

Original article

Formation and Characterization of mini-emulsion P3HT PCBM Nanoparticles

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Abstract

This report presents the synthesis of nanoparticulate suspensions of P3HT:PCBM for organic photovoltaic active layer through a mini-emulsion process with the used of sodium dodecyl sulphate (SDS) as the surfactant. A series of characterization for the nanoparticles using Dynamic Light Scattering (DLS), Ultraviolet-visible spectroscopy, (UV-VIS), Photolumination (PL), Transmission, Electron Microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) also demonstrated. The P3HT/PCBM nanoparticle performances are comparable to P3HT/PCBM solution in chloroform and met the requirement for use in organic Photovoltaic fabrication.

INTRODUCTION

Current attention in electronic devices based on polymers and other organic materials is increasing including the rising interest given for organic products based on organic nanoparticle active layers (Landfester *et al.*, 2002; Landfester, 2009; Stapleton *et al.*, 2012). The key competitive advantages of these nanoparticle materials compare to the conventional solution processed approach are the opportunity to pre-organise the morphology of active layer on a nano-scale, and the chance to use printing techniques to fabricate various polymer based devices from aqueous polymeric ink rather than volatile and flammable solvents (Shimizu *et al.*, 2007; Hu and Gesquiere, 2009; Hu *et al.*, 2010; Millstone *et al.*, 2010).

Here, we present semiconducting nanoparticulate suspensions of P3HT:PCBM for OPV have been synthesized via a micro-emulsion process with the used of sodium dodecyl sulphate (SDS) as the surfactant.

MATERIAL AND METHODS

Semiconducting polymeric P3HT PCBM nanoparticles was prepared in aqueous media through a micro-emulsion method. The synthesis is based upon the method that was first introduced by Landfester *et al.* and subsequently modified by other researchers (Landfester *et al.*, 2002; Landfester, 2009; Stapleton *et al.*, 2012; Vaughan *et al.*, 2012).

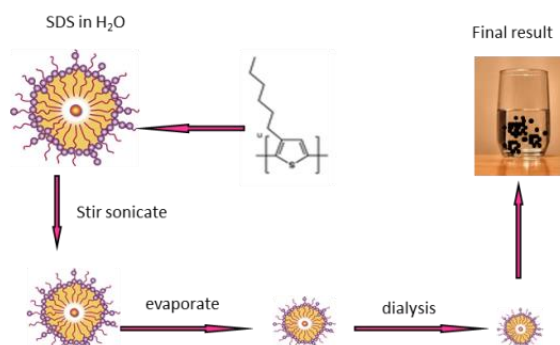


Fig 1. Mini-emulsion procedure representative schematic.

Semiconducting P3HT and PCBM materials were obtained from Lumtec were dissolved into chloroform and then put into SDS aqueous solution (33 mg SDS in 2.8 mL Milli-Q water). The next step was the formation of a macro-emulsion by stirring the solution at 1200 rpm for 1 hour and then sonicating by using a Branson 450 analogue sonifier for 2 minutes to produce a mini-emulsion. After sonication the mini-emulsion was then softly stirred at 1200 rpm whilst heated at 60 °C for a minimum of 4 hours to evaporate the chloroform. A schematic of this process is shown in Figure 1.

The aqueous suspension obtained after evaporation (volume of approximately 2.8 mL) was transferred into the centrifuge dialysis tube purchased from Millipore and centrifuged at 4000 rpm for 7 minutes by using a centrifuge unit Benchtop Hettict Rotofix 32A. This process remains filtrate which collected in the bottom of the tube which can be disposed. The dispersion was then topped up with Milli-Q water until the volume back to its pre-centrifuge volume about 2.8 mL. This action was repeated six times or until a final volume of 0.5 mL was reached. The samples were then placed into pre-cleaned glass vials until they were required for dispersion characterisation or device manufacture. The sample properties were characterized using DLS, UV-Vis, PL, TEM and XPS (with temperature optimization) methods (Yang and Heeger, 1996; De Bettignies *et al.*, 2006; Woo *et al.*, 2008; Millstone *et al.*, 2010; Xie *et al.*, 2010).

RESULT AND DISCUSSIONS

Figure 2(b) shows TEM image of microemulsion nanoparticles synthesised for film and device fabrication. The presence of discrete particles confirming the DLS measurements for these nanoparticles, which showing indication of a z-average diameter for the miniemulsion nanoparticles of 31 nm (Figure 2(a)). Whilst the size of nanoparticle could easily be scaled by altering the concentration of organic materials P3HT:PCBM solutions used in nanoparticle fabrication, this size has been used in this research as it is optimal parameter for the fabrication of organic photovoltaic devices using the method.

Figure 3 shows the UV-Vis spectra for the nanoparticle suspension synthesized by the mini-emulsion processes. The UV-Vis peaks of the dispersion show the typical P3HT-based spectra at 520 nm with a relative size of the P3HT shoulder at about 600 nm indicate the degree of inter-chain ordering and PCBM-based bands at 330 and 260 nm. However, the miniemulsion nanoparticle

suspension showing a significant contribution of larger vibronic band at ~600 nm suggests a more phase segregation combination and/or local order of the P3HT chains in these NPs (Brown *et al.*, 2003).

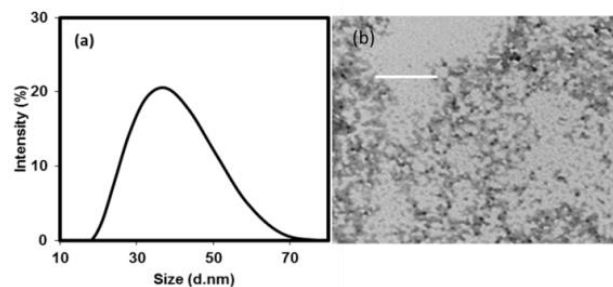


Fig 2. DLS of surfactant-containing P3HT/PCBM nanoparticle (a) TEM image of Surfactant containing (b) A 500 nm scale bar is shown in the TEM image

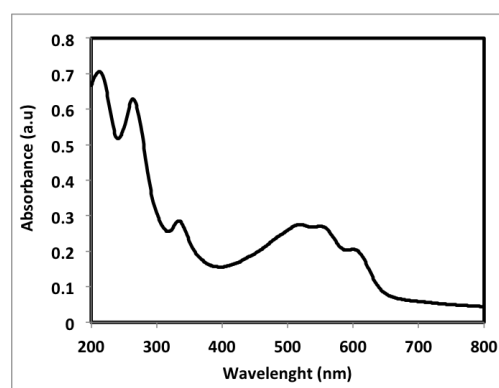


Fig 3. UV-Vis spectra of surfactant-containing P3HT/PCBM nanoparticle suspension.

The photoluminescence peaks in figure 4 are also similar for the nanoparticles and showing the expected 0-0 and 0-1 transitions at approximately 640 and 710 nm respectively (Motaung *et al.*, 2009; Hu *et al.*, 2010; Ulum *et al.*, 2013).

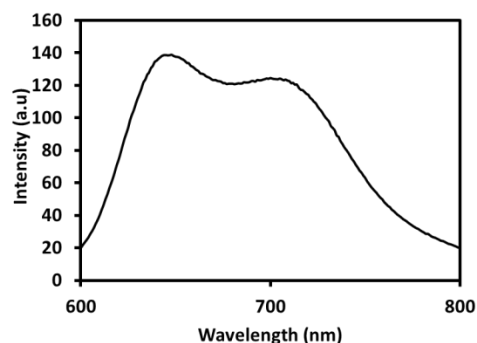


Fig 4. PL spectra for the nanoparticles P3HT/PCBM suspension

Figure 5 shows the XPS spectra of the Na 1s, S 2p, O 1s and C 1s regions for the P3HT:PCBM NP samples, fabricated using the miniemulsion technique, at room temperature and after annealing. The Na 1s signal is present at room temperature (Figure 5a), but disappears from the surface at

elevated annealing temperatures, indicating sodium ions are likely to move away from the surface after annealing. The relative height of the P3HT sulphur signal at 164.0 eV compared to the SDS sulphur signal at 170.0 eV is quite strong even at room temperature (figure 5b), suggesting there is much less SDS on the surface at the room temperature for P3HT:PCBM blend NP film than that for P3HT only NP film. Annealing to 120°C and above there is a little change in SDS sulphur intensity. In contrast, P3HT sulphur intensity increases at the higher annealing temperature suggesting P3HT likely move toward surface region of the P3HT:PCBM NP film. This is also in a good accordance to the rising of the S/C intensity ratio after annealing. The S/C intensity ratio is 0.073 at the room temperature, and increases to 0.091 after annealing to 120°C and 130°C. However, S/C ratio decreases for 0.072 at 140°C sample, followed by a rising in O 1s intensity (Figure 5c) and concurring a high-energy shoulder in carbon 1s (Figure 5d) at this temperature. This C 1s shoulder could be due to C=O contribution from PCBM and, at this annealing temperature some increase of PCBM at the film surface (provided it does not reduce the concentration in the bulk of the film) which provides a better electron transport pathway to the cathode. Therefore, 140°C annealing was ready to be used in the OPV device fabrication.

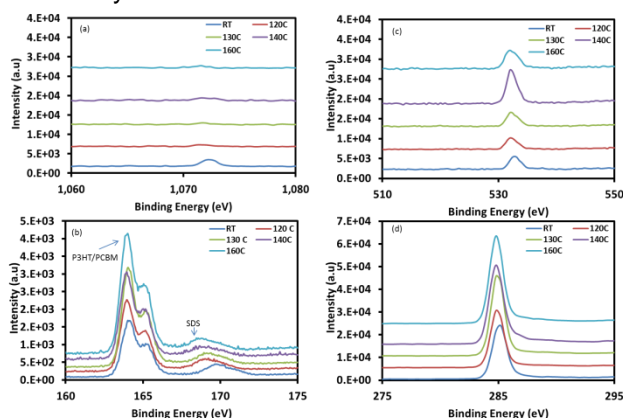


Fig 5. XPS spectra of the surfactant-containing P3HT/PCBM nanoparticle thin films (a) Sodium, (b) Sulphur, (c) Oxygen, (d) Carbon.

With this set XPS experiment, there is much less SDS on the surface of low temperature samples compare to the P3HT samples. Sodium is present at room temperature (Figure 5a), but it moves away from the surface at annealing temperatures of 120°C and above. The P3HT sulphur signal is quite strong even at room temperature and grows with annealing temperature (figure 5b) (Darwis *et al.*, 2011; Shrotriya *et al.* 2005). The SDS sulphur signal is relatively weak, and, like the P3HT sample, appear to shift to lower binding energy with temperature

(figure 5c). The oxygen signal is also weak to start with, but increases at 140°C and decreases again at 160 °C. This oxygen signal relates to PCBM concentration at the surface (Figure 5d). There is a high-energy shoulder in carbon signal at 140°C, which is consistent with C=O contribution from PCBM at the sample surface. However, this is the only C peak to have this shoulder.

CONCLUSION

Taken together, semiconductor nanoparticulate has been synthesised by the used of a surfactant-containing mini-emulsion method using sodium dodecyl sulphate as the surfactant. This method was used to form P3HT/PCBM suspension for fabrication organic photovoltaic devices. This report demonstrated formation and a series of characterization experiments of surfactant containing nanoparticles. The results showing a better way to prepare low cost nanoparticle active layer for organic photovoltaic fabrication.

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