Deposition of hole-transport materials in solid-state dye-sensitized solar cells by doctor-blading

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ABSTRACT

We report using doctor-blading to replace conventional spin coating for the deposition of the hole-transport material spiro-OMeTAD (2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9′-spirobifluorene) in solid-state dye-sensitized solar cells. Doctor-blading is a roll-to-roll compatible, large-area coating technique, is capable of achieving the same spiro-OMeTAD pore filling fraction as spin coating, and uses much less material. The average power conversion efficiency of solid-state dye-sensitized solar cells made from doctor-blading is 3.0% for 2-μm thick films and 2.0% for 5-μm thick films, on par with devices made with spin coating. Directions to further improve the filling fraction are also suggested.

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1. Introduction

Dye-sensitized solar cells (DSCs) have received international research focus due to their high power conversion efficiency and low cost [1–4]. However, liquid-based DSCs suffer from potential problems such as solvent evaporation and leakage [5]. Such disadvantages can be solved by replacing the liquid-electrolyte with solid-state hole-transport materials (HTMs), such as spiro-OMeTAD (2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene) [6–9]. Solid-state dye-sensitized solar cells (ss-DSCs) made with spiro-OMeTAD have attained efficiencies over 5% [10] and have exhibited good stability under elevated-temperature light-soaking [11]. To date, all efficient ss-DSCs have been fabricated using spin-coating techniques to infiltrate the spiro-OMeTAD. This method wastes material and cannot scale up for larger area devices. Doctor-blading, a roll-to-roll compatible, large-area coating technique, is an attractive alternative to spin coating. It has

been used to deposit the active layer of several types of solar cells, such as the mesoporous TiO_2 layer in dye-sensitized solar cells [12], the polymer–fullerene blend in bulk heterojunction solar cells [13,14], and $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells [15]. In this work, doctor-blading is used to deposit spiro-OMeTAD into mesoporous TiO_2 films. To the best of our knowledge, this is the first report of efficient ss-DSCs made from doctor-blading.

2. Results and discussion

2.1. Pore filling mechanism

Pore filling of TiO_2 mesoporous films with spiro-OMeTAD has been proposed as one of parameters that limits the ss-DSC power conversion efficiency [16,17]. The mechanism of pore filling has been explained in detail in previous publications [18,19]. Here we provide a brief description of the pore filling mechanism. Pore filling of spiro-OMeTAD in mesoporous TiO_2 films is usually accomplished by depositing a concentrated solution of

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spiro-OMeTAD on top of the TiO$_2$ film. Immediately after solution deposition, the solution fills the pores effectively, and the filling fraction of spiro-OMeTAD inside the pores is the same as the volumetric concentration of the solution. The wet layer on top of the film then acts as a reservoir to increase the filling fraction beyond the macroscopic solubility of spiro-OMeTAD in the solvent. As the solution evaporates, the concentration of spiro-OMeTAD in the reservoir increases, and more spiro-OMeTAD diffuses into the pores. This infiltration process stops when enough solvent has evaporated for the spiro-OMeTAD to become immobile. For thicker films, the maximum filling fraction is further limited kinetically by the quantity of spiro-OMeTAD that can infiltrate into the pores before the critical solution concentration is reached. The filling fraction of thick films may increase if the solution evaporation is slowed down. Doctor-blading allows for slower solvent evaporation than spin coating because it does not introduce rapid air flow during film deposition. The size of the reservoir on top of the dyed TiO$_2$ film is very important in pore filling. An under-sized reservoir leads to low filling fraction and oversized reservoir leads to a thick spiro-OMeTAD overlayer. Both scenarios result in suboptimal charge transport. In developing a new deposition technique for HTMs in ss-DSCs, optimizing the reservoir size is required to maximize performance.

2.2. Effect of solution concentration

The first parameter we varied in optimizing the reservoir size is the spiro-OMeTAD solution concentration. We performed pore filling on TiO$_2$ films with two different thicknesses (2.5 and 5.0 μm) and compared the filling fraction from doctor-blading and spin coating. The parameters for doctor-blading are documented in the experimental section. The detailed procedure for measuring the filling fraction is reported elsewhere [18]. First, the overlayer thickness is measured with SEM cross-section. Then, the sample is immersed in a known volume of chlorobenzene to dissolve the spiro-OMeTAD out from the pores. The spiro-OMeTAD can be quantified by measuring the absorption in the solution phase.

Fig. 1a and b shows the filling fraction and overlayer thickness of 2.5- and 5-μm thick TiO$_2$ films as a function of spiro-OMeTAD solution concentration. It shows that a solution concentration below 270 mg/mL results in an under-sized reservoir (evident from the absence of overlayer) and low filling fraction. When the solution concentration was raised above 360 mg/mL, there was a spiro-OMeTAD overlayer on top of TiO$_2$ film. The formation of an overlayer usually indicates that the filling fraction can no longer be increased by increasing solution concentration [18]. Indeed, when the solution concentration was further
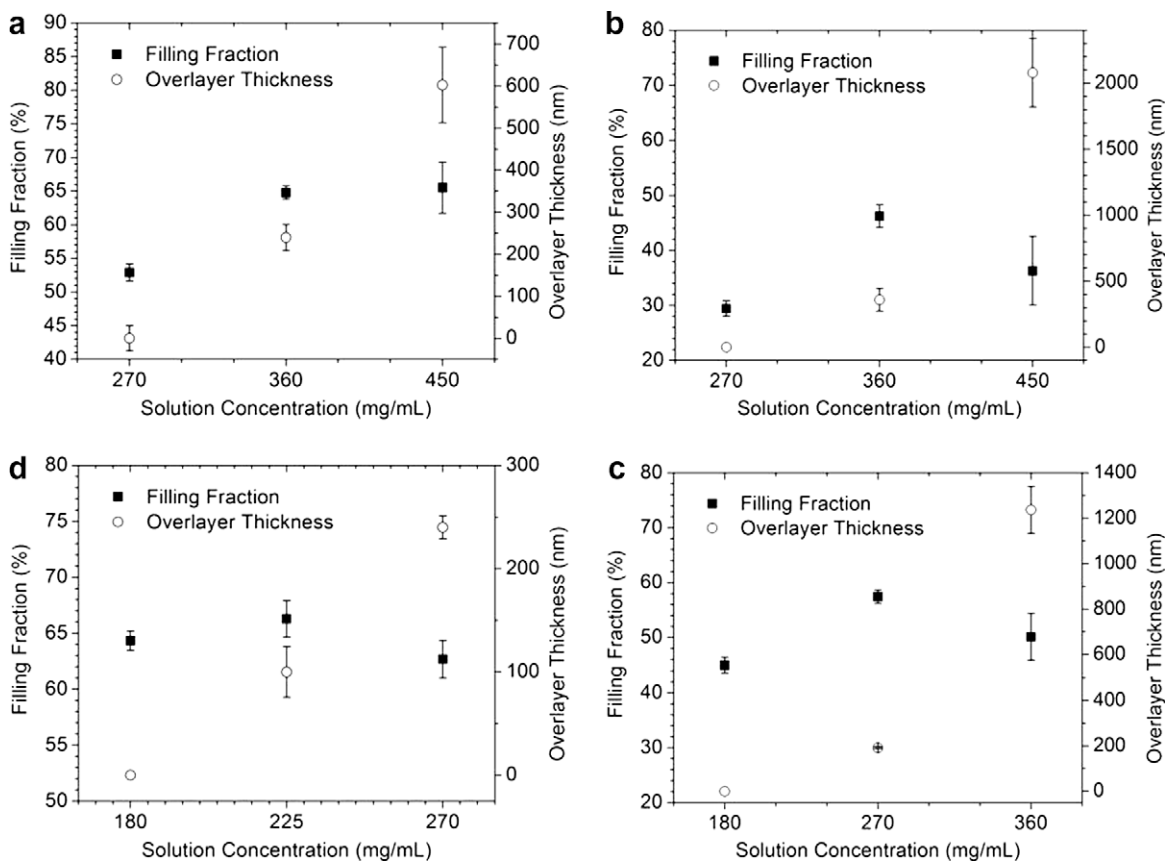

Fig. 1. Filling fractions and overlayer thicknesses of TiO$_2$ films with two different thicknesses and spiro-OMeTAD deposition techniques. (a) 2.5 μm, doctor-blading; (b) 5.0 μm, doctor-blading; (c) 2.5 μm, spin coating; (d) 5.0 μm, spin coating.

increased to 450 mg/mL, the filling fraction remained relatively constant and the overlayer became much thicker.

The 5-μm thick TiO_2 film infiltrated with 450 mg/mL solution appears to have lower filling fraction than other samples. The reason is as follows: in measuring the filling fraction, the spiro-OMeTAD in the pores is calculated by the total spiro-OMeTAD amount minus the amount presented in the overlayer. When the overlayer thickness becomes comparable with TiO_2 film thickness, any error in overlayer thickness measurement causes large error in the filling fraction.

For comparison purposes, the filling fractions and overlayer thicknesses of samples filled with spin coating are shown in Fig. 1c and d. For spin coating, the optimized solution concentration depends strongly on the TiO_2 film thickness. The optimized solution concentration changed from 180 mg/mL for 2.5-μm thick TiO_2 films to 270 mg/mL for 5-μm thick films. Also, for 2.5-μm thick TiO_2 films, doctor-blading at room temperature can already attain a filling fraction around 65%, which is comparable to the value obtained from spin coating. However, for 5-μm thick TiO_2 films, the filling fraction from doctor-blading at room temperature is lower than that obtained from spin coating. To increase the filling fraction, the spiro-OMeTAD solution is doctor-bladed at elevated temperature.

2.3. Effect of solution temperature

The advantages of doctor-blading at an elevated temperature are twofold: it lowers the solution viscosity and increases the solubility of spiro-OMeTAD in chlorobenzene. Both factors facilitate the infiltration of spiro-OMeTAD and consequently increase the filling fraction.

The effect of increasing the doctor-blading temperature on the filling fraction of 5-μm TiO_2 films is shown in Fig. 2. When the temperature was raised from 20 to 80 °C, the filling fraction increased from 46% to 53%, while the overlayer thicknesses remained relatively unchanged. The filling fraction of 53% at 80 °C is comparable with the value obtained from optimized spin-coating condition as shown in Fig. 1d. We note that increasing the deposition temperature only increased filling fraction for doctor-blading samples and not for spin-coating samples, possibly because spin-coating samples cool much more rapidly. It is conceivable that raising the temperature even higher may further increase filling fraction. However, when the temperature was raised to 100 °C, the rapid evaporation of chlorobenzene made the doctor-blading process hard to control and resulted in non-uniform overlayers. Therefore, we stopped the temperature study at 80 °C and used this temperature in the fabrication of the solar cell.

2.4. Solar cell performance

After deposition of spiro-OMeTAD, the silver electrodes were thermally evaporated onto the sample, and the J–V curves of the solar cell were measured under simulated one-sun illumination. Fig. 3 shows the current density–voltage (J–V) curves of devices made from doctor-blading and spin coating. The two deposition techniques give approximately equal device efficiencies, which is expected because of the equal filling fractions. Devices from doctor-blading tend to have a slightly higher fill factor and lower open-circuit voltage compared with spin coating. The nature of these differences is outside the scope of this study, but it is possible that these differences resulted from different spiro-OMeTAD overlayer thicknesses of films deposited by doctor-blading and spin coating.

The reproducibility of the device performances from doctor-blading was also tested. For each device thickness, we made at least four identical devices, and the standard deviations of the efficiencies were within 7%. Table 1 compares the average device performances of ss-DSCs made from two spiro-OMeTAD deposition techniques.

In addition to delivering equally efficient devices as spin coating, doctor-blading also uses far less material. The loss of coating solution can be as high as 95% for spin coating [20] and as low as 5% for doctor-blading [21]. The efficient usage of materials by doctor-blading is demonstrated for
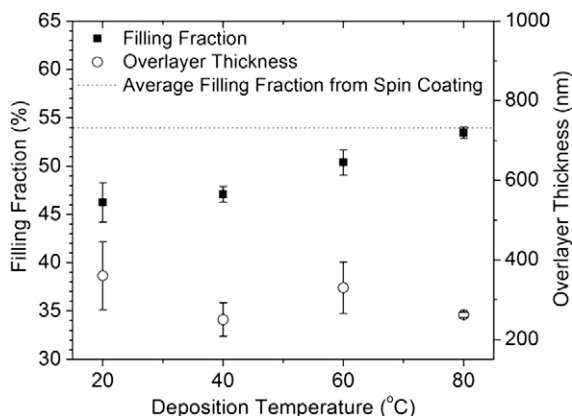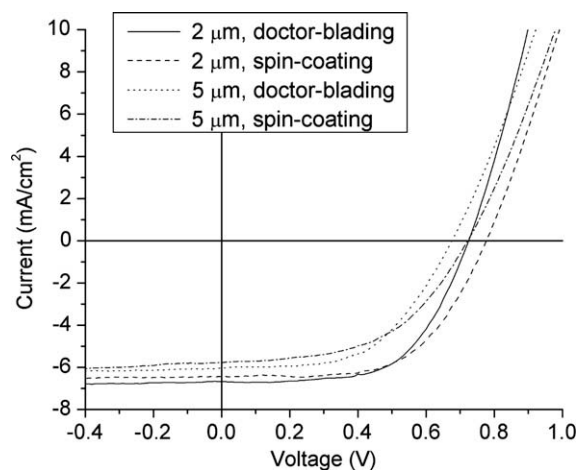
Fig. 2. Filling fractions and overlayer thicknesses of 5-μm thick TiO_2 films doctor-bladed at different temperatures with 360 mg/mL spiro-OMeTAD solution in chlorobenzene. The dotted line indicates the average filling fraction of 5-μm thick TiO_2 films from spin coating.

Fig. 3. Current density–voltage (J–V) curves of solid-state dye-sensitized solar cells made from doctor-blading and spin-coating spiro-OMeTAD. Two different device thicknesses were tested: 2 and 5 μm.

Table 1
The device performance of ss-DSCs made from spin coating and doctor-blading deposition of spiro-OMeTAD. The values shown above are averaged values and standard deviations of at least four devices made under identical conditions.

	Jsc (mA/cm^2)	Voc (V)	Efficiency (%)	Fill factor
2 µm, doctor-blading	6.86 ± 0.37	0.73 ± 0.01	3.01 ± 0.13	0.61 ± 0.03
2 µm, spin coating	6.80 ± 0.26	0.76 ± 0.03	3.02 ± 0.16	0.58 ± 0.02
5 µm, doctor-blading	5.88 ± 0.45	0.68 ± 0.01	2.13 ± 0.13	0.54 ± 0.02
5 µm, spin coating	5.77 ± 0.90	0.71 ± 0.02	2.00 ± 0.10	0.49 ± 0.04

our relatively small device areas as well. For 5-µm thick TiO$_2$ films (1.5 cm by 2 cm), we used 35 µL of 270 mg/mL spiro-OMeTAD solution for spin coating, and 10 µL of 360 mg/mL solution for doctor-blading; in this case, doctor-blading uses 60% less spiro-OMeTAD than spin coating. When the device area is further increased, the reduction of material usage by doctor-blading will be much more pronounced.

2.5. Directions to improve filling fraction

The optimized thickness of ss-DSCs is approximately 2 µm due to the compromise between light absorption and charge collection [19]. Devices made with TiO$_2$ films thicker than 4 µm are usually less than 2% [22]. In contrast, the 5-µm thick ss-DSCs reported here, made from either doctor-blading or spin-coating concentrated spiro-OMeTAD solution, achieved an average efficiency well over 2%. We propose that the improved efficiency results directly from the enhanced filling fraction. When spiro-OMeTAD is deposited on 5-µm thick TiO$_2$ film by conventional recipe of spin coating a 180 mg/mL solution, the filling fraction is extrapolated to be only 41% [18], much lower than the 53% filling fraction reported in our optimized recipe. This indicates that one of the possible directions of improving the performance of thick ss-DSCs is to increase the filling fraction because higher filling fraction results in better charge collection. However, the fact that 5-µm thick devices still have a lower short-circuit current and open-circuit voltage than 2-µm thick ones means there is room for improvement.

It is instructive to consider what limits the filling fraction at values substantially below unity. For 2-µm films, we found that changing the particle size from 20 to 45 nm does not increase the filling fraction. This indicates the filling fraction for 2 µm films is not limited by the constrictions inside the porous network, but by the viscosity-concentration curve of the spiro-OMeTAD solution. We propose that when the spiro-OMeTAD-chlorobenzene mixture contains 65% spiro-OMeTAD by volume, the viscosity is too high for spiro-OMeTAD to easily diffuse; this is when the infiltration stops. If this hypothesis is right, it has the following implications: (1) solution-based infiltration methods will never be able to achieve 100% filling fraction because there have to be some solvent molecules inside

the HTM film to make HTM molecules mobile. Void formation occurs when the solvent molecules evaporates. (2) To get to 100% filling fraction, a solvent-free method such as melt infiltration has to be used [23,24]. Unfortunately spiro-OMeTAD has very high melting temperature (248 °C as determined by differential scanning calorimetry), which makes it impossible to be used for melt infiltration since the sensitizing dye is damaged at this temperature [25]. To get to 100% filling fraction, new HTMs that have lower glass transition temperatures and stay amorphous even when being heated above T_g must be developed [26].

Despite the aforementioned fundamental limitation of spiro-OMeTAD pore filling, the filling fraction for thick films can still be improved by optimizing the solution deposition techniques. It was mentioned previously in Section 2.1 that using doctor-blading to deposit spiro-OMeTAD solution results in a slower evaporation, which gives spiro-OMeTAD more time to infiltrate prior to the drying of solution. In our previous studies, slowing down the evaporation by decreasing the spin-coating speed appears to improve filling fraction [18]. However, in this study, the slightly slower evaporation rate from doctor-blading did not result in substantial increase of filling fraction. A more detailed study on the evaporation rate and its influence on pore filling with doctor-blading deposition will be necessary to further optimize this technique. We have tried treating the deposited spiro-OMeTAD film with solvent vapor to soften the film to enhance diffusion [27], but it led to extensive crystallization of spiro-OMeTAD that can be observed in the optical microscope, which hurts the device performance. Other possible methods to accomplish higher filling fraction include switching to a high boiling point solvents during doctor-blading or spin coating.

3. Conclusions

We have demonstrated the use of doctor-blading to deposit spiro-OMeTAD in solid-state dye-sensitized solar cells. After optimizing the solution concentration and temperature, we achieved an equal pore filling fraction with doctor-blading and spin coating for 2.5 and 5-µm thick films. The efficiencies of devices made with these two deposition techniques are comparable, and the materials utilization of spiro-OMeTAD is significantly better for doctor-blading. This demonstrates the potential for doctor-blading to be used in future commercial production of solid-state dye-sensitized solar cells.

4. Experimental

4.1. Sample preparation

FTO substrates (Hartford Glass TEC 15) were first patterned through etching with Zinc powder and HCl (12%). Then, the substrates were cleaned by sonication sequentially in 10% Extran solution, acetone and isopropanol [28]. Samples used for solar cell measurements were coated with a compact layer of TiO$_2$ (50 nm) by aerosol spray pyrolysis using air as carrier gas [29]. Mesoporous

TiO$_2$ films were then deposited from commercially-available paste (Dyesol 18NR-T) using screen-printing. These sheets were slowly heated to 500 °C and baked for 30 min in air. Samples used for solar cell measurements are treated with acidic TiCl$_4$ solution [30] by immersing the samples in 0.02 M TiCl$_4$ aqueous solution overnight at room temperature. The samples were then heated to 450 °C and subsequently cooled to 80 °C before being immersed in Z907 dye solution for 12–18 h. The dye solution comprised of 0.3 mM of Z907 (Solaronix SA) in 1:1 mixture of acetonitrile and tert-butyl alcohol. Prior to making the solution, Z907 dye has been purified by column chromatography following published procedure [31].

4.2. Spiro-OMeTAD infiltration

The formulation of spiro-OMeTAD solution has been published elsewhere [18]. For spin coating, a small quantity (30–50 µL) of the spiro-OMeTAD solution was deposited onto each TiO$_2$ film (1.5 cm by 2 cm) at room temperature and left for 1 min before spin coating at 2000 rpm for 45 s in air. Doctor-blading was done with a commercially-available machine (CX-4 motorized film applicator, mtv Messtechnik oHG) with blade speed of 15 mm/s. The blade height was controlled by adjusting the screws on the doctor-blade (UA 3000 universal film applicator, mtv Messtechnik oHG). The blade height was 40 µm for TiO$_2$ films of 2 µm thick, and 80 µm for TiO$_2$ films of 5-µm thick. The solution (10 µL) was first deposited using a micropipette onto an area of the FTO substrate not covered by TiO$_2$, then spread onto TiO$_2$ film with doctor-blade. For the temperature-dependence experiment, we first put the both the spiro-OMeTAD solution and the TiO$_2$ film on top of a hot plate that has been set to the desired temperature, and let the system equilibrate for 5 min. Then, the TiO$_2$ film was transferred onto the doctor-blading machine and the solution was immediately deposited. We note that because the doctor-blading machine does not contain a heating element, the true doctor-blading temperature may be slightly lower than the value reported. After spiro-OMeTAD deposition, the film was left to dry overnight in air at room temperature.

4.3. Device fabrication and photovoltaic measurements

For efficiency measurements, silver electrodes (200 nm) were thermally evaporated onto the film under vacuum below 10^{-6} torr.

Current density–voltage (J–V) measurements were carried out with a Keithley 2400 source meter and a 91160 300 W Oriel solar simulator equipped with a 6258 ozone-free Xenon arc lamp and an air mass (AM 1.5 G) filter. The lamp intensity was measured with an NREL calibrated silicon photodiode, with spectral mismatch accounted for.

Acknowledgements

References

[1] C.Y. Chen, M. Wang, J.Y. Li, N. Pootrakulchote, L. Alibabaei, N.-L. Cevey-Ha, J.D. Decoppet, J.H. Tsai, C. Gratzel, C.G. Wu, S.M. Zakeeruddin, M. Grätzel, Highly efficient light-harvesting ruthenium sensitizer for thin-film dye-sensitized solar cells, ACS Nano 3 (2009) 3103–3109.
[2] B.C. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO$_2$ films, Nature 353 (1991) 737–740.
[3] J.R. Durrant, S.A. Haque, E. Palomares, Towards optimisation of electron transfer processes in dye sensitised solar cells, Coord. Chem. Rev. 248 (2004) 1247–1257.
[4] M. Grätzel, Photoelectrochemical cells, Nature 414 (2001) 338–344.
[5] A.F. Nogueira, C. Longo, M.A. De Paoli, Polymers in dye sensitized solar cells: overview and perspectives, Coord. Chem. Rev. 248 (2004) 1455–1468.
[6] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Grätzel, Solid-state dye-sensitized mesoporous TiO$_2$ solar cells with high photon-to-electron conversion efficiencies, Nature 395 (1998) 583–585.
[7] J.-H. Yum, P. Chen, M. Grätzel, M.K. Nazeeruddin, Recent developments in solid-state dye-sensitized solar cells, ChemSusChem 1 (2008) 699–707.
[8] S.-J. Moon, J.-H. Yum, R. Humphry-Baker, K.M. Karlsson, D.P. Hagberg, T. Marinado, A. Hagfeldt, L. Sun, M. Grätzel, M.K. Nazeeruddin, Highly efficient organic sensitizers for solid-state dye-sensitized solar cells, J. Phys. Chem. C 113 (2009) 16816–16820.
[9] H.J. Snaith, L. Schmidt-Mende, Advances in liquid-electrolyte and solid-state dye-sensitized solar cells, Adv. Mater. 19 (2007) 3187–3200.
[10] H.J. Snaith, A.J. Moule, C. Klein, K. Meerholz, R.H. Friend, M. Grätzel, Efficiency enhancements in solid-state hybrid solar cells via reduced charge recombination and increased light capture, Nano Lett. 7 (2007) 3372–3376.
[11] M. Wang, S.-J. Moon, M. Xu, K. Chittibabu, P. Wang, N.-L. Cevey-Ha, R. Humphry-Baker, S.M. Zakeeruddin, M. Grätzel, Efficient and stable solid-state dye-sensitized solar cells based on a high-molar-extinction-coefficient sensitizer, Small 6 (2009) 319–324.
[12] J.-H. Yum, B.E. Hardin, S.-J. Moon, E. Baranoff, F. Nüesch, M.D. McGehee, M. Grätzel, M.K. Nazeeruddin, Panchromatic response in solid-state dye-sensitized solar cells containing phosphorescent energy relay dyes, Angew. Chem. Int. Ed. 48 (2009) 9277–9280.
[13] Y.H. Chang, S.R. Tseng, C.Y. Chen, H.F. Meng, E.C. Chen, S.F. Horng, C.S. Hsu, Polymer solar cell by blade coating, Org. Electron. 10 (2009) 741–746.
[14] P. Schilinsky, C. Waldauf, C.J. Brabec, Performance analysis of printed bulk heterojunction solar cells, Adv. Funct. Mater. 16 (2006) 1669–1672.
[15] M. Kaelin, D. Rudmann, A.N. Tiwari, Low cost processing of CIGS thin film solar cells, Sol. Energy 77 (2004) 749–756.
[16] L. Schmidt-Mende, M. Grätzel, TiO$_2$ pore-filling and its effect on the efficiency of solid-state dye-sensitized solar cells, Thin Solid Films 500 (2006) 296–301.
[17] D.M. Huang, H.J. Snaith, M. Gratzel, K. Meerholz, A.J. Moule, Optical description of solid-state dye-sensitized solar cells. II. Device optical modeling with implications for improving efficiency, J. Appl. Phys. 106 (2009) 073112.
[18] I.-K. Ding, N. Tetreault, J. Brillet, B.E. Hardin, E.H. Smith, S.J. Rosenthal, F. Sauvage, M. Gratzel, M.D. McGehee, Pore-filling of spiro-OMeTAD in solid-state dye sensitized solar cells: quantification, mechanism, and consequences for device performance, Adv. Funct. Mater. 19 (2009) 2431–2436.
[19] H.J. Snaith, R. Humphry-Baker, P. Chen, I. Cesar, S.M. Zakeeruddin, M. Grätzel, Charge collection and pore filling in solid-state dye-sensitized solar cells, Nanotechnology 19 (2008) 424003.
[20] C.J. Brabec, J.R. Durrant, Solution-processed organic solar cells, MRS Bull. 33 (2008) 670–675.
[21] F.C. Krebs, Fabrication and processing of polymer solar cells: a review of printing and coating techniques, Sol. Energy Mater. Sol. Cells 93 (2009) 394–412.
[22] L. Schmidt-Mende, S.M. Zakeeruddin, M. Grätzel, Efficiency improvement in solid-state-dye-sensitized photovoltaics with an amphiphilic ruthenium-dye, Appl. Phys. Lett. 86 (2005) 013504.

[23] K. Fredin, E.M.J. Johansson, T. Blom, M. Hedlund, S. Plogmaker, H. Siegbahn, K. Leifer, H. Rensmo, Using a molten organic conducting material to infiltrate a nanoporous semiconductor film and its use in solid-state dye-sensitized solar cells, Synth. Met. 159 (2009) 166–170.

[24] K.M. Coakley, Y. Liu, M.D. McGehee, K.L. Frindell, G.D. Stucky, Infiltrating semiconducting polymers into self-assembled mesoporous titania films for photovoltaic applications, Adv. Funct. Mater. 13 (2003) 301–306.

[25] K. Fredin, K.F. Anderson, N.W. Duffy, G.J. Wilson, C.J. Fell, D.P. Hagberg, L. Sun, U. Bach, S.-E. Lindquist, Effect on cell efficiency following thermal degradation of dye-sensitized mesoporous electrodes using N719 and D5 sensitizers, J. Phys. Chem. C 113 (2009) 18902–18906.

[26] M.Y. Lo, C. Zhen, M. Lauters, G.E. Jabbour, A. Sellinger, Organic-inorganic hybrids based on pyrene functionalized octavinylsilsesquioxane cores for application in OLEDs, J. Am. Chem. Soc. 129 (2007) 5808–5809.

[27] F. Pschenitzha, J.C. Sturm, Three-color organic light-emitting diodes patterned by masked dye diffusion, Appl. Phys. Lett. 74 (1999) 1913–1915.

[28] G.F. Burkhard, E.T. Hoke, S.R. Scully, M.D. McGehee, Incomplete exciton harvesting from fullerenes in bulk heterojunction solar cells, Nano Lett. 9 (2009) 4037–4041.

[29] H.J. Snaith, M. Grätzel, The role of a "Schottky Barrier" at an electron-collection electrode in solid-state dye-sensitized solar cells, Adv. Mater. 18 (2006) 1910–1914.

[30] P.M. Sommeling, B.C. O'Regan, R.R. Haswell, H.J.P. Smit, N.J. Bakker, J.J.T. Smits, J.M. Kroon, J.A.M. van Roosmalen, Influence of the $TiCl_4$ treatment on nanocrystalline TiO_2 films in dye-sensitized solar cells, J. Phys. Chem. B 110 (2006) 19191–19197.

[31] P. Wang, B. Wenger, R. Humphry-Baker, J.-E. Moser, J. Teuscher, W. Kantlehner, J. Mezger, E.V. Stoyanov, S.M. Zakeeruddin, M. Grätzel, Charge separation and efficient light energy conversion in sensitized mesoscopic solar cells based on binary ionic liquids, J. Am. Chem. Soc. 127 (2005) 6850–6856.