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Received 21 Apr 2016 | Accepted 27 Jun 2016 | Published 10 Aug 2016

DOI: 10.1038/ncomms12374

OPEN

Ultrafast formation of air-processable and high-quality polymer films on an aqueous substrate

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Polymer solar cells are attracting attention as next-generation energy sources. Scalable deposition techniques of high-quality organic films should be guaranteed to realize highly efficient polymer solar cells in large areas for commercial viability. Herein, we introduce an ultrafast, scalable, and versatile process for forming high-quality organic films on an aqueous substrate by utilizing the spontaneous spreading phenomenon. This approach provides easy control over the thickness of the films by tuning the spreading conditions, and the films can be transferred to a variety of secondary substrates. Moreover, the controlled Marangoni flow and ultrafast removal of solvent during the process cause the films to have a uniform, high-quality nanomorphology with finely separated phase domains. Polymer solar cells were fabricated from a mixture of polymer and fullerene derivatives on an aqueous substrate by using the proposed technique, and the device exhibited an excellent power conversion efficiency of 8.44 %. Furthermore, a roll-to-roll production system was proposed as an air-processable and scalable commercial process for fabricating organic devices.

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Control of the nanomorphology in polymer solar cells (PSCs) is a key factor for maximizing the module power conversion efficiency (PCE) and enhancing the electrical properties related to exciton dissociation at the interfaces between donors and acceptors^{1–3}, diffusion of charge carriers^{4,5}, and charge collection at each electrode^{6–8}. The nanomorphology of the blended film can be engineered via thermal and solvent annealing^{9,10} or the use of processing additives and so on, to achieve selective solubility¹¹. Effective manipulations may favorably influence the crystallization and orientation of the polymers¹².

Although spin-coating is the most appropriate laboratory-scale film formation process, scale-up of this process does not ensure uniformity, even within a device. This makes the spin-coating process incompatible with roll-to-roll (R2R) production under ambient conditions, where the latter is desirable for successful commercialization.

Furthermore, air processability of PSCs is a critical issue given that an inert environment is currently required for the entire process, unless the devices are stable under ambient conditions. Although poly(3-hexylthiophene) (P3HT)-based devices exhibit good air processability due to reversible degradation by oxygen, highly efficient polymers containing the benzodithiophene (BDT) group, such as poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) and poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2,6-diyl]] (PTB7-Th), tend to undergo significant degradation on exposure to oxygen and light^{13–16}.

Here we propose a new approach to form high-quality organic films on an aqueous (water based) substrate under ambient conditions. A drop of organic material blended into a solvent, when dropped onto an aqueous surface, spreads spontaneously and rapidly by the Marangoni effect¹⁷, leading to the rapid and uniform formation of an organic layer that can be functionalized on various substrates once transferred. Interestingly, the nanomorphology of blended films can be efficiently managed in seconds during the process of spreading on the aqueous substrate. We verify that the ultrafast solvent removal by the spontaneous spreading process can impede the infiltration of oxygen into the film via the remaining solvent effectively.

The utility of the films in functional devices is demonstrated by applying the new film formation technique to the fabrication of highly efficient PSCs. PTB7-based PSCs are successfully fabricated by exploiting the high-quality nanomorphology within the bulk heterojunction (BHJ) films. Last, we demonstrate the potential of our method as a scalable process by transferring the spontaneously spreading (SS) film from water surface to a large plastic substrate using a custom-made R2R process.

Results

Spontaneously spreading process of polymer solutions. When chemical agents with low surface energy (for example, hydrocarbon solvents or detergents) are dropped into high-surface-energy media (for example, water), local surface tension gradients occur on the boundary between the surrounding materials, leading to surficial flow toward regions of higher surface tension. This spontaneous spreading is called Marangoni flow^{17,18}. The spreading coefficient (S) dictates the speed of the spreading flow and is defined by the surface tensions at the three-phase contact line between a liquid droplet and liquid substrates¹⁹, where $S = \gamma_1 - \gamma_2 - \gamma_{12}$ (γ_1 and γ_2 are the surface tensions of the base and polymer solutions, respectively, and γ_{12} is the interfacial surface tension of the two solutions). Figure 1a illustrates the different

behaviours of the polymer solution depending on S when a drop of polymer solution is dropped on the base solution. The flow of the solution is determined by the net force direction of the surface tensions. If S is positive, that is, the surface tension of the base solution, γ_1 (red arrow), is larger than the sum of γ_2 (green arrow) and γ_{12} (blue arrow), the polymer solution will spread over the aqueous substrate surface and form a uniform polymer film. Otherwise, the polymer solution will ball on the aqueous substrate without dispersion.

The proportion $S^{1/2}$ describes the spreading speed of the solution^{20,21}, and the solution is unlikely to spread if S is negative. The spreading coefficients of 1,2-dichlorobenzene (*o*-DCB) and chlorobenzene (CB) are -4.25 and $2.35 \text{ dyne cm}^{-1}$, respectively^{21,22}; thus only CB would exhibit spontaneous spreading flow on water. Dissolution of the solvent in water further accelerates drying and formation of the polymer films on aqueous substrates. Figure 1b illustrates the formation of a SS film on an aqueous substrate (here water is used as the aqueous substrate). (I) The polymer solution is dropped onto the aqueous substrate; (II) the solution quickly spreads (if $S > 0$) over the aqueous surface within a few seconds; (III) because the solvents evaporate and dissolve into the liquid simultaneously, the drying process occurs instantaneously to form a thin solid polymer layer (the SS film) on the liquid; (IV) this thin film can readily be transferred to a variety of target substrates, for example, by stamping the substrates on the SS film gently (see Supplementary Movie 1, Supplementary Note 1 and Supplementary Fig. 1).

Because the photoactive films of polymer solar cells have dimensions below the wavelengths of visible light ($< \sim 200 \text{ nm}$), control of the thickness within tens of nanometers is very important for achieving optimized performance²³. Herein, the SS film formation method is shown to be extremely reliable for controlling the thickness of polymer films over a wide range (tens to hundreds of nanometers). The ultimate thickness of organic films forming on water depends on the volume and concentration of the polymer solution, the size of the water bath, and the number of layers transferred (see Supplementary Note 2 and Supplementary Fig. 2a–d). PTB7:PC₇₁BM solution was used for the thickness experiments.

Uniform and conformal transfer on various substrates. The SS films formed in the water bath exhibited controllable thickness and high uniformity over large areas. The SS-PTB7:PC₇₁BM film was deposited in a square PET Petri dish ($12 \times 12 \text{ cm}^2$), leading to a thickness of $43.9 \pm 4.1 \text{ nm}$ (see Supplementary Note 3 with Supplementary Figs 3 and 4) as determined from 16 positions on the substrate.

The SS films were also successfully transferred to various secondary substrates including polydimethylsiloxane (PDMS), polyethylene terephthalate (PET), paper, and the curved surface of a vial by the stamping method (Fig. 1c–f). An interference pattern was still apparent on the polyurethane (PU) substrate with sinusoidal gratings (period: 556 nm) after transfer of the SS films to the substrate (Supplementary Note 4; Supplementary Fig. 5a,b). Scanning electron microscope (SEM) images also confirmed successful formation of the SS films.

Nanomorphology within BHJ films. The universality of SS film formation was demonstrated by generating the SS films using several types of common polymers. AFM images (Supplementary Note 5 and Supplementary Fig. 6) show that poly(3-hexylthiophene-2,5-diyl) (P3HT), poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), PTB7, and PTB7-Th formed uniform and smooth SS films. The SS phenomenon

Figure 1 | Principle and formation process of spontaneous spreading. (a) Spreading of polymer solution dropped onto the base solution is determined by the spreading coefficient, S . Positive S results in a uniform polymer film; otherwise, polymer drops aggregate; (b) Schematic illustrations of formation of an SS BHJ film on water and transfer to target substrates. Actual processing images are shown. (c–f) Transferred SS-PTB7:PC₇₁BM films on various substrates: PDMS (c), PET (d), copy paper (e) and a curved surface of a vial (f).

appeared to be uninfluenced by the presence of PC₇₁BM and an additive such as DIO.

High-resolution transmission electron microscope analysis of the BHJ films was performed under the same defocused imaging conditions (10 μm) to compare the domain sizes of PTB7 (refs 24,25). To fabricate top-down transmission electron microscope (TEM) samples, the SS-PTB7:PC₇₁BM film was directly transferred to 300 mesh copper TEM grids, while the spin-coated (SC-)PTB7:PC₇₁BM films (air and N₂) were floated on deionized water and transferred. To highlight the PC₇₁BM cluster domains (dark regions) and PTB7 crystallite domains (bright regions), the bright regions are coloured red (Supplementary Note 5; Supplementary Fig. 6d–f). The PC₇₁BM cluster domains and domains of PTB7 crystallites in the SC-PTB7:PC₇₁BM films processed in air and in N₂ were slightly larger than those of the SS-PTB7:PC₇₁BM film (Fig. 2a–c)²⁶. Figure 2c illustrates the more uniformly formed nanomorphology of the SS-PTB7:PC₇₁BM film with finely dispersed phase separation between the PTB7 and PC₇₁BM domains, suggesting efficient spatial interaction between these species during the SS process. The size distribution of the PTB7 domains was determined from at least five samples using ImageJ software (Fig. 2d; see Supplementary Note 6 and Supplementary Fig. 7 for details). The average size of the PTB7 domains in the SS-PTB7:PC₇₁BM film was 5.50 nm, while that of the SC-PTB7:PC₇₁BM films was 8.79 nm on average; the PTB7 domains in the SS film had a narrower size distribution.

The final morphology of a BHJ film with solvent additives is governed by the dynamics of solvent evaporation and liquid-liquid phase separation^{26,27}. Immediately on dropping the solution on the water, the solvent (that is, CB) volume decreases due to evaporation and dissolution of the solvent into the water (Fig. 1a); the PTB7 chains start to form aggregated fine structures within a few seconds. This is much faster than the drying of spin-coated BHJ films (a few tens of seconds)²⁸.

However, too rapid solvent evaporation and a higher initial concentration of the polymer in the solution at the air/liquid interface may enhance the nucleation rate, leading to a high

number of small crystallites^{29,30}. Therefore, inducing optimized-scale phase separation with appropriately sized crystallites is desirable. To properly control the phase separation, the DIO content in the PTB7:PC₇₁BM solution was varied²⁶. Because DIO has a higher boiling point (~170 °C) and higher surface tension (43.25 dynes cm⁻¹) than CB, mixing 10 vol% DIO with PTB7:PC₇₁BM solution leads to increased surface tension of the droplet, which slows the rate of spreading over the water^{31,32}. Furthermore, DIO molecules with greater specific gravity (1.84 g cm⁻³) than water are steadily removed from films into water during SS process although DIO is insoluble in water (water solubility at 25 °C: 0.2301 mg l⁻¹). This results in sufficient plasticity to allow the aggregated polymer chains to be mobile enough to assume the optimal conformations^{31,33}. At the same time, the PC₇₁BM molecules remain dissolved in DIO, preventing large-scale liquid-liquid phase separation³⁴. Subsequently, the PC₇₁BM molecules captured in DIO are slowly integrated into the PTB7 crystallites before complete solidification, resulting in larger interface areas between smaller PTB7 and PC₇₁BM domains²⁶. The larger interfacial areas between domains result in efficient exciton dissociation in the BHJ PSCs, as discussed below³⁵.

Figure 2e shows photoluminescence spectra (excited at 633 nm) of the SC- and SS-PTB7:PC₇₁BM films on silicon wafers. Significant quenching of the photoluminescence intensity for the SS-PTB7:PC₇₁BM film confirms facilitated exciton dissociation in the increased interfacial area between the finely dispersed phase-separated domains, as revealed in the TEM images (Fig. 2c).

The influence of the SS process on the degree of molecular order was probed using resonant Raman spectroscopy (excited at 633 nm) of the SC- and SS-PTB7:PC₇₁BM films because these spectra can reveal the intramolecular conformational order of polymer chains (Fig. 2g)^{36,37}. The wavelength of 633 nm is close to the maximum absorption of PTB7 (Fig. 2h), which allows excitation of even the disordered phase of PTB7 in strong resonance with electronic transitions³⁷. The Raman spectra were background corrected and the spectra from three different regions of the samples were averaged. Spectra were also acquired from

Figure 2 | High-quality polymer from spontaneous spreading process. (a–c) TEM images of N_2 processed (a) air-processed SC-BHJ (b) and SS-BHJ (c) films measured at the same defocusing distance. (d) PTB7 domain size distribution histograms of N_2 -processed SC-BHJ and SS-BHJ films. (e) Photoluminescence spectra of both films when excited at 633 nm. (f) SC-BHJ and SS-BHJ films immediately after film formation process. (g–i) Raman spectra (g) and ultraviolet-visible absorption spectra (h) for SC-BHJ and SS-BHJ films, and S2p and C1s XPS spectra (i) of N_2 and air-processed SC-BHJ, and SS-BHJ films. (j–l) 2D GIWAXS images of SC-BHJ (j) and SS-BHJ films (k) and out-of-plane and in-plane GIWAXS profiles (l).

three samples prepared at different times to exclude sample-to-sample variation and measurement error. The Raman peaks of the SS-PTB7:PC₇₁BM film at $\sim 1435\text{ cm}^{-1}$ (C–C intra-ring stretch mode) and at $\sim 1490\text{ cm}^{-1}$ (symmetric C=C stretch mode) were almost identical to those of the SC-films. The ratio of the intensity of the peaks of the C–C and C=C modes ($I_{C-C}/I_{C=C}$ of the SS film) increased from 0.46 to 0.49, and the full width at half maximum (FWHM) of the C=C mode became narrower, reflecting the enhanced degree of molecular order of the PTB7 chains in the SS film.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was also used to verify enhanced crystallization and orientation of the

molecules during the spontaneous spreading process. The intensity of the (010) scattering peak at $1.6\text{ \AA}^{-1}$ for the SS-PTB7:PC₇₁BM film increased markedly compared with that of the SC-PTB7:PC₇₁BM film (Fig. 2j–l), indicating enhanced face-on orientation of the PTB7 chains in relation to the substrate in the SS-PTB7:PC₇₁BM film processed in air. The enhanced face-on orientation of the SS-PTB7 film is most likely due to the interplay of Van der Waals interaction from alkyl side chains and the attractive interactions occurring between the less hydrophobic backbone of PTB7 and the water surface^{38,39}. The intensity ratio (I_{out}/I_{in}) of the out-of-plane to in-plane PTB7 lamellar peaks (100) at around $0.35\text{ \AA}^{-1}$ was also calculated for quantitative

analysis of the edge-on PTB7 lamellar to face-on crystallite ratio⁴⁰. The I_{out}/I_{in} ratio of the SS-PTB7:PC₇₁BM film was 3.96, whereas that of the SC-PTB7:PC₇₁BM film was 29.1, indicating a significantly lower degree of edge-on orientation.

Enhanced crystallization and orientation of the molecules in the SS-PTB7:PC₇₁BM film can affect the air stability of the film^{41–43}. The mass density of an organic thin film, which is determined by the degree of crystallinity, can alter the ability of chemical reactants to permeate to the reaction site of molecules⁴¹. Enhanced molecular packing can also strengthen chemical bonds in the film due to more rigid and planar backbones, extending the regions of delocalization, leading to a chemically more robust film^{42,43}. (Supplementary Note 7; Supplementary Fig. 8)

Air processability. The air stability of the films formed by various processes was evaluated based on the Raman spectra of the SC- and SS-PTB7:PC₇₁BM films obtained under 514 nm excitation. Raman peaks corresponding to phenylene-alkoxy (–R–O–) stretching ($\sim 1,250$ and $\sim 1,350$ cm^{–1}) and the C=C stretching mode of the BDT group ($\sim 1,500$, $\sim 1,550$ cm^{–1} and $\sim 1,580$ cm^{–1}) were observed for the air-processed SC-PTB7:PC₇₁BM film (Supplementary Note 8; Supplementary Fig. 9). The intensity of these peaks was significantly lower than that of the peaks of the N₂-processed SC-PTB7:PC₇₁BM film. This suggests that oxygen that infiltrated into the film during the spin-coating and drying processes contributes to cleavage of the alkoxy groups and insertion of oxygen into the C=C bonds in the backbone, resulting in disruption of the π -conjugation. This is consistent with the decreased and slightly blue-shifted absorption and photoluminescence of the air-processed SC-PTB7:PC₇₁BM film (Fig. 2h,e).

A survey scan using X-ray photoelectron spectroscopy (XPS) was also performed to confirm the air stability of the SS films^{44,45}. Figure 2i shows a considerable shift and peak broadening of the S2p peak for the air-processed SC-PTB7:PC₇₁BM film, which can be ascribed to chain scissions in the polymer backbone, or to loss of the side chains. The C1s spectrum of the air-processed SC-PTB7:PC₇₁BM film shows the emergence of a peak at 287 eV, derived from oxygenated carbon species, including a carboxyl group¹³. In contrast, no detectable S2p peak broadening or C1s peak from oxygenated carbon species was observed for the SS-BHJ and N₂-processed SC-BHJ films (Fig. 2i).

Surprisingly, no indication of degradation was observed for the SS-PTB7:PC₇₁BM films based on the XPS and Raman spectra (Fig. 2i; Supplementary Fig. 9) although the film was formed on water in air. For the air-processed SC-BHJ films, CB remaining between the polymer chains before complete drying may work as effective percolation pathways for diffusion of oxygen to the PTB7 molecules because of the significantly higher oxygen diffusivity of CB (1.16×10^{-5} cm² s^{–1}) than that of PTB7 (1.2×10^{-8} cm² s^{–1})^{46,47}, which can facilitate reactions between oxygen and the BDT group of PTB7 (Fig. 3a)^{47–49}.

To examine the aftermath effects of remaining solvent on degradation of the BHJ films, the atomic ratio of oxygen to sulfur in the polymer films exposed to ambient conditions versus the drying time was probed by using XPS. Briefly, the BHJ films were spin-coated under N₂ and subsequently exposed to air for different periods; finally, the films were completely dried in a N₂-filled glove box (Supplementary Note 9; Supplementary Fig. 10a). The films exposed to air for a longer time exhibited greater oxygen permeation with a broad distribution of oxygen in the films, implying that the CB molecules could provide pathways for oxygen diffusion into the BHJ film, as presented in Fig. 3a. In contrast, the O/S ratio and the atomic distribution of oxygen in SS-PTB7:PC₇₁BM film were comparable to that of the

N₂-processed SC-PTB7:PC₇₁BM film, suggesting excellent air processability by the spontaneous spreading process (Supplementary Note 9; Supplementary Fig. 10b).

The effect of solvent (here, CB) on oxidation of polymer films was evaluated. DIO additive as a co-solvent was not considered because DIO molecules are steadily removed from films during the SS process due to greater specific gravity of DIO than water, as previously mentioned. (Supplementary Table 1, Supplementary Note 10 and Supplementary Fig. 11) For the experiments, PTB7 only (that is, without fullerenes) films were prepared using different post-treatments. PTB7 films spun in nitrogen were treated under different conditions (Fig. 3a) before exposure to air for 3 h, that is, (i) as-spun without removal of solvent, (ii) thermally treated at 70 °C for 20 min. After exposure to air for 3 h, the intensity of the absorption peaks of the as-spun PTB7 film with excess solvent were considerably reduced (Fig. 3b), indicating degradation of the PTB7 polymer chains due to air exposure, as compared with the thermally treated PTB7 films. Moreover, the Raman peaks of the as-spun PTB7 film obtained under excitation at 514 nm were also significantly diminished relative to those of the other films, suggesting cleavage of the alkoxy groups and insertion of oxygen into the C=C bonds in the backbone (Fig. 3c). Oxygen within the three PTB7 films was tracked using time-of-flight secondary ion mass spectrometry (TOF-SIMS), as shown in the depth profile in Fig. 3d. Figure 3e–g shows the 3D iso-surface overlay of the intensity of the oxygen ion peaks (¹⁶O and ¹⁸O). The intensity of oxygen near the surface of the as-spun PTB7 film was considerably higher than that of the thermally-treated PTB7 film (Fig. 3e–f), confirming that oxygen molecules penetrated the PTB7 film via the excess solvent between the PTB7 chains as explained above. In contrast, the oxygen intensity near the surface region of the SS-PTB7 film was comparable to that of the thermally treated film (Fig. 3f,g). In addition, performed studies on the effect of solvent on exposure to light and air on the oxidation of PTB7 films also suggest that oxygen adsorbed through the solvent path in the film during illumination in air contributes to accelerated disruption of the backbone conjugation of BDT group in PTB7 molecules. (Supplementary Note 11; Supplementary Fig. 12)

It can be inferred that the spontaneous spreading process can induce rapid formation of a condensed and well-packed thin film due to the ultrafast solvent removal, which can prevent the intrusion of oxygen via the CB solvent, impeding oxidation and redistribution of the polymer and PC₇₁BM molecules in the BHJ film.

Photovoltaic performances. Polymer solar cells (hereafter, SS-PSCs) were fabricated to evaluate the applicability of the SS films to high-efficiency functional devices fabricated in air. For comparison with the SS-PSCs, SC-PSCs were fabricated under two different sets of environmental conditions, that is, in a N₂ filled glove box (hereafter, SC-PSCs (N₂)) and under ambient atmosphere (hereafter, SC-PSCs (air)). The air exposure time of the SC-PSCs (air) and SS-PSCs during the coating process in air was set to under 10 min. The post-drying process for the SC-PSCs (air and N₂) was performed in a N₂ filled glove box (see Methods section). The device structure (Fig. 4a,e) was ITO/CBA (or ZnO)/PTB7 (or PTB7-Th):PC₇₁BM/BCP/Al (or MoO₃/Ag).

Figure 4b,f show the representative current density–voltage (*J*–*V*) characteristics of the SS-PSCs, SC-PSCs (N₂) and SC-PSCs (air) based on a mixture of PTB7:PC₇₁BM and PTB7-Th:PC₇₁BM. The SC-PSCs (air) exhibited much lower performance than the SS-PSCs and SC-PSCs (N₂), attributed to degradation of the air-processed BHJ films by oxidation as explained in relation to Fig. 2f.

Figure 3 | Oxygen diffusion into polymer films via solvent. (a) Oxygen diffusion mechanism in PTB7 films during drying process for spin-coated PTB7 films treated under different conditions and for SS-PTB7 film. (b) Ultraviolet-visible absorption spectra and (c) Raman spectra of spin-coated PTB7 films treated under different conditions, (d–g) TOF-SIMS depth profile and 3D iso-surface overlay of oxygen ions (¹⁶O and ¹⁸O) intensity as a function of sputter time for the spin-coated PTB7 films treated under different conditions.

The PCE of the PTB7-based SS-PSC was 6.27% (Table 1, Supplementary Note 12 and Supplementary Table 2), which is comparable to that of the SC-PSC (N₂; 6.21%). However, the PCE of the SC-PSCs (air) was significantly reduced (3.74%). The PCE of the PTB7-Th-based SS-PSC reached 8.44%, and this is the highest PCE reported for air-processed organic solar cells to date to the best of our knowledge. Details of the device performance are summarized in Table 1.

Both polymer-based SS-PSCs exhibited performance comparable to that of the SC-PSCs (N₂) with an almost identical spectral response in the external quantum efficiency (EQE) data (Fig. 4c,g). To evaluate the reliability of the SS-PSCs processed in air, statistical data for the PCEs of 30 PTB7 and PTB7-Th devices are presented in Fig. 4d,h and Supplementary Figs 13 and 14 with Supplementary Note 13, respectively.

We demonstrated the potential of our method as a scalable process by transferring the SS film to a large PET substrate using an R2R process. Figure 4i shows a SS-PTB7:PC₇₁BM film on the water bath (30 × 120 cm² size), made by dropping only 200 µl of the polymer solution as a point source for spontaneous spreading (Supplementary Movie 2). After the solution spread, a 1 m long SS film was obtained in a few seconds. A custom-made R2R system was used to transfer the large SS film to the PET substrate (Fig. 4j). The SS-film was transferred successfully from the water

surface to the PET substrate (Supplementary Movie 3). Figure 4k shows a PET film coated with a PTB7:PC₇₁BM layer ~60 nm thick. We anticipate that this new polymer film formation method will have great potential as a new process for R2R-processed modules with low material consumption and drying time, and consequently lower fabrication cost.

In summary, we developed an air-processable technique to form polymer films on an aqueous surface within a few seconds, using the spontaneous spreading phenomenon. Ultrafast removal of solvent during the process causes the films to have uniform and high-quality nanomorphology because oxygen diffuses into the polymer films rapidly through the remaining solvent between the polymer chains. Furthermore, the polymer films were successfully transferred onto various substrates. Finally, we demonstrated high performance of PSCs prepared using the proposed process, comparable to that of PSCs prepared by spin coating. We expect that this approach can be extended by roll-to-roll production to achieve high-quality films.

Methods

Preparation of the polymer solution. For the SC films, PTB7:PC₇₁BM (1-Materials: Nano-C) and PTB7-Th:PC₇₁BM (1-Materials: Nano-C) at a weight ratio of 1:1.5 were dissolved in chlorobenzene (CB):1,8-diiodooctane (DIO) (97:3 v/v) at 50 °C. This mixture was stirred for 12 h under N₂. For the SS-films, PTB7:PC₇₁BM

Figure 4 | Fabrication of organic solar cells using SS films and potential for scalable process. (a,b) Device structure of n-PSC (PTB7:PC₇₁BM) and i-PSC (PTB7-Th:PC₇₁BM); (c-f) J-V characteristics and EQE spectra of PTB7-based (c,e) and PTB7-based PSCs (d,f) under AM 1.5G 100 mW cm⁻² illumination. (g,h) statistics for PCEs of 30 samples. (i) Formation of a single SS film on a large water bath (30 × 120 cm²). (j) Homemade R2R coating system for large-scale transfer on flexible substrates. (k) 25 × 100 cm² PET film coated with a SS-PTB7:PC₇₁BM film.

Table 1 | Representative photovoltaic performance parameters for SC- and SS-PSCs.

PSCs	Performance	SC-PSC (N ₂)	SC-PSC (air)	SS-PSC (air)
PTB7:PC ₇₁ BM	PCE (%)	5.90 ± 0.27 (6.34)	3.32 ± 0.25 (3.74)	5.84 ± 0.25 (6.24)
	J _{sc} (mA cm ⁻²)	14.22 ± 0.83 (15.71)	12.27 ± 0.67 (13.28)	14.71 ± 0.57 (15.45)
	V _{oc} (V)	0.74 ± 0.03 (0.77)	0.65 ± 0.03 (0.69)	0.74 ± 0.01 (0.76)
	FF	0.56 ± 0.03 (0.60)	0.42 ± 0.02 (0.46)	0.54 ± 0.02 (0.57)
PTB7-Th:PC ₇₁ BM	PCE (%)	8.41 ± 0.24 (8.86)	5.89 ± 0.46 (6.29)	7.95 ± 0.28 (8.44)
	J _{sc} (mA cm ⁻²)	16.80 ± 0.27 (16.72)	14.71 ± 0.84 (15.85)	16.66 ± 0.34 (16.80)
	V _{oc} (V)	0.80 ± 0.01 (0.79)	0.78 ± 0.01 (0.79)	0.79 ± 0.01 (0.79)
	FF	0.63 ± 0.02 (0.67)	0.51 ± 0.03 (0.50)	0.60 ± 0.02 (0.64)

PSCs, polymer solar cells; PTB7, poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophenediyl]]; SS, spontaneously spreading.
Means and s.d. are obtained from 30 devices. The values in brackets illustrates the best cell performance for each device.

and PTB7-Th:PC₇₁BM at a weight ratio of 1:1.5 were dissolved in 10 vol% of DIO in CB (CB:DIO = 90:10 v/v).

Solar cell fabrication for PTB7:PC₇₁BM. PTB7:PC₇₁BM PSCs were fabricated on ITO-deposited glass substrates (R_{sh} : 22 ohm sq⁻¹). A layer of 4-chlorobenzoic acid (CBA, Sigma-Aldrich) as a hole transfer layer (HTL) was spun onto the substrates at 3,000 r.p.m. for 30 s; the substrates were then annealed at 70 °C for 5 min (ref. 50). Surplus molecules of CBA on the substrates were removed by spin coating with methanol at 6,000 r.p.m. for 30 s. Two layers of SS-PTB7: PC₇₁BM films were transferred sequentially onto the substrates and dried at 70 °C for 10 min under N₂. SC-PTB7: PC₇₁BM films were spun at 2,500 r.p.m. for 30 s and then dried at 70 °C for 10 min under N₂. Subsequently, bathocuproine (BCP, 8 nm) and Al (150 nm) were deposited through a shadow mask by thermal evaporation onto the devices⁵¹.

Solar cell fabrication for PTB7-Th:PC₇₁BM. PTB7-Th:PC₇₁BM PSCs were fabricated on the same ITO glass substrates with PTB7:PC₇₁BM PSCs. A layer of

ZnO for electron transfer layer (ETL) was spun onto the substrates at 6,000 r.p.m. for 30 s, and the substrates were then annealed at 200 °C for 20 min (ref. 25). Two layers of SS-PTB7:PC₇₁BM films were transferred sequentially onto the substrates. The SC-PTB7: PC₇₁BM films were spun at 2,000 r.p.m. for 30 s. There was no additional drying process or annealing. Subsequently, MoO₃ (9 nm) and Ag (150 nm) were deposited through a shadow mask by thermal evaporation onto the devices⁵².

Measurement of polymer solar cells. The current density-voltage (J - V) characteristics of the cells were measured from 1.0 to -0.2 V using a solar simulator (K201 LAB55, McScience) under irradiance of 100 mW cm⁻² from a 150 W Xe short-arc lamp filtered by an air mass 1.5 G filter. Light intensity was calibrated with a Si reference cell (McScience, K801S-K302). The voltage scan rate was 100 mV s⁻¹ and no device preconditioning was applied before starting the measurement, such as light soaking. A 6.25 mm² aperture mask was attached to the device to define the illuminated area clearly. The quantum efficiency (QE) spectra of the solar cells were obtained using a spectral (K3100 IQX, McScience Inc.)

measurement system. The integrated response (J_{SC}) under the standard reference spectrum was compared with the J_{SC} value measured under the simulator, and they showed an $\sim 2\%$ J_{SC} difference.

Film analysis. The surface morphology of the BHJ films was observed using atomic force microscopy in tapping mode under ambient conditions (AFM, Nanoman, Veeco) using a field emission scanning electron microscope (FE-SEM, FEI Sirion) and a field emission transmission electron microscope (FE-TEM, FEI Tecnai G2 f30 S-Twin, 300 KeV). Photoluminescence quenching was evaluated for the SC- and SS-PTB7:PC₇₁BM films without metal electrodes using a Horiba Jobin Yvon NanoLog spectrophotometer. We performed the measurement with at least three samples to reduce the sample-to-sample variation and measurement error. The XPS and ultraviolet photoelectron spectroscopy spectra were recorded with a Sigma Probe (Thermo VG Scientific) instrument, using a micro-focused monochromatic Al X-ray source with a beam energy of 1468.74 eV and a takeoff angle of 45°. Raman spectra were obtained using a micro-Raman system (LabRam HR spectrometer, JY Horiba). A 514 nm solid-state laser and a 633 nm He-Ne laser were used as the excitation light sources and were kept to less than 0.5 mW to prevent photo-degradation of the BHJ films. The laser was focused to a beam diameter of $\sim 5 \mu\text{m}$ on the sample using a $\times 50$ objective microscope lens. The Raman spectra were background corrected and obtained by averaging the spectra obtained from three different regions of each sample. The spectra from the different regions were almost the same, demonstrating the reliability of the results. We also confirmed the outcomes by measuring three samples prepared at different times. The spectral resolutions are within 0.4 and 0.2 cm^{-1} for the 514 and 633 nm excitations, respectively. GIWAXS measurement was performed using X-rays with a wavelength of $\lambda = 1.54 \text{ \AA}$ at the 8C1 beam line of the Pohang Accelerator Laboratory. The 3D profiles for oxygen distribution in the PTB7 films were obtained using a TOF-SIMS 5 system (ION-TOF GmbH, Münster, Germany) equipped with a 30 KeV liquid metal ion gun and a time-of-flight mass spectrometer. To sputter the PTB7 film, a 1 KeV beam of Cs^+ ions was used to remove material by sputtering a $300 \mu\text{m} \times 300 \mu\text{m}$ region, whereas a 30 KeV beam of Bi^{3+} ions was employed to analyse the composition distribution by acquiring the mass-to-charge ratios (m/q) of the negatively charged secondary ions, for example, C^- ($m/q = 12$), S^- ($m/q = 32$), $^{16}\text{O}^-$ ($m/q = 16$), $^{18}\text{O}^-$ ($m/q = 16$) from the analysis area ($100 \mu\text{m} \times 100 \mu\text{m}$) centered at the sputtered region. Data acquisition and subsequent data processing and analysis were performed using SurfaceLab 6 software (ION-TOF GmbH).

Data availability. The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information.

References

- Yang, X. N. *et al.* Nanoscale morphology of high-performance polymer solar cells. *Nano Lett.* **5**, 579–583 (2005).
- Bredas, J. L., Norton, J. E., Cornil, J. & Coropceanu, V. Molecular understanding of organic solar cells: the challenges. *Acc. Chem. Res.* **42**, 1691–1699 (2009).
- Seo, J.-W., Lee, S.-H. & Lee, J.-Y. Enhancing quantum efficiency of parallel-like bulk heterojunction solar cells. *Appl. Phys. Lett.* **103**, 123301 (2013).
- Kim, Y. *et al.* A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene: fullerene solar cells. *Nat. Mater.* **5**, 197–203 (2006).
- Vithanage, D. A. *et al.* Visualizing charge separation in bulk heterojunction organic solar cells. *Nat. Comm.* **4**, 2334 (2013).
- Dibb, G. F. A. *et al.* Influence of doping on charge carrier collection in normal and inverted geometry polymer: fullerene solar cells. *Sci. Rep.* **3**, 3335 (2013).
- Jeong, S. *et al.* Nanoimprinting-induced nanomorphological transition in polymer solar cells: enhanced electrical and optical performance. *ACS Nano* **9**, 2773–2782 (2015).
- Lee, S.-H., Seo, J.-W. & Lee, J.-Y. Stable inverted small molecular organic solar cells using a p-doped optical spacer. *Nanoscale* **7**, 157–165 (2015).
- Campoy-Quiles, M. *et al.* Morphology evolution via self-organization and lateral and vertical diffusion in polymer: fullerene solar cell blends. *Nat. Mater.* **7**, 158–164 (2008).
- Li, G. *et al.* 'Solvent annealing' effect in polymer solar cells based on poly(3-hexylthiophene) and methanofullerenes. *Adv. Funct. Mater.* **17**, 1636–1644 (2007).
- Peet, J. *et al.* Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols. *Nat. Mater.* **6**, 497–500 (2007).
- Hammond, M. R. *et al.* Molecular order in high-efficiency polymer/fullerene Bulk heterojunction solar cells. *Acs Nano* **5**, 8248–8257 (2011).
- Norrman, K., Madsen, M. V., Gevorgyan, S. A. & Krebs, F. C. Degradation patterns in water and oxygen of an inverted polymer solar cell. *J. Am. Chem. Soc.* **132**, 16883–16892 (2010).
- Alem, S. *et al.* Degradation mechanism of benzodithiophene-based conjugated polymers when exposed to light in air. *ACS Appl. Mater. Interf.* **4**, 2993–2998 (2012).
- Lu, L. & Yu, L. Understanding low bandgap polymer PTB7 and optimizing polymer solar cells based on it. *Adv. Mater.* **26**, 4413–4430 (2014).
- Li, N. & Brabec, C. J. Air-processed polymer tandem solar cells with power conversion efficiency exceeding 10%. *Energy Environ. Sci.* **8**, 2902–2909 (2015).
- Poulard, C. & Damman, P. Control of spreading and drying of a polymer solution from Marangoni flows. *Europhys. Lett.* **80**, 64001 (2007).
- Morita, T. *et al.* Enhancement of transport characteristics in poly(3-hexylthiophene) films deposited with floating film transfer method. *Appl. Phys. Express* **2**, 111502 (2009).
- Harkins, W. D. *The Physical Chemistry of Surface Films* (Reinhold, 1952).
- Dussaud, A. D. & Troian, S. M. Dynamics of spontaneous spreading with evaporation on a deep fluid layer. *Phys. Fluids* **10**, 23–38 (1998).
- Demond, A. H. & Lindner, A. S. Estimation of interfacial-tension between organic liquids and water. *Environ. Sci. Technol.* **27**, 2318–2331 (1993).
- Lyman, W. J., Reehl, W. F. & Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds* 2nd edn 960 (American Chemical Society, 1990).
- Krebs, F. C. Fabrication and processing of polymer solar cells: A review of printing and coating techniques. *Sol. Energy Mater. Sol. Cells* **93**, 394–412 (2009).
- Moon, J. S., Lee, J. K., Cho, S. N., Byun, J. Y. & Heeger, A. J. 'Columnlike' structure of the cross-sectional morphology of bulk heterojunction materials. *Nano Lett.* **9**, 230–234 (2009).
- Liang, Y. Y. *et al.* For the bright future-bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%. *Adv. Mater.* **22**, E135–E138 (2010).
- Liu, F. *et al.* Understanding the morphology of PTB7: PCBM blends in organic photovoltaics. *Adv. Energy Mater.* **4**, 1301377 (2014).
- Schmidt, K. *et al.* A Mechanistic understanding of processing additive-induced efficiency enhancement in bulk heterojunction organic solar cells. *Adv. Mater.* **26**, 300–305 (2014).
- Abdelsamie, M., Zhao, K., Niazi, M. R., Chou, K. W. & Amassian, A. *In situ* UV-visible absorption during spin-coating of organic semiconductors: a new probe for organic electronics and. *J. Mater. Chem. C* **2**, 3373–3381 (2014).
- Ma, W., Zhang, J. & Wang, X. Effect of initial polymer concentration on the crystallization of poly(vinylidene fluoride)/poly(methyl methacrylate) blend from solution casting. *J. Macromol. Sci. Phys* **47**, 139–149 (2008).
- Young, T. H., Huang, J. H. & Chuang, W. Y. Effect of evaporation temperature on the formation of particulate membranes from crystalline polymers by dry-cast process. *Eur. Polym. J.* **38**, 63–72 (2002).
- Deegan, R. D. Pattern formation in drying drops. *Phys. Rev. E* **61**, 475–485 (2000).
- Peet, J., Cho, N. S., Lee, S. K. & Bazan, G. C. Transition from solution to the solid state in polymer solar cells cast from mixed solvents. *Macromolecules* **41**, 8655–8659 (2008).
- de Gans, B. J. & Schubert, U. S. Inkjet printing of well-defined polymer dots and arrays. *Langmuir* **20**, 7789–7793 (2004).
- van Franeker, J. J., Turbiez, M., Li, W., Wienk, M. M. & Janssen, R. A. J. A real-time study of the benefits of co-solvents in polymer solar cell processing. *Nat. Commun.* **6**, 6229 (2015).
- Heeger, A. J. 25th Anniversary article: bulk heterojunction solar cells: understanding the mechanism of operation. *Adv. Mater.* **26**, 10–28 (2014).
- Gao, Y. & Grey, J. K. Resonance chemical imaging of polythiophene/fullerene photovoltaic thin films: mapping morphology-dependent aggregated and unaggregated C=C species. *J. Am. Chem. Soc.* **131**, 9654–9662 (2009).
- Tsoi, W. C. *et al.* The Nature of in-plane skeleton raman modes of P3HT and their correlation to the degree of molecular order in P3HT:PCBM blend thin films. *J. Am. Chem. Soc.* **133**, 9834–9843 (2011).
- Yin, J., Zhou, Y., Lei, T. & Pei, J. A butterfly-shaped amphiphilic molecule: solution-transferable and free-standing bilayer films for organic transistors. *Angew. Chem. Int. Ed.* **50**, 6320–6323 (2011).
- Park, J. Y. & Advincula, R. C. Nanostructuring polymers, colloids, and nanomaterials at the air-water interface through Langmuir and Langmuir-Blodgett techniques. *Soft Matter* **7**, 9829–9843 (2011).
- Osaka, I., Saito, M., Koganezawa, T. & Takimiya, K. Thiophene-thiazolothiazole copolymers: significant impact of side chain composition on backbone orientation and solar cell performances. *Adv. Mater.* **26**, 331–338 (2014).
- Ramamurthy, V. & Venkatesan, K. Photochemical reactions of organic crystals. *Chem. Rev.* **87**, 433–481 (1987).
- Brown, W. H. & Poon, T. *Introduction to Organic Chemistry* 5th edn 1–792 (John Wiley & Sons, 2012).
- Mateker, W. R. *et al.* Molecular packing and arrangement govern the photo-oxidative stability of organic photovoltaic materials. *Chem. Mat* **27**, 6455–6453 (2015).
- Zhou, H. *et al.* High-efficiency polymer solar cells enhanced by solvent treatment. *Adv. Mater.* **25**, 1646–1652 (2013).

45. Kim, J. *et al.* Efficient charge extraction in thick bulk heterojunction solar cells through infiltrated diffusion doping. *Adv. Energy Mater.* **4**, 1301502 (2014).
46. Eckenfelder, W. W., Bowers, A. R. & Roth, J. A. *Chemical Oxidation: Technologies for the Nineties*. 1–334 (Technomic, 1997).
47. Shoaee, S. & Durrant, J. R. Oxygen diffusion dynamics in organic semiconductor films. *J. Mater. Chem. C* **3**, 10079–10084 (2015).
48. Jorgensen, M., Norrman, K. & Krebs, F. C. Stability/degradation of polymer solar cells. *Sol. Energy Mater. Sol. Cells* **92**, 686–714 (2008).
49. Seemann, A., Egelhaaf, H.-J., Brabec, C. J. & Hauch, J. A. Influence of oxygen on semitransparent organic solar cells with gas permeable electrodes. *Org. Electron.* **10**, 1424–1428 (2009).
50. Choi, H., Kim, H.-B., Ko, S.-J., Kim, J. Y. & Heeger, A. J. An organic surface modifier to produce a high work function transparent electrode for high performance polymer solar cells. *Adv. Mater.* **27**, 892–896 (2015).
51. Chu, T.-Y. *et al.* Morphology control in polycarbazole based bulk heterojunction solar cells and its impact on device performance. *Appl. Phys. Lett.* **98**, 253301 (2011).
52. Chang, Y.-M. & Leu, C.-Y. Conjugated polyelectrolyte and zinc oxide stacked structure as an interlayer in highly efficient and stable organic photovoltaic cells. *J. Mater. Chem. A* **1**, 6446–6451 (2013).

Acknowledgements

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean Government (MSIP; no. NRF-2015R1A2A2A01006689 and no. NRF-2015M1A2A2057509). We gratefully acknowledge support from the EEWS Research Project of the office of the KAIST EEWS Initiative (EEWS-2016-N11160015). We thank Changyeon Lee for GIWAXS measurement.

Author contributions

J.N, S.J. and J.L. conceived and designed the experiments and prepared the manuscript. J.N. and S.J. fabricated the spontaneous spreading films and solar cells, and performed PCE and QE measurements. S.J. analysed organic films using SEM, TEM, ToF-SIMS and XPS. J.N. designed the R2R machine and performed the large-scale transfers of the organic thin films. All authors discussed the results and commented on the manuscript.

Additional Information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Noh, J. *et al.* Ultrafast formation of air-processable and high-quality polymer films on an aqueous substrate. *Nat. Commun.* **7**:12374 doi: 10.1038/ncomms12374 (2016).

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