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Graphical abstract

Fabrication of highly transparent and conducting PEDOT:PSS films using a formic acid treatment

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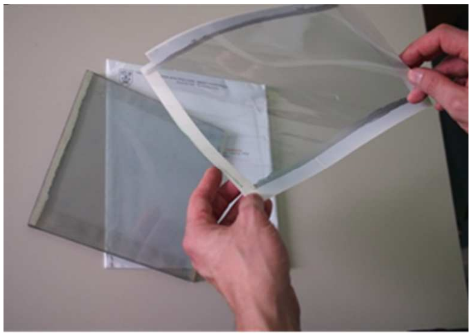
In this work the improvement in the conductive properties of thin nanoscale films of the polymer PEDOT: PSS was achieved by spraying and post treatment of the films using methanol and formic acid. This resulted in a huge improvement in sheet resistance values in the range of 3-4 orders of magnitude from the untreated films. This improvement in conductive properties of PEDOT:PSS films and the easily up scalable fabrication by automated spraying opens up a range of potential applications including flexible displays, light emitting diodes, photovoltaic cells, sensors and other optical and electronic devices.



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ARTICLE

Fabrication of highly transparent and conducting PEDOT:PSS films using a formic acid treatment

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The present work is focused on the development of transparent conductive polymer films and improving their conductivity. The films were produced using a commercially available poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate (PEDOT:PSS) aqueous dispersion. To deposit the PEDOT:PSS an automated programmable spray system was used. This enabled to spray the PEDOT:PSS onto reasonably large heated substrates creating a smooth homogeneous film. The dimensions and thickness of the film can be controlled and size of area of the film is only limited by spraying system dimensions providing a readily up scalable film deposition technique. The sprayed films were produced on a range of polymer (e.g. PET, polycarbonate and dielectric elastomer 3M VHB) or glass substrates. Varying PEDOT:PSS film thicknesses (corresponding to films of various %T values of <95% to >75%) were deposited and characterised primarily by UV-vis and Raman spectroscopy, Atomic Force Microscopy (AFM) and 4-point resistance measurements. The untreated films showed as expected a relatively poor sheet resistance to transparency ratio. However, treatment of these films using methanol and formic acid resulted in a huge improvement in sheet resistance values in the range of 3-4 orders of magnitude from the untreated films. In addition, the FA treated PEDOT:PSS films showed greater stability and only a slight reduction in their conductivity over the 200 hrs under atmospheric exposure. We believe that the improvement in conductive properties of PEDOT:PSS films and the easily up scalable fabrication by automated spraying opens up a range of potential applications including flexible displays, light emitting diodes, photovoltaic cells, sensors, window defrost systems, photo-chromic windows and sunroofs in cars.

1. Introduction

In recent years the demand for transparent flexible and conductive electrodes has risen sharply, in particular the need to find a replacement for indium tin oxide (ITO) based electrodes[1]. Many alternatives to ITO including various transparent conducting oxides (e.g. ATO, FTO, AZO),[2, 3] metal nanowires (e.g. Ag nanowires)[4] and carbon nanomaterial based electrodes[5-8] have been explored. However, due to various drawbacks and limitations of new alternative materials, ITO is still used as the primary material for transparent electronics. Conducting polymers, specifically poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), have attracted a great deal of attention for applications requiring flexible and transparent conductors. PEDOT is a conducting polymer which has relatively high optical transparency and good ductility. One problem is that it has quite low solubility in most common solvents.[9] This problem is circumvented by an addition of PSS which stabilises the PEDOT to form a coil structure enabling to produce stable aqueous solutions. PEDOT:PSS based electrodes have shown to be durable with a reasonable transparency and good mechanical properties under stress.[10, 11] One of its original drawbacks was its relatively low conductivity compared to metal oxide films. However with improved commercial formulations available along with a number of recent reports on treatments improving its conductivity, PEDOT:PSS has re-staked a claim as a viable alternative to traditional technologies in the world of transparent conductors. PEDOT:PSS is now heavily used in emerging photovoltaic applications and devices[12-14] along with other applications such as OLEDs[15] and electrochromic devices.[16, 17]

In this work we present an efficient and readily up scalable method for producing PEDOT:PSS films on polymer substrates combined with a new post treatment method to obtain highly transparent and conducting flexible electrodes.

There are several recent papers on the fabrication[18, 19] and treatment of PEDOT:PSS (specifically based on Clevios

PH1000 formulation) films in order to improve conductivity. It is reasonably well known about the improvement in conductive properties of PEDOT:PSS by the addition of high boiling point solvents such as sorbitol[20] and ethylene glycol (even reported on manufacturers sites) to produce the films with sheet resistance values of 65-176 Ω/□ and transparency of 80-88%.[21] Xia et al.[22-24] previously reported on a solvent treatment for PEDOT:PSS films spun coated onto glass substrates. Various solvents were tested with the most successful candidate being H_2SO_4 treated films with a thermal treatment of 160°C with top results reported of 67 Ω/□ and 39 Ω/□ sheet resistances with 87% and 80% transparency (quoted at 550nm) respectively. The authors also reported interesting results using carboxylic acids treatment[24] with varied success (relatively low conductivity reported in comparison to more recent relevant publications) however notably formic acid treatment was not studied in the work. Bao et al.[10, 11] reported using mixtures of DMSO and a Zonyl fluorosurfactant as additives to the PEDOT:PSS formulation and spin coating onto glass and PDMS substrates with thermal treatment at 120 °C. They achieved resistances of 46 – 240 Ω/□ at the 82-97% transmittance range. The best results in PEDOT:PSS treatments so far has been reported by Alemu et al.[25] which used a simple methanol treatment of spin coated glass samples. This enabled the authors to achieve ~25 Ω/□ – 147 Ω/□ sheet resistances at ~78-90% transmittance (apparently including the glass substrate). However one of the limits in these reports is the spin coating method employed to produce the samples with maximum size of about 1.5 cm x 1.5 cm with the vast majority being produced on glass substrates. Spin coating is a fast and efficient method of producing films however it is not a readily viable technology for scaling up to larger substrates and continuous production. Very recently Tait et al.[26] described a spray method to produce PEDOT:PSS films on glass, silicon and plastic substrates. Using an EG post treatment they achieved very good results (in comparison to other investigated EG treatments) with sheet resistance and transmittance (@550 nm) values of 24 – 259 Ω/□ and 71-95% respectively. Their spray system employed a technique allowing droplets to coalesce into film over a small area (2x2 cm for their PET substrates) and then solvent evaporation at a mild temperature (50 °C) before annealing at 120 °C. Whereas the films they produced were sufficient for the OPV cells they fabricated it is questionable whether a similar spray method using droplet coalescence into film would work over a large area film fabrication.

In this paper we report a modified method for readily producing PEDOT:PSS thin films of varying thickness using an automated spraying system. PEDOT:PSS films have been sprayed on various substrates (including a range of polymers) to a size of up to 20 cm x 24 cm. This approach can also be used to produce much larger samples and potentially for an industrial scale fabrication. In addition to this we report an alternative post solvent treatment method using formic acid which results in highly conductive and transparent flexible electrodes.

2. Experimental

2.1 Materials

All chemicals unless otherwise stated were obtained from Sigma-Aldrich. Poly (3,4-ethylenedioxythiophene) poly (styrenesulfonate) as an aqueous dispersion was purchased from Heraeus (Clevios PH1000 formulation). Quick drying silver paint was purchased from Agar scientific. Polycarbonate (PC) substrate was provided by Centro Ricerche Fiat (CRF). VHB 4910F (Clear) tape™ was purchased from 3M UK.

2.2 Spray Deposition System

Pure PEDOT:PSS solutions were prepared in water to the desired dilution factor. This solution was then loaded into a graduated reservoir attached to a Harden and Steinback Evolution airbrush. This was then integrated into a Janome JR 2300N automatic robot system along with a pressurised N_2 hose (see Fig. 1). Polyethylene terephthalate (PET) substrates were cut to required sizes and thoroughly washed using soapy water followed by through rinsing with acetone and iso-propanol (IPA) and left to dry at ambient conditions. The cleaned PET substrate was placed flat on the hotplate set at @ 110 °C. The robotic arm and moveable tray was set to spray the desired film area on the PET by activating the airbrush trigger releasing a fine controllable jet of solution (at 40 psi air pressure) onto the substrate. This process resulted in the formation of PEDOT:PSS composite films. The thickness of the films can be controlled by altering the number of layers sprayed i.e. the amount of solution deposited.

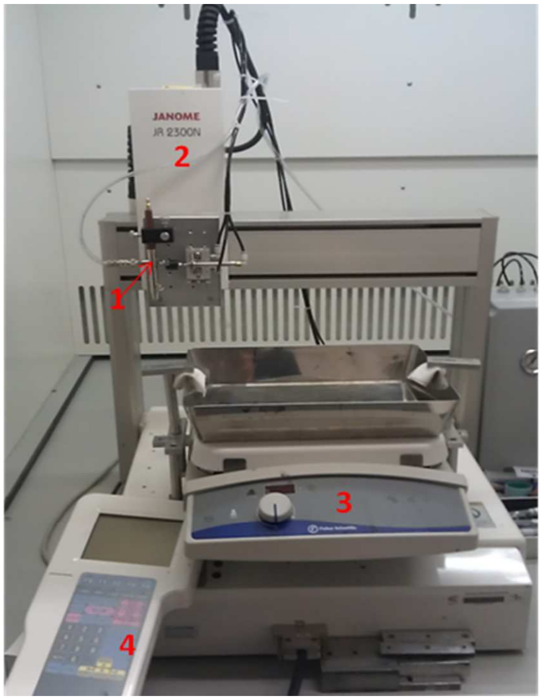

Fig. 1 Spray set up of the Janome JR 2300N automatic robot showing; 1: airbrush with compressed air feed attached 2: mechanical robot with pneumatic arm 3: hot plate where substrate is placed and 4: programmable controller.

2.3 Post-treatment of deposited films

The PEDOT-PSS coated substrates were cut to desired test size and typically treated by slowly dipping the film into a methanol (MeOH) or formic acid (FA) solutions as desired and removing the film slowly (duration of ~5 seconds). The films were then dried in an oven at 70 °C and used for testing.

2.4 Characterisation of films

The optical transmission of the films was tested using a Cary Varian 6000i UV-vis spectrometer. %T values quoted were corrected for the transmission of the PET substrate. Sheet resistance measurements were carried out on thin strips using the in-line four terminal method. The samples were cut into strips of length ~5 cm and with ~0.5 cm. Four contacts were placed onto the films by delicately painting 4 thin lines at even spacing using quick drying silver paint and attaching thin silver wire to each. I-V curves were obtained using a Keithley 2400 source meter. Raman spectra were recorded using Renishaw 1000 micro-Raman system fitted with a Leica microscope and Grams Research™ analysis software. The excitation wavelength was 633 nm from a Renishaw RL633 HeNe laser. The 50X magnifying objective of the Leica microscope was capable of focusing the beam onto a spot of approximately 2-3 μm in diameter. The PEDOT:PSS samples for Raman analysis were prepared by drop-casting thick samples and drying in an oven at 70 °C for characterisation as the spectra taken from the highly transparent thin films did not generate sufficient signal intensity to be analysed in detail. Surface roughness and thickness measurements were performed using an Omniscan MicroXam white light interferometer with Mapvue AE 2.27.1 capture software and SpiP 4.4.3 analysis software. AFM images of the polymer films were acquired in tapping mode using the inverted configuration of the NTEGRA Spectra (NT-MDT). NCH tips (nanoworld) with a resonant frequency of approximately 275 kHz are employed for capturing the phase images.

3. Results and Discussion

3.1 Spray system and production of PEDOT:PSS films

In our work we used the spray setup which consists of an automated mechanical horizontal system and adjustable vertical position with a pneumatic arm that activates and engages the spray gun (Fig. 1). The system (X-Y coordinates, speed of movement and arm activation) were all controlled using the programmable controller. The spray system such as the height of the spray gun above the substrate, nozzle aperture and air pressure were set up accordingly to optimally produce a uniform thin film over the sprayed area. The steady fine spray jet deposits the PEDOT:PSS solution onto the heated substrate whereupon the fine droplets spread and rapidly evaporate when in contact with the substrate. The most concentrated part of the spray cone is optimised to the spray pattern programmed into the system so that the trace pattern forms an even coat over the sprayed area. Diluting the stock PEDOT:PSS solution allows for an even coating to be built up over a number of passes on the spray area and also for a greater degree of control over the film thickness deposited as desired. PET has been primarily used as the substrate in the work presented in this article however the technique is versatile to be used with a variety of substrates such as polycarbonate (PC), glass and a stretchable polymer, 3M VHB tape TM (see Fig. 2). These substrates have also been successfully tested for spray coating and for some solvent treatments.

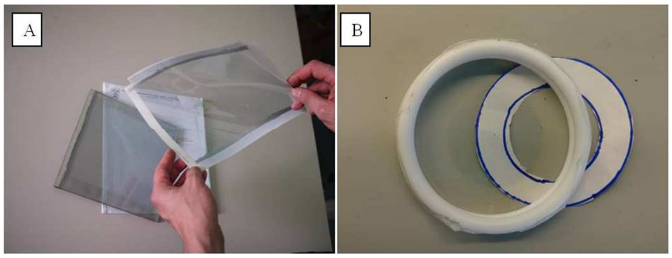

Fig. 2 Images of PEDOT:PSS films fabricated using the spray system A; polycarbonate and PET (in flex) B; a stretched VHB substrate mounted on Teflon ring.

3.2 Conductivity and transmittance characterisation of films

The sprayed substrates with PEDOT:PSS films were cut into testing strips, treated methanol or formic acid, dried and the transmission and sheet resistance was measured for each. Fig. 3 A shows a plot of %T versus sheet resistance (Rs) for films of varying thickness on PET treated with formic acid and methanol. The trend of the plot is in line with other reported thin film electrodes. The dramatic and large improvement in conductivity of treated films in comparison to untreated films has been documented previously as outlined above [10, 20, 22, 23, 25], a similar large decrease of the sheet resistance in the untreated films (with sheet resistances of kΩ/□) upon treatment was observed in this work. More informative was the comparison of our FA treatment to a MeOH treatment. The comparison of the effect of MeOH and FA treatment on the sheet resistance has clearly demonstrated that FA treated films show an average of 60% improvement in sheet resistance. The FA treated films displayed sheet resistances as low as 35 Ω/□, while still maintaining nearly 80% transmittance at 550 nm. At the other end of the scale, films demonstrated transmittance values of 95-97% at 550 nm and sheet resistances of 130-160 Ω/□ respectively. These values are well within the range of performance to be relevant for many potential industrial applications. Variations on the dipping treatment procedure were performed to test the efficacy of the procedure. The number of successive dips in a short time scale was tested along with drying intervals between successive dips. Also combined MeOH and FA dipping combinations were experimented with. The results obtained showed an insignificant difference in the treatment methods within the confidence of the measurement method, with the single dip procedure showing to be at least equal if not superior in sheet resistance values. Typically the sheet resistance values varied ~1 Ω/□ for the different treatment tests. Also excessive dipping procedures could in cases (more frequently for thicker films) damage the film due to delamination of PEDOT:PSS layers from the PET substrate.

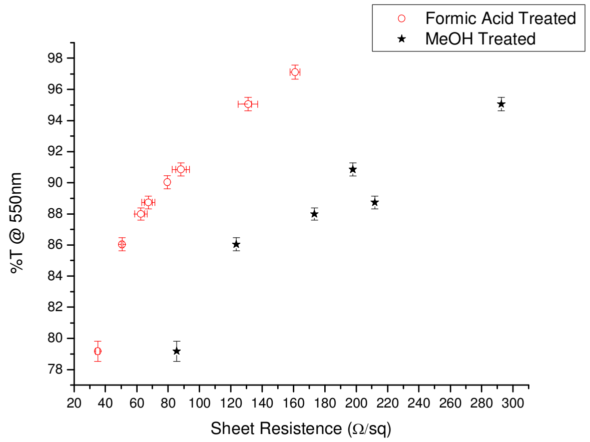

Fig. 3 Plot of % transmission quoted at 550 nm versus sheet resistance for PEDOT:PSS films on PET treated with formic acid and methanol.

Fig. 4 shows an example of some typical transmission spectra of PEDOT:PSS films of carrying thickness. Transmission percentage measurements were taken at least 5 times from different areas of the sprayed film to ensure uniformity of the film and account for experimental errors. Standard deviation of %T values of a particular film at 550nm typically was less than 0.2%. As is commonly observed for PEDOT films the transmission is at a maximum in the blue end of the spectrum and decreases when moving into the red.[25, 26] This has more dramatic impact in the case of the thicker films where the blue PEDOT colour is quite visible and the transmission changes by ~20% over the range of the visible spectrum (~85-65%). However for thin films (with a %T value of ≥90% at 550 nm) the change in transparency is much less affected over the range in the region of 5-10%. The solvent dipping treatment of the films with FA and MeOH does not show a significant change to the transmission of the films (Fig. 4 B). The reasoning behind this is that the post solvent treatment removes the transparent polymer PSS stabiliser from the film, thus having a negligible effect on the film transparency. This finding is consistent with previous reports of effects on transparency with post treatment of films with solvents.

The effect on the thickness of treated PEDOT:PSS films were investigated using a thick film (%T = 52%). Thickness measurements before and after treatment showed a reduction in thickness from ~790 nm to ~635 nm with an associated surface roughness reduction of ~20 nm to ~14 nm. These results are consistent with the theory of PSS removal and PEDOT chain conformational change in the film upon treatment. The surface roughness of the more transparent films had a value approaching ~6 nm.

A figure of merit (FOM) of σ_{DC}/σ_{OP} describing the ratio of the bulk DC conductivity (σ_{dc}) and the optical conductivity (σ_{op}) is commonly used to classify transparent conductors.[23, 27] This ratio is obtained by substituting the transmission (at 550 nm) and sheet resistance (Rs) into the following equation:

$$T = \left(1 + \frac{Z_0}{2R_s}\frac{\sigma_{op}}{\sigma_{dc}}\right)^{-2} \qquad (1)$$

where Z_0 is the impedance of free space (377 Ω). A FOM value of 35 representing %T and Rs values of 90% and 100 Ω/□ respectively is considered to be the minimum standard for transparent conductors to be relevant for industrial applications. The FOM values obtained for the FA treated films in this work had an average value of 50 with a maximum recorded value of 79 for the highest transparency film and no film showing a FOM lower than 43.5. The difference in the highest value from the average would seem dramatic however at the higher end of the results small differences of 1-2% in transparency for example results in large changes in the FOM. These results to the best of our knowledge are among the highest FOM values for PEDOT:PSS films and the highest for this technique of producing flexible PEDOT:PSS films to date.

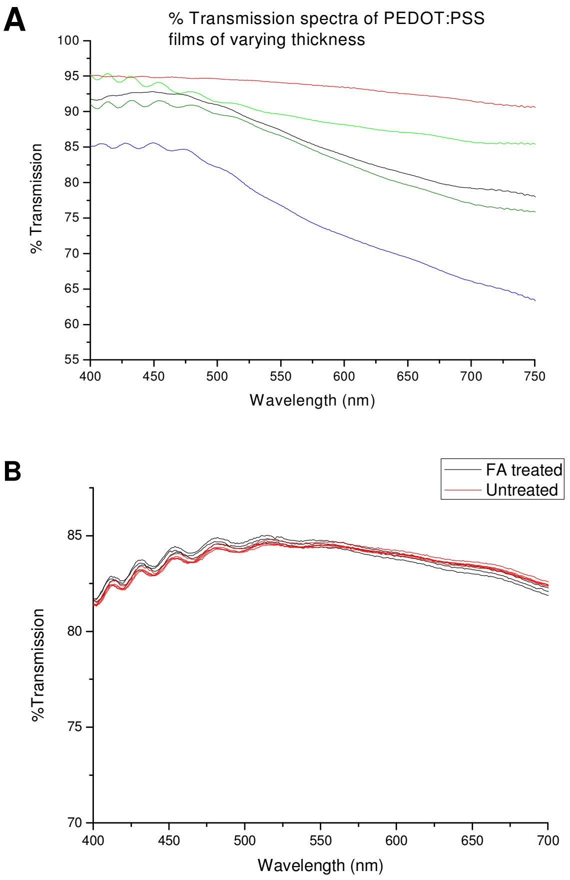

Fig. 4 A - Typical transmission spectra of PEDOT:PSS films (PET corrected) of varying thickness. **B** - Transmission spectra of a FA treated and untreated PEDOT:PSS film.

3.3 Raman spectroscopy studies of treated PEDOT:PSS

Raman spectroscopy was performed on treated and untreated PEDOT:PSS films to investigate the effect of FA treatment on the properties of films. Fig. 5 shows the Raman spectra of FA treated and untreated PEDOT:PSS films. The annotated peak highlighted in Fig. 5 centred around 1428 cm^{-1} for the untreated film corresponds to the stretching vibration on the $C_\alpha = C_\beta$ of the constituent five member ring of PEDOT.[28, 29] This band is red shifted to ~1415 cm^{-1} upon treatment with FA. This shift results from a change from the benzoid structure to the quinoid structure in the PEDOT chains.[28, 30] An interesting work by Ouyang et al.[31] reported similar observations in their Raman analysis of ethylene glycol treated PEDOT:PSS films. They proposed an explanation that this structural change in the PEDOT is associated to a conformational change of the PEDOT:PSS chains changing from a predominantly coiled structure to a more mixed linear-coil formation thus facilitating a stronger interaction between the chains and an increase in conductivity. This explanation is plausible given the evidence of a decrease in thickness and surface roughness values of treated films compared to untreated films.

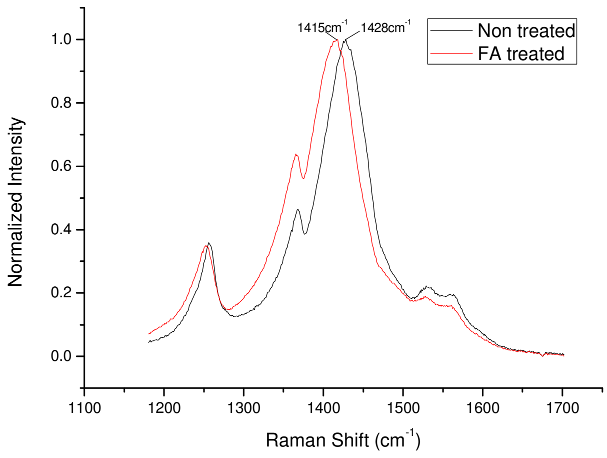

Fig. 5 Raman spectra of a FA treated and untreated PEDOT:PSS film (excitation at 633 nm).

3.4 AFM microstructure characterisation of films

The microstructure of the films was investigated using phase imaging Atomic Force Microscopy (AFM). Phase imaging is useful here as it can more clearly identify the difference between two mixed polymers[32] as opposed to topographical imaging due to the interaction of the tip with regions of changing material properties (i.e. the change in areas of film with more or less of a particular polymer). Fig. 6 shows the phase images of untreated, MeOH treated and FA treated films. The images indicate there is a clear microstructure change in the films upon treatment with both MeOH and FA. The untreated films (Fig. 6 A) show a greater degree of phase change in the film morphology. This is due to changing areas of PSS and PEDOT rich grains in the films. After treatment the films exhibit a much lower degree of phase contrast in the film (Fig 6 B). This is due to the removal of PSS from the film (mostly from the surface) and conformational change in the PEDOT chains to a more linear formation (this is discussed in detail in a later section below), thus resulting in a more even PEDOT distribution in the film and a lower degree of phase shift in the AFM tapping oscillation.

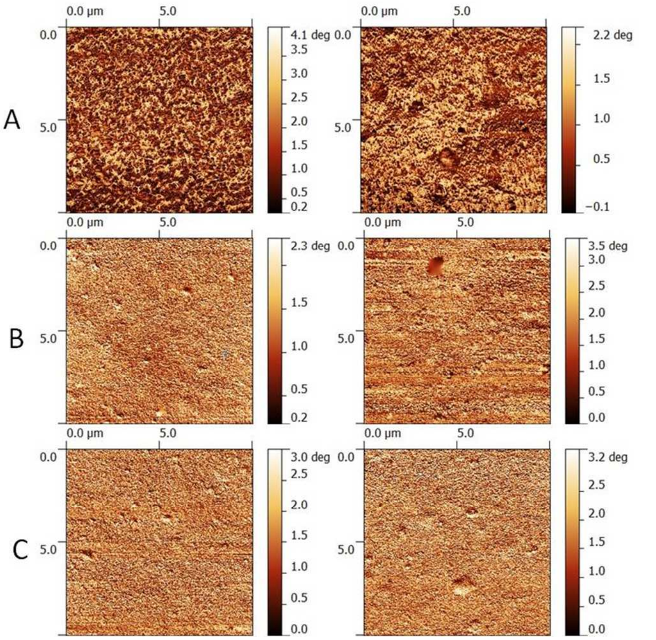

Fig. 6 AFM phase images of A: untreated films, B: MeOH treated films and C: FA treated films

3.5 Discussion of conductivity increase

The exact theory behind the cause of the conductivity increase in treated PEDOT:PSS films is still the subject some debate however it is generally accepted that the solvent treatment results in the removal of the stabilising PSS polymer which can act as an insulating barrier to conduction between the PEDOT thus reducing interchain charge hopping barrier coupled with a conformational change of the PEDOT:PSS[31, 33] chains leading to a higher degree of connectivity between the chains (as it schematically displayed in Fig. 7). Polar high dielectric constant solvents which are weakly protic causes the removal of the negatively charged PSS chains by effectively screening them from the positively charged hydrophobic PEDOT chains. This causes a phase separation between the chains and removal of PSS from the film.[21, 25] Also postulated additionally for an acidic post treatment is the replacement of the negatively charged PSS^- ion with the protonated acidS PSSH derivative which is phase separated from the PEDOT chains and easily removed into solution. This removal of the PSS also causes a conformational change in the PEDOT which are curled up in a coil structure in the pure PEDOT:PSS film.[23] Thus we believe that the higher dielectric constant of FA coupled with the added effect of its much greater acidity than MeOH is the main reason for the improved conductive properties of the PEDOT:PSS films treated with FA comparing to the pure and MeOH treated films.

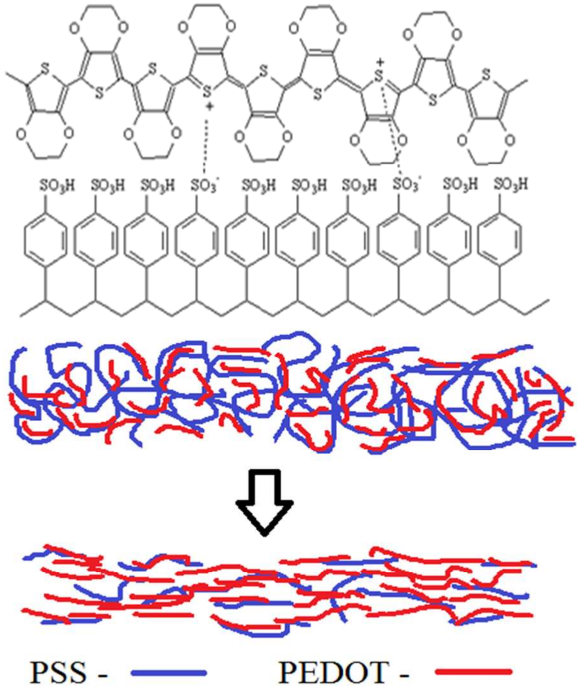

Fig. 7 Top: atomic structure of PEDOT:PSS Bottom: sketch illustrating the change in PEDOT:PSS film after solvent treatment.

3.6 Testing of film stability in atmosphere

The effects of the solvent treatments on the PEDOT:PSS films were investigated in terms of their conductivity stability upon exposure the films to the atmosphere at 20 °C for the period of 200 hrs (Fig 8). PEDOT:PSS films were left exposed to the air and their resistance was monitored over time. The results for untreated films were in line with previous reports on atmospheric exposure of PEDOT:PSS films.[20, 21, 25] As expected we observed the gradual increase in resistance of the PEDOT:PSS films with exposure to atmosphere at ambient conditions (Fig 8). This increase is due to the ready uptake of atmospheric water by the hydroscopic PSS component in the film. Thusly the removal of PSS from the film upon treatment should result in a comparative lesser uptake of water and corresponding reduction rate of resistance increase. Fig 8 shows that this is indeed the case with the FA treated films showing the lowest resistance increase in comparison to MeOH treated and untreated films. This further demonstrated the greater efficiency of the FA treatment in comparison to the similarly treated MeOH films in the removal of PSS from the film and as a result showed greater stability under atmospheric exposure.

4. Conclusions

In summary we have presented in this work a fast and efficient method for producing high quality, conductive transparent and relatively large area PEDOT:PSS films on various substrates. The method is highly reproducible and can be easily up scaled to accommodate future desired film requirements. We have also demonstrated that a formic acid treatment method for the PEDOT:PSS films results in a vast improvement in the conductive properties of PEDOT:PSS films and a significant improvement when compared to a methanol treatment performed on the films. The figure of merit results achieved for the films is one of the best reported for flexible and transparent PEDOT:PSS films. This increase in conductive properties of the films is attributed to the removal of the PSS chains and a conformational change in the PEDOT chains brought about through a Coulombic screening effect of the formic acid upon treatment due to its acidity and high dielectric constant. Moreover by contrast to the untreated samples, the FA treated PEDOT:PSS films showed greater stability and only a slight reduction in their conductivity over the 200 hrs in atmospheric exposure. The combined readily scalable process employed in producing the films and improvement in film properties opens up a range of potential applications in optical and electronic devices varying from flexible displays to photovoltaic cell technologies. In addition these materials might find a variety of important applications in automotive industry such as integrated flexible solar panels, window defrost systems, photo-chromic windows and sunroofs in cars.

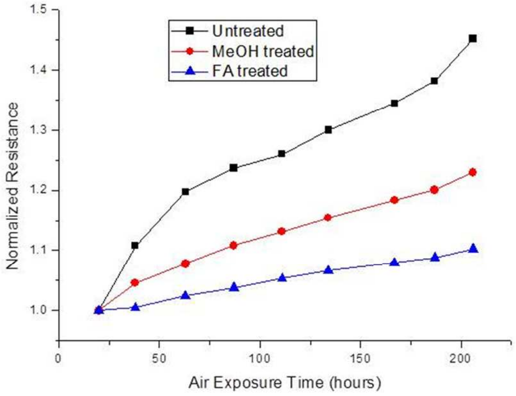

Fig. 8 Plot of normalised resistance versus air exposure time for untreated, MeOH treated and FA treated PEDOT:PSS films.

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References and notes

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