT:C-GO(pH 9)/SY/LiF/Al	106700 (10.8 V)	21.74 (6.4 V)	13.38 (4.0 V)	7.48 (6.4 V)	2.0

from 1451 cm^{-1} to 1438 cm^{-1} indicates that the quinoid structure of the PEDOT chain can be described as more dominant in the well-dispersed PEDOT:GO composite layer. The GO-specific peaks of a D band at 1348 cm^{-1} and a G band at 1600 cm^{-1} in the well-dispersed PEDOT:GO composite layer (red-line) provide evidence that the GO is well-mixed with the PEDOT:PSS in Figure S2a in the Supporting Information.³⁸

Operating characterizations of the PLEDs with the well-dispersed PEDOT:GO composite, the aggregated PEDOT:GO composite, and the PEDOT:PSS layers are shown in terms of (a) the current density versus the applied voltage (J - V), (b) the luminance versus the applied voltage (L - V), (c) the luminous efficiency versus the applied voltage (E - V), (d) the power efficiency versus the voltage (P - V), (e) the external quantum efficiency versus the applied voltage (EQE - V), and (f) the electroluminescence (EL) spectra of the devices in

Figure 2. The reference device with PEDOT:PSS presented a maximum luminance of $77\,100\text{ cd}/\text{m}^2$ (at 11.0 V), a luminous efficiency of $10.04\text{ cd}/\text{A}$ (at 7.4 V), and a power efficiency of $5.41\text{ lm}/\text{W}$ (at 4.4 V). On the other hand, the PLEDs with the PEDOT:GO composite showed improved device efficiency, in comparison with the reference PLEDs with PEDOT:PSS. In particular, optimized PLEDs with a well-dispersed PEDOT:GO composite layer exhibited remarkably improved maximum luminous efficiency of $21.74\text{ cd}/\text{A}$ (at 6.4 V), a maximum power efficiency of $13.38\text{ lm}/\text{W}$ (at 4.0 V), and a maximum luminance at $106\,700\text{ cd}/\text{m}^2$ (at 10.8 V), which were improved by ~ 220 , 250 , and 140% , respectively, compared to the reference PLED with PEDOT:PSS. The detailed device performance values of the PLEDs with the well-dispersed PEDOT:GO composite, the aggregated PEDOT:GO composite and the PEDOT:PSS layers are summarized in Table 1. The optimum volume ratio of PEDOT:PSS and GO for PLEDs

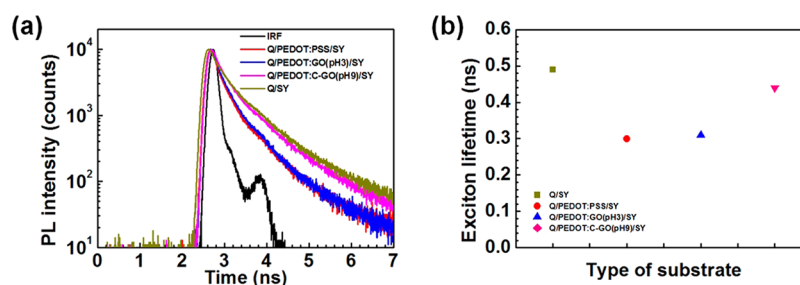


Figure 3. (a) Time-resolved PL signal and (b) exciton lifetime of the quartz/SY, quartz/PEDOT:PSS/SY, quartz/PEDOT:GO (pH 3) composite/SY, and quartz/PEDOT:C-GO (pH 9) composite/SY films with a 50-nm thickness of SY.

Table 2. Detailed Exciton Lifetime of SY, PEDOT:PSS/SY, PEDOT:GO(pH 3)/SY, and PEDOT:C-GO(pH 9)/SY Films on Quartz with a 60-nm Thickness of SY

sample	$\tau_1 (f_1)$ [ns]	$\tau_2 (f_2)$ [ns]	χ^2	τ_{ave} [ns]	PLQE [%]
quartz/SY	1.29 (0.15)	0.36 (0.85)	1.277	0.49	14.8
quartz/PEDOT:PSS/SY	1.17 (0.06)	0.24 (0.94)	1.246	0.30	8.0
quartz/PEDOT:GO(pH 3)/SY	1.05 (0.08)	0.25 (0.92)	1.286	0.31	8.1
quartz/PEDOT:GO(pH 9)/SY	1.21 (0.14)	0.31 (0.86)	1.343	0.44	9.5

is shown in Figures S3 and S4 and Tables S2 and S3 in the Supporting Information. As GO increased to the optimum volume ratio, the device efficiencies increased due to enhanced hole carrier transport caused by improved conductivity by benzoid–quinoid transitions and reduced exciton quenching between PEDOT:PSS and SY with electron blocking behavior. However, the use of an excessive volume ratio of GO in PEDOT:PSS decreased the device efficiency, because the hole injection was lower after the adding of an excessive amount of the GO insulator into the PEDOT:GO composite layer, leading to lower device efficiency.³⁹

The photoluminescence decay profiles were measured to observe the exciton quenching of the SY, SY/PEDOT:PSS, SY/aggregated PEDOT:PSS:GO composite, and well-dispersed PEDOT:PSS:GO composite layers shown in Figure 3. As shown in Figures 3a and 3b, the exciton lifetime at 545 nm is substantially decreased from 0.49 ns in the SY to 0.30 ns in the SY/PEDOT:PSS on quartz substrates. The exciton lifetime of the SY/aggregated PEDOT:GO composite (0.31 ns) is similar to that of SY/PEDOT:PSS, whereas the exciton lifetime of the SY/well-dispersed PEDOT:GO composite layer is 0.44 ns, leading to a decrease of the exciton quenching because of the existence of GO in well-dispersed PEDOT:GO composite layer. The results of the corresponding exciton lifetimes are also summarized in Table 2. The photoluminescence quantum efficiency (PLQE) values measured inside an integration sphere are 14.8% for SY, 8% for SY/PEDOT:PSS, and 9.5% for the SY/well-dispersed PEDOT:GO composite layer. [See Table 2.] The excitation wavelength for PLQE is 450 nm. The PLQE of the SY/well-dispersed PEDOT:GO composite film is higher than that of PEDOT:PSS/SY, and the results for PLQE also support reduced exciton quenching using the well-dispersed PEDOT:GO composite layer.

In addition, J – V characterizations of PSCs with the well-dispersed PEDOT:GO composite, the aggregated PEDOT:GO composite, and the PEDOT:PSS hole transport layers as HTL in the dark condition, as shown in Figure S5 in the Supporting Information. The dark current density of the PSC with the well-dispersed PEDOT:GO composite layer under the reverse bias was roughly more than 10 times lower than that of PSC with the PEDOT:PSS layer, which demonstrated that the

suppression of the recombinations was confirmed by using the well-dispersed PEDOT:GO composite layer.⁴⁰

The enhanced conductivity of the well-dispersed PEDOT:GO composite transport layer in relation to the hole transport was confirmed by a hole-only device. In Figure S6 in the Supporting Information, the $\log J$ vs $\log V$ curves of hole-only devices with ITO/well-dispersed PEDOT:C-GO/SY/MoO₃/Au and ITO/PEDOT:PSS/SY/MoO₃/Au were fitted with the Mott–Gurney space-charge-limited-current (SCLC) model.^{41–43}

$$J_{\text{SCLC}} = \frac{9}{8} \mu_{\text{eff}} \epsilon_0 \epsilon_r \frac{V^2}{d^3} \quad (1)$$

where J is the current density, d the thickness of the SY layer ($d = 100$ nm), V the applied voltage, $\epsilon_0 \epsilon_r$ the permittivity of the polymer ($\epsilon_0 \epsilon_r = 2.654 \times 10^{-11}$ mA S V⁻¹ cm⁻¹), and μ_{eff} is the effective carrier mobility. The effective hole mobility (μ_{eff}) of the hole-only device with a PEDOT:PSS layer, using the Mott–Gurney Law, was calculated to be 1.328×10^{-8} cm² V⁻¹ S⁻¹, whereas the device with the PEDOT-well-dispersed GO composite layer showed higher effective mobility (μ_{eff}) of 2.308×10^{-7} cm² V⁻¹ S⁻¹, showing more than 10-fold enhancement, compared to the reference cell. A quantitative comparison of the hole mobility levels of two hole-only devices confirmed that the use of the well-dispersed PEDOT:GO composite HTL promoted hole transport and extraction. In a conventional structure with the ITO/PEDOT:PSS/SY/LiF/Al configuration, holes are minority charge carriers, and increased hole mobility using a well-dispersed PEDOT:GO composite layer can lead to balanced charge carrier transport with an electron-blocking ability and a reduction of the quenching between the HTL and the active layer. Thus, highly efficient PLEDs were realized using a well-dispersed PEDOT:GO composite layer.

Figure 4 presents the J – V characteristics behavior and incident photon-to-current efficiency (IPCE) of PSCs with the well-dispersed PEDOT:GO composite, the aggregated PEDOT:GO composite and the PEDOT:PSS as measured under 1000 W m⁻² air mass 1.5 global (AM 1.5G) illumination. The PSCs with the PEDOT:PSS (reference device) represented a short circuit current (J_{SC}) of 14.75 mA cm⁻², an open circuit

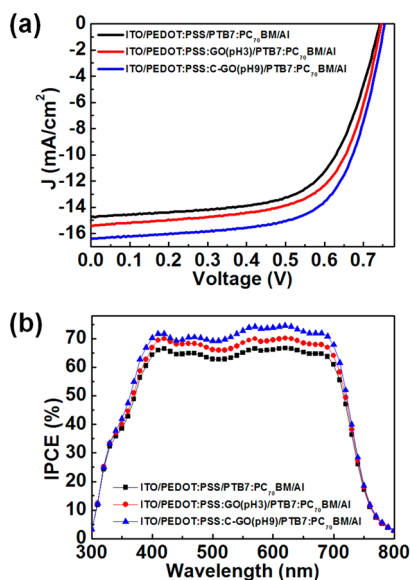


Figure 4. (a) J - V characteristics and (b) IPCE of PSCs with the well-dispersed PEDOT:GO composite, the aggregated PEDOT:GO composite and the PEDOT:PSS layers as the HTLs measured under AM 1.5G illumination, 1000 W m^{-2} .

voltage (V_{OC}) of 0.75 V, a fill factor (FF) of 63.6%, and a power conversion efficiency (η) of 7.04%, whereas the PSCs with the PEDOT:GO composite layer exhibited remarkably improved power conversion efficiencies, compared to the reference PSCs. Among the PSCs with the PEDOT:GO composite layer, the PSCs with the well-dispersed PEDOT:GO composite layer exhibited the highest device efficiency value, with values of $J_{SC} = 16.42 \text{ mA cm}^{-2}$, FF = 65.8%, and PCE = 8.21% with $V_{OC} = 0.76 \text{ V}$, similar to that of a reference cell. The main increases in the device efficiency came from the enhancement of J_{SC} and FF, because of the suppression of recombinations between the active layer and the PEDOT-well dispersed GO composite layer and the enhanced extraction of charges toward electrodes as confirmed by the charge carrier mobility measurements using the well-dispersed PEDOT:GO composite layer in PSCs. The IPCE data support this improvement of J_{SC} , showing higher values of 74% at 630 nm using the well-dispersed PEDOT:GO composite layer, as shown in Figure 4b. The detailed results of PSCs are shown in Table 3.

CONCLUSION

In summary, we demonstrated highly efficient PLEDs and PSCs using a solution-processable PEDOT:GO composite layer, which showed enhanced electric conductivity, in comparison with a PEDOT:PSS film. PLEDs and PSCs with a PEDOT:GO composite film as a HTL show a maximum LE of 21.74 cd/A (at 6.4 V) for PLEDs, as well as a PCE value of 8.21% for PSCs, respectively. The dramatically improved efficiency of PLEDs and PSCs with a PEDOT:GO composite layer originate from

the improved hole mobility and the remarkably reduced exciton quenching and recombinations at the contact between the PEDOT:GO composite layer and the active layer. The introduction of GO materials in combination with PEDOT:PSS to create a composite layer is a simple and effective route to achieve highly efficient organic optoelectronics such as organic light-emitting diodes, organic diode laser devices, organic thin-film transistors, organic photovoltaics, and flexible device applications.

ASSOCIATED CONTENT

Supporting Information

AFM image of pristine GO and additional data, Raman spectra of PEDOT:PSS and PEDOT:GO thin films, J - V characteristic of PSCs in the dark, J - V curves was fitted with SCLC model and conductivity of the composite film. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541.
- Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15–26.
- Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864–868.
- Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222–225.
- Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477–479.
- De Arco, L. G.; Zhang, Y.; Schlenker, C. W.; Ryu, K.; Thompson, M. E.; Zhou, C. W. *ACS Nano* **2010**, *4*, 2865–2873.
- Steim, R.; Kogler, F. R.; Brabec, C. J. *J. Mater. Chem.* **2010**, *20*, 2499–2512.
- Ma, H.; Yip, H. L.; Huang, F.; Jen, A. K. Y. *Adv. Funct. Mater.* **2010**, *20*, 1371–1388.

Table 3. Summarized Device Performance of PSCs with the Well-Dispersed PEDOT:GO Composite, the Aggregated PEDOT:GO Composite, and the PEDOT:PSS Hole Transport Layers, Measured under AM 1.5G Illumination, 1000 W m^{-2}

device configuration	J_{SC} [mA/cm ²]	V_{OC} [V]	FF [%]	η [%]	$J_{SC}(\text{calc.})$ [mA/cm ²]
ITO/PEDOT:PSS/PTB7-PC ₇₁ BM/Al	14.75	0.75	63.6	7.04	14.61
ITO/PEDOT:PSS-GO(pH 3)/PTB7-PC ₇₁ BM/Al	15.39	0.75	64.8	7.48	15.35
ITO/PEDOT:PSS-C-GO(pH 9)/PTB7-PC ₇₁ BM/Al	16.42	0.76	65.8	8.21	16.15

- (9) Jonda, C.; Mayer, A. B. R.; Stolz, U.; Elschner, A.; Karbach, A. J. *Mater. Sci.* **2000**, *35*, 5645–5651.
- (10) Brown, T. M.; Kim, J. S.; Friend, R. H.; Cacialli, F.; Daik, R.; Feast, W. J. *Appl. Phys. Lett.* **1999**, *75*, 1679–1681.
- (11) Cao, Y.; Yu, G.; Zhang, C.; Menon, R.; Heeger, A. J. *Synth. Met.* **1997**, *87*, 171–174.
- (12) Kirchmeyer, S.; Reuter, K. J. *Mater. Chem.* **2005**, *15*, 2077–2088.
- (13) Karg, S.; Scott, J. C.; Salem, J. R.; Angelopoulos, M. *Synth. Met.* **1996**, *80*, 111–117.
- (14) Kim, Y. H.; Lee, S. H.; Noh, J.; Han, S. H. *Thin Solid Films* **2006**, *510*, 305–310.
- (15) van de Lagemaat, J.; Barnes, T. M.; Rumbles, G.; Shaheen, S. E.; Coutts, T. J.; Weeks, C.; Levitsky, I.; Peltola, J.; Glatkowski, P. *Appl. Phys. Lett.* **2006**, *88*, 233503/1–233503/3.
- (16) Kim, J. S.; Ho, P. K. H.; Murphy, C. E.; Seeley, A.; Grizzi, I.; Burroughes, J. H.; Friend, R. H. *Chem. Phys. Lett.* **2004**, *386*, 2–7.
- (17) Yan, H.; Lee, P.; Armstrong, N. R.; Graham, A.; Evmenenko, G. A.; Dutta, P.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 3172–3183.
- (18) Lim, Y.; Park, Y. S.; Kang, Y.; Jang, D. Y.; Kim, J. H.; Kim, J. J.; Sellinger, A.; Yoon, D. Y. *J. Am. Chem. Soc.* **2011**, *133*, 1375–1382.
- (19) Niu, Y. H.; Liu, M. S.; Ka, J. W.; Bardeker, J.; Zin, M. T.; Schofield, R.; Chi, Y.; Jen, A. K. Y. *Adv. Mater.* **2007**, *19*, 300–304.
- (20) Yang, X. H.; Muller, D. C.; Neher, D.; Meerholz, K. *Adv. Mater.* **2006**, *18*, 948–954.
- (21) Han, T. H.; Choi, M. R.; Woo, S. H.; Min, S. Y.; Lee, C. L.; Lee, T. W. *Adv. Mater.* **2012**, *24*, 1487–1493.
- (22) Kim, J. S.; Friend, R. H.; Grizzi, I.; Burroughes, J. H. *Appl. Phys. Lett.* **2005**, *87*, 023506/1–023506/3.
- (23) Nakayama, Y.; Morri, K.; Suzuki, Y.; Machida, H.; Kera, S.; Ueno, N.; Kitagawa, H.; Noguchi, Y.; Ishii, H. *Adv. Funct. Mater.* **2009**, *19*, 3746–3752.
- (24) Lee, B. R.; Choi, H.; Park, J. S.; Lee, H. J.; Kim, S. O.; Kim, J. Y.; Song, M. H. *J. Mater. Chem.* **2011**, *21*, 2051–2053.
- (25) Chu, T. Y.; Chen, J. F.; Chen, S. Y.; Chen, C. J.; Chen, C. H. *Appl. Phys. Lett.* **2006**, *89*, 053503–053506.
- (26) Tao, C.; Ruan, S.; Xie, G.; Kong, X.; Shen, L.; Meng, F.; Liu, C.; Zhang, X.; Dong, W.; Chen, W. *Appl. Phys. Lett.* **2009**, *94*, 043311–043314.
- (27) Chan, I. M.; Hsu, T. Y.; Hong, F. C. *Appl. Phys. Lett.* **2002**, *81*, 1899–1901.
- (28) Irwin, M. D.; Buchholz, D. B.; Hains, A. W.; Chang, R. P.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 2783–2787.
- (29) Lee, B. R.; Kim, J. W.; Kang, D.; Lee, D. W.; Ko, S. J.; Lee, H. J.; Lee, C. L.; Kim, J. Y.; Shin, H. S.; Song, M. H. *ACS Nano* **2012**, *6*, 2984–2991.
- (30) Li, S. S.; Tu, K. H.; Lin, C. C.; Chen, C. W.; Chhowalla, M. *ACS Nano* **2010**, *4*, 3169–3174.
- (31) Tung, V. C.; Kim, J.; Cote, L. J.; Huang, J. X. *J. Am. Chem. Soc.* **2011**, *133*, 9262–9265.
- (32) Gao, Y.; Yip, H. L.; Chen, K. S.; O'Malley, K. M.; Acton, O.; Sun, Y.; Ting, G.; Chen, H. Z.; Jen, A. K. Y. *Adv. Mater.* **2011**, *23*, 1903–1908.
- (33) Erickson, K.; Erni, R.; Lee, Z.; Alem, N.; Gannett, W.; Zettl, A. *Adv. Mater.* **2010**, *22*, 4467–4472.
- (34) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2006**, *442*, 282–286.
- (35) Fan, X. B.; Peng, W. C.; Li, Y.; Li, X. Y.; Wang, S. L.; Zhang, G. L.; Zhang, F. B. *Adv. Mater.* **2008**, *20*, 4490–4493.
- (36) Ouyang, J.; Xu, Q. F.; Chu, C. W.; Yang, Y.; Li, G.; Shinar, J. *Polymer* **2004**, *45*, 8443–8450.
- (37) Keawprajak, A.; Koetnuyom, W.; Piyakulawat, P.; Jiramitmongkon, K.; Pratontep, S.; Asawapirom, U. *Org. Electron.* **2013**, *14*, 402–410.
- (38) Kudin, K. N.; Ozbas, B.; Schniepp, H. C.; Prud'homme, R. K.; Aksay, I. A.; Car, R. *Nano Lett.* **2008**, *8*, 36–41.
- (39) Zhong, Z.; Dai, Y. F.; Ma, D. G.; Wang, Z. Y. *J. Mater. Chem.* **2011**, *21*, 6040–6045.
- (40) Yang, T.; Wang, M.; Duan, C.; Hu, X.; Huang, L.; Peng, J.; Huang, F.; Gong, X. *Energy Environ. Sci.* **2012**, *5*, 8208–8214.
- (41) Lampert, M. A.; Mark, P. *Current Injection in Solids*; Academic Press: New York, 1970.
- (42) Shen, Y. L.; Jacobs, D. B.; Malliaras, G. G.; Koley, G.; Spencer, M. G.; Ioannidis, A. *Adv. Mater.* **2001**, *13*, 1234–1238.
- (43) Blom, P. W. M.; de Jong, M. J. M.; van Munster, M. G. *Phys. Rev. B* **1997**, *55*, R656–R659.
- (44) Han, J. T.; Kim, B. J.; Kim, J. S.; Jeong, B. H.; Jeong, S. Y.; Jeong, H. J.; Cho, J. H.; Lee, G. W. *ACS Nano* **2011**, *5*, 8884–8891.
- (45) Han, J. T.; Kim, J. S.; Lee, S. G.; Bong, H.; Jeong, H. J.; Jeong, S. Y.; Cho, K.; Lee, G. W. *J. Phys. Chem. C* **2011**, *115*, 22251–22256.
- (46) Liang, Y. Y.; Wu, D. Q.; Feng, X. L.; Mullen, K. *Adv. Mater.* **2009**, *21*, 1679–1683.
- (47) Lee, B. R.; Jung, E. D.; Nam, Y. S.; Jung, M.; Park, J. S.; Lee, S.; Choi, H.; Ko, S.-J.; Shin, N. R.; Kim, Y.-K.; Kim, S. O.; Kim, J. Y.; Shin, H.-J.; Cho, S.; Song, M. H. Amine-Based Polar Solvent Treatment for Highly Efficient Inverted Polymer Solar Cells. *Adv. Mater.* **2014**, *26* (3), 494–500 (DOI: 10.1002/adma.201302991).
- (48) Heo, M.; Cho, H.; Jung, J. R.; Park, S.; Kim, J. Y. *Adv. Mater.* **2011**, *23*, 5689–5693.