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Solution modification of PEDOT:PSS inks for ultrasonic spray coating

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Highlights

- Ultrasonic spray coating was used to explore the deposition of PEDOT:PSS films from a series of different ink formulations.
- It was demonstrated that the addition of a ternary solvent blend and high molecular weight polyethylene glycol additive to PEDOT:PSS improves its solution processability.
- We find that spray-cast PEDOT:PSS films incorporating a polyethylene glycol have similar surface roughness to spin coated films, but have superior conductivity and enhanced air stability.

Abstract

PEDOT:PSS is a high-conductivity hole-transporting polymer that is widely used in polymer and perovskite photovoltaic devices, as well as in a host of other antistatic applications. Here we show that modification of PEDOT:PSS inks using ternary solvents and by the addition of small amounts of a high molecular weight polymer make it possible to deposit highly uniform thin films via ultrasonic spray coating. Such films can be deposited using a single pass in the wet phase without the use of surfactants; a process that greatly simplifies their deposition. Using this technique we create films having thickness and roughness comparable to that of spin coated films, whilst properties such as the conductivity and stability can be improved.

Key Words Ultrasonic Spray Coating; PEDOT:PSS; Printable Electronics; Photovoltaic-materials;

1. Introduction

The properties of the polymer PEDOT:PSS have made it an extremely versatile material with wide reaching applications such as an anti-static coating, a transparent conductor, a thermoelectric material and a work-function modifier.[1-3] There are several advantages that PEDOT:PSS possesses over alternative conductive materials, including low material cost, high optical-transparency, high electrical-conductivity, low thermal-conductivity and ease of processing.[1,2,4] PEDOT:PSS is also employed as a transparent electrode and a work function modifier for several types of printed-electronic device including photovoltaics, light emitting diodes and thin-film transistors.[1,2,4]

To process PEDOT:PSS it is most often solubilised in water, however this can result in surface wetting problems and the formation of non-uniform films due to water's high surface tension. To counter this problem, solutions are often mixed with surfactants, however such additives can compromise the electronic functionality of the film. Using such an approach, thin films of PEDOT:PSS have been deposited via scalable techniques such as blade coating,[5,6,7] spray coating,[8-12] or gravure printing.[13,14] Unfortunately the use of techniques such as multi-pass deposition or the incorporation of surfactants can result in a reduction in performance of the PEDOT:PSS film deposited, such as reduced conductivity, low surface uniformity, the creation of thicker films (and thus reduced optical transparency), or spatially non-uniform work function.[15-17] For many applications in printable electronic devices, control over optical and electronic properties is critical in order to optimise device performance and efficiency.

To optimise the properties of PEDOT:PSS for device applications and to maintain a wide processing window, it is desirable to develop improved processing routes. Here, we explore the deposition of PEDOT:PSS by spray-casting. The use of spray-casting in electronics fabrication is of growing importance, as it combines low wastage, high precision, rapid-deposition and high-volume scalability. We show that improved processability of ternary blends of PEDOT:PSS, incorporating isopropyl alcohol and ethylene glycol, can be achieved by the addition of polyethylene glycol. Here, the use of EG creates films having high conductivity without the use of any post deposition treatment to aid film formation. [19.20]

By adding a small quantity (~0.015 mg ml^{-1}) of an extremely high molecular weight polymer (polyethylene glycol) to the PEDOT:PSS ink, it is possible to increase solution viscosity and further improve film forming qualities. We show that such solutions can be used to deposit thin films of PEDOT:PSS via ultrasonic spray deposition using a single pass without the need for any surface modification. The PEDOT:PSS films deposited combine high surface uniformity, high optical transmission and improved conductivities over spin coated films. Our work adds to the growing capability to deposit functional electronic materials over large areas for applications in thin film electronics and photovoltaics.

2. Experimental methods

PEDOT:PSS (Clevios Al 4083 Ltd) was purchased from Ossila Ltd, and had a solid content of approximately 1.3% to 1.7% by weight in water and a PEDOT:PSS ratio of 1:6 by weight. Isopropanol (IPA) (99.5%) and ethylene glycol (EG) (99%) were purchased from Sigma Aldrich. Polyethylene glycol (PEG) having a molecular weight of 7 MDa was purchased from Sigma Aldrich.

Glass substrates were purchased from Ossila Ltd having dimensions of 20mm x 15mm, each substrate was cleaned sequentially in a 3% Hellmanex III solution, de-ionized water, and isopropyl alcohol. The cleaning solutions were heated to 50°C and placed within an ultrasonic bath for 10 minutes each. After being cleaned in isopropyl alcohol the substrates were dried under a nitrogen stream before deposition of the PEDOT:PSS solutions.

PEDOT:PSS films of 40 nm thickness were deposited either by spin coating (at 4,000 RPM) or by ultrasonic spray casting. Spray casting was conducted using a Prism 300 ultrasonic spray coater supplied by Ultrasonic Systems Inc. This spray coater is a so-called 'nozzle-less system' that is based on a spray tip that vibrates at ultrasonic frequency onto which the liquid of interest is fed by a syringe driver. The oscillations of the spray-head break the liquid into a very fine mist that is then directed to a surface via a focussed jet of compressed gas. This technique has been used by us [19-22] and others [23-26] to deposit high-quality, uniform polymeric films for optoelectronic devices without the use of surfactants. Indeed, we have previously deposited PEDOT:PSS by spray coating [19,20], with the film forming properties of the PEDOT:PSS solution being modified by the addition of IPA and EG. Such a process however required the use of a time-consuming multistage anneal routine, with the films created often characterized by non-uniformities towards the edge of the substrate. Here however we modify a standard PEDOT:PSS formulation (Clevios Al 4083 Ltd) creating a blend of PEDOT:PSS : Isopropanol : Ethylene Glycol at a ratio of 2 : 8 : 1. Critically, we also add 0.015 mg ml^{-1} PEG that as we show below, controls thin-film viscosity and helps to improve film uniformity. This allows us to increase the processing time window significantly and to improve film uniformity across the substrate (characteristics important in any practical manufacture process). To deposit films by spray-casting, the solution was sprayed onto substrates held at 45°C from a height of 40 mm, using a pass speed of 40 mm s^{-1}, and a gas overpressure of 50 mbar. Once the IPA had evaporated (after ~30 s) the substrate was transferred onto a second hotplate held at 180°C for approximately 10 seconds to remove any remaining solvent.

To characterise thin films, we performed **c**ontact angle measurements using a Theta optical tensiometer, with a droplet of solution deposited onto the surface of a cleaned glass substrate. A sequence of images were recorded every 0.02 seconds for a total of 5 seconds, with contact angles taken by fitting a curve across the surface of the droplet. The angle of the curve to the surface was recorded from both sides of the droplet, with values plotted being an average of the two measurements. Scanning force microscopy scans were taken using a Veeco Dimension 3100 across an area of 10µm x 10µm using a tip from Budget Sensors (300G-Al). Data analysis was performed using Gwyddion software. Sheet resistance measurements were recorded using an Ossila 4-point probe measuring station attached to a Keithley 2400 source measure unit.

To quantify the solution evaporation rates, viscosities, and surface tensions of the various inks, we used Hansen solubility parameters in practice (HSPIP) software, assuming that the solid content of the PEDOT:PSS did not change solution viscosity or surface tension. We used values of surface tension and viscosity for undiluted Clevios Al 4083 of 78 Dynes and 5 cp respectively (manufacturer's data). All calculations assumed a solution deposition temperature of 45°C (determined from the temperature of the hot plate during deposition), a surface area of evaporation of $3x10^{-4}$ m^{2}, and an air flow rate across the surface of 15 m s^{-1} (determined from the air extraction rate of the spray deposition system). HSPiP software calculates a relative evaporation rate of each solvent relative to both n-butylacetate and diethylether (these are the most popular industrial reference solvents in the USA and Europe respectively), this is done by taking the vapour pressure curves for each solvent calculated using the August Equation and the Antoine coefficients for each solvent. The time it takes to evaporate a given amount of the reference solvent under specific test conditions can be calculated; which include the temperature of the solvent, the air flow across the surface, and the surface area of the evaporating surface. From this and the relative evaporation rates of the solvents the evaporation rate as a function of volume, and or mass can be determined.

3 Results and Discussion

3.1 Solution Formulation

To deposit a functional semiconductor by spray-casting, it is preferable to deposit it as a single wet layer that is then allowed to dry. Films that are formed from either ‘dry’ sprays or from sprays that very rapidly dry upon hitting a surface can result in the formation of rough surfaces or films characterised by regions of preferential wetting that contribute towards poor device performance.[27-29] For the formation of uniform layers from wet films, the solution deposited must wet the surface, forming a continuous film, with such wetting maintained throughout the film drying phase. To spray cast PEDOT:PSS using an ultra-sonic spray-coater, it is necessary to optimise both the ink formulation and the spray coating parameters. We have found that to create films by ultrasonic spray coating having comparable thickness to those created by spin-coating, it is necessary to use inks in which the weight percentage of solid material within the solution is significantly reduced. This requires the dilution of the ink solution either with the host solvent or with other miscible solvents. We note that commercial formulations of PEDOT:PSS are often solubilised in deionised (DI) water, however the addition of further DI to PEDOT:PSS can lead to poor spreading across a surface as a result of the high surface tension of water. This problem can be overcome by diluting PEDOT:PSS in IPA as it has a lower surface tension than DI, resulting in improved initial spreading of the solution across the surface. This approach permits PEDOT:PSS to be diluted to a point where is can be successfully deposited by spray casting.

The effect of the addition of different solvents to PEDOT:PSS is illustrated in **Figure 1,** where we show the evolution in film contact angle over time. (To avoid confusion in the presentation of the various formulation ratios, we henceforth refer to the Clevios PEDOT:PSS formulation as ‘PEDOT’). Here PEDOT was diluted as follows; PEDOT:DI (2:8), PEDOT:IPA (2:8), PEDOT:IPA:EG (2:8:1) and PEDOT:IPA:EG (2:8:1) + 0.015 mg ml^{-1} PEG. The first three blends have previously been reported within the literature as being suitable for large area deposition of PEDOT:PSS thin films with varying degrees of success.[11,12,19,25,27] It can be seen that all formulations have similar initial values of contact angle (between 20 and 40 degrees), however the contact angle for the formulation that includes a small amount of PEG drops to ~ 2° (the limit of measurement for the instrument) within 2 seconds. This indicates that PEG significantly improves the initial wetting of solution onto the surface of the substrate compared to all other ink formulations explored. Our measurements indicate therefore that all other solution formulations except those containing PEG will not fully wet the substrate however – as we show below – the eventual uniformity of the film is also strongly dependent on the drying dynamics of the solutions.

Interestingly whilst the amount of PEG added to the solution is very small, it has (as we show below) a profound effect on the film forming effect of the PEDOT:PSS through changes in the film viscosity. This is because even when dissolved into a solution at 0.015 mg ml^{-1} (equivalent to a concentration by mass of polymer in solution of 0.0015%), the length of the polymer molecules is such that they are already overlapped. Here, we can estimate the concentration at which the polymer molecules overlap from their radius of gyration (R_g), that is the volume that is swept out by the coil in solution. For a Gaussian coil this is most simply given by ‾, where N is the degree of polymerisation and b is the length per monomer unit. The overlap concentration, c*, is defined as the concentration at which the coils first interact and is given by , where M is the molar mass of the polymer and N_A is Avogadro’s number.[30] Using the molecular weight of the PEG of 10^7 g mol^{-1} and a statistical segment length of b = 0.637 nm we obtain an overlap concentration of 6.5 x 10^{-5} mg ml^{-1}. This is three orders of magnitude smaller than the solutions used here and we expect that the polymer molecules will start to interact through entanglements at a concentration of 0.00001%. Because of such intermolecular interactions, the viscosity of the solution will be very sensitive to concentration, with - for example - a doubling of the polymer concentration easily causing a tenfold increase in the solution viscosity.

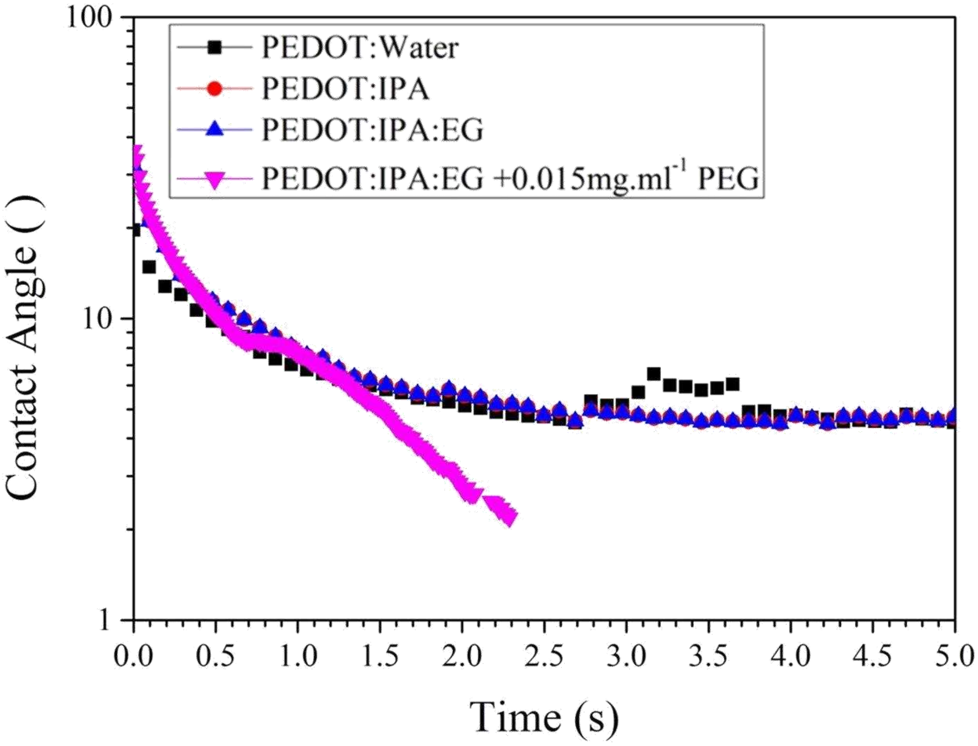

Figure. 1 The evolution of contact angle over time for PEDOT:DI (2:8), PEDOT:IPA (2:8), PEDOT:IPA:EG (2:8:1), and PEDOT:IPA:EG + PEG (2:8:1 + 0.015 mg ml^{-1}).

We now consider the formation of thin PEDOT:PSS films from the various inks. In **Figure 2(a), (b) (c)** and **(d)** we show images of spray-cast PEDOT:PSS films cast from PEDOT:DI (2:8), PEDOT:IPA (2:8), PEDOT:IPA:EG (2:8:1) and PEDOT:IPA:EG (2:8:1) + 0.015 mg ml^{-1} PEG respectively. We also show surface profile measurements made from the PEDOT:DI, PEDOT:IPA, PEDOT:IPA:EG, PEDOT:IPA:EG + PEG 0.015mg.ml^{-1} cast films recorded using a Dektak surface profiler in parts (e), (f) and (g) respectively. It can be seen that films cast from the DI water (part (a) and (e)) undergo significant pooling during the drying phase as a result of solution dewetting. For films diluted using IPA (part (b) and (f)), there is a rapid evaporation of the solvent that creates a series of droplets across the surface. These droplets then dry to create spots of PEDOT dispersed across the surface. Here, the effect of the IPA is to reduce the surface energy of the solution to improve spreading, however as IPA has a lower boiling point than DI, it evaporates leaving a solution composed of PEDOT dispersed in DI. This results in the solution undergoing spinodal decomposition, creating a series of localised regions that undergo dewetting. The origin of this decomposition is unknown but may be due to surface defects or due to local composition differences within the wet film.

Upon the addition of EG to the IPA based solution (see part (c)), we find that the PEDOT film is deposited continuously across the entire substrate, although film quality is reduced towards the edge of the substrate due to edge effects (limited to a distance of <1mm from the edge). 3D profiles of the surface are shown around a scratch made in the surface (see part (g)). Here it can be seen that the thickness of the film is uniform across a central (2 x 2) mm area indicating high uniformity. The improved film quality upon the addition of EG most likely results from an increase in solution viscosity following the evaporation of the IPA. Increases in viscosity reduce the shear rate of a fluid resulting in a reduced mobility of the wet film and supressed pooling and dewetting.[27, 31] However the slow subsequent evaporation of the EG from the film (following the 'fast' initial evaporation of the IPA) still offers an opportunity for the film to undergo partial dewetting, resulting in reduced film quality at the edge of the substrate. To optimise film quality using this solvent mixture, we have found that it is critical to rapidly evaporate any remaining EG present within the film using a second high temperature annealing stage.[19, 20]

In parts (d) and (h) we show a film in which a small concentration of PEG has been added to a solution containing IPA and EG. The addition of the very high molecular weight PEG is found to increase the viscosity of the deposited solution resulting from a physical entanglement between the polymer chains. This modification in rheological properties reduces the shear rate of the wet film and thus reduces its mobility during dewetting. We find that with the addition of PEG, the edge effects are reduced in comparison to films cast from

IPA and EG. The increase in solution viscosity is known to be proportional to the concentration of the polymer used and also its molecular weight. [32] Usefully, this technique permits solution viscosity to be increased through the addition of a very small amount of PEG; an approach that minimises any effect of the PEG on the electrical or optical properties of the PEDOT:PSS.

We have explored the effect of varying the PEG concentration as shown in in **Figure S1.** Here, we find that films cast from PEG at a concentration lower than 0.015 mg ml^{-1} exhibit edge effects similar to the those cast from IPA and EG. We also find when the PEG concentration exceeds 0.03 mg ml^{-1}, the solution can no longer be cast by ultrasonic spray deposition as its viscosity and shear resistance become too high and it can no longer be broken into a spray by the vibrating tip. **Figure S2** shows a video of this change in spraying dynamics and is consistent with the viscosity of the solution increasing by an order of magnitude in this concentration range.

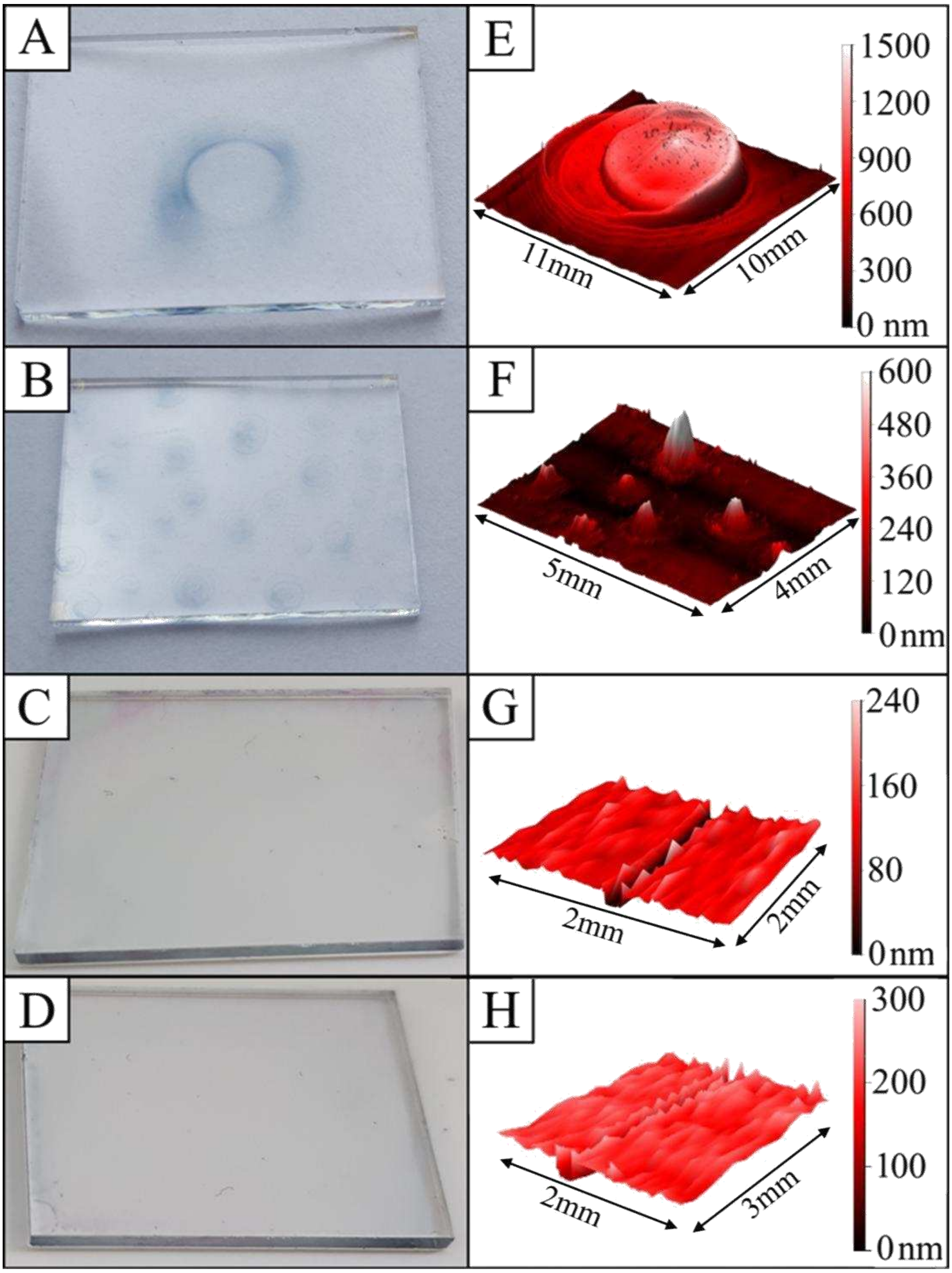

Figure. 2 (a-d) show images of films sprayed using DI water, IPA, IPA:EG, and IPA:EG + PEG 0.015 mg ml^{-1} all substrates are 20mmx 15mm in size. Parts (e-h) show 3d surface profilometry of regions of interest for films cast from DI water, IPA, IPA:EG, and IPA:EG + PEG 0.015mg.ml^{-1}. Note that the scratches were deliberately made into the films shown in part (g and h) to help illustrate the uniformity of the surface.

We can obtain further insight into the effect of the solution modifiers by calculating the relative evaporation rates of the different components within the solution as a function of time. This in turn allows us to determine a time-dependent measurement of relative solution composition, surface tension and viscosity. This is shown in **Figures 3(a)** and **(b)**, where we plot volumetric concentration as a percentage for different solvents, solution viscosity and surface tension of a Water:IPA and Water:IPA:EG solution respectively as a function of time. We find that in the Water:IPA solution (see Fig 3(a)), there is a rapid evaporation of IPA during the drying phase that results in a small decrease in the viscosity (from 1.42 cP to 0.75 cP) and a large increase in surface tension (from 17.4 dyne cm^{-1} to 72 dyne cm^{-1}). This reduction in solution viscosity results in increased lateral flow of the wet film across the substrate, however the increased surface tension leads to poorer wetting of the solution; a result consistent with the dewetting observed of films deposited from Water:IPA. However, on addition of EG to the solution, we find that the viscosity of the solvent system increases during the drying phase of the IPA (from 2.82 cP to 6.90 cP); an effect that results from the significantly lower evaporation rate of EG which has a higher viscosity and a lower surface tension than water. It is this increase in viscosity and reduction in surface tension that reduces the flow rate of the wet film across the surface during casting and suppresses the tendency of the solution to de-wet. In Figure 3(c), we plot the calculated concentration of PEG in a Water:IPA:EG solution as a function of time after casting. Here, it can be seen that during the evaporation of IPA, the concentration of PEG increases from 0.015 mg ml^{-1} to 0.063 mg ml^{-1}; an effect likely to lead to an exponential increase in solution viscosity. [32] During this initial, rapid IPA drying phase, this increase in solution viscosity will result in a significantly reduced lateral flow rate within the wet film; a process that we speculate results in the observed improvement in film uniformity. It should be noted that the presence of both

PEDOT:PSS and PEG within the solutions can lead to variations within the evaporation rates of solvents due to ion-dipole interactions.

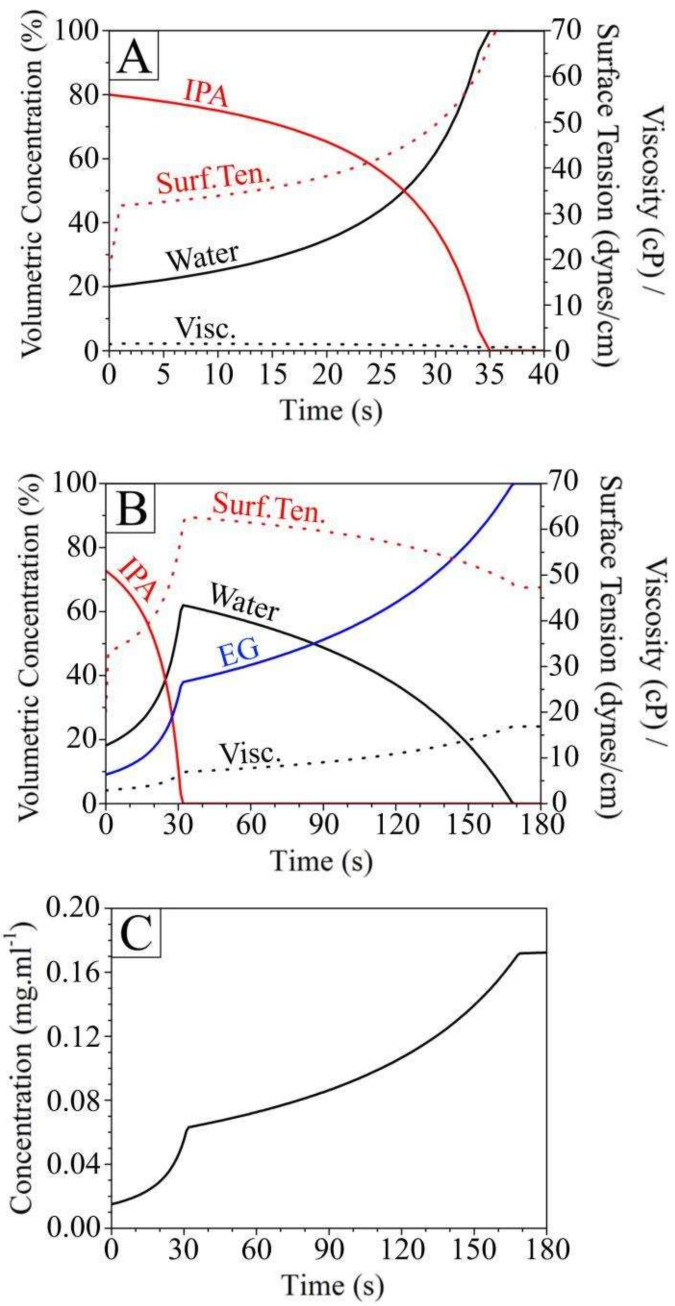

Figure 3 (a) shows the calculated volumetric concentration (%) of water (DI) and IPA in a DI:IPA blend as a function of time after casting (— DI, —IPA). In the same figure we also plot the calculated viscosity (- - -) and surface tension (- - -) of the solution. Part **(b)** also shows concentration, viscosity and surface tension of a DI:IPA:EG solution (— DI, —IPA,

— EG). Part **(c)** plots the concentration of PEG as a function of time following casting of a DI:IPA:EG solution.

3.2 Thin Film Properties

We have shown that films spray-cast from a solvent composed of a mixture of IPA:EG and PEG apparently are characterised by promising uniformity over length scales of 100s of microns to a few mm. However, to fully understand the properties of such films it is important to characterise film morphology over length-scales commensurate with their thickness. To do this we have used scanning force microscopy (SFM) to explore film roughness on films prepared by spin-casting and spray-casting as shown in **Figure 4.** Here, we show (10 x 10) µm scans of (a) spin coated PEDOT:PSS (cast from a Clevios PEDOT:PSS solution), and (b) a spray coated PEDOT:PSS film deposited from a PEDOT:IPA:EG (2:8:1) + 0.015 mg ml^{-1} PEG solution. It can be seen that there is some variation in the roughness of the two films, however they are the same order of magnitude. Specifically, we determine RMS values for the spin coated and spray-coated films to be 1.2 nm and 3.6 nm respectively.

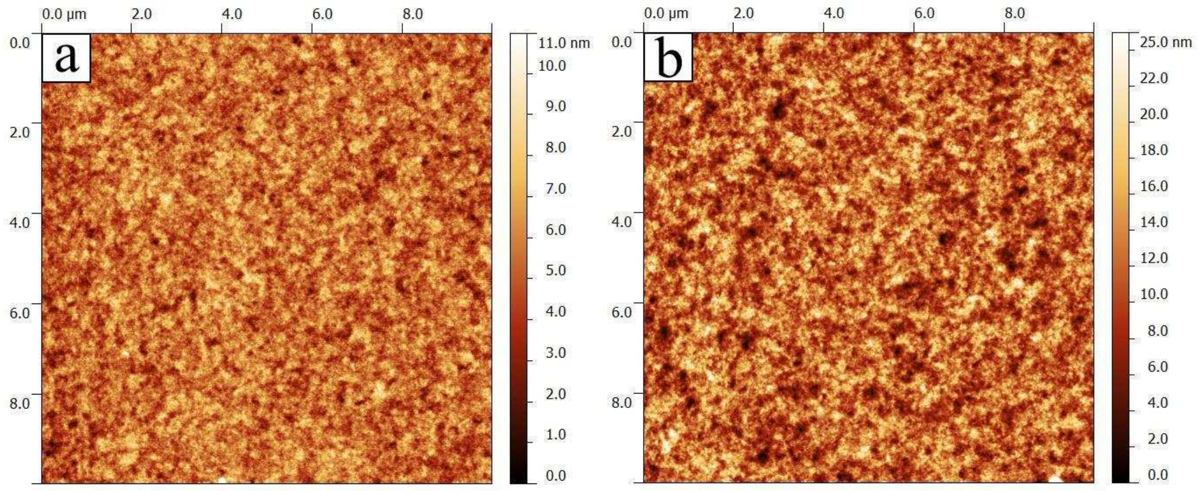

Figure. 4 Scanning force microscopy images of PEDOT:PSS films deposited by (a) spin coating, and (b) spray-coating from a PEDOT:IPA:EG + 0.015 mg ml^{-1} PEG solution.

It is important that the electronic properties of the PEDOT:PSS are not compromised by the techniques or materials used in its deposition. To explore this further, we have measured the sheet resistance of PEDOT:PSS films deposited using both spin-coating from an as purchased Clevios PEDOT:PSS solution and spray-coated PEDOT:PSS from a mixture of PEDOT:IPA:EG (2:8:1). Here we have explored spray-coating both with and without the addition of 0.015 mg ml^{-1} PEG. **Table 1** details sheet resistance values immediately after deposition and after films have been left in air for 14 days. The measurements presented are average values recorded at 5 points across the film surface. We find that the initial sheet resistance of films deposited by spray deposition is significantly lower than those deposited via spin coating; an effect resulting from the presence of the EG which facilitates the close intermixing of the PEDOT and PSS components. In contrast, films spin-cast from a water based solution have a lower conductivity as they are composed of PEDOT rich regions interspersed within the highly resistive PSS matrix.[33]

For the spray-cast films, we find that the addition of PEG leads to a slight increase of film resistance (by ~ 100 $\Omega\ \square^{-1}$). After 14 days in air, the sheet resistance of all films increase, with this increase being particularly pronounced in films spray-cast from an IPA:EG solution. This increase however appears to be significantly supressed in films that contain PEG. Previous work suggests that changes in PEDOT:PSS films left in air result from the absorption of moisture which acts as a plasticiser and drives morphological change resulting in the formation of a PSS-rich resistive layer at the film surface. [33] The origin of the reduced initial conductivity of films containing PEG is at present unclear. We speculate that it may be due to the absorption of water, which causes a change in nanomorphology that reduces the density and interconnectivity of PEDOT percolation pathways within the film, [32] however more work is required to confirm this hypothesis. It is clear that the high molecular weight PEG acts as a binder within the film, reducing the physical mobility of both the PEDOT and PSS molecules within the film. This apparently helps to stabilise film morphology even when exposed to the atmosphere for a prolonged period.

	Sheet resistance (0 days) [Ω square^{-1}]	Sheet resistance (14 days) [Ω square^{-1}]	Percentage Change
Spin Coated	18.7×10^6	23.0×10^6	+23%
Spray Coated (IPA:EG)	672	47.3×10^3	+6939%
Spray Coated (IPA:EG + PEG)	784	2.10×10^3	+168%

Table. 1 Sheet resistance values for 30 nm thick films of PEDOT:PSS deposited via spin and spray deposition.

4. Conclusions

We have explored the formulation of PEDOT:PSS solutions that are typical of those used in thin film photovoltaic and light-emitting diode devices. We show that by using a volatile primary solvent combined with secondary solvents that have high viscosity and lower volatility, it is possible to create an ink that can be spray-cast, forming a highly uniform film. The processing properties of the film on spray-casting can be further improved through the addition of a small amount of the high molecular weight polymer PEG. We find that films that have been spray-cast have a similar surface roughness to those deposited via conventional spin coating methods, and critically also have a significantly lower sheet resistance. Our work demonstrates that spray-casting is likely to be an increasingly important tool in the fabrication of large-area electronic devices.

Acknowledgements

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Supplementary Information

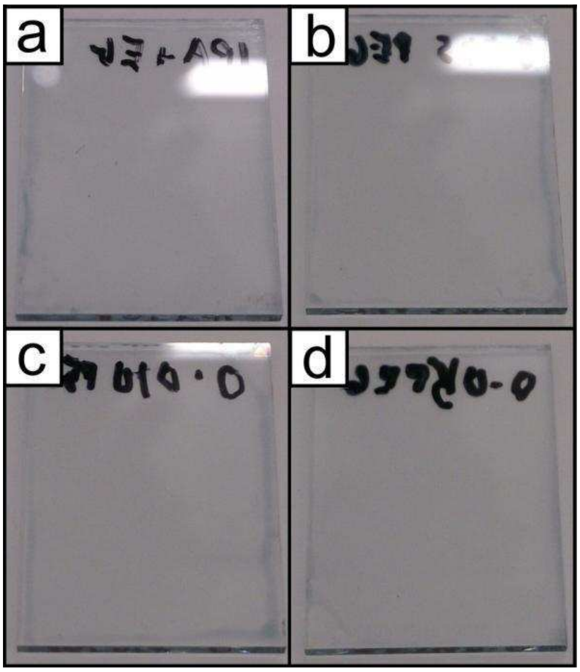

Figure. S1 Spray coated PEDOT:PSS films with varying amounts of PEG within the film (a) no PEG, (b) 0.005 mg ml^{-1}, (c) 0.01 mg ml^{-1}, and (d) 0.015 mg ml^{-1}.

Figure. S2 Video of spray upon addition of excessive amounts of PEG