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PAPER

Aqueous-solution-processed PPV– $Cd_xHg_{1-x}Te$ hybrid solar cells with a significant near-infrared contribution[†]

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Aqueous poly(*p*-phenylene-vinylene) (PPV): $Cd_xHg_{1-x}Te$ nanocrystal (NC) hybrid solar cells are prepared with heat-introduced aggregation and growth of the NCs. The morphology of the active layer is easily controlled by tuning the composition of the donor and acceptor and the charge carrier mobility is largely improved after annealing for 1 h. Through passivating the surface traps on the NCs with the UV-ozone radiation, the V_{oc} can be improved. The photovoltaic devices present a wide response range in the solar spectrum from UV to 1200 nm. The near-infrared absorption is attributed to the $Cd_xHg_{1-x}Te$ NCs and the absorption extends to near-infrared as the Cd/Hg ratios decrease, which favors the stability of the NCs due to the strong ionic bond of HgTe. The power conversion efficiency (PCE) of such photovoltaic devices exhibits about 1.5% under AM 1.5G illumination with a high shortcircuit current density (J_{sc}) of 12.84 mA cm⁻². 11.4% near-infrared contribution is observed from the external quantum efficiency (EQE) measurement with only simple device structures.

Introduction

Because they can be solution-processed, π -conjugated polymers have been considered as competitive candidates to produce large area, low cost, and flexible solar cells.¹⁻⁹ The power conversion efficiency (PCE) of polymer solar cells (PSC) has approached to 9% since the bulk heterojunction structure was employed. $^{10-12}$ Meanwhile, the low charge carrier mobility of the polymer materials greatly stimulates the construction of organic-inorganic hybrid solar cells (HSC)¹³⁻¹⁷ because inorganic materials are capable of overcoming the electron transport limitations associated with the organic materials.^{13,16,18,19} In particular, the recent advances in colloidal synthesis of high quality nanocrystals (NCs) allow the band gaps of inorganic materials to be tailored, 20-22 thus opening the door for further enhancing the performance of HSC. With respect to the light harvesting, employing NCs with nearinfrared absorption is another effective method to increase the photocurrent, because half of the Sun's power reaching the surface of the Earth belongs to the infrared.²³ In this aspect, Pbcontaining NCs, such as PbS and PbSe, are mostly investigated.²³⁻²⁶ It should be mentioned that the near-infrared NCs have been synthesized in organic media, and the device fabrication is carried out in organic solvents. To exploit the merit of the solution-processed nature of HSC as well as avoiding

environmental pollution, aqueous solution-processed materials are welcome in the construction of solar cells.²⁷⁻³² However, the fabrication of aqueous solution-processed HSC is still challenging due to the limitation of too many surface traps of the aqueous NCs, leading from the complex aqueous environment in the NCs synthesis. What's more, most aqueous solution-processed HSC are composed of NCs with UV–visible absorption, while nearinfrared NCs are rarely applied in device construction.

As a conventional material in construction of thin film solar cells, bulk Cd_xHg_{1-x} Te crystal has a changeable band gap, from 0 to 1.6 eV, potentially suitable for fabrication of HSC with proper conjugated polymers. In this paper, aqueous $Cd_xHg_{1-x}Te$ NCs with tunable band gap were synthesized using mercaptocompounds as the capping ligands. Moreover, the Cd/Hg ratio in Cd_xHg_{1-x} Te NCs could be altered in a broad range, which made the absorption of $Cd_xHg_{1-x}Te$ tunable from visible to nearinfrared region. We reported the fabrication of the HSC from aqueous solution-processed materials, employing the watersoluble poly (p-phenylene-vinylene) (PPV) precursor, which were converted to the PPV (donor) after annealing under nitrogen, and aqueous Cd_xHg_{1-x}Te NCs (acceptor) with near-infrared absorption. Efficient HSC with the PCE of 1.5% was fabricated through the controllable heat-introduced aggregation and growth of the NCs, which involved a near-infrared contribution up to 11.4%.

Experimental

Materials

Tellurium powder (200 mesh, 99.8%), R, R_0 -dichloro-p-xylene (98%), tetrahydrothiophene (99%) and 3-mercaptopropionic

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acid (MPA) were all purchased from Aldrich Chemical Corp. $CdCl_2$ (99+ %), $HgCl_2$ (99+ %) were commercially available. All of the solvents were analytical grade and used as received.

The preparation of the PPV

The synthesis method of the PPV precursor could be found elsewhere.³³ Briefly, 0.4 M NaOH 10 ml was added to 10 ml of 0.4 M *p*-xylylenebis (tetrahydrothiophenium chloride) methanol solution. This solution was cooled to 0-5 °C in an ice bath. The reaction proceeded for 1 h and then was terminated by the addition of 0.4 M HCl aqueous solution to neutralize the reaction solution. The PPV precursor aqueous solution was dialyzed against deionized water for one week. The PPV precursor can be converted to conjugated PPV after annealing under nitrogen, and the synthesis route is presented in Scheme 1.

The synthesis of aqueous Cd_xHg_{1-x}Te NCs

 $Cd_xHg_{1-x}Te$ NCs covered with 3-mercaptopropionic acid were prepared according to the previous method.³⁴ Freshly prepared NaHTe solution was added to a N₂-saturated aqueous solution of CdCl₂ and HgCl₂ at pH 9 in the presence of MPA as a stabilizing agent. The ratio of (Cd + Hg) : MPA : HTe⁻ was 1 : 2.9 : 0.5 and the concentration of metal ion (Cd + Hg) was 3.75 × 10⁻³ M. The precursor solution was then placed in an oven at 40 °C for 30 min. For the CdTe NCs fabrication, the precursor solution was suffered refluxing for 5 h instead of oven. The absorption of the NCs solution can be found in Fig. S1.[†]

Devices fabrication

ITO-coated glasses first underwent ultrasonic treatment in chloroform, acetone, isopropyl, then were rinsed by deionized water before drying in N₂ flow, followed by the oxygen plasma treatment for 5 min; then spin-coating of the PEDOT:PSS layer (45 nm) at 3000 rpm for 60 s followed by annealing at 250 °C for 30 min under N_2 in order to avoid dissolution by the active layer. Before blending the donor and acceptor, $Cd_xHg_{1-x}Te$ NCs underwent ligand exchange with 0.2 mg ml⁻¹ 2-mercaptoethylamine water solution (2-MAW), and the precipitate was obtained by centrifugation at 6000 r per min for 5 min. The precipitated NCs were redissolved in 2-MAW and further centrifugated by the addition of isopropanol to remove the superfluous salts and ligands, and this process was repeated two times. The precipitated NCs were redissolved in deionized water with a concentration of 84 mg ml⁻¹. The photoactive layer was formed by spin-coating (at 600 r per min), with an aqueous solution containing 1 mg ml⁻¹ PPV precursor and 42 mg ml⁻¹ N⁻¹Cs.



Scheme 1 The synthetic route for the conjugated PPV.

The blend film was annealed at 300 $^{\circ}$ C in the glove box, followed by the evaporation of Al electrode with a 4 mm² mask.

Characterization

UV-vis spectra were acquired on a Shimadzu 3600 UV-vis-NIR spectrophotometer. Fluorescence spectra were acquired on a Shimadzu RF-5301 PC spectrofluorimeter and the excitation wavelength was 365 nm. Atomic force microscopy (AFM) images were recorded in tapping mode with a Digital Instruments NanoScope IIIa under ambient conditions. Transmission electron microscopy (TEM) images were recorded on a JEOL-2010 electron microscope operating at 200 kV. The film thicknesses were measured on an Ambios Tech. XP-2 profilometer. EQE was measured under illumination of monochromatic light from the xenon lamp using a monochromator (Jobin Yvon, TRIAX 320) and detected by a computer-controlled Stanford SR830 lock-in amplifier with a Stanford SR540 chopper. The current density-voltage (J-V) characterization of PV devices under white-light illumination from an SCIENCETECH 500-W solar simulator (AM 1.5G, 100 mW cm⁻²) was carried out on computer-controlled Keithlev 2400 Source Meter measurement system in a glove box filled with nitrogen atmosphere (<1 ppm H_2O and <1 ppm O_2). All the other measurements were performed under ambient atmosphere at room temperature.

Results and discussion

The PPV precursor converts to PPV with a conjugated structure during annealing under nitrogen and the formation process of the PPV can be found in Scheme 1, while the surface ligands of the NCs are also removed and the electron transport path forms as the NCs aggregate and grow. The process can be illustrated by the scheme in Fig. 1(a). Before the annealing process, the NCs disperse in the polymers and less interlinking exists. During the annealing process, the aggregation and growth of the NCs take place. The growth of the NCs results in interlinking of the NCs, and an effective path is generated for the charge carrier



Fig. 1 (a) The scheme describes the annealing process of the photoactive layer, and the interpenetrating network structure forms after annealing. (b) The absorption spectra of the blend films with different $Cd_{0.75}Hg_{0.25}Te$ NC contents. (c) The PL emission quenching process as the $Cd_{0.75}Hg_{0.25}Te$ NC content increases.

transport. Fig. 1(b) presents the absorption of the blend films after annealing as the weight percent of the $Cd_{0.75}Hg_{0.25}Te$ NCs (3:1 Cd/Hg ratio) changes and the PPV film seems to absorb little light above 600 nm, while the absorption of the NCs after annealing covers from UV to 1200 nm. The broad absorption of the NCs illustrates a broad size distribution caused by the inhomogeneous growth of the NCs because of the limitation of the PPV chains. The photons absorbed by the PPV form the excitons, and exciton dissociation is able to take place at the heterojunction, as a result, the electron is transferred from PPV to NCs. This transferred process is demonstrated by the photoluminescence (PL) quenching of PPV described in Fig. 1(c). The PL emission of the PPV film with strong π - π interacting chains is located at 546 nm, while the PL emission of the weak interactions without π - π scaffold can be also detected at 516 nm. The PL of the PPV is gradually quenched by the NCs as the NC content increases and the relative PL emission intensity of the chains with strong $\pi - \pi$ interactions is decreased compared to that of weak interacting chains because the interactions is largely relaxed by the NCs.³⁴ The energy structure of the HSC is described in Fig. 2. The highest occupied molecular orbital (HOMO) level of the PPV is -5.1 eV, and the lowest unoccupied molecular orbital (LUMO) level of the PPV is about -2.8 eV. While the conduction band of the NCs is -4.0 eV, and the valence band of the NCs is -5.3 eV relative to the vacuum level. This energy band favors the electron transport from PPV to the Cd_{0.75}Hg_{0.25}Te NCs.³⁴

Since the nanoscopic morphology of the blend film directly determines the charge separation and transport, tapping mode AFM is employed to study the film morphology. Because of the excellent membrane forming properties of PPV, the blend film with 30 wt% NCs shows a smooth surface with a root-mean-square (RMS) roughness of 1.15 nm as presented in Fig. 3(a) and the NCs are separately distributed in the blend film. As the weight percent of the NCs reach 60 wt%, the RMS roughness of the blend films (1.43 nm) doesn't change much while the two phase structure presents apparent as shown in Fig. 3(e). The large aggregation region of the NCs appears though no interpenetrating network forms. However, the photocurrent is often supplied with a path in the form of network. Fig. 3(c) and (f) show that the interpenetrating network structure is established as the content of the NCs reaches 97 wt%. The network structure



Fig. 2 The energy structure of the HSC.



Fig. 3 AFM (5 μ m × 5 μ m) topography (a–c) and the corresponding phase images (d–f) of the PPV:Cd_{0.75}Hg_{0.25}Te NCs active layer with various compositions: (a and d) 30 wt% NCs, (b and e) 60 wt% NCs, (c and f) 97 wt% NCs. The active layer is suffered from annealing for 60 min under N₂.

ensures the charge separation and clear transport at the heterojunction and apparent phase separation occurs. Generally, too rough an active layer surface may lead to poor contact with the metal cathode. However, the RMS roughness of the blend films is only 4.62 nm after the larger NCs formed.

The internal morphology of the blend films are explored by using TEM. From Fig. 4 we can see that the size of the NCs is inhomogeneous and the average size is about 40 nm, what's more, this growth process mainly takes place during the first 10 min for the little change of the morphology after annealing for 10 min.³⁵ However, we observe that the electron-only carrier mobility increases a lot after annealing for 1 hour compared to that after only 30 min as shown in Fig. 4(d).^{11,13} The electron mobility of the blend film heated for 10 min is 3.90×10^{-7} cm² V⁻¹ s⁻¹, and that of the blend film is improved after annealing for 30 min (5.18 × 10^{-7} cm² V⁻¹ s⁻¹). Both of the values are too low for an effective photovoltaic device. However, after annealing for 1 hour, the electron mobility of the hybrid film increases to 1.47×10^{-4} cm² V⁻¹ s⁻¹. Therefore, 30 min is not sufficient to remove most ligands



Fig. 4 (a–c) TEM images of the PPV:Cd_{0.75}Hg_{0.25}Te blend films with different annealing time (10 min, 30 min and 60 min). (d) $J^{0.5}$ vs. V plots for the blend film with different annealing time and the insert is the corresponding amplification image. The solid line is a fit of the data points. The films thicknesses are about 80 nm.

covering the surface of the NCs. X-ray photoelectron spectroscopy (XPS) analysis for the S2p is used to calculate the ligand content on the NCs' surface after annealing as shown in Fig. 5(a). As the annealing time increases, the ligands are gradually removed. Through the S/M (Cd + Hg) atom ratios, the weight percents of the ligands can be calculated and the corresponding calculation results are plotted in Fig. 5(b). From Fig. 5(b) we can see that the contents of the ligands after 30 min annealing of the NCs films (68.0 wt%) is similar to that of 10 min (73.1 wt%). However, there are only 29.4 wt% ligands left after 60 min annealing which ensures the interpenetrating network structure and the enhancement of the electron mobility. Hole-only charge carrier mobility was measured according to a similar method using a diode configuration of ITO/poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/PPV:Cd_{0.75}-Hg_{0.25}Te/MoO₃/Au by using the space-charge-limited-current (SCLC) model at low voltage which is described by:

$J = 9\varepsilon_0\varepsilon_{\rm r}\mu V^2/8L^3$

where ε_0 is the permittivity of free space (8.85 × 10⁻¹² F m⁻¹), ε_r is the dielectric constant of the PPV (assumed to 3), μ is the hole mobility of the PPV, V is the applied voltage, and L is the film thickness.^{13,36,37} By fitting the results to a space charge limited form, $J^{0.5}$ versus V_{appl} is plotted in the Fig. 6. The thickness of the blend film was about 80 nm, which was determined by the Ambios Tech. XP-2 profilometer. The hole mobility of the PPV was about 1.12×10^{-4} cm² V⁻¹ s⁻¹, which was similar to the electron mobility of the Cd_{0.75}Hg_{0.25}Te. The electron mobility is measured according to a similar method with an electron-only device structure of ITO/Al/PPV:Cd_{0.75}Hg_{0.25}Te/LiF/Al. The balanced carrier mobility results in the effective performance of the HSC.

Fig. 7(a) depicts the current density–voltage (J-V) curves of the PPV:Cd_{0.75}Hg_{0.25}Te HSC devices measured under AM 1.5 G illumination (100 mW cm⁻²). As the annealing time increases, both of the short-circuit current density (J_{sc}) and the open-circuit voltage (V_{oc}) are enhanced, and this is also consistent with the electron mobility increase. The device performance with an annealing time of 30 min is better than that of 10 min. However, efficient HSC is obtained after annealing for 60 min with J_{sc} of 12.84 mA cm⁻², V_{oc} of 0.34 V, fill factor (FF) of 34.3% and PCE of 1.5%. Sufficient annealing time allows the surface ligands to be removed as much as possible, and efficient interpenetrating network is formed as the NCs grow, which are beneficial to the



Fig. 5 (a) XPS spectra of S2p in the $Cd_{0.75}Hg_{0.25}Te$ NCs films with different annealing time. (b) The weight contents of the ligands in the NCs calculated with the S atom in the ligands employing metal elements as a reference.



Fig. 6 Hole mobility of the PPV: $Cd_{0.75}Hg_{0.25}Te$ hybrid device.



Fig. 7 (a) Device performance of the PPV:Cd_{0.75}Hg_{0.25}Te HSC annealed at 300 °C for different time. (b) Devices performance of the PPV:Cd_xHg_{1-x}Te HSC with different Cd/Hg ratios. For the CdTe NCs and Cd_{0.91}Hg_{0.09}Te NCs, the HSC performs better if UV-ozone is used to treat the blend films. (c) The external quantum efficiency measurement of the PPV:Cd_{0.75}Hg_{0.25}Te HSC device with 60 min annealing.

Table 1Current–voltage characteristics of the photovoltaic devices withdifferent Cd/Hg ratio. For the CdTe and $Cd_{0.91}Hg_{0.09}Te$ NCs, UV-ozoneradiation is used to reduce the surface traps

Cd/Hg ratio ^a	UV-ozone time (min)	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}$ (V)	FF (%)	PCE (%)
3:1	0	12.84	0.34	34.3	1.50
5:1	0	9.05	0.32	35.0	1.01
10:1	0	6.81	0.12	31.4	0.26
10:1	10	6.37	0.26	30.2	0.50
1:0	0	3.04	0.12	28.4	0.10
1:0	10	3.62	0.34	33.2	0.41

 a The corresponding NCs compositions with different Cd/Hg ratios (3:1, 5:1, 10:1, and 1:0) are described as Cd_{0.75}Hg_{0.25}, Cd_{0.83}Hg_{0.17}Te, Cd_{0.91}Hg_{0.09}Te and CdTe respectively.

PCE enhancement. The low V_{oc} of the devices is caused by the decrease of the conduct band level of the NCs during the annealing process. Fig. 7(b) presents the J-V curves of the PPV: Cd_xHg_{1-x} Te HSC devices with different Cd/Hg ratios. The J_{sc} is 3.04 mA cm⁻² for the CdTe, 6.37 mA cm⁻² for the Cd_{0.91}Hg_{0.09}Te (10 : 1), 9.05 mA cm⁻² for the Cd_{0.83}Hg_{0.17}Te (5 : 1) and 12.84 mA cm⁻² for the Cd_{0.75}Hg_{0.25}Te (3 : 1). This proves that near-infrared absorption plays an important role in the enhanced photocurrent. The $V_{\rm oc}$ of the CdTe NCs is only 0.12 V due to the surface traps caused by oxidation, and the $V_{\rm oc}$ can be effectively improved to 0.34 V after UV-ozone radiation for 10 min. However, there is no effect for Cd_{0.83}Hg_{0.17}Te NCs and Cd_{0.75}Hg_{0.25}Te NCs which may be due to the strong oxidation resistance resulting from the strong ionic bond of the HgTe compared to the CdTe. The corresponding external quantum efficiency (EQE) of HSC with Cd_{0.75}Hg_{0.25} NCs is presented in Fig. 7(c), and we can see that the PPV:Cd_{0.75}Hg_{0.25}Te HSC has a broad response range of the spectra from 300 to 1000 nm as expected from the absorption spectra. The maximum value reaches 50% at 370 nm and the contribution of near-infrared (800-1000 nm) to the photocurrent reaches 11.4% which is assigned to the absorption of the Cd_{0.75}Hg_{0.25}Te NCs. The devices performance of NCs with different Cd/Hg ratios are also summarized in Table 1, from which we can see that the J_{sc} of the device is enhanced as the Cd/Hg ratio increases and the $V_{\rm oc}$ can be improved by reducing the surface traps of the NCs with UV-ozone radiation.^{23,38}

Conclusions

In summary, we have reported the fabrication and characterization of the aqueous PPV: $Cd_xHg_{1-x}Te$ HSC with broad coverage of the solar spectrum. By employing the method of controllable heat-introduced aggregation and growth of the NCs, the blend film morphology can be easily controlled and the charge carrier mobility can be easily improved by increasing the annealing time. The largely improved charge carrier mobility is also derived from the elimination of the surface ligands of the NCs and the formation of the interpenetrating network structure. The coverage range of the absorption spectra can be easily tuned by changing the Cd/Hg ratio and the surface traps of the aqueous NCs can be reduced to some extent by UV-ozone radiation. The PCE of such photovoltaic devices exhibit about 1.5% under AM 1.5G illumination. 11.4% near-infrared contribution is observed from the EQE measurement with only simple devices structure. All the present findings prove that the aqueous PPV:Cd_xHg_{1-x}Te HSC is promising and attractive for organic–inorganic optoelectronic devices for the clean, environment-friendly, renewable energy application.

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Notes and references

- 1 J. Peet, A. J. Heeger and G. C. Bazan, Acc. Chem. Res., 2009, 42, 1700–1708.
- 2 R. C. Coffin, J. Peet, J. Rogers and G. C. Bazan, *Nat. Chem.*, 2009, **1**, 657–661.
- 3 H. Chen, J. H. Hou, S. Q. Zhang, Y. Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649–653.
- 4 C. Mayer, S. R. Scully, B. E. Hardin, M. W. Rowell and M. D. McGehee, *Mater. Today*, 2007, 10, 28–33.
- 5 R. Søndergaard, M. Helgesen, M. Jørgensen and F. C. Krebs, Adv. Energy Mater., 2011, 1, 68–71.
- 6 R. Søndergaard, M. Hösel, D. Angmo, T. T. Larsen-Olsen and F. C. Krebs, *Mater. Today*, 2012, 15, 36–49.
- 7 N. Espinosa, M. Hösel, D. Angmo and F. C. Krebs, *Energy Environ. Sci.*, 2012, 5, 5117–5132.
- 8 F. C. Krebs, J. Fyenbo, D. M. Tanenbaum, S. A. Gevorgyan, R. Andriessen, B. V. Remoortere, Y. Galagan and M. Jørgensen, *Energy Environ. Sci.*, 2011, 4, 4116–4123.
- 9 H. J. Son, W. Wang, T. Xu, Y. Y. Liang, Y. Wu, G. Li and L. P. Yu, J. Am. Chem. Soc., 2011, **133**, 1885–1894.
- 10 Z. C. He, C. M. Zhong, X. Huang, W. Y. Wong, H. B. Wu, L. W. Chen, S. J. Su and Y. Cao, *Adv. Mater.*, 2011, 23, 4636–4643.
- 11 Y. Y. Liang, Z. Xu, J. B. Xia, S. Tsai, Y. Wu, G. Li, C. Ray and L. P. Yu, *Adv. Mater.*, 2010, **22**, E135–E138.
- 12 L. T. Dou, J. B. You, J. Yang, C. Chen, Y. J. He, S. Murase, T. Moriarty, K. Emery, G. Li and Y. Yang, *Nat. Photonics*, 2012, 6, 180–185.
- 13 H. Chen, C. Lai, I. Wu, H. Pan, I. P. Chen, Y. Peng, C. Liu, C. Chen and P. Chou, *Adv. Mater.*, 2011, 23, 5451–5455.
- 14 S. Dowland, T. Lutz, A. Ward, S. P. King, A. Sudlow, M. S. Hill, K. C. Molloy and S. A. Haque, *Adv. Mater.*, 2011, 23, 2739–2744.
- 15 S. Q. Ren, L. Chang, S. Lim, J. Zhao, M. Smith, N. Zhao, V. Bulović, M. Bawendi and S. Gradecak, *Nano Lett.*, 2011, 11, 3998–4002.
- 16 D. Celik, M. Krueger, C. Veit, H. F. Schleiermacher, B. Zimmermann, S. Allard, I. Dumsch, U. Scherf, F. Rauscher and P. Niyamakom, *Sol. Energy Mater. Sol. Cells*, 2012, **98**, 433–440.
- 17 T. T. Xu and Q. Q. Qiao, Energy Environ. Sci., 2011, 4, 2700-2720.
- 18 W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, Science, 2002, 295, 2425–2427.
- 19 G. Grancini, R. S. S. Kumar, A. Abrusci, H. Yip, C. Li, A. Y. Jen, G. Lanzani and H. J. Snaith, *Adv. Funct. Mater.*, 2012, 22, 2160.
- 20 L. Rogach, A. Eychmüller, S. G. Hicker and S. V. Kershaw, *Small*, 2007, 3, 536–557.
- 21 S. Dayal, M. O. Reese, A. J. Ferguson, D. S. Ginley, G. Rumbles and N. Kopidakis, *Adv. Funct. Mater.*, 2010, **20**, 2629–2635.
- 22 K. F. Jeltsch, M. Schädel, J. Bonekamp, P. Niyamakom, F. Rauscher, H. W. A. Lademann, I. Dumsch, S. Allard, U. Scherf and K. Meerholz, *Adv. Funct. Mater.*, 2012, **22**, 397–404.
- 23 N. Zhao, T. P. Osedach, L. Chang, S. M. Geyer, D. Wanger, M. T. Binda, A. C. Arango, M. G. Bawendi and V. Bulovic, ACS Nano, 2010, 4, 3743–3752.
- 24 J. Tang and E. H. Sargent, Adv. Mater., 2011, 23, 12-29.
- 25 E. H. Sargent, Adv. Mater., 2005, 17, 515-522.
- 26 W. L. Ma, S. L. Swisher, T. Ewers, J. Engel, V. E. Ferry, H. A. Atwater and A. P. Alivisatos, ACS Nano, 2011, 5, 8140–8147.
- 27 T. R. Andersen, T. T. Larsen-Olsen, B. Andreasen, A. P. L. Böttiger, J. E. Carlé, M. Helgesen, E. Bundgaard, K. Norrman,

J. W. Andreasen, M. Jørgensen and F. C. Krebs, *ACS Nano*, 2011, **5**, 4188–4196.

- 28 G. Krishna, V. V. Thalluri, J. Bolsée, A. Gadisa, M. Parchine, T. Boonen, J. D'Haen, A. E. Boyukbayram, J. Vandenbergh, T. J. Cleij, L. Lutsen, D. Vanderzande and J. Manca, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 3262–3268.
- 29 J. H. Yang, A. Garcia and T. Nguyen, Appl. Phys. Lett., 2007, 90, 103014.
- 30 Q. Q. Qiao, Y. Xie and J. T. Mcleskey, J. Phys. Chem. C, 2008, 112, 9912–9916.
- 31 M. Q. Wang and X. G. Wang, Polymer, 2008, 49, 1587–1593.
- 32 Q. Q. Qiao and J. T. Mcleskey, Appl. Phys. Lett., 2005, 86, 153501.

- 33 H. T. Wei, H. Z. Sun, H. Zhang, C. Gao and B. Yang, Nano Res., 2010, 3, 496–505.
- 34 H. T. Wei, H. Z. Sun, H. Zhang, W. L. Yu, F. Zhai, Z. X. Fan, W. J. Tian and B. Yang, *J. Mater. Chem.*, 2012, **22**, 9161–9165.
- 35 W. L. Yu, H. Zhang, H. R. Tian, H. T. Wei, W. X. Liu, J. Zhu, J. H. Zhang and B. Yang, J. Phys. Chem. C, 2012, 116, 1322–1328.
- 36 Y. Cheng, C. Hsieh, P. Li and C. Hsu, *Adv. Funct. Mater.*, 2011, **21**, 1723–1732.
- 37 Y. S. Liu, X. J. Wan, F. Wang, J. Y. Zhou, G. K. Long, J. G. Tian and Y. S. Chen, *Adv. Mater.*, 2011, 23, 5387–5391.
- 38 C. E. Small, S. Chen, J. Subbiah, C. M. Amb, S. Tsang, T. Lai, J. R. Reynolds and F. So, *Nat. Photonics*, 2012, 6, 115–120.