Polymer solar cells

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Recent progress in the development of polymer solar cells has improved power-conversion efficiencies from 3% to almost 9%. Based on semiconducting polymers, these solar cells are fabricated from solution-processing techniques and have unique prospects for achieving low-cost solar energy harvesting, owing to their material and manufacturing advantages. The potential applications of polymer solar cells are broad, ranging from flexible solar modules and semitransparent solar cells in windows, to building applications and even photon recycling in liquid-crystal displays. This Review covers the scientific origins and basic properties of polymer solar cell technology, material requirements and device operation mechanisms, while also providing a synopsis of major achievements in the field over the past few years. Potential future developments and the applications of this technology are also briefly discussed.

arnessing solar energy is one of the most promising ways to tackle today's energy issues. Although the present dominant photovoltaic (PV) technology is based on inorganic materials, high material and manufacturing costs limit its wide acceptance¹. Intensive research has been conducted towards the development of low-cost PV technologies, of which organic photovoltaic (OPV) devices are one of the promising. OPV devices are based on organic semiconductors - carbon-based materials whose backbones are comprised mainly of alternating C-C and C=C bonds. Electron delocalization along the conjugated backbone is responsible for the semiconducting properties of OPV devices². One of the major differences between organic semiconductors and inorganic semiconductors is the presence of tightly bonded excitons (electron-hole pairs) resulting from their low dielectric constant ($\varepsilon_r \approx 2-4$). The binding energy of the Frenkel exciton is in the range of 0.3-1 eV (refs 2,3). Such a large binding energy prevents exciton dissociation by an electrical field (a non-radiative decay channel) and can achieve a high electroluminescent efficiency in organic light-emitting devices. The weak intermolecular van de Waals interaction enables the realization of low-cost, large-area deposition technologies such as roll-toroll printing³. In recent years, organic electronic devices such as organic light-emitting diodes (OLEDs), organic thin film transistors, OPVs and organic memory devices have attracted considerable attention, owing to their potential low cost and high performance characteristics. OLED displays have gained a considerable share in the portable electronics market, for use in devices such as smart phones. However, research into OPV cells continues to lag behind, despite the first patent⁴ and the first paper⁵ by Tang appearing ahead of those of OLEDs, probably owing to the fact that developing alternative energy sources has been viewed, until recently, as being relatively unimportant.

OPVs are divided into two different categories according to whether their constituent molecules are either small or large (polymers). These two classes of materials are rather different in terms of their synthesis, purification and device fabrication processes. Polymer solar cells (PSCs) are processed from solution in organic solvents, whereas small-molecule solar cells are processed mainly using thermal evaporation deposition in a high-vacuum environment. Using the solution process to fabricate small-molecule solar cells has recently been gaining momentum⁶, although the film quality and crystallization is expected to be an issue. PSCs are attractive owing to a number of advantageous features⁷, including their thin-film architecture and low material consumption resulting from a high absorption coefficient, their use of organic materials, which are abundant, their utilization of efficient solution processes and low manufacturing energy requirements. Other advantages include their low specific weight, mechanical flexibility, tunable material properties and high transparency. This Review is primarily devoted to recent progress in the development of PSCs.

Tang^{4,5} introduced the donor-acceptor bilayer planar heterojunction to the OPV cell in 1979, and achieved power-conversion efficiencies (PCEs) of around 1%. The energy difference between the lowest unoccupied molecular orbital (LUMO) of the donor and highest occupied molecular orbital (HOMO) of the acceptor provides the driving force for the dissociation of Frenkel excitons. The separated holes and electrons are then collected at the anode and cathode, respectively. One of the major breakthroughs in OPV technology was the adoption of C₆₀ fullerene and its derivatives (such as [6,6]-phenyl-C₆₁-butyric acid methyl ester⁸, PCBM) to replace the n-type molecules in OPV devices. Owing to their strong electronegativity and high electron mobility, C60 derivatives have become standard n-type molecules in OPV devices. In the early 1990s, Heeger et al. and Yoshino et al. independently demonstrated electron transfer between a conjugated polymer and fullerene derivatives9,10. They observed an extremely fast photoinduced electron transfer process of around 50-100 fs, which dominates over all other photophysical processes present. These discoveries provided a solid foundation for OPV technology. In 1993, researchers made the first demonstrations of planar heterojunction PSCs11.

The planar junction concept has certain limitations, including a small surface area between the donor–acceptor interfaces and the requirement of long carrier lifetime to ensure that the electrons and holes reach their respective electrodes. This problem can be addressed by introducing a bulk heterojunction, which involves mixing donor–acceptor materials in the bulk body of an OPV device. This concept was first demonstrated by Hiramoto *et al.* through the co-evaporation of donor and acceptor molecules under high-vacuum conditions¹². The first efficient bulk heterojunction PSCs were independently realized in 1995 by the groups of Heeger and Friend in polymer–fullerene and polymer–polymer blends^{13,14}. Polymer–fullerene systems currently dominate the field of high-efficiency PSCs. PSC efficiencies are now approaching 10%, which indicates remarkable progress towards a promising future.

Although the bulk heterojunction concept is powerful as a solution for addressing the issue of exciton disassociation, in 2005 researchers discovered that the morphology (the donor-acceptor phase separation) also plays a critical role in achieving

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proper charge transport channels for collecting the electrons and $holes^{15,16}$.

A typical PV process involves the creation of free carriers from incident photons. The physics and the energy diagram of polymer-fullerene-based PSCs are illustrated in Fig. 1a¹⁷. The external quantum efficiency (EQE) as a function of wavelength (λ) is the ratio between the collected photogenerated charges and the number of incident photons, ultimately being the product of four efficiencies (η): absorption (A), exciton diffusion (ED), charge separation (CS) and charge collection (CC), giving $EQE(\lambda) = \eta_A(\lambda) \times \eta_{ED}(\lambda) \times \eta_{CS}(\lambda) \times \eta_{CC}(\lambda)$. The photovoltage (or open-circuit voltage, $V_{\rm OC}$) is directly linked to the energy difference between the LUMO level of the acceptor and the HOMO level of the donor, thereby providing the primary driving force for charge separation. Figure 1b compares the solar spectrum to the EQE spectrum of the representative PSCs (bandgap of 1.9 eV). The short-circuit current density (J_{SC}) is equal to the integral of the product between cell responsivity and incident solar spectral irradiance. Thus, it is necessary to utilize a broader solar spectrum and enlarge the energy level difference between the LUMO level of the donor and the HOMO level of the acceptor, resulting in high values of $J_{\rm SC}$ and $V_{\rm OC}$, respectively. Innovations in materials science have provided efficient ways of achieving these goals. Morphology is another critical factor in bulk heterojunction PSCs. The preferred morphology of bulk heterojunctions is a bicontinuous interpenetration network (Fig. 1c)¹⁸. Donor and acceptor domains should be twice the size of the exciton diffusion length (around 10 nm), which allows excitons to diffuse to the donor-acceptor interface and thus achieves efficient $\eta_{\rm FD}(\lambda)$ and $\eta_{\rm CS}(\lambda)$ for charge generation. After charge separation at the donor-acceptor interface, holes and electrons must travel to the positive and negative electrodes through donor and acceptor networks, respectively. The third key factor is the organic-electrode interface, where the charges are extracted to external circuits. The charge collection efficiency $\eta_{\rm CC}(\lambda)$ accounts for both carrier transport in the networks and the extraction steps.

Building efficient PSCs therefore requires a systematic consideration and understanding of three key areas: materials design, morphology and manipulation, and interface engineering. It is worth pointing out that inorganic materials such as nanostructures of zinc oxide, titanium oxide and cadmium selenium can also function as acceptors for polymer donors, for which efficiencies of over 3% have been demonstrated¹⁹⁻²¹. This type of solutionprocessed solar cell is typically categorized as a hybrid solar cell, and will therefore not be discussed in this Review.

Materials development

The development of PSCs has always been accompanied by innovations in materials science. Figure 2 shows the chemical structures of some representative materials. One of the earliest PSC polymers is poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV), which was developed by Wudl et al.²². Wudl also invented one of the most important fullerene derivatives, PCBM⁸, which represents a milestone in the development of PSC acceptors and is still widely used today. In 1995, Yu et al. blended MEH-PPV with C₆₀ and its derivatives to give the first PSC with a high PCE¹³. This work opened up a new era of polymer materials for use in solar energy conversion. After significant optimization, researchers achieved PCEs of more than 3.0% for PPV-based PSCs^{23,24}. However, further improvement was limited by the relatively low hole mobility and narrow light absorption range. Soluble polythiophenes, especially poly(3-hexylthiphene) (P3HT)²⁶, with their higher hole mobility²⁵ and therefore a broader spectrum coverage than MEH-PPV, have become a standard for PSC materials in the 2000s. Morphology optimization^{15,16} has provided PCEs of 4-5%, thus attracting worldwide interests in PSCs.



Figure 1 | Introduction to PSCs. a, The operating mechanism of a PSC. **b**, Comparison between solar spectrum and the photoresponse of a P3HT:PCBM solar cell. **c**, Conceptual morphology model with bicontinuous interpenetration network of the polymer and the acceptor¹⁸. Figure **c** reproduced with permission from ref. 18, © 2007 ACS.

Many more high-performance polymers have been developed in recent years. One of these is poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), a low-bandgap polymer whose absorption extends up to 900 nm. PSCs made from this polymer have showed an initial efficiency of around $3\%^{27}$. However, by incorporating alkanedithiol additives, researchers were able to achieve efficiencies of around $5.5\%^{28}$. Leclerc *et al.* developed poly[*N*-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), which gave a PCE of $3.6\%^{29}$. In 2009, researchers increased this to 6.1% by incorporating a titanium oxide (TiO_x) layer as an optical spacer³⁰. The most impressive high-performance polymers are those designed by Yu *et al.*, which are composed of thieno[3,4-*b*]-thiophene (TT) and benzodithiophene (BDT) alternating units³¹⁻³³. This was the first polymer donor system capable



Figure 2 | Chemical structures of representative donor and acceptor molecules used in PSCs.

of reaching PCEs of 7–8%. Following this work, PCEs of more than 7% were frequently reported with either new materials or novel device optimization techniques³⁴⁻⁴⁰.

Materials innovation is one of the major forces currently driving the performance of PSCs. The key issues of polymer design include^{41,42} engineering the bandgap and energy levels to achieve high J_{SC} and V_{OC} , enhancing planarity to attain high carrier mobility, and materials processability and stability. All of these issues are correlated with each other. In the ideal case, all factors should be optimized in a single polymer, but this remains a significant challenge. The efficiency of a PSC is given by $\eta = V_{OC} \times J_{SC} \times FF$, where FF is the fill factor. Knowledge of the link between the design of a polymer and these parameters has been significantly improved over the past decade.

The value of $V_{\rm OC}$ for a PSC can be expressed by the empirical equation $V_{\text{OC}} = e^{-1} \times (|E_{\text{HOMO}}^{\text{donor}}| - |E_{\text{LUMO}}^{\text{acceptor}}| - 0.3 \text{ eV})$, where *e* is the elementary charge, E is the energy level and 0.3 eV is an empirical value for efficient charge separation⁴³. A donor polymer with a lower HOMO level will give a higher $V_{\rm OC}$. P3HT is by far the most popular donor, with a HOMO level of ~4.9 eV (ref. 44), which corresponds to a $V_{\rm OC}$ value of around 0.6 V and serves as a reference for polymer design¹⁵. Thiophene is an electron-rich group^{45,46}. The HOMO level of the polymer in a PSC can be effectively lowered by utilizing groups that are less electron-rich^{29,47-49}. For example, fluorene and carbazole are commonly used units in wide-bandgap materials because they are less electron-rich than thiophene. By incorporating these units into a polymer donor, $V_{\rm OC}$ can be significantly increased. Cao et al. demonstrated a polymer containing a fluorene unit that achieved $V_{\rm OC} \approx 1.0$ V (ref. 47). Inganäs et al. also reported a polymer composed of fluorene and quinoxaline alternating units⁴⁸ that reached $V_{\rm OC} \approx 1.0$ V. Another example is PCDTBT, which incorporates carbazole units in the polymer chain, from which researchers achieved $V_{\rm OC} \approx 0.89$ V (ref. 29). $V_{\rm OC}$ is also affected by non-radiative recombination between the donor and the acceptor. Eliminating these non-radiative pathways⁵⁰ will help to maximize $V_{\rm OC}$. However, linking polymer design with such an elimination process remains a significant challenge.

 $J_{\rm SC}$ is another important parameter that determines the performance of a PSC. The most powerful strategy for achieving high

 $J_{\rm SC}$ is to narrow the bandgap (<1.8 eV) for a broader coverage of the solar spectrum^{41,42,51}. Methods for achieving this include designing an alternating donor-acceptor structure, stabilizing the quinoid structure, controlling the polymer chain planarity, and tuning the effective conjugation length. Designing an alternating donor-acceptor structure is the most common approach, in which the push-pull driving forces between the donor and acceptor units, together with the photoinduced intramolecular charge transfer, facilitates electron delocalization and the formation of low-bandgap quinoid mesomeric structures over the polymer backbone^{41,52,53}. According to molecular orbital perturbation theory, electron delocalization leads to the hybridization of molecular orbitals, resulting in electron redistribution throughout the interacting orbitals. This provides two new hybridized orbitals — a higher HOMO level and a lower LUMO level — resulting in a narrower bandgap. One of the most successful examples of this donor-acceptor structure is PCPDTBT^{27,28}. By combining a dialkyl-cyclopentabithiophene donor unit and benzothiadiazole acceptor unit, the bandgap of PCPDTBT spans 1.4 eV (around 900 nm). This donor-acceptor structure is not limited to the polymer main chain. Huang et al. demonstrated that a donor-acceptor structure comprising an acceptor-based side chain and a donorbased main chain also results in a lower bandgap⁵⁴. Another successful way of reducing the bandgap is to stabilize the quinoid structure of conjugated units^{31,51}. The ground state of a conjugated structure has two resonance structures: an aromatic form and a quinoidal form⁴¹. The quinoidal form is energetically less stable because of its smaller bandgap; achieving a stable quinoidal form therefore reduces the bandgap. Yu et al. have found that a thieno[3,4-*b*]thiophene unit can stabilize the quinoidal structure through a fused thiophene ring^{31,32,51}. Polymers containing TT and BDT alternating units have bandgaps of around 1.6 eV.

Narrowing the bandgap alone is not necessarily enough to achieve high $J_{\rm SC}$. Other parameters, such as carrier mobility, intermolecular interaction and molecular chain packing, also affect $J_{\rm SC}$. For example, tuning the chemical structure provides effective ways to improve hole mobility. Yang *et al.* developed poly(4,4-dioctyldithieno(3,2-*b*:2,'3'-*d*)silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl) (PSBTBT) by replacing the bridging carbon atom in PCPDTBT with a silicon atom^{55,56}. PSBTBT has a higher crystallinity than PCPDTBT and therefore has improved hole mobility, leading to a higher value of $J_{\rm SC}$. Using a large planar structure can also improve transport by enhancing molecule packing^{57,58}.

Although $V_{\rm OC}$ and $J_{\rm SC}$ can indeed be improved by employing these strategies, it remains a challenge to improve both values simultaneously. Narrowing the bandgap can improve $J_{\rm SC}$, but $V_{\rm OC}$ may correspondingly be decreased because of the higher HOMO level that results. Researchers recently demonstrated that structural fine-tuning is a powerful approach for improving both $V_{\rm OC}$ and $J_{\rm SC}$ simultaneously (refs 32–35). For example, introducing a fluorine atom into the TT unit reduces both HOMO and LUMO levels simultaneously, while also improving $V_{\rm OC}$ and retaining the bandgap^{32,35}. Fine-tuning the side-chain structure can also result in a similar effect. One example is to simultaneously lower both the HOMO and LUMO levels by replacing the electron-rich alkoxy side chain with the less electron-rich alkyl chain³³.

The third parameter for achieving high efficiency in a PSC is the FF, which is currently the least understood one among the three. The FF is the ratio between the maximum obtainable power and the product of $J_{\rm SC}$ and $V_{\rm OC}$. It is affected by many factors, including charge carrier mobility and balance, interface recombination, series and shunt resistances, film morphology and miscibility between the donor and acceptor⁵⁹. However, obtaining a clear understanding and the ability to modulate the FF still remains a

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Figure 3 | **Morphology in PSCs. a**, Tapping mode atomic force microscopy image of a solvent-annealed P3HT:PCBM film⁷¹. **b**, TEM image of a thermally annealed P3HT:PCBM film⁷³. **c**, Defocused cross-sectional TEM image of a P3HT:PCBM film⁷⁴. **d**, Three-dimensional electron tomography image of thermally annealed P3HT-PCBM film⁷⁶. Figure reproduced with permission from: **a**, ref. 71, © 2007 Wiley; **b**, ref. 73, © 2005 ACS; **c**, ref. 74, © 2009 ACS; **d**, ref. 76, © 2009 ACS.

hurdle in the development of PSCs. From the materials design point of view alone, molecular planarity, intermolecular interactions, molecular chain packing and crystallinity, and high-mobility units should be taken into consideration in structure designs. Side-chain tuning also has considerable effects on improving the FF. For example, Fréchet *et al.* optimized the side-chain patterns for *N*-alkylthieno[3,4-*c*]pyrrole-4,6-dione (TPD)-based polymers⁶⁰. Side-chain tuning helped to optimize π -stacking, polymer crystallinity and material miscibility, and caused the FF to increase from 55% to 68%. Researchers also recently achieved an efficiency of 7% for a TPD–silole copolymer³⁹.

Developing novel acceptors can also improve the PCE⁶¹⁻⁶⁵. For example, C_{70} derivatives exhibit better absorption than those of C_{60} . Replacing C_{60} derivatives with C_{70} derivatives often enhances J_{SC} by around 10%. Moreover, V_{OC} can also be enhanced by using novel acceptor materials. From the energy diagram in Fig. 1a, it can be seen that V_{OC} is also determined by the LUMO level of the acceptor. Achieving an upshifted LUMO level leads to a larger value of V_{OC} . One of the most impressive examples of this is C_{60} with an indene bisadduct^{62,64,65}. Symmetrically adding such electron-rich indene units to fullerene upshifts the LUMO level by 0.17 eV compared with PC₆₁BM, resulting in a 40% improvement in V_{OC} (0.84 V) in P3HT-based PSCs. Although indene C_{60} bisadduct exhibits superior performance over P3HT, improving its compatibility with other polymer donors remains a challenge.

The development of PSC materials is being intensely pursued. In 2010, four groups^{60,66-68} independently published the same structure design of a TPD–BDT copolymer, although with performances varying in the range of 4.1–6.8% due primarily to differences in material quality and device fabrication processes. This work highlights the importance of interactive collaboration between scientists working in materials synthesis and those working in device fabrication.

Morphology in PSCs

Morphology control is critical in bulk-heterojunction PSCs. Thermal annealing²⁶ and solvent annealing¹⁵ are currently the most popular methods for controlling morphology. It was not until 2005 that both thermal and solvent annealing were shown to enhance PSC efficiency by a significant amount^{15,16}. Many other approaches are also effective for improving polymer–fullerene morphology, such as solvent selection⁶⁹ and solvent mixture⁷⁰ techniques, and the use of additives²⁸.

The characterization of polymer morphology involves a variety of different technologies. Microscopic techniques provide a direct view of polymer morphology. Atomic force microscopy in tapping mode is suitable for soft PSC films and can provide highresolution surface topographical and surface donor–acceptor distribution data on the nanoscale. Figure 3a shows a phase image of a high-crystallinity P3HT:PCBM film⁷¹. The polymer nanofibrillar structure is consistent with that of a pure P3HT film⁷². The nanofibrillar width of P3HT is 20–30 nm, which is consistent with the morphology model. Another powerful imaging technique is transmission electron microscopy (TEM). Yang *et al.* studied a P3HT:PCBM film using bright-field TEM⁷³ (Fig. 3b). The specific density difference of P3HT and PCBM enables the polymer- and

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Figure 4 | Grazing-incidence X-ray diffraction images of polymer-acceptor films. a, Highly crystalline P3HT:PCBM blend film by solvent annealing⁷¹. **b**, BDT-TPD copolymer:PCBM films⁶⁰, showing the different polymer orientations in the two systems. Figure reproduced with permission from: **a**, ref. 71, © 2007 Wiley; **b**, ref. 60, © 2010 ACS.

fullerene-rich regions to be mapped, and thus provides information on the dimensions of the P3HT nanostructure. Cross-section TEM provides another critical piece of morphological information. Heeger *et al.* observed bicontinuous interpenetrating polymer and fullerene domains in cross-sectional TEM images of a P3HT:PCBM solar cell (Fig. 3c)⁷⁴. The combination of surface topological and cross-sectional imaging tools provides important information regarding the morphology of quasi-optimized P3HT:PCBM solar cells.

Electron tomography⁷⁵ involves reconstructing threedimensional (3D) objects from a series of 2D images by sequential tilting of the sample about a single axis. This technique, although originally designed for use in the life sciences, has also been applied to the study of polymer blends using bright-field TEM as a nanoscale 3D imaging tool. Loos *et al.* studied the 3D morphology of MEH-PPV:PCBM¹⁸ and P3HT:PCBM⁷⁶ systems. The contrast between crystallized polymer nanostructures with PCBM (Fig. 3d) enables the crystallinity of P3HT to be estimated (found to be around 60%). The volume percentage of crystalline P3HT nanorods varies in the vertical direction, which indicates a more complex 3D morphology than that of an active layer with uniform material distribution.

Variable-angle spectroscopic ellipsometry⁷⁷ and X-ray photoemission spectroscopy⁷⁸ have also been used to investigate vertical phase separation in P3HT:PCBM films. Researchers observed a concentration gradient, with PCBM-rich regions being present near the substrate and a P3HT-rich region being adjacent to the surface. Near-edge X-ray absorption fine structure spectroscopy studies by DeLongchamp⁷⁹ have shown that the concentration of P3HT at the buried interface depends strongly on the substrate surface energy. Similar results were also obtained in recent neutron reflectometry studies^{80,81}.

Grazing-incidence X-ray diffraction (GIXRD) is a technique used to measure the crystalline structural details of a thin film⁸². Obtaining accurate structural information for a material of weak polymer crystallinity requires a synchrotron beamline with a high X-ray photon flux and beam collimation⁸³. Figure 4a shows a synchrotron GIXRD pattern of a P3HT:PCBM film⁷¹. The prominent (*n*00) diffraction peaks indicate high crystallinity with edge-on chain orientation. GIXRD can also be applied to new high-efficiency, low-bandgap copolymer systems. In some BDT-containing polymer–PCBM systems^{32,60}, GIXRD shows a clear face-on orientation. Figure 4b shows GIXRD images of BDT–TPD copolymers with different side chains⁶⁰. A large planar BDT unit prefers a face-on orientation in film formation. Different polymers need different orientations to achieve high performance, thus requiring customization in the film processing stage.

Interface and device structure

Interface layers have multiple functions in a PSC⁸⁴. First, they are able to reduce the energy barrier between the photoactive layer and the electrode, thus forming Ohmic contacts for effective charge extraction. Second, they can form selective contacts for a single type of carrier, such as an electron-transporting layer that also serves as a hole-blocking layer. Some interface materials, such as TiO_x and caesium carbonate (CsCO₃), can modify the electrode work function and thus enable the inverted structure of a PSC to be realized. Optical field modulation and protection of the underlying active layer are also important functions that can be provided by the interface layer.

The bottom layer of a PSC is traditionally a layer of the transparent conductive material indium tin oxide (ITO), which has a high work function of around 4.7 eV. A p-type interface layer of PEDOT:PSS (work function of around 5.0 eV) applied on top forms an Ohmic contact with the photoactive layer for effective charge collection, and also smoothes the ITO surface to remove potential pinholes. The acidic nature of PEDOT:PSS, however, causes issues regarding the device's long-term stability. To get around this problem, researchers introduced various transition metal oxides^{38,85,86} — V₂O₅, MoO₃, WO₃ and NiO — as replacements to PEDOT:PSS. Solution-processed transition metal oxides have recently become popular for use in PSCs, with several groups achieving promising results^{87,88}.

On the cathode side, low-work-function metals such as calcium, barium and magnesium are used to provide Ohmic contacts at the cathode–polymer interface. Researchers introduced inorganic compounds to replace such reactive metals and thus improve the stability of the device. Tang *et al.* introduced LiF as

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an n-type interface layer in small-molecule OLEDs⁸⁹. Brabec *et al.* then demonstrated that LiF–Al can achieve efficiencies comparable to the Ca–Al electrode in MDMO–PPV:PCBM solar cells²³. Jönsson *et al.* reported that aluminium decomposes LiF for submonolayer coverage, thus causing any subsequent lithium doping of the organic material to lower the contact's work function⁹⁰. Employing a thicker layer of LiF creates a dipole layer that also lowers the work function⁹¹. Other fluorides such as CsF have exhibited similar effects⁹².

Solution-processed interface layers are often preferred over vacuum processes such as thermal evaporation or sputtering for realizing the full potential of bulk-heterojunction PSCs. n-type inorganic metal oxides such as sol-gel-based TiO_x (ref. 93) and zinc oxide $(ZnO_x)^{94}$ have been shown to be good candidates for organic electronics. Low-temperature (150 °C) hydrolysis sol-gel process amorphous TiO_x was shown to be effective for use in OLEDs and PSCs⁹⁵. TiO_x also functions as a hole-blocking layer and optical spacer, which enhances absorption inside a thin device by modulating the optical field. The use of a TiO_x optical spacer has been shown to cause a 40% enhancement in photocurrent and EQE for a P3HT:PCBM system⁹³ and nearly a 100% enhancement in internal quantum efficiency for a PCDTBT:PCBM system³⁰. Crystalline TiO_x nanoparticles from non-hydrolysis sol-gel processes have also been shown to work well in this respect⁹⁶. By incorporating Cs₂CO₃ into nanocrystalline TiO₂₂, Park et al. observed the Cs-doping of TiO_x, which lowers the TiO_x work function and improves OLED and PSC performance⁹⁶.

Materials with permanent dipole moments can also be used to modify polymer–electrode interfaces. The work function can be increased or decreased by employing self-assembled monolayers with electron-withdrawing or electron-donating groups, respectively. By controlling the dipole moment of self-assembled monolayers, researchers have improved PSC efficiency using combined ZnO and self-assembled monolayers⁹⁷. Polyelectrolyte is another successful n-type interface material^{98,99}. Wu *et al.* demonstrated a PSC efficiency of 8.37% by using conjugated polyelectrolyte as an n-type interface layer for devices based on the TT–BDT copolymer¹⁰⁰.

Although most research into PSCs has involved the traditional device structure (with ITO as the anode contact), the inverted architecture has received increasing attention since 2006. Removing the reactive metal and introducing an air-stable transition metal oxide layer as a p-type interface layer has provided a significant boost in PSC stability. This structure is also more compatible with roll-to-roll manufacturing processes than the traditional device structure¹⁰¹.

Yang *et al.* observed that Cs_2CO_3 can 'convert' ITO into a cathode by lowering its work function^{102,103}. With V_2O_5 as the top p-type interface layer, Yang *et al.* demonstrated an inverted PSC structure with the same ITO bottom and top metal electrodes. White *et al.* subsequently demonstrated a solution-processed ZnO_x n-type interface layer for an inverted PSC¹⁰⁴. Brabec *et al.* showed the effectiveness of combining TiO_x and PEDOT:PSS in an inverted PSC¹⁰⁵. Nanostructure forms such as the TiO₂ nanotube¹⁰⁶ and ZnO nanoridge¹⁰⁷ have also been applied in the inverted PSC design. The most popular n-type buffer materials are TiO_x, ZnO_x and Cs-doped TiO_x, while the most popular p-type buffers are V₂O₅, MOO₃, WO₃, NiO and PEDOT:PSS. Very recently, graphene oxide¹⁰⁸ was also shown to be an effective p-type interface layer.

New concepts in PSC and future prospects

The maximum power conversion efficiencies of PSCs must rise above 15% in the laboratory (corresponding to a module efficiency of around 10–12%) before they can become practically useful. The tandem solar cell concept¹⁰⁹, which combines two or more







Figure 5 | Novel structure and applications of PSCs. a, Solution-processed tandem PSC (regular)¹¹². **b**, Stretchable PSC¹¹³. **c**, Integrating a PV polarizer¹¹⁴ into a liquid-crystal display. Figure **b** reproduced with permission from ref. 113, © 2011 Wiley.

sub-cells with different absorption ranges (Fig. 5a), is obviously a very attractive way to improve power efficiencies because it can significantly enhance photon utilization efficiencies and thus preserve $V_{\rm OC}$. The typical structure of a solution-processed tandem PSC is shown in Fig. 5a. The key components include high-efficiency sub-cells with maximized $V_{\rm OC}$, sub-cell spectra matching, and robust and transparent solution-processing interconnection layers. Over the past two years, device innovation, in combination with the development of photoactive materials and improvements to the interface layer, have provided a solid foundation for all solution-processed tandem PSCs. Several groups^{110–112} have demonstrated the feasibility of this concept, for which the current state-of-the-art cell efficiency is 8.6%.

The unique properties of PSCs open the door for many novel applications. Stretchable PSCs (Fig. 5b) enable the concept of conformal photovoltaics on curved or wrinkled surfaces, such

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as textiles and fabrics¹¹³. PSCs can also be integrated into liquidcrystal displays (LCDs) to recycle wasted photons by creating a PV polarizer, as shown in Fig. 5c¹¹⁴. In this work, the researchers oriented the conjugated polymer chain by employing a simple rubbing process, which caused the material to polarize incoming light. This PV LCD panel can harvest energy from sunlight, ambient light or the backlight of LCDs. Guo *et al.* demonstrated a PV colour filter concept for integrated PV-LCD panels¹¹⁵.

Stability is one of the major hurdles that must be tackled before PSCs can enter the market. Brabec *et al.* investigated the requirements that PSC technology must meet for it to become competitive⁷. They claim that a module efficiency of 7% and a lifetime of seven years is the threshold for roll-to-roll-processed PSCs. Many research groups have shown that inverted PSCs have a much longer lifetime than traditional PSCs. McGehee *et al.* recently showcased a PCDTBT-based PSC rigid device with a lifetime of seven years¹¹⁶. In industry, Konarka's first-generation flexible PSC panel has a three-year lifetime with flexible encapsulation. All of these technological advances are encouraging. Progress in the OLED industry has shown that realizing a long-lifetime PSC, although challenging, is not impossible. Rapid progress in the development of PSCs in recent years provides significant confidence in this promising technology.

During the preparation of this manuscript, we have successfully demonstrated a solution-processed tandem PSC with an NREL-certified PCE of $10.6\%^{117}$, which represents a substantial improvement over the previous record of $8.6\%^{118}$.

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Additional information

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