High-Performance Thin Film Transistor from Solution-Processed P3HT Polymer Semiconductor Nanoparticles

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Abstract. Nanoparticulate suspensions of semiconducting polymer poly-3-hexylthiophene (P3HT) have been prepared in water through a mini-emulsion process using sodium dodecyl sulphate (SDS) as the surfactant. Using these suspensions, we have fabricated organic thin film transistors (OTFTs) in a top gate configuration. These devices operate at a low voltage and show output characteristics similar to those achieved when the P3HT film is spun from chloroform. To characterize the properties of the film made from the nanoparticle suspension, differential thermal analysis (TGA), differential scanning calorimetry (DSC), atomic force microscopy (AFM), fluorescence spectra analysis, ultraviolet/visible (UV/VIS) spectrophotometry and X-ray photoelectron spectroscopy (XPS) have been used.

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INTRODUCTION

Electronic products based on polymers and other organic materials have been rapidly emerging as a significant new technology. As a result, devices such as OLED-displays (both front planes and backplanes), integrated circuits, organic photovoltaic cells and transistors are becoming common place [1-6]. The organic transistor is a key component in many organic electronic devices. The main reason that studies of organic thin film transistors (OTFTs) have increased in recent times is due to their ease of fabrication. The deposition and patterning of all layers of an OTFT can be performed at low temperature by a combination of solution-based techniques, which makes them suitable devices for the realization of low-cost, large-area electronic functions on flexible substrates. Although the performance and stability of organic transistors still lag behind those of inorganic devices, the inexpensive and simple processing methodology of organic electronics still provides great potential to replace current alternatives in some areas. As well as sensing devices and active matrix liquid crystals, flexible, active-matrix electronic-paper displays and high-performance RFID tags compatible with existing communication standards are some desired applications of OTFTs [7]. In the majority of cases, the active layers of those devices have been applied from organic polymer solutions which are dissolved in organic solvents such as chloroform. However, significant problems exist in deposition from those solvents, particularly when dealing with large areas or multilayer devices [8]. For instance, interdiffusion and undefined interfaces can be the result of depositing several layers on top of each other because most processing of the gate dielectric or active layers use the same solvents. Another problem is the very rapid drying of most organic solvents which can be a problem when they are used in inkjet printing.

Deposition of the first layer and then crosslinking by thermal treatment is one major approach used to solve the interdiffusion problem, after which the next layer can be readily applied [8,9]. However, reaction side products and the chemical reaction itself can potentially influence the device performance [8]. A more desirable approach is to produce high quality aqueous polymeric dispersions that can be used to deposit a conductive layer or an active layer for building organic electronic devices. A common approach involves the use of water-based dispersions of the polymeric conductor polyethylenedioxythiophene (PEDOT) doped with polv (styrenesulfonate) (PSS) [10,11], but the focus of this approach is the aqueous deposition of potentially any electrically conducting polymer [8-13]. Here, we demonstrate high performance top-gate OTFT prepared from aqueous semiconducting P3HT nanoparticles as the active layer.

NANOPARTICLE PREPARATION AND CHARACTERIZATION

We prepared semiconducting polymeric nanoparticles in aqueous media via a mini-emulsion process. This method was first introduced by Landfester et al. and subsequently modified by other researchers [8,14,15]. P3HT (purchased from Lumtec) was dissolved in chloroform and then mixed into SDS solution (42 nm SDS in 2.8 mL milliQ water). A macroemulsion was then formed by stirring the solution at 1200 rpm for 1 hour and subsequently sonicating for 2 minutes. The resulting mini-emulsion was then gently stirred at 60 °C to evaporate the chloroform. After evaporation of the solvent, dialysis of the nanoparticle suspension is required to concentrate the samples and remove excess surfactant from the suspension. A Zetasizer Nano-ZS (Malvern Instrumenet, UK) was used to characterize the dispersion particle size and a polymer particle size of about 60 nm was obtained (Figure 1).



FIGURE 1. Particle size distribution of the P3HT nanoparticulate dispersion.

To fully investigate the properties of the nanoparticles, X-ray photoelectron spectroscopy (XPS), differential thermal analysis (TGA), atomic force microscopy (AFM) and differential scanning calorimetry (DSC) measurements were conducted. Figure 2 shows the XPS plots of the P3HT nanoparticles for a range of annealing conditions as has been used to analyze the surface chemical composition of the nanoparticle film. It is clear from Figure 2 that the characteristic sulfur peaks of the P3HT (~164 eV) increase in intensity as the annealing temperature is increased whist the sulfur peaks assigned to the SDS surfactant (~ 169 eV) are stable

from 'unannealed' to 120 $^{\circ}$ C and subsequently decrease in intensity beyond 120 $^{\circ}$ C [15]. This indicates that as the annealing temperature is increased the relative amount of P3HT at the surface of the particles increases and, indeed, SDS is lost from the surface.



FIGURE 2. XPS plot of the sulfur peak region of P3HT nanoparticles for varying annealing temperatures (5 minute annealing time).

The XPS result directly relates to the DSC measurements (Figure 3) which show a distinct phase transition in the nanoparticles at about $120 \,^{\circ}C$ [15].



FIGURE 3. DSC plot of the P3HT nanoparticles.

Figure 4 shows the TGA weight change of the nanoparticles, as well as pure P3HT and SDS samples, as a function of temperature. These data clearly demonstrate the onset of a major mass loss from the nanoparticle at 190 $^{\circ}$ C which is attributed to the SDS since there is no change in the P3HT plot until above 450 $^{\circ}$ C.



FIGURE 4. TGA of P3HT nanoparticulate, pure P3HT and SDS samples.

An AFM investigation of the nanoparticle film (Figure 5) reveals that annealing at 140 °C for 5 minutes results in some coalescence of particles, and the P3HT film becomes smoother (rms surface roughness for the unannealed film is 4.2 nm compared to 3.5 nm for the post annealed film). Using this method we can really deposit multiple nanoparticulate layers to form a continuous multi-layer film of the nanoparticle material, allowing for the fabrication of semiconducting layers of a variety of thicknesses.



FIGURE 5. AFM images of the P3HT nanoparticulate film (a) unannealed (b) annealed at 140 °C for 5 minutes.

FABRICATION AND CHARACTERIZATION OF THE OTFT

The P3HT nanoparticle suspension has been used to deposit the active semiconducting channel material of an OTFT. The devices were fabricated in a top gate to produce devices of the architecture shown in Figure 6a. Prepatterned indium tin oxide (ITO) glass slides with a 20µm channel were cleaned with acetone and isopropyl alcohol, and subsequently dried by using nitrogen. A 60 nm thick active layer of P3HT was deposited on the ITO by spin coating 35 µL of the P3HT nanoparticle dispersion at 3500 rpm in air and then drying at 140 °C for 5 minutes. A 100 nm thick film of polyvinylphenol (PVP) dielectric polymer, was the spin coated from an ethanol solution onto the P3HT. Finally, a PEDOT/PSS gate electrode was dropcast, in air, onto the PVP layer such that the PEDOT overlapped fully the P3HT channel.





FIGURE 6. a) Schematic of the top gate organic thin film transistor architecture. b) Output characteristic (drain voltage, Vd vs. drain current, Id) of the top gate OTFT measured under ambient conditions.

All OTFT devices were fabricated under ambient conditions and their IV characteristics were

(a)

determined using a Keithley 2400 Sourcemeter. Figure 6b shows the influence of gate voltage on the I-V characteristics for nanoparticle OTFT devcies. This device shows typical transistor behavior. The more negative the gate voltage that is applied the higher the current flow between drain and source electrodes. When a negative voltage is applied to the gate, positive charges are induced at the organic semiconductor/organic insulator interface (at the channel) resulting in more charge carriers in the channel material. Importantly, the characteristics for this device are identical to those obtained for devices fabricated with an organic solvent processed P3HT channel material [6, 7].

CONCLUSION

conclusion, In we have synthesized a nanoparticulate polymer semiconductor (P3HT) via a mini-emulsion process and used this dispersion to produce functioning The OTFTs. device's performance is comparable to other transistors fabricated with non-nanoparticulate materials, from organic solvents, without the need for precautionary measures such as excluding oxygen, light, and moisture during fabrication and characterization.

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REFERENCES

- 1. Subarman, *Progress Toward Development of All-Printed* RFID Tags: Materials, Processes, and Devices, Proceeding of IEEE, 2005.
- 2. S. Holdcroft, Adv. Mater. 13, 1753-1756 (2001).
- 3. A.C. Arias, Appl. Phys. Lett. 85, (2004).
- 4. H. Sirringhaus, et al., Science 290, 2123-2126 (2000).
- 5. L. Yi-Kang, Y. Cheng Han, and Y. Hsiao-Ching, *Polymer International* **59**, 16-21 (2010).
- R.J. Chesterfield, et al., J. Phys. Chem. B 108, 19281-19292 (2001).
- 7. H.G.O. Sandberg, et al., Org. Electron. 6, 142-146 (2005).
- 8. K. Landfester, et al., Adv. Mater. 14, 651-655 (2002).
- W.H. Wang, H.Y. Bai, and W.K. Wang, J. Appl. Phys. 74, 2471-2474 (1993).
- 10. S.H. Eom, et al., Org. Electron. 10, 536-542 (2009).
- 11. K. Hong, et al., Org. Electron. 9, 864-868 (2008).
- 12. A.M. Nardes, M. Kemerink, and R.A.J. Janssen, *Phys. Rev. B* : Condens Matter **76**, 085208 (2007).

- 13. F. Xue, Y. Su, and K. Varahramyan, *IEEE Trans. Electron Devices* **52**, 1982-1987 (2005).
- 14. L. Katharina, Angew. Chem. Int. Ed. 48, 4488-4507 (2009).
- 15. A.J. Stapleton, *Nanoparticle Based Organic Photovoltaic Devices*. Thesis. Newcastle University, 2010.