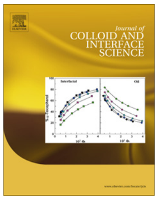
Journal of Colloid and Interface Science 401 (2013) 65–69

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



Novel low voltage and solution processable organic thin film transistors based on water dispersed polymer semiconductor nanoparticulates

Darmawati Darwis [a,b], Daniel Elkington [a], Syahrul Ulum [a,b], Glenn Bryant [a], Warwick Belcher [a], Paul Dastoor [a], Xiaojing Zhou [a,*]

[a] Centre for Organic Electronic, University of Newcastle, Callaghan, NSW 2308, Australia
[b] Department of Physics, Faculty of Science, Tadulako University, Kampus Bumi Tadulako Tondo kota Palu 94118, Indonesia

ARTICLE INFO

Article history:
Received 4 February 2013
Accepted 29 March 2013
Available online 8 April 2013

Keywords:
Polymer nanoparticulates
OTFT
P3HT
Surfactant
SDS

ABSTRACT

Two novel organic thin film transistor structures that combine a hygroscopic insulator with the use of water-dispersed polymer nanoparticles as the active layer are presented. In the first device structure, the semiconducting layer was fabricated from a nanoparticulate suspension of poly-(3-hexylthiophene) prepared through a mini-emulsion process using sodium dodecyl sulfate as the surfactant whereas a surfactant-free precipitation method has been used for the second device structure. In both cases, fully solution processable transistors have been fabricated in a top gate configuration with hygroscopic poly(4-vinylphenol) as the dielectric layer. Both device structures operate at low voltages (0 to −4 V) but exhibit contrasting output characteristics. A systematic study is presented on the effect of surfactant on the synthesis of semiconducting nanoparticles, the formation of thin nanoparticulate films and, consequently, on device performance.

1. Introduction

Electronic products based on polymer and other organic materials are emerging rapidly, and encompass items such as: organic light emitting diode (OLED) displays, integrated circuits, organic photovoltaic cells and transistors [1–6]. Organic transistors are key components in many of these organic electronic devices. The main driver for this rapidly increasing interest in organic thin film transistors (OTFTs) is their ease of fabrication. In particular, the deposition and patterning of all layers in an OTFT is possible at low temperature using a combination of solution-based techniques, which makes them ideally suited for the realization of low-cost, large-area electronics on flexible substrates. As such, the inexpensive and simple processing capabilities of organic electronics means that they have the potential to replace conventional devices in many applications [4].

A key advantage of OTFT technology is that conventional printing techniques can be implemented to provide rapid mass production of devices. However, a challenge for printing OTFTs is that the organic semiconducting solutions that are used generally involve chlorinated solvents which are highly toxic and volatile [7,8]. In addition, the fabrication of high performance OTFTs requires optimization of polymer crystallinity in the active layer, which in turn is highly dependent upon the choice of solvents, deposition techniques and post-deposition treatments such as annealing [9]. Thus, from a fabrication point of view, the development of alternative more environmentally compatible semiconducting solutions capable of producing crystalline semiconducting polymer layers would be highly attractive.

Recently, methods have been reported to prepare semiconducting polymer films through pre-formed polymer nanoparticulate dispersions. These nanoparticles can be prepared either by a precipitation approach [10,11] or a surfactant-assisted mini-emulsion method [12–15]. Previous studies have shown that it is possible to form stable suspensions with a tunable nanoparticle size using both methods, thus offering a new pathway to fabricate OTFT active layers with controlled polymer domain size and thin film morphology [10–16]. Furthermore, the polymer chains can be highly crystalline within each particle [10,11].

Many applications for organic transistors also require low voltage operation driven by the need for devices with low power consumption [17]. One approach to low-voltage OTFT operation is to use hygroscopic materials as the dielectric layer [18–20]. Poly(4-vinylphenol) (PVP) is one such hygroscopic polymer and the moisture adsorbed by it plays a central role in modulating drain current under low gate voltage values [21]. The current modulation mechanism in these devices involves chemical doping of the semiconducting channel stemming from ion diffusion at the dielectric-semiconductor interface [20]. These devices operate at a few volts and have maximum output currents (I_{ON}) comparable to, or even higher than, many conventional OFETs operating at many tens of volts [11].

---

* Corresponding author.
E-mail address: Xiaojing.Zhou@newcastle.edu.au (X. Zhou).

0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.03.052

Significantly, the use of a polymer top-gate architecture in these transistors allows for a fully solution-processable device, which can ultimately be printed on flexible substrates [22]. A challenging aspect of fabricating this architecture with nanoparticulate materials is that it requires a pinhole-free semiconductor layer. We have shown that using surfactant-containing nanoparticles (NPs) we can obtain high-quality active layers and subsequently fabricate low-voltage OTFT devices with a PEDOT:PSS top gate electrode [23].

In this work, we compare NP OTFTs fabricated with and without surfactant to probe the mechanism of operation in these devices. The NP thin film morphologies, chemical and electronic properties and performance of OTFTs fabricated from these two types of nanoparticles are characterized. We show that the performance of the surfactant-containing OTFTs is dictated by counter-ions associated with SDS in the film. By removing the surfactant from the active layer, substantial improvements in the performance of these low-voltage all-solution processable OTFTs are obtained. This novel device structure offers the twin advantages of low-voltage operation combined with the elimination of harmful solvents from the device fabrication process.

2. Materials and methods

Semiconducting polymeric nanoparticles were prepared in aqueous media via a mini-emulsion process (Type I). P3HT (Mn = 22 K, PDI 2.58, purchased from Lumtec) was dissolved in chloroform at a concentration of 30 mg/mL and then mixed into an aqueous sodium dodecyl sulfate (SDS) solution (42 mg SDS in 2.8 mL MilliQ water). A macroemulsion was then formed by stirring the solution at 1200 rpm for 1 h and this was then sonicated for 2 min to form a mini-emulsion. The mini-emulsion was then gently stirred at 60 °C to evaporate the chloroform. After evaporation of the solvent, the nanoparticle suspension was dialysed to concentrate the samples and remove excess surfactant. Stable polymer dispersions with a polymer particle size of about 60 nm, as measured by a Zetasizer Nano-ZS (Malvern Instruments, UK), were obtained. Semiconducting polymeric nanoparticles were prepared without surfactant using the direct precipitation method (Type II). P3HT was dissolved in 1 mL chloroform (0.25 wt.%) and stirred for 10 min at room temperature. This solution was transferred into a syringe and rapidly dropped into 4 mL anhydrous ethanol while simultaneously stirring the mixture (200 rpm). After injection, stable nanoparticle suspensions were obtained. Both types of suspensions were subsequently used in the fabrication of OTFTs.

OTFTs were fabricated on glass substrates with pre-patterned indium-tin-oxide (ITO) source and drain electrodes. The channel length and width was 20 μm and 3 mm respectively. A 100 nm thick P3HT nanoparticle layer was spin-coated (60 s at 2000 rpm) from the suspensions onto the substrate as measured by a KLA Tencor profilometer. A hot plate with a controlled temperature was used to anneal the formed films. For the dielectric layer, PVP (Aldrich) was dissolved in ethanol at a concentration of 80 mg/mL and then spin-coated (60 s at 2000 rpm) to a thickness of approximately 500 nm. The P3HT/PVP two-layer structures were annealed at 85 °C in air to remove any remaining solvent. Lastly, PEDOT:PSS (Aldrich, pH = 1–2) was drop-cast on the top of gate dielectric layer and dried on a hot plate at 40 °C in air. Two Keithley 2400 source meters were used for the device characterization. All output characteristic measurements were conducted at a scan rate of 0.1 V/s. All fabricated devices were measured in air immediately after drying the PEDOT:PSS layer. The relative humidity (RH) of the laboratory was consistently recorded as 50 ± 10%.

Atomic force microscopy (AFM) images of the films formed from these suspensions were measured using a Cypher scanning probe microscopy system in non-contact mode. X-ray photoelectron spectroscopy (XPS) analysis was performed using a multi-technique ultrahigh-vacuum imaging XPS system (Thermo VG Scientific ESCALab 250) equipped with a hemispherical analyzer (of 150 mm mean radius) and a monochromatic Al KR (1486.60 eV) X-ray source. An ultraviolet–visible (UV–Vis) absorption spectrophotometer (Varian Cary 6000i) was used to measure the absorption of the nanoparticle suspensions and the films.

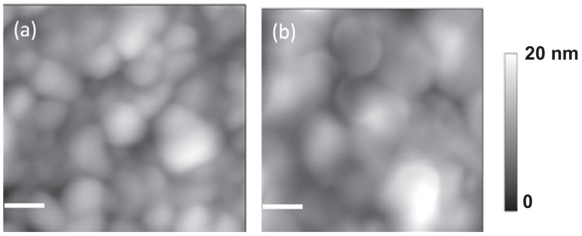


Fig. 1. AFM images of the Type I (surfactant-containing) P3HT nanoparticle (NP) thin films: (a) unannealed NP film (rms roughness of 4.2 nm) and (b) NP film after annealing for 5 min at 140 °C (rms roughness of 3.5 nm), the scale bars are 50 nm.

3. Results and discussion

Fig. 1a and b show AFM images of the Type I (surfactant-containing) nanoparticle (NP) thin film before and after annealing at 140 °C respectively. A particle size distribution from 30 nm to 100 nm is observed in Fig. 1a in good agreement with transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements (see Supporting information in Figs. S1 and S2). The AFM images also show that multiple particles stack together; resulting in a continuous film with a thickness of 60 nm as measured by profilometry. Annealing at 140 °C for 5 min results in the coalescing of particles shown in Fig. 1b and, based on the AFM roughness analysis, a slightly smoother film is obtained. The surface roughness (based on RMS) of the film decreases from 4.2 nm to 3.5 nm upon annealing.

Fig. 2 compares the UV–Vis spectra of the surfactant-containing NPs in suspension with that of the thin film before and after annealing at 140 °C. Consistent with previous reports, the absorption spectra of P3HT are all red-shifted compared to the absorption spectrum of P3HT in $CHCl_3$ solution [24]. In addition, the red-shifts for solid state NP films are larger than that observed for NPs in suspension and exhibit an increased background signal. The increased red-shift in the UV–Vis spectra for the NP films can be attributed to more crystalline NPs being preferably retained during the spin-casting process, whilst the higher background signal is consistent with increased optical scattering due to the particulate nature of the film. Three pronounced absorption peaks are observed for both the P3HT NPs in suspension (510 nm, 535 nm and 585 nm) and for the NP thin films (525 nm, 550 nm and 600 nm). The three adsorption features are attributed to the π–π stacking of the P3HT backbone and the intermolecular π–π stacking interaction and are consistent with the absorption features for nanoparticle P3HT reported by Millstone [11]. The pronounced vibronic shoulders at 550 nm and 600 nm indicate highly ordered polymer chains in the NPs and, given that these shoulders increase in magnitude upon annealing, shows that annealing at 140 °C enhances polymer crystallinity within the NPs themselves.

X-ray photoelectron spectroscopy (XPS) was used to investigate the relative SDS:P3HT concentration ratio at the thin film surface before the PVP dielectric layer is deposited. Fig. 3a and b shows the XPS S 2p and C 1s spectra respectively. In Fig. 3a, the peak doublet located at 164.0 eV and 164.5 eV corresponds to the S 2p signal for P3HT [25] while the other doublet at 170.0 eV and 171.2 eV