

Improvement of power conversion efficiency of P3HT:CdSe hybrid solar cells by enhanced interconnection of CdSe nanorods *via* decomposable selenoureat

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We introduce a novel method to improve the device performance of P3HT:CdSe hybrid solar cells by using selenourea (SeU) for ligand exchange. SeU induces interconnection of CdSe nanorods in the nanoscale range without severe aggregation. The power conversion efficiency of the devices with SeU is improved from 1.71% to 2.63% due to efficient charge transport through interconnected CdSe nanorods.

Hybrid solar cells consisting of conjugated polymers and inorganic nanocrystals have received much attention as next-generation solar cells due to high absorption coefficients,¹ tunable band gap depending on size and shape,² facilitated charge transport,³ stability of nanostructures,⁴ and excellent solution processibility of inorganic nanocrystals. Inorganic nanocrystals act as electron acceptors, while conjugated polymers act as electron donors, in which photo-generated carriers are transported to the respective electrodes to generate current.^{3,5–7} One of the widely used inorganic nanocrystals for hybrid solar cells is CdSe in the form of quantum dots,⁸ nanorods,⁹ tetrapods,¹⁰ and hyperbranches.¹¹

As-synthesized CdSe nanocrystals are usually capped with long chain ligands, such as trioctylphosphine oxide (TOPO) and alkylphosphonic acid, fatty acid, or long alkyl amine to prevent the aggregation of nanocrystals.¹² But, because these long alkyl chain ligands function as insulators between CdSe nanocrystals, they should be replaced by short chains, for instance, pyridine, to facilitate electron hopping between CdSe nanocrystals.¹³ Thus, CdSe nanocrystals treated with pyridine (CdSe-py) have

been widely used for hybrid solar cells.^{3,14–17} The device performance of the hybrid solar cells depends significantly on the dispersion of CdSe nanocrystals in an electron-donating polymer (for instance, poly(3-hexylthiophene) (P3HT)), which in turn is greatly affected by the types and lengths of the ligands on the CdSe nanocrystals, as schematically shown in Fig. 1(a)–(c).

Even after pyridine treatment, some long alkyl chain ligands (for instance, TOPO and alkylphosphonic acid) still remain on CdSe-py. Although these remaining ligands help in good dispersion of nanocrystals in P3HT (Fig. 1(a)), they prevent effective electron transport, which results in poor device performance. On the other hand, even when long alkyl chains on CdSe nanocrystals could be removed completely by multiple pyridine treatment, the performance of hybrid solar cells is not improved.¹⁸ This is because of severe aggregation of CdSe nanocrystals during multiple pyridine treatments, namely, the dispersion of CdSe nanocrystals in P3HT becomes very poor (Fig. 1(b)). Thus, the dispersion of CdSe nanocrystals in P3HT for the best device performance is the interconnection of CdSe nanocrystals in the nanoscale range without severe aggregation (Fig. 1(c)).

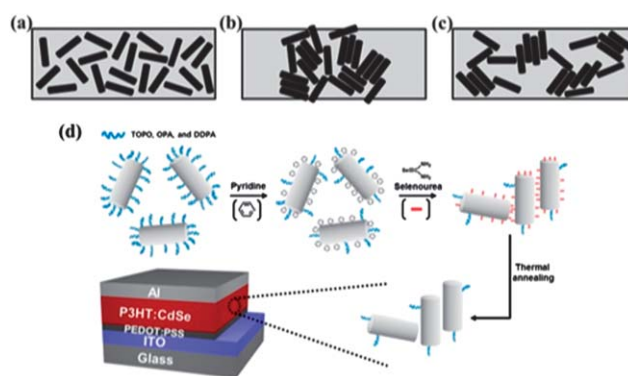


Fig. 1 Schematic illustrations of morphology of P3HT:CdSe films with (a) well-dispersed, (b) agglomerated, and (c) interconnected CdSe nanocrystals in the nanoscale range and (d) schematic of the preparation of P3HT:CdSe hybrid solar cells with SeU.

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Several research groups have investigated the effect of the dispersion of ligand-exchanged CdSe nanocrystals in P3HT on the device performance of P3HT:CdSe hybrid solar cells. Radychev *et al.*¹⁹ replaced the remaining oleic acid ligands on CdSe by short alkyl chain ligands (for instance, butylamine) and showed improved device performance. Wu and Zhang²⁰ used chemical vapor of 1,3-benzenedithiol to directly replace alkylphosphonic acid groups of CdSe nanocrystals in P3HT:CdSe-py thin films. The good dispersion of CdSe nanocrystals in the P3HT matrix is maintained even after the remaining alkylphosphonic acid groups are replaced by 1,3-benzenedithiol, because the replacement reaction was done in thin film, not in the solution state. Seo *et al.*²¹ introduced cleavable ligands into CdSe. Due to the existence of cleavable ligands, good dispersion of CdSe nanocrystals is achieved in solution. Once the thin film is fabricated by spin coating, the length of the ligand on CdSe nanocrystals is reduced due to the cleavage groups during the thermal annealing process. However, electron transport is still hindered by insulating short alkyl chains or benzenedithiol ligands between CdSe nanocrystals. Therefore, the best approach to improve device performance of hybrid solar cells is that the alkyl chain ligands on the CdSe nanocrystals should be replaced by non-insulating materials, while there is no severe aggregation of CdSe nanocrystals.

In this study, we introduce a novel method to improve the device performance of P3HT:CdSe hybrid solar cells by using selenourea (SeU, $\text{Se}=\text{C}(\text{NH}_2)_2$) for the ligand exchange in P3HT:CdSe-py. SeU was used as a Se source of metal chalcogenide.^{22,23} First, SeU is added to P3HT:CdSe-py in solution for the ligand exchange. Then, P3HT:CdSe-SeU solution is spin-coated to prepare the thin film where the interconnection of CdSe nanorods in the nanoscale range is obtained. SeU on CdSe nanorods is easily decomposed into selenide during thermal annealing of the thin film. Consequently, the nanoscale interconnection of CdSe nanorods without severe aggregations is maintained, while SeU is converted into selenide. This device provides good charge transport by efficient charge hopping through interconnected CdSe nanorods. We found that the short-circuit current density (J_{SC}) of the hybrid solar cell was increased from 5.0 to 8.4 mA cm^{-2} by the use of SeU; thus, the power conversion efficiency (PCE) was improved from 1.71 to 2.63%.

Fig. 1(d) gives a schematic of fabrication of P3HT:CdSe-SeU hybrid solar cells. Two solutions ((i) P3HT and pyridine-treated CdSe nanorods in mixed solvent of 1,2-dichlorobenzene (DCB) and pyridine, and (ii) SeU in pyridine) were stirred separately for 12 h at room temperature and then combined in a nitrogen-filled glove box. The SeU exchange reaction was performed at 55 °C for 12 h. The ratio of SeU/CdSe nanorods (w/w) (SeU ratio) in the mixed solution varied from 0 to 0.1. P3HT:CdSe-SeU solution was spin-coated on top of the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)-coated ITO glass and then thermally annealed at various temperatures. Aluminum (Al) electrode with a thickness of 100 nm was evaporated on top of the substrates. Experimental details of synthesis of CdSe nanorods and ligand treatment as well as the fabrication and the characterization of the hybrid solar cells are given in the ESI.†

The plots of current density *versus* voltage (J - V characteristics) of P3HT:CdSe hybrid solar cells were obtained under AM 1.5 G illumination from a calibrated solar simulator with an incident light intensity of 100 mW cm^{-2} . Fig. 2(a) shows the J - V curves of hybrid solar cells without and with two different amounts of SeU (SeU ratio = 0.033 and 0.1). These cells were thermally annealed at 215 °C before the Al electrode deposition. The effect of annealing temperature on device performance will be discussed later. J_{SC} increases from 5.0 to 8.4 mA cm^{-2} with increasing the SeU ratio from 0 to 0.033, and then decreases to 8.0 mA cm^{-2} at an SeU ratio of 0.05 (Fig. 2(b)). But, compared with a device without SeU, the device with an SeU ratio of 0.033 shows a slightly lower open circuit voltage (V_{OC}) and fill factor (FF) (Fig. 2(c)) in spite of decreased series and sheet resistances as well as the same UV-Vis absorption spectrum as that of CdSe

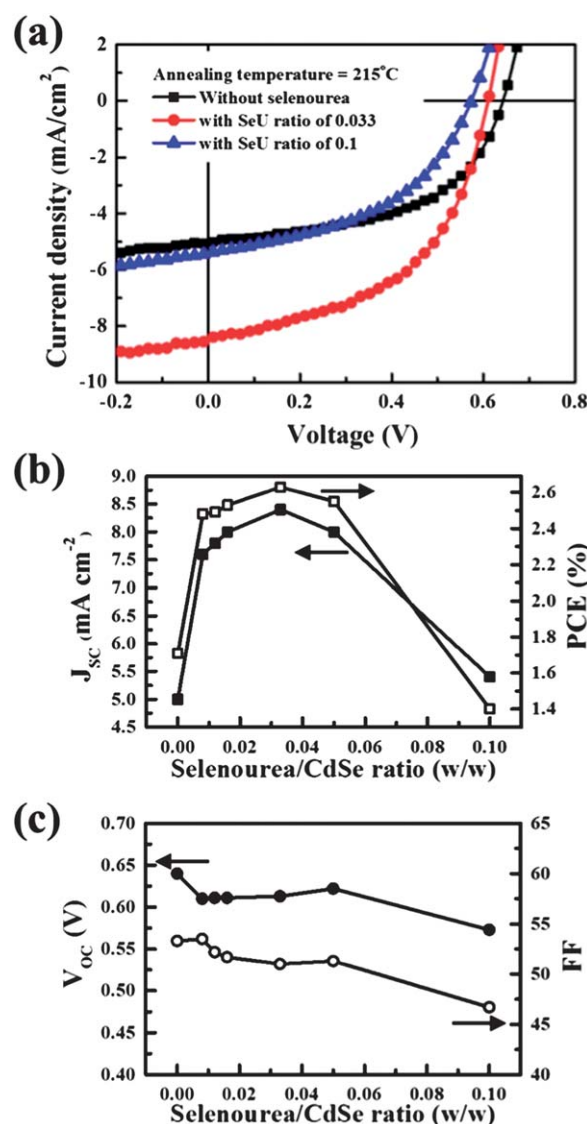


Fig. 2 (a) J - V characteristics of P3HT:CdSe hybrid solar cells without (squares) and with SeU ratios of 0.033 (circles) and 0.1 (triangles) annealed at 215 °C. (b) Plots of J_{SC} and PCE *versus* SeU ratio, and (c) plots of V_{OC} and FF *versus* SeU ratio for P3HT:CdSe hybrid solar cells annealed at 215 °C.

nanorods without SeU (Table S1 and Fig. S1†). A small reduction of V_{OC} and FF might arise from a slight decrease in the shunt resistance due to the surface recombination of a few Se dangling bonds at CdSe/Al after the decomposition of SeU to selenide.²⁴ Also, we found that the incident-photon-to-current conversion efficiency (IPCE) increases with increasing the SeU ratio from 0 to 0.033 (Fig. S2†). Consequently, PCE increases from 1.71% to 2.63%. However, at an SeU ratio of 0.1, J_{SC} and FF sharply decrease to 5.4 mA cm^{-2} and 46.7%, respectively. The device performance of the hybrid solar cells depending on SeU ratios is summarized in Table S2 of the ESI.†

To explain the large difference in PCE of P3HT:CdSe depending on the SeU ratio, we performed a transmission electron microscopy (TEM) experiment. We prepared the films by spin coating of P3HT:CdSe–SeU (1 : 9 w/w) solution and thermal annealing at 215 °C. Since the weight fraction of CdSe nanorods in the films was 0.9, it was not easy to distinctly observe the dispersion of the sample depending on the amount of SeU.

However, CdSe nanorods (dark) are more or less uniformly dispersed in P3HT phases (bright) throughout the entire film without SeU (Fig. 3(a)). On the other hand, a film prepared from P3HT:CdSe–SeU with an SeU ratio of 0.1 exhibited a large area of dark regions, indicating that CdSe nanorods are severely aggregated (Fig. 3(c)). Interestingly, for the film having an SeU ratio of 0.033 (Fig. 3(b)), the size of the dark area in Fig. 3(b) is larger than that in Fig. 3(a), but smaller than that in Fig. 3(c). Thus, the film with an SeU ratio of 0.033 might have the interconnected CdSe nanorods in the nanoscale range in the P3HT phase. To clearly demonstrate the dispersion of CdSe nanorods with the amount of SeU in the film, we decreased the amount of CdSe nanorods, that is, we prepared P3HT:CdSe (1 : 1 w/w) films with various amounts of SeU ratios (see Fig. S3 in the ESI†). P3HT:CdSe (1 : 1 w/w) without SeU shows uniform dispersion of CdSe nanorods, and CdSe nanorods are not connected in some regions. On the other hand, P3HT:CdSe (1 : 1 w/w) with an SeU ratio of 0.1 shows severe aggregation of CdSe nanorods. However, P3HT:CdSe (1 : 1 w/w) with an SeU ratio of 0.033 shows that almost all of the CdSe nanorods are interconnected without severe aggregation. As a result, the performance enhancement comes from formation of the electron pathway by

interconnected CdSe nanorods in the nanoscale range with an SeU ratio of 0.033, while the performance at an SeU ratio of 0.1 decreases due to large-scale phase separation by severe aggregation of CdSe nanorods.

The effect of the thermal annealing temperature on the device performance is summarized in Fig. 4. Here, the SeU ratio is fixed to be 0.033. Fig. 4(a) shows J – V curves of P3HT:CdSe–SeU hybrid solar cells annealed at various temperatures. J_{SC} and FF

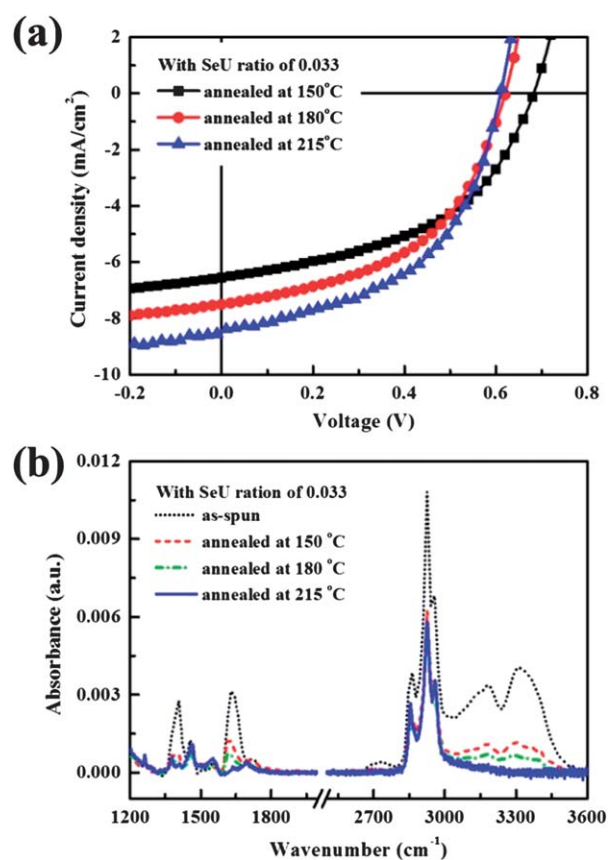


Fig. 4 (a) J – V curves of P3HT:CdSe hybrid solar cells annealed at 150 °C (squares), 180 °C (circles), and 215 °C (triangles). (b) FT-IR spectra of CdSe nanorod films with an SeU ratio of 0.033 annealed at various temperatures.

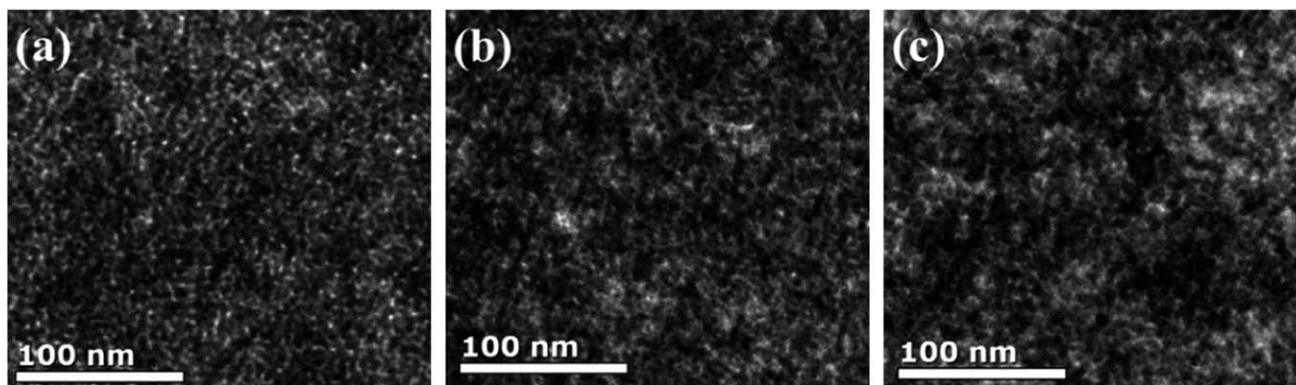


Fig. 3 TEM images of the P3HT:CdSe thin film with SeU ratios of (a) 0, (b) 0.033 and (c) 0.1.

increase from 6.5 to 8.4 mA cm⁻² and from 48.0% to 51.0%, respectively, with increasing the annealing temperature from 150 to 215 °C. As a result, PCE was increased from 2.12% to 2.63% (see also Table S3†). To explain the change of PCE with thermal annealing temperature, we performed FT-IR spectroscopy and the results are given in Fig. 4(b). Before thermal annealing, SeU was attached to the surface of CdSe nanorods by replacing the remaining TOPO and alkylphosphonic acid groups in py-CdSe nanorods (see Fig. S4 in the ESI†). However, when the device was annealed at 150 °C (or 180 °C) the intensity of absorption bands of C–N (1410 cm⁻¹) and N–H (1640 cm⁻¹ and 3000–3500 cm⁻¹) dramatically decrease compared with the sample before thermal treatment, but these bands still remain. However, after the device was annealed at 215 °C, these bands disappeared, which suggests that the urea in SeU was completely removed. This is confirmed by thermogravimetric analysis (TGA), from which the urea in the SeU was completely decomposed at ~205 °C (Fig. S5†). After the complete decomposition of SeU, the distance between the CdSe nanorods decreased. On the other hand, when the device was annealed at higher temperatures (for instance, 250 °C) than the melting temperature of P3HT ($T_m \sim 230$ °C), it shows poorer device performance than another device annealed at 215 °C (Fig. S6†). This might be because the grain sizes of the P3HT crystals of a sample crystallized at a constant temperature lower than the T_m of P3HT are different from those of crystals prepared by cooling from temperatures higher than T_m of P3HT.^{25,26}

Finally, we found by the X-ray photoelectron spectroscopy (XPS) experiment that SeU on CdSe nanorods was successfully converted into selenide without the formation of selenium (Se–Se linkage) (Fig. S7 in the ESI†). Although the exact mechanism of the decomposition of SeU to selenide in the presence of CdSe is not clear, a plausible explanation would be as follows. During the decomposition of SeU, selenium might become a very reactive species (for instance, Se²⁽⁻⁾), which easily combines with Cd in the CdSe nanorods. A similar behavior was reported for the decomposition of selenadiazole at high temperatures under inert atmospheres.²⁷

Conclusion

In summary, we demonstrated that the device performance of P3HT:CdSe hybrid solar cells was greatly enhanced by SeU treatment. A P3HT:CdSe hybrid solar cell with an SeU ratio of 0.033 shows a J_{SC} of 8.4 mA cm⁻² and PCE of 2.63%, which are increased by 68% and 54%, respectively, compared to those of other P3HT:CdSe hybrid solar cells without SeU. When an appropriate amount of SeU was added to the solar cell, the dispersion of CdSe nanorods in P3HT showed good interconnection in the nanoscale range without severe aggregation. Once the solar cell was thermally annealed at 215 °C, SeU was completely decomposed into selenide; thus electron transport toward the cathode was greatly enhanced. Interconnection of various inorganic nanocrystals in the nanoscale range without severe aggregation could also be achieved by using various decomposable organochalogen compounds for further improving the device performance of hybrid solar cells.

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Notes and references

- 1 A. P. Alivisatos, *Science*, 1996, **271**, 933.
- 2 L.-S. Li, J. Hu, W. Yang and A. P. Alivisatos, *Nano Lett.*, 2001, **1**, 349.
- 3 W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, 2002, **295**, 2425.
- 4 L. Fang, J. Y. Park, Y. Cui, P. Alivisatos, J. Shrier, B. Lee, L. W. Wang and M. Salmeron, *J. Chem. Phys.*, 2007, **127**, 184704.
- 5 W. Yue, S. Han, R. Peng, W. Shen, H. Geng, F. Wu, S. Tao and M. Wang, *J. Mater. Chem.*, 2010, **20**, 7570.
- 6 Y.-Y. Lin, C.-W. Chen, T.-H. Chu, W.-F. Su, C.-C. Lin, C.-H. Ku, J.-J. Wu and C.-H. Chen, *J. Mater. Chem.*, 2007, **17**, 4571.
- 7 W. J. E. Beek, M. M. Wienk and R. A. J. Janssen, *J. Mater. Chem.*, 2005, **15**, 2985.
- 8 J. D. Olson, G. P. Gray and S. A. Carter, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 519.
- 9 B. Sun and N. C. Greenham, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3557.
- 10 B. Sun, H. J. Snaith, A. S. Dhoot, S. Westenhoff and N. C. Greenham, *J. Appl. Phys.*, 2005, **97**, 014914.
- 11 I. Gur, N. A. Fromer, C. P. Chen, A. G. Kanaras and A. P. Alivisatos, *Nano Lett.*, 2007, **7**, 409.
- 12 L. Qu, Z. A. Peng and X. Peng, *Nano Lett.*, 2001, **1**, 333.
- 13 A. J. Moulé, L. Chang, C. Thambidurai, R. Vidu and P. Stroeve, *J. Mater. Chem.*, 2012, **22**, 2351.
- 14 B. Sun, E. Marx and N. C. Greenham, *Nano Lett.*, 2003, **3**, 961.
- 15 I. Gur, N. A. Fromer and A. P. Alivisatos, *J. Phys. Chem. B*, 2006, **110**, 25543.
- 16 Y. Li, R. Mastria, A. Fiore, C. Nobile, L. Yin, M. Biasiucci, G. Cheng, A. M. Cucolo, R. Cingolani, L. Manna and G. Gigli, *Adv. Mater.*, 2009, **21**, 4461.
- 17 K. F. Jeltsch, M. Schadel, J. B. Bonekamp, P. Niyamakom, F. Rauscher, H. W. A. Lademann, I. Dumsch, S. Allard, U. Scherf and K. Meerholz, *Adv. Funct. Mater.*, 2012, **22**, 397.
- 18 I. Lokteva, N. Radychev, F. Witt, H. Borchert, J. Parisi and J. Kolny-Olesiak, *J. Phys. Chem. C*, 2010, **114**, 12784.
- 19 N. Radychev, I. Lokteva, F. Witt, J. Kolny-Olesiak, H. Borchert and J. Parisi, *J. Phys. Chem. C*, 2011, **115**, 14111.
- 20 Y. Wu and G. Q. Zhang, *Nano Lett.*, 2010, **10**, 1628.
- 21 J. Seo, W. J. Kim, S. J. Kim, K. S. Lee, A. N. Cartwright and P. N. Prasad, *Appl. Phys. Lett.*, 2009, **94**, 133302.
- 22 M. E. Rincón, O. Gómez-Daza, C. Corriplo, E. A. Vázquez-Martínez and J. Ruiz-García, *Semicond. Sci. Technol.*, 1999, **14**, 390.
- 23 M. Epifani, E. Pellicer, J. Arbiol, N. Sergent, T. Pagnier and J. R. Morante, *Langmuir*, 2008, **24**, 11182.
- 24 C. S. Solanki, *Solar Photovoltaics: Fundamentals, Technologies, and Applications*, PHI Learning Pvt. Ltd, 2009.

- 25 S. Hugger, R. Thomann, T. Heinzl and T. Thurn-Albercht, *Colloid Polym. Sci.*, 2004, **282**, 932; C. Müller, T. A. Ferenczi, M. Campoy-Quiles, J. M. Frost, D. D. C. Bradley, P. Smith, N. Stingelin-Stutzmann and J. Nelson, *Adv. Mater.*, 2008, **20**, 3510.
- 26 D. B. Choi, S. W. Jin, Y. M. Lee, S. H. Kim, D. S. Chung, K. P. Hong, C. W. Yang, J. W. Jung, J. K. Kim, M. H. Ree and C. E. Park, *ACS Appl. Mater. Interfaces*, 2010, **2**, 48.
- 27 P. K. Khanna, R. M. Gorte and C. P. Morley, *Mater. Lett.*, 2002, **57**, 1464.