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Graphene quantum dots as the hole transport layer material for high-performance organic solar cells†

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We present an investigation of organic photovoltaic (OPV) cells with solution-processable graphene quantum dots (GQDs) as hole transport layers (HTLs). GQDs, with uniform sizes and good conductivity, are demonstrated to be excellent HTLs in both polymer solar cells (PSCs) and small-molecule solar cells (SMSCs) with the blend of poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT:PC₆₁BM) and small molecule DR₃TBDT:[6,6]-phenyl-C₇₁-butyric acid methyl ester (DR₃TBDT:PC₇₁M) as the active layer, respectively. The PSCs and SMSCs based on GQDs yield power conversion efficiencies of 3.51% and 6.82%, respectively, both comparable to those of solar cells with PEDOT:PSS as the HTLs. In addition, the cells with GQDs as HTLs exhibit much more reproducible performance and longer lifetime. In light of the high stability, low cost and easy processing, these results indicate that GQDs can be potentially used to replace PEDOT:PSS for producing high-performance and stable organic photovoltaic cells.

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1 Introduction

Organic photovoltaic (OPV) cells, as a promising renewable energy source, have attracted more and more interest due to their light-weight, low cost, ease of fabrication, solution-based process, and mechanical flexibility.^{1–5} In OPV cells, the interface between the active layer and the two electrodes plays an essential role in achieving both required high performance and good stability.^{6–8} The functions of interfacial layers include adjusting the energy barrier between the active layer and the electrodes, forming a selective contact for carriers of one sort, and determining the polarity of the cell.^{9,10} For the use of the interfacial layer, several key factors that need consideration are transparency, good stability, solution processability, appropriate work function, high conductivity, homogeneity, *etc.* Currently, the commercially available conducting polymer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), is widely employed as the solution-processable interfacial layer to increase the work-function of ITO for effective hole collection in organic electronic devices. However, PEDOT:PSS is

highly acidic, hygroscopic, and electrically inhomogeneous, resulting in instability in the long term.^{11,12} Therefore, seeking substitute hole transport materials for PEDOT:PSS to achieve high-performance and stable OPV cells is in high demand.

Recently, graphene oxide (GO) based hole transport layer materials have been widely studied to replace PEDOT:PSS for high-efficiency OPV cells.^{13–17} But GO hole transport layers (HTLs), with the low conductivity, lead to high series resistance, low fill factor (FF), and hence a low power conversion efficiency (PCE). In this regard, a number of approaches have been developed to enhance the conductivity of GO layers, such as adding single-walled carbon nanotubes to the GO layer,¹⁴ using *p*-toluenesulfonyl hydrazide to reduce GO,¹⁵ and using sulfuric acid to prepare sulfated GO.¹⁶ These approaches all enhance the performance of the solar cells with GO as HTLs. However, besides the poor conductivity, GO possesses non-uniform sizes, which makes GO interfacial layers inhomogeneous and thus gives rise to the problem of reproducibility for solar cell performance. To further improve the hole transport capability of GO, therefore, it is necessary to prepare GO sheets with both high conductivity and uniform sizes. With narrow size distribution, high mobility and tunable band gap, graphene quantum dots (GQDs) have drawn great attention and been applied in bioimaging, light emitting diodes and photovoltaics.^{18–21} GQDs with small sizes and high loading of oxygen-containing groups exhibit excellent dispersibility in water, and hence are able to avoid aggregation during partial reduction. Herein, GQDs with uniform sizes were prepared, and were partially reduced by ammonia water. The resultant GQDs were introduced into

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† Electronic supplementary information (ESI) available: Photoluminescence (PL) spectra of GQDs, UV/vis absorption spectra of the solution of GO and GQDs, XPS analysis, Raman spectra, FT-IR spectra and UPS spectra of GO and GQDs, optical transmission spectra of the GO and GQD films deposited on ITO glass, and AFM height images of GO and GQD films with different thickness. See DOI: 10.1039/c3cp53283f

organic solar cells as the hole transport material. As a result, the overall performance of polymer solar cells (PSCs) with P3HT:PC₆₁BM as the active layer and GQDs as HTLs was far superior to the cells based on GO. More importantly, high-performance OPV cells were fabricated by using GQDs as HTLs in both the polymer solar cells (PSCs) and the small-molecule solar cells (SMSCs). GQD-based PSCs with P3HT:PC₆₁BM as the active layer yielded a PCE of 3.51%, and GQD-based SMSCs with the recent high-performance small molecule DR₃TBDT²² as the donor and PC₇₁BM as the acceptor achieved a PCE of 6.82%, the highest so far for using graphene material as the HTL for small-molecule solar cells. The PCEs of GQD-based PSCs and GQD-based SMSCs are both comparable to the PEDOT:PSS-based solar cells. Furthermore, the cells with GQDs as HTLs exhibit excellent reproducibility and much better stability. These results indicate that GQDs could be an effective alternative to the conventional PEDOT:PSS as hole transport layers for high-performance OPV cells.

2 Experimental section

2.1 Preparation of graphene quantum dots (GQDs) and graphene oxide (GO)

GQDs were synthesized from carbon fibers by a facile one-step acid treatment based on the method described elsewhere.^{23,24} During the final work-up of the preparation of GQDs, ammonia water was added to neutralize the redundant acidity and to reduce the GQDs partially. In detail, carbon fibers (9 g) were added into a mixture of concentrated H₂SO₄ (600 mL) and HNO₃ (200 mL). The solution was sonicated for 4 hours at room temperature and stirred for 30 hours at 100 °C. After being cooled to room temperature, the mixture was diluted with deionized (DI) water. The pH was tuned to 7 with saturated ammonia solution. The resulting solution was further dialyzed in a dialysis bag (retained molecular weight: 2000 Da) to remove impurity ions. The sizes of most GQDs range from 20 to 30 nm. The GQDs solution presents a yellow luminescence under UV light with 365 nm excitation. The solution is stable in water for several months without any changes. In comparison, GO was also prepared using the common modified Hummer's method,²⁵ without adding ammonia water that could lead to irreversible aggregation of GO sheets.

2.2 Instrument and characterization

The morphology of GO and GQDs thin films deposited on SiO₂/Si substrates was examined by AFM (Nanoscope IIIa Multimode 8, Bruker, operating in ScanAsyst mode). The thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 409PC instrument at a heating rate of 10 °C per minute under nitrogen flow. Photoluminescence characterization was done using a Fluoro Max-P luminescence spectrometer using a xenon lamp as the source of excitation. UV-vis absorption spectra were obtained using a JASCO V-570 spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was done using an AXIS HIS 165 spectrometer (Kratos Analytical) with a monochromatized Al K α X-ray source (1486.71 eV photons). Raman scattering was

performed using a Renishaw inVia Raman spectrometer using laser excitation at 514.5 nm. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 spectrometer (Germany). The Ultraviolet Photoelectron Spectroscopy (UPS) measurements (Thermo ESCALAB 250) were carried out using the He I ($h\nu = 21.2$ eV) source.

2.3 Device fabrication and characterization

The solar cells were fabricated with a conventional structure of glass/ITO/HTLs/donor:acceptor/LiF/Al using a solution process. ITO/glass substrates were cleaned in detergent, deionized water, acetone, and isopropyl under ultrasonication for 15 min each, and then dried by nitrogen flow. The HTLs were then spin-coated on the clean ITO glass under the following conditions. PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45 μ m) was spin-coated onto the ITO substrates at 3000 rpm for 20 s. GO and GQDs were spin-coated from their aqueous solutions onto the ITO substrates at 2000 rpm for 60 s. The thickness of GO and GQDs layers was controlled through the variation in the concentration of GO and GQDs dispersion. The thickness of GO and GQDs layers was measured by atomic force microscopy (AFM) on the silicon substrate with the materials spin-coated under the same conditions as those used for device fabrication. The AFM height images of GO and GQDs with different thickness are shown in Fig. S8 (ESI[†]). The PEDOT:PSS films and graphene-based hole transport layers (GO and GQDs) were baked at 120 °C for 15 min under ambient conditions. The substrates were then transferred into an argon-filled glovebox. Subsequently, the active layer was spin-coated on the HTLs. For the polymer solar cells, the *o*-dichlorobenzene (*o*-DCB) solution containing 18 mg mL⁻¹ of P3HT and 18 mg mL⁻¹ of PC₆₁BM was spin-coated at 800 rpm for 18 s. The resulting active-coated substrates were kept in a petri-dish at room temperature for 1 h to allow the *o*-DCB solvent to evaporate slowly, and then they were annealed inside the glove box at 110 °C for 10 min. For the small-molecule solar cells, the chloroform solution containing 8 mg mL⁻¹ of DR₃TBDT and 6.4 mg mL⁻¹ of PC₇₁BM was spin-cast onto the HTLs at 1700 rpm for 20 s. In the final stage, 0.8 nm LiF and 50 nm Al were thermally evaporated onto the active layer at high vacuum ($< 2 \times 10^{-4}$ Pa) with a metal mask. The effective area of each cell was ~ 4 mm² as defined by the mask. The current density-voltage (J - V) curves of OPV cells were obtained using a Keithley 2400 source-measure unit. The photovoltaic characteristics were measured under illumination simulated 100 mW cm⁻² AM1.5G irradiation using an Oriel 96 000 solar simulator, calibrated with a standard Si solar cell.

3 Results and discussion

The prepared GO and GQDs were investigated by several analyzing methods, such as atomic force microscopy (AFM), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy (PL), ultraviolet-visible spectroscopy (UV-vis), Raman, and Fourier transform infrared spectroscopy (FT-IR). Fig. 1a shows the AFM images of GO and GQDs. The thickness of GO and GQDs is both in the

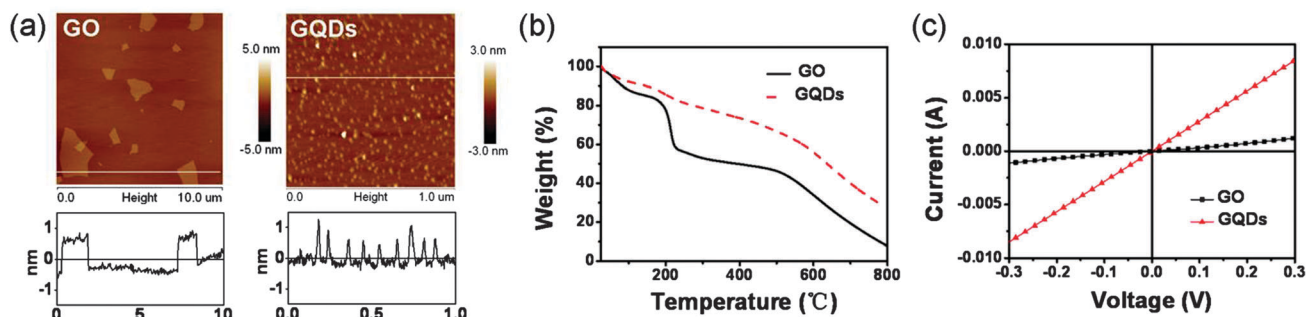


Fig. 1 (a) AFM height images of GO and GQDs. (b) TGA of GO and GQDs. (c) Current–voltage curves of the GO and GQDs films.

range of 0.7–1.4 nm, corresponding to the thickness of single layer graphene oxide.^{26,27} The GQDs are of uniform sizes and have a narrow distribution from ~20 to 30 nm, while the GO sheets are non-uniform with a size distribution from hundreds of nanometers to a few microns. Besides, GQDs possess less degree of oxidation than GO. After ammonia water was added, partial reduction of GQDs was observed as indicated by the significant enhancement of the darkness of the product, and GO showed a brown color that was much more lighter than GQDs. Furthermore, as shown in the TGA (Fig. 1b), GO and GQDs exhibit a mass loss of ~30% and ~10% in the range of 110–230 °C under N₂, corresponding to the removal of oxygen-containing groups. The less oxygen-containing groups of GQDs are due to the partial reduction of GQDs. We also measured the resistance of GO and GQDs films from resistive devices with the structure of ITO/GO or GQDs/Al. The current–voltage measurement is shown in Fig. 1c. The thickness of GO and GQDs films is both ~30 nm. The current–voltage measurements from these devices indicate the resistance values of GO and GQDs films are 184.5 and 35.3 Ω, respectively. The resistance of GO film is 5 times greater than that of GQD film, which is believed to be associated with the low oxygen content and partially recovered conjugation in GQDs. Besides, prior to the use of GQDs as HTL materials in OPV cells, we measured the work function of GQDs by Ultraviolet Photoelectron Spectroscopy (UPS). The work function values obtained from UPS plots (Fig. S7, ESI[†]) was found to be 4.9 eV similar to GO (4.7–5.0 eV).^{13,16,17} These values match the highest occupied molecular orbital (HOMO) level of P3HT (−5.0 eV) for an ohmic contact.

In order to select the optimum thickness of GO and GQDs HTLs, we fabricated PSCs with different thickness of GO and GQDs layers. The cell structure is ITO/HTLs/P3HT:PC₆₁BM (200 nm)/LiF (0.8 nm)/Al (50 nm). Fig. 2 shows the measured current density–voltage curves of the PSCs. The short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) values for PSCs are listed in Table 1. As shown, the cells with too thin layers of GO (1 nm) or GQDs (1 nm) show relatively poor performance, because the graphene-based interfacial layers cannot cover the entire electrode. But too thick graphene-based interfacial layers lead to decreased J_{sc} , FF, and thus the decreased PCEs. The decrease in J_{sc} and FF can be attributed to the increased series resistance of cells with thicker graphene interfacial layers. Excellent PCEs were

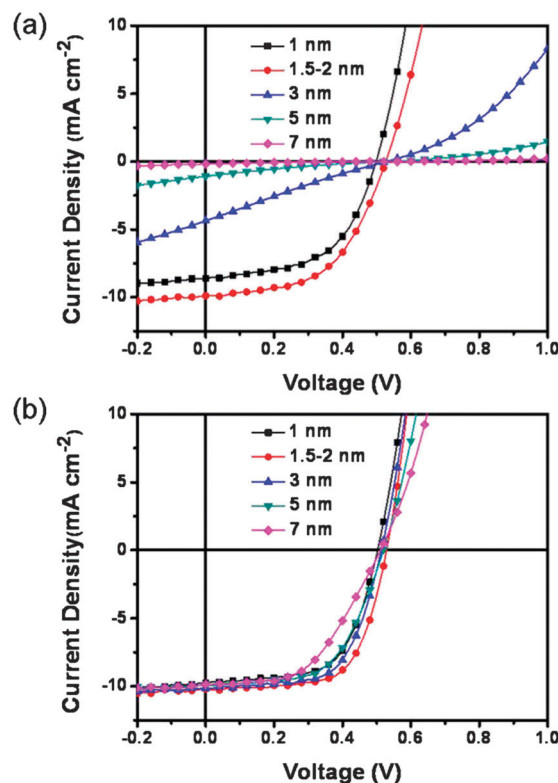


Fig. 2 Current density–voltage curves of the PSCs using different thicknesses of GO (a) or GQDs (b) as HTLs.

Table 1 The summary of typical photovoltaic parameters of the PSCs without HTLs, and with PEDOT:PSS, GO and GQDs as HTLs

	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
ITO only	0.44	8.15	56.4	2.02
PEDOT:PSS	0.54	10.51	62.1	3.52
GO (1 nm)	0.50	8.62	54.8	2.36
GO (1.5–2 nm)	0.52	9.88	54.0	2.77
GO (3 nm)	0.52	4.34	23.5	0.53
GO (5 nm)	0.52	0.19	1.1	0.11
GO (7 nm)	0.52	0.17	0.17	0.015
GQDs (1 nm)	0.50	9.77	62.1	3.03
GQDs (1.5–2 nm)	0.52	10.20	66.3	3.51
GQDs (3 nm)	0.52	10.15	62.2	3.28
GQDs (5 nm)	0.52	9.89	58.5	3.01
GQDs (7 nm)	0.52	9.86	50.2	2.57

achieved with the optimized layer thickness of GO (1.5–2 nm) and GQDs (1.5–2 nm). In addition, as the thickness of the GO layers increases from 1.5–2 nm to 7 nm, the J_{sc} and FF decrease by 98.3% and 99.7% respectively, and hence the PCE decreases sharply from 2.77% to 0.015% (Table 1). In contrast, when the thickness of GQDs layers changes from 1.5–2 nm to 7 nm, the PCE of the cells with GQDs decreases within a narrow range from 3.51% to 2.57%. These results indicate that the performance of PSCs with GQDs shows relatively weak dependence on the thickness of GQDs layer, resulting in the more reproducible cell-performance.

With the optimized thickness, we fabricated PSCs without HTLs and with PEDOT:PSS, GO (1.5–2 nm) or GQDs (1.5–2 nm) as HTLs. The current density–voltage (J – V) curves are reported in Fig. 3a, and the corresponding photovoltaic parameters are summarized in Table 1. It can be seen that the ITO-only cell shows V_{oc} of 0.44 V, J_{sc} of 8.15 mA cm^{-2} , FF of 56.4% and a PCE of 2.02%. All solar cell parameters are enhanced by the introduction of PEDOT:PSS, GO (1.5–2 nm) and GQDs (1.5–2 nm) as HTLs. The PCEs of the cells with PEDOT:PSS, GO (1.5–2 nm) and GQDs (1.5–2 nm) are 3.52%, 2.77% and 3.51%, respectively. The cell with GO (1.5–2 nm) as HTLs shows relatively poor photovoltaic performance compared to the PEDOT:PSS-based cell. By contrast, the overall photovoltaic characteristics of the cell with the GQDs (1.5–2 nm) are highly comparable to those of the cell with PEDOT:PSS, indicating that the GQDs have a similar function in the solar cell as PEDOT:PSS, and it is possible to substitute the PEDOT:PSS with the GQDs.

The excellent performance of GQDs cells can be due to the homogeneous morphology and the good conductivity of GQDs layers. AFM images of the GO film and the GQDs film with the thickness of (1.5–2 nm) are shown in Fig. 3b. The root-mean-square

Table 2 Standard deviations (σ) of photovoltaic parameters (V_{oc} , J_{sc} , FF, and PCE), R_s and R_{sh} of PSCs with PEDOT:PSS, GO and GQDs as HTLs

HTL	$\sigma_{V_{oc}}$	$\sigma_{J_{sc}}$	σ_{FF} (%)	σ_{PCE} (%)	R_s ($\Omega \text{ cm}^2$)	R_{sh} ($\Omega \text{ cm}^2$)
ITO	0.0105	0.3681	2.15	0.0798	4.37	409.84
PEDOT:PSS	0.0100	0.3771	2.06	0.0731	4.55	909.09
GO (1 nm)	0.0170	0.3886	3.05	0.1421	4.20	380.89
GQDs (1 nm)	0.0115	0.3520	2.03	0.0478	3.47	523.56
GO (1.5–2 nm)	0.0184	0.3960	3.05	0.1455	4.66	427.35
GQDs (1.5–2 nm)	0.0111	0.3485	2.03	0.0478	2.23	833.40
GO (3 nm)	0.0181	0.3892	2.01	0.1218	37.45	117.23
GQDs (3 nm)	0.0110	0.3489	2.00	0.0362	2.97	724.63
GO (5 nm)	0.0178	0.0537	0.46	0.0478	213.67	297.62
GQDs (5 nm)	0.0119	0.3534	2.12	0.0456	3.31	617.28
GO (7 nm)	0.0189	0.0462	0.06	0.0042	1462.84	1642.03
GQDs (7 nm)	0.0121	0.3518	2.05	0.0397	3.96	581.40

(rms) roughness of GO film and GQDs film are 0.76 nm and 0.34 nm, respectively, showing that the GQDs film is smoother and more uniform than GO film. For better comparison, the series resistance (R_s) and shunt resistance (R_{sh}) of the solar cells are shown in Table 2. Compared with the cell using GO (1.5–2 nm) as HTLs, the cell based on GQDs (1.5–2 nm) exhibits a lower R_s ($2.23 \Omega \text{ cm}^2$ vs. $4.66 \Omega \text{ cm}^2$), a much higher R_{sh} ($833.40 \Omega \text{ cm}^2$ vs. $427.35 \Omega \text{ cm}^2$) and hence a significantly improved FF (66.3% vs. 54.0%) and PCE (3.51% vs. 2.77%). The lower R_s and the higher R_{sh} of the cells with GQDs should result from the better

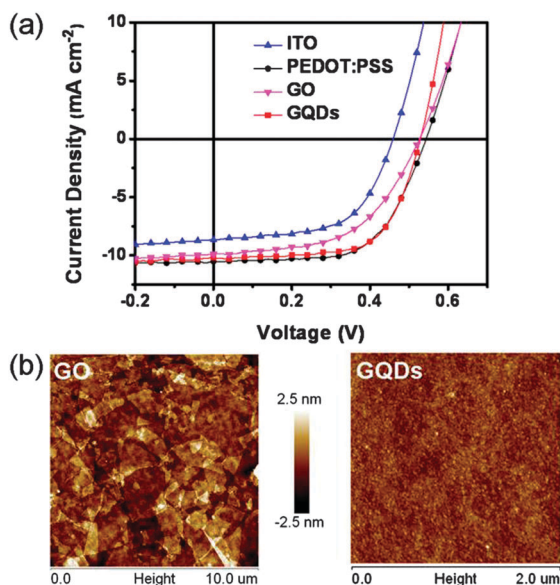


Fig. 3 (a) Current density–voltage curves of PSCs without the hole transport layer (the curve labeled as ITO), and with PEDOT:PSS, GO (1.5–2 nm) and GQDs (1.5–2 nm) as HTLs. (b) AFM images of GO and GQDs thin films with the thicknesses of 1.5–2 nm deposited on SiO_2/Si substrates.

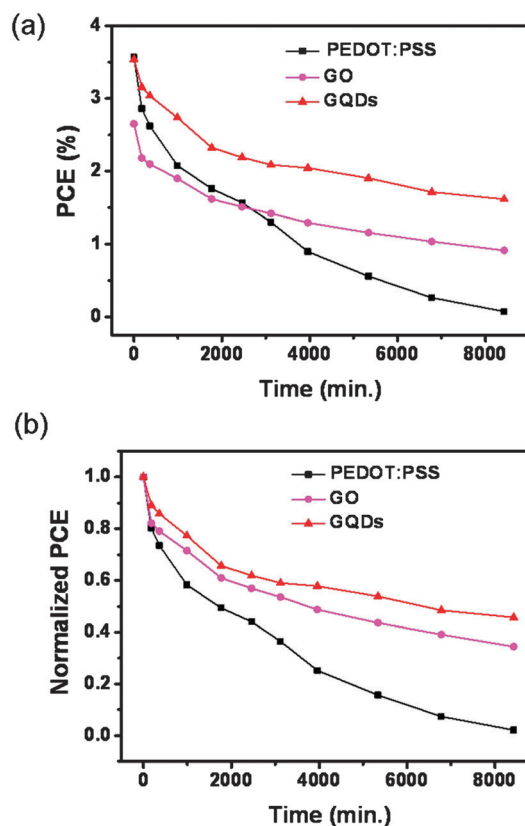


Fig. 4 (a) Changes in PCE of PSCs with PEDOT:PSS, GO (1.5–2 nm) and GQDs (1.5–2 nm) as HTLs during exposure to air. (b) The normalized PCE of PSCs with PEDOT:PSS, GO (1.5–2 nm) and GQDs (1.5–2 nm) as HTLs.

conductivity and homogeneous morphology of the GQDs layer. In addition, Table 2 compiles a statistical analysis of 30 individual devices for each HTLs, showing the reproducible differences in the V_{oc} , J_{sc} , FF and PCE. The photovoltaic parameters of GQDs-based PSCs show overall significantly lower standard deviations (σ), confirming that the cells with GQDs as HTLs exhibit better reproducibility for cell-performance.

To investigate the stability and feasibility of PSCs with different hole transport layers, lifetime testing experiments were conducted. The performance of un-encapsulated cells with PEDOT:PSS, GO and GQDs as HTLs was recorded in air at $\sim 50\%$ relative humidity and 25°C room temperature. Fig. 4 shows the PCE decay over time for cells using PEDOT:PSS, GO (1.5–2 nm) and GQDs (1.5–2 nm) as HTLs. In the lifetime testing, the degradation of photovoltaic performance in the cells with GQDs as HTLs is slower than that in the cells based on PEDOT:PSS and GO. The PCE of PEDOT:PSS-based cells dropped rapidly to $\sim 0\%$ after exposure to air for 8430 min. In contrast, the GO-based cells and GQDs-based cells remained a PCE of 0.91% (34% of initial PCE) and

Table 3 Summary of typical photovoltaic parameters of the SMSCs without HTLs and with PEDOT:PSS and GQDs as HTLs

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
ITO only	0.46	10.54	47.0	2.28
PEDOT:PSS	0.93	11.40	65.3	6.92
GQDs (1.5–2 nm)	0.92	11.36	65.2	6.82
GQDs (5 nm)	0.90	10.83	63.0	6.15
GQDs (7 nm)	0.88	10.78	61.7	5.86

1.62% (45% of initial PCE) after 8430 min, respectively. The PEDOT:PSS-based cells with quicker degradation in cell performance could be attributed to the high acidity and hygroscopic properties of PEDOT:PSS. These results indicate that the GQDs are better suitable than both PEDOT:PSS and GO for the fabrication of more stable organic photovoltaic cells.

To further test the applicability of GQDs in OPV cells, we applied GQDs HTLs in small-molecule-based solar cells (SMSCs). SMSCs are drawing more and more attention recently due to the small molecule donor with some promising advantages, such as high purity, well-defined structure, and versatile molecular structure.^{28–31} Hence, it is important that GQDs hole transport layer material is also suitable for SMSCs. To directly evaluate the performance of GQDs as HTLs in SMSCs, three types of SMSCs with a blend of DR₃TBDT (Fig. 5a) and PC₇₁BM as the active layer were fabricated: the cell without HTLs, and the cell with either PEDOT:PSS or GQDs as HTLs. The typical J - V curves of cells are shown in Fig. 5b, and the values of J_{sc} , V_{oc} , FF, and PCE for each set of cell are summarized in Table 3. It can be seen that the PEDOT:PSS-based cell yields a PCE of 6.92%.²² The cell using GQDs (1.5–2 nm) as the hole transport layer exhibits V_{oc} of 0.92 V, J_{sc} of 11.36 mA cm^{-2} , FF of 65.2% and a PCE of 6.82%. These values are all close to those of the PEDOT:PSS-based SMSCs. These results indicate the wide applicability of GQDs to be efficient hole transport layers. Additionally, we also investigated the influence of GQDs layer thickness on the performance of SMSCs. The results are shown in Fig. 5c and Table 3. Similar to PSCs, with increasing GQDs layer thickness from 1.5–2 nm to 7 nm, a trend of decreasing PCE can be observed, and the optimized thickness is around 1.5–2 nm.

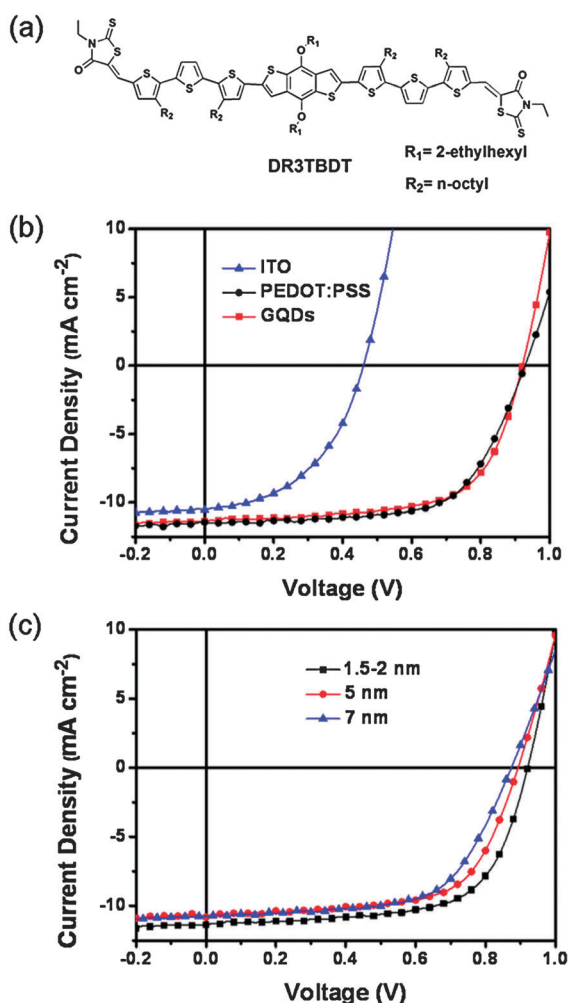


Fig. 5 (a) Chemical structure of the small molecule DR₃TBDT. (b) Current density–voltage curves of SMSCs without hole transport layers (curve labeled as ITO), and with PEDOT:PSS and GQDs (1.5–2 nm) as HTLs. (c) Current density–voltage curves of SMSCs based on GQDs with the different thickness.

4 Conclusions

GQD thin films with homogenous morphology and high conductivity have been demonstrated to be efficient hole transport layers for organic solar cells. The performances of PSCs and SMSCs with GQDs as the HTLs are both comparable to those of the cells using the conventional PEDOT:PSS. Furthermore, the overall photovoltaic characteristics of cells based on GQDs exhibit significant improvement compared with GO-based cells. Importantly, the solar cells using GQDs as HTLs also show longer lifetime and more reproducible photovoltaic performance. These results indicate that as a promising hole transport layer material for organic solar cells, GQDs have great potential to replace the conventional hole transport layer material PEDOT:PSS.

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Notes and references

- 1 B. C. Thompson and J. M. J. Frechet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58–77.
- 2 Y. J. Cheng, S. H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868–5923.
- 3 D. J. Lipomi, H. Chong, M. Vosgueritchian, J. Mei and Z. Bao, *Sol. Energy Mater. Sol. Cells*, 2012, **107**, 355–365.
- 4 Y. Lin, Y. Li and X. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245–4272.
- 5 A. Mishra and P. Baeuerle, *Angew. Chem., Int. Ed.*, 2012, **51**, 2020–2067.
- 6 Z. He, C. Zhong, X. Huang, W. Y. Wong, H. Wu, L. Chen, S. Su and Y. Cao, *Adv. Mater.*, 2011, **23**, 4636–4643.
- 7 Y. Sun, M. Wang, X. Gong, J. H. Seo, B. B. Y. Hsu, F. Wudl and A. J. Heeger, *J. Mater. Chem.*, 2011, **21**, 1365–1367.
- 8 J. You, C. C. Chen, L. Dou, S. Murase, H.-S. Duan, S. A. Hawks, T. Xu, H. J. Son, L. Yu, G. Li and Y. Yang, *Adv. Mater.*, 2012, **24**, 5267–5272.
- 9 R. Steim, F. R. Kogler and C. J. Brabec, *J. Mater. Chem.*, 2010, **20**, 2499–2512.
- 10 L. M. Chen, Z. Xu, Z. Hong and Y. Yang, *J. Mater. Chem.*, 2010, **20**, 2575–2598.
- 11 M. Jorgensen, K. Norrman and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 686–714.
- 12 L. S. C. Pingree, B. A. MacLeod and D. S. Ginger, *J. Phys. Chem. C*, 2008, **112**, 7922–7927.
- 13 S. S. Li, K. H. Tu, C. C. Lin, C. W. Chen and M. Chhowalla, *ACS Nano*, 2010, **4**, 3169–3174.
- 14 J. Kim, V. C. Tung and J. Huang, *Adv. Energy Mater.*, 2011, **1**, 1052–1057.
- 15 J. M. Yun, J. S. Yeo, J. Kim, H. G. Jeong, D. Y. Kim, Y.-J. Noh, S.-S. Kim, B. C. Ku and S.-I. Na, *Adv. Mater.*, 2011, **23**, 4923–4928.
- 16 J. Liu, Y. Xue and L. Dai, *J. Phys. Chem. Lett.*, 2012, **3**, 1928–1933.
- 17 D. Yang, L. Zhou, L. Chen, B. Zhao, J. Zhang and C. Li, *Chem. Commun.*, 2012, **48**, 8078–8080.
- 18 Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou and L. Qu, *Adv. Mater.*, 2011, **23**, 776–780.
- 19 J. Shen, Y. Zhu, X. Yang and C. Li, *Chem. Commun.*, 2012, **48**, 3686–3699.
- 20 H. Sun, L. Wu, N. Gao, J. Ren and X. Qu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1174–1179.
- 21 V. Gupta, N. Chaudhary, R. Srivastava, G. D. Sharma, R. Bhardwaj and S. Chand, *J. Am. Chem. Soc.*, 2011, **133**, 9960–9963.
- 22 J. Zhou, X. Wan, Y. Liu, Y. Zuo, Z. Li, G. He, G. Long, W. Ni, C. Li, X. Su and Y. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 16345–16351.
- 23 J. Peng, W. Gao, B. K. Gupta, Z. Liu, R. Romero-Aburto, L. Ge, L. Song, L. B. Alemany, X. Zhan, G. Gao, S. A. Vithayathil, B. A. Kaiparettu, A. A. Marti, T. Hayashi, J.-J. Zhu and P. M. Ajayan, *Nano Lett.*, 2012, **12**, 844–849.
- 24 J. Luo, L. J. Cote, V. C. Tung, A. T. L. Tan, P. E. Goins, J. Wu and J. Huang, *J. Am. Chem. Soc.*, 2010, **132**, 17667–17669.
- 25 L. Zhang, J. Liang, Y. Huang, Y. Ma, Y. Wang and Y. Chen, *Carbon*, 2009, **47**, 3365–3368.
- 26 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228–240.
- 27 S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature*, 2006, **442**, 282–286.
- 28 D. Demeter, T. Rousseau, P. Leriche, T. Cauchy, R. Po and J. Roncali, *Adv. Funct. Mater.*, 2011, **21**, 4379–4387.
- 29 R. Fitzner, E. Mena-Osteritz, A. Mishra, G. Schulz, E. Reinold, M. Weil, C. Koerner, H. Ziehlke, C. Elschner, K. Leo, M. Riede, M. Pfeiffer, C. Uhrich and P. Baeuerle, *J. Am. Chem. Soc.*, 2012, **134**, 11064–11067.
- 30 S. Loser, C. J. Bruns, H. Miyauchi, R. P. Ortiz, A. Facchetti, S. I. Stupp and T. J. Marks, *J. Am. Chem. Soc.*, 2011, **133**, 8142–8145.
- 31 G. C. Welch, L. A. Perez, C. V. Hoven, Y. Zhang, X. D. Dang, A. Sharenko, M. F. Toney, E. J. Kramer, N. Thuc-Quyen and G. C. Bazan, *J. Mater. Chem.*, 2011, **21**, 12700–12709.