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Water-based high-performance polymer field effect transistors enabled by heat-assisted surfactant elimination

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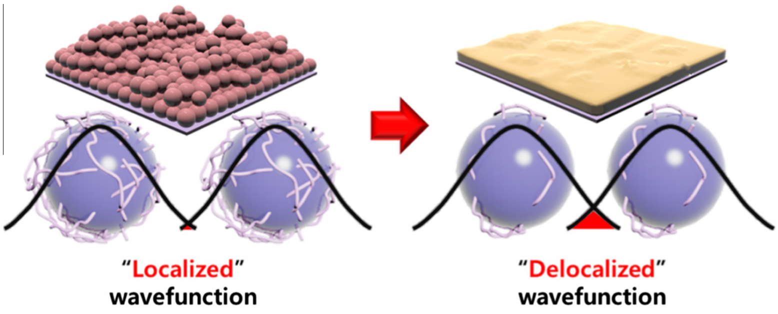
HIGHLIGHTS

- We demonstrate polymer nanoparticle technique for organic electronics.
- Nanoparticle techniques enable green technology.
- High mobility of 0.19 cm^2/Vs is demonstrated from sintering of polymer particle annealed at high temperature.
- X-ray study supports the well aligned ordering of semiconductor in particles by second transition temperature.
- Stable polymer nanoparticles are fabricated by miniemulsion polymerization process.

GRAPHICAL ABSTRACT



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ABSTRACT

Environmentally benign processing technology of polymeric semiconductor is demonstrated to facilitate industrial application of organic electronics. By employing sodium dodecyl sulfate (SDS) as a surfactant and Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT) as a polymeric semiconductor, a water-borne colloid was synthesized and used for forming the active layer of a field effect transistor. Traditionally, this technology was not successful in realizing high charge carrier mobility, owing to difficulties in identifying an optimal temperature for eliminating the surfactant while maintaining the long-range-ordered π–π stacked structure of the semiconductors. In this work, by utilizing the liquid crystalline nature of the PBTTT, we identified the optimal thermal treatment condition (~270 °C), which is sufficient both for eliminating the SDS and stimulating a second phase transition of the PBTTT. As a result, the PBTTT nanoparticle film cast from the water-borne colloid was successfully sintered to form continuously π–π stacked polymeric semiconductor films, whose high charge carrier mobility of 0.19 cm^2/Vs, is comparable to those of organic solvents.

1. Introduction

In recent years, polymeric semiconductors have received significant attention as potential low-cost alternatives to Si-based inorganic semiconductors [1–3]. Polymeric semiconductors are especially well-suited for various opto-electronic applications, owing to multiple inherent merits, such as solution-processability, compatibility with plastic substrates, and ease of large-scale production, most of which cannot be realized by inorganic semiconductors [4,5]. Recent achievements in design and synthesis of novel donor–acceptor co-polymers have produced

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high-performance polymer field effect transistors (PFETs), for example diketopyrrolopyrrole (DPP)- and isoindigo-based copolymers, with unprecedented high charge carrier mobility [6,7]. The development of deposition and patterning techniques such as offset, gravure, inkjet, and screen printing, will also enable the application of polymeric semiconductors to various opto-electronic devices [8].

However, still there is an important but unsolved issue of polymeric semiconductors: the polymeric semiconductor can only be dissolved and be optimized by toxic organic solvents [9]. This results in significant harm to the environment during the production, use, and waste removal stages of these semiconductors. As such, many recent efforts have focused on developing a novel polymer semiconductor that can be processed in eco-friendly solvents. For example, Yun et al. obtained a high-mobility (>5 cm^2/Vs) PFET from a non-chlorinated solvent by applying a random co-polymerization strategy that used DPP-based planar repeating units [10]. They also developed PFETs with charge carrier mobilities of up to 8.2 cm^2/Vs [11], the highest value ever achieved for PFETs processed in non-chlorinated solvents; these PFETs were fabricated by applying a pseudo-regular alternating co-polymer strategy, using an asymmetric monomer. Although the aforementioned achievements are impressive, non-chlorinated solvents (such as tetralin) used in these syntheses, are still toxic organic solvents, as confirmed by their materials safety data sheets and other reports [12].

Another experimental methodology for processing of polymeric semiconductors away from organic solvents is fabricating water-based, aqueous nanoparticles of polymeric semiconductors. For example, Landfester et al. reported the first-ever aqueous semiconducting polymer colloid fabricated via the mini-emulsion process [13]. The aqueous nanoparticles of polymeric semiconductors typically have shown low ($\sim 10^{-3}$ cm^2/Vs) charge carrier mobilities [14]. These low mobilities are attributed to the presence of surfactants (sodium dodecyl sulfate, SDS), between the nanoparticles; these surfactants prevent the overlap of frontier orbitals of pi (π)-conjugated polymeric semiconductors. In other words, SDS has a strong ionic polarity and can therefore inhibit charge transport by acting as either charge trapping centers or dopants; this inhibited transport results in both low charge carrier mobility and on/off ratio of the PFET. Surfactant-free nanoparticles fabricated via the quick-precipitation method resulted in a slightly improved charge carrier mobility of ~0.01 cm^2/Vs [14]. Furthermore, compared to the typical value of $\sim 10^{-3}$ cm^2/Vs, a significantly higher mobility of ~1 cm^2/Vs was realized for an alcohol-based colloid fabricated by using a simple surfactant-free dispersion method [15]. However, these surfactant-free colloids are unstable and become rapidly agglomerated, and hence their use in commercial applications is limited. Developing surfactant-based water-borne colloid technology with surfactant-elimination capability is therefore essential.

Low-molecular weight surfactants have relatively low thermal degradation temperatures (T_{ds}). For example, the SDS has a T_d of <200 °C. As such, high-temperature (>200 °C) thermal annealing may be effective in removing the surfactants present in the films. However, this attempt has never been successful in the case of traditional poly(3-hexylthiophene) (P3HT)-based colloid technique, possibly due to relatively low inherent charge carrier mobility of pristine polymer ($\sim 10^{-2}$ cm/Vs) [16]. Therefore, in this work, we fabricated a water-borne colloid using a liquid–crystalline polymer (Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene]), PBTTT), which is known to undergo a second phase transition at annealing temperatures above 250 °C [17]. At temperatures higher than this second phase transition, the PBTTT film undergoes a smectic-like conformation in which the polymer chains assemble into crystalline nanoribbons, thereby resulting in a high charge carrier mobility [18]. Therefore, by performing high-temperature (>250 °C) annealing, we successfully eliminated the surfactant while maintaining the well-ordered polymer crystalline phase. Various characterization tools were employed to verify the formation of stable water-borne colloids of PBTTT, successful elimination of the SDS after film formation, and effective sintering of the polymer nanoparticles. This elimination resulted in a high mobility PFET (from a water-borne colloid of PBTTT) whose high mobility, ~0.19 cm^2/Vs, is similar to those obtained from organic solvents.

2. Experimental

2.1. Colloid synthesis

In preparation for the mini-emulsion process, 5 mg of PBTTT (purchased from Sigma–Aldrich and used without further purification) were dissolved in 2 mL of chloroform and added to water colloids of a surfactant (50 mg of SDS in 3 mL of DI-water); the chloroform evaporated completely after 1 h of stirring at 90 °C. The prepared water-borne colloid of polymer nanoparticles was then repeatedly (i.e., more than 5 times) washed via precipitation and re-dispersion.

2.2. Device fabrication

The fabricated water-borne colloids of PBTTT were spin-coated onto the Si/SiO_2 substrate to form the thin film. In order to eliminate the SDS, the prepared films were washed by water (dipping for a second) and further annealed at 200 for 30 min or 270 °C for 5 s and then slowly cooled. In addition, the PFET geometry was completed by depositing Au source–drain electrodes onto the annealed films.

2.3. Characterization

Scanning electron microscopy (SEM) images were obtained by using a field emission scanning electron microscope (FE-SEM; Sigma/Carl Zeiss) equipped with a Schottky field emitter. Moreover, thermogravimetric analysis (TGA; TGA-2050, TA Instruments, USA) was performed at a heating rate of 20 °C/min under nitrogen atmosphere. The GIXD measurements were performed using the PLS-II 3C beamline at the Pohang Accelerator Laboratory (PAL) in Korea. Furthermore, Fourier transform infrared spectroscopy (FT-IR) absorbance peaks were acquired using an FTIR 4700 spectrometer (JASCO). The corresponding electrical characteristics of the transistors were measured by using 4156A Precision semiconductor parameter analyzers (Agilent Technologies).

3. Results and discussion

We determined the values of the zeta potential (ζ) after synthesizing colloids of the PBTTT via the mini-emulsion method; a ζ value of ~ -60 mV, which is consistent with values reported for the SDS-based colloids, was obtained by using the electrophoretic light scattering technique. The fabricated colloid remained very stable for more than 3 months. The particle size and distribution of the PBTTT colloid were determined from SEM images (Fig. 1(a)) of the deposited films; the nanoparticles with spherulite shape were typically smaller than 100 nm. In fact, the size distribution of the PBTTT nanoparticles (Fig. 1(b)) revealed an average particle size of ~83 nm. As previously mentioned, selective elimination of SDS surfactants from the films is essential to their use in opto-electronic applications. The corresponding thermal characteristics of the nanoparticles were determined by performing TGA on the PBTTT and the SDS. As the resulting curves show, with onset