

# Blends of polythiophene nanowire/fluorine rubber with multiscale phase separation suitable for stretchable semiconductors



Yun-Chi Chiang<sup>a</sup>, Chien-Chung Shih<sup>a</sup>, Shih-Huang Tung<sup>b,c,\*</sup>, Wen-Chang Chen<sup>a,b,c,\*\*</sup>

<sup>a</sup> Department of Chemical Engineering, National Taiwan University, Taipei, 10617, Taiwan

<sup>b</sup> Institute of Polymer Science and Engineering, National Taiwan University, Taipei, 10617, Taiwan

<sup>c</sup> Advanced Research Center for Green Materials Science and Technology, National Taiwan University, Taipei, 10617, Taiwan

## HIGHLIGHTS

- The blending of P3HT with fluorine rubber creates stretchable semiconductors.
- The charge transporting and the stretchability of the films are both enhanced.
- The unique multiscale phase-separated structures contribute to the performance.

## ARTICLE INFO

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## ABSTRACT

We report an effective approach to prepare stretchable semiconductors by simply blending P3HT nanowires with fluorine rubber. The hole mobility of the field-effect transistors with the blend films as active layers is higher than that of pristine P3HT, and the mobility can maintain over  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  under 100% strain or even after 400 stretching/releasing cycles at 60% strain. The structures of the blend films were probed by TEM, AFM, X-ray diffraction, and polarized UV-vis spectrometry, which was then correlated to the electrical and the mechanical properties of the films. We find that because of the low miscibility between P3HT and fluorine rubber as well as the highly crystalline nature of P3HT, the blends phase separate into unique multiscale structures that can simultaneously enhance the charge transporting capability and the stretchability of the blend films.

## 1. Introduction

Polymeric semiconductors are emerging as a promising material for applications in wearable or deformable electronic devices due to their preferable mechanical resilience in comparison to their inorganic counterparts [1–7]. Numerous studies on stretchable thin film transistors using conjugated polymers as the active layer have been demonstrated [8–11]. Meanwhile, thanks to the substantial progress on the enhancement of carrier mobility in the past few years, conjugated polymers based thin film transistors show an ever-growing possibility for manufacturing of flexible and light-weight electronic devices as used in practice [12–21]. However, the conjugated polymers are rather stiff and brittle comparing to rubbers and plastic polymers [22–25]. Consequently, the mechanical instability of the electronic devices under applied tensile strain is inevitable. It is therefore importance to exploit high performance semiconductors with good mechanical durability able to endure high tensile deformation.

Unfortunately, efficient charge-transport in  $\pi$ -conjugated system strongly relies on their conjugated backbone with well-ordered intermolecular packing [20,26,27]. As known, high crystalline domains in a polymer matrix cause enhancement of film stiffness and brittleness because the rigid grain boundary restrict the strain release through the disordered polymer chains [24]. In this regard, some research groups have designed conjugated polymer with optimized alkyl chains or soft segments in the side chain position to meet the balance between incompatibility of crystallinity and ductility [13,28–31]. However, this approach usually accompanies a deterioration of charge mobility because the long side chains lead to less ordered packing and increase the amorphous regions, which results in inefficient delocalization of  $\pi$ -electrons.

An alternative approach to prepare stretchable semiconductors is to create elastomer/semiconductor blends [32]. The blending of conjugated polymers with insulated polymers have been widely investigated [33–36]. The vertical phase separation in a blend system is

\* Corresponding author. Institute of Polymer Science and Engineering, National Taiwan University, Taipei, 10617, Taiwan.

\*\* Corresponding author. Department of Chemical Engineering, National Taiwan University, Taipei, 10617, Taiwan.

E-mail addresses: [shtung@ntu.edu.tw](mailto:shtung@ntu.edu.tw) (S.-H. Tung), [chenwc@ntu.edu.tw](mailto:chenwc@ntu.edu.tw) (W.-C. Chen).

thought to be necessary to maintain charge carrier mobility because it provides opportunity to form the continuous semiconducting layers [34]. In contrast, if semiconductors are well dispersed in the matrix or the blends form bulk heterojunction structures, the charge current density may be diminished due to the lack of continuous channels for charge transport, thus resulting in a poor mobility. By controlling solvent solubility, surface energy, and substrate wetting conditions, vertical phase separation can be induced during the solution casting process. Recently, several elastomer/conjugated polymer blends have been developed to enhance the endurance of semiconductors under strain [32,37–39]. Although the stretchability of the semiconductors is improved by incorporation of the elastomers, the charge carrier mobility is generally inferior to the pristine conjugated polymer due to the dilution effect. Hence, a new type of morphology in the elastomer/conjugated polymer blends with balanced electrical performance and mechanical properties is highly in demand [40].

Instead of vertical phase separation, we demonstrated in this study that the lateral phase separation of the blend films prepared simply by mixing P3HT with poly(vinylidene fluoride-hexafluoropropylene) (fluorine rubber) can induce local aggregated bundles of P3HT nanowires and create a suitable morphology for stretchable semiconductors. The fluorine rubber is an elastomer with a higher polarity than other common elastomers like PDMS and SEBS [41,42]. The low miscibility between P3HT and fluorine rubber, coupled with the crystallization of P3HT, cause the blends to be highly inhomogeneous, different from the previous studies using other rubbers that show dispersion of conjugated polymer nanofibrils in the rubber matrices [38,39]. The phase-separated structures, electric performances, and charge transport behaviors of the films under varying tensile strains were systematically investigated by TEM, AFM, GIWAXS/GISAXS, and UV-vis spectrometry. We report for the first time that the addition of fluorine rubber into P3HT can effectively improve both the electrical performance and mechanical stretchability of the blend films. The transistors with the blend films as active layers are demonstrated to be more capable of charge transport and more stretchable than those with pristine P3HT films. Such an improvement is closely correlated with the multiscale phase-separated structures in the P3HT/fluorine rubber blends.

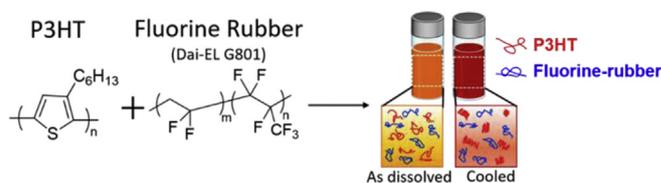
## 2. Experimental section

### 2.1. Materials

Poly(3-hexylthiophene-2,5-diyl) ( $M_w$ : 48k, PDI: 4.53) was purchased from Lumtec (Taiwan) and fluorine rubber (DAI-EL G-801) was purchased from Daikin (Japan), respectively. Anhydrous tetrahydrofuran (THF) was purchased from Sigma-Aldrich (U.S.A.). All the materials were used directly without further purification.

### 2.2. Sample preparation and structure characterization

To prepare the blend films with P3HT nanowires, P3HT and fluorine rubber were first dissolved in THF, a solvent of good miscibility with both P3HT and fluorine rubber. After completely dissolved, the solution was slowly cooled down to room temperature, and then stored in the refrigerator at 4 °C overnight, which facilitated the formation of self-assembled nanowires (Scheme 1). The solution exhibits brown color after the cooling process as shown in Fig. S1 of the Supporting Information. The blend films cast from the solutions were named as  $F_x$ -P3HT $_y$ , where  $x$  is the concentration of fluorine rubber and  $y$  is the concentration of P3HT in the solutions, both in the unit of  $\text{mg mL}^{-1}$ . Transmission Electronic Microscope (TEM) images were collected by a JEOL 1230 at acceleration voltage set at 100 kV with thin films prepared on the carbon-supported grids. Surface morphology of thin films was probed by atomic force microscope (AFM) in tapping mode under ambient atmosphere via the Bruker, Innova system. The spring constant of the cantilevers (Nanosensor PPP-NCHR) was  $\sim 42 \text{ N m}^{-1}$  and the



**Scheme 1.** Illustration of the preparation of P3HT and fluorine rubber blends. Temperature-dependent solubility was controlled to induce the self-assembly of P3HT chains into nanowires before film casting.

resonant frequency was  $\sim 330 \text{ kHz}$ . UV-vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer with the wavelength range from 300 to 800 nm. For polarized UV-vis spectroscopy, a rotational polarizer was introduced to measure the absorption with the polarized incident light parallel or perpendicular to the stretching direction. The dichroic ratio ( $R$ ) of thin films were calculated as  $R = A_{\parallel}/A_{\perp}$ , where  $A$  is the absorption intensity at 555 nm. Grazing-incident small-angle and wide-angle X-Ray scattering (GISAXS and GIWAXS) for thin films were carried out on beamline 23A1 and beamline 13A1 in National Synchrotron Radiation Research Center (NSRRC), Taiwan, with monochromatic beams of wavelength  $\lambda = 0.82656 \text{ \AA}$  and  $1.0227 \text{ \AA}$ , respectively. The incident angle was set at  $0.12^\circ$  for both experiments and the scattering intensities are reported as intensity versus  $q$ , where  $q = (4\pi/\lambda) \times \sin(\theta/2)$  and  $\theta$  is the scattering angle.

### 2.3. Fabrication and characterization of field-effect transistors

Field-effect transistors were fabricated with a bottom-gate/top-contact configuration. A 300 nm  $\text{SiO}_2$  layer with capacitance per unit area =  $10 \text{ nF cm}^{-2}$  as gate dielectric was thermally grown onto the highly n-type doped Si (100) substrates. The substrates were modified with an octadecyltrimethoxysilane (ODTS) self-assembled monolayer according to the reported method [43]. The polymer thin films were spin-coated onto modified  $\text{SiO}_2/\text{Si}$  substrates, and a post-annealing process at 150 °C under vacuum for 30 min was consequently introduced to promote the molecular packing that enhances the resultant FET performance. The top-contact source/drain gold electrodes with thickness of 65 nm were thermally evaporated through a regular shadow mask, with the channel length ( $L$ ) and width ( $W$ ) being 50 and 1000  $\mu\text{m}$ , respectively. For the measurements of the electrical characteristics of the stretched thin films, the thin films were spin-cast on ODTS-modified silicon substrate first, followed by transferred onto PDMS slabs (15:1 base to cross-linker by mass ratio) where the films are stretched to desired strain level. The stretched thin films were transferred again from PDMS slabs back onto silicon substrates for transistor fabrication and characterization.

## 3. Results and discussion

### 3.1. Phase-separated structures of blend films

P3HT nanowires and their distributions in thin films before and after blending with fluorine rubber were observed by TEM. In the case of pristine P3HT (Fig. 1a), the TEM image shows randomly distributed nanowires with lengths around several hundred nanometers. After blending with fluorine rubber at a weight ratio of 1:4 ( $F_1$ -P3HT $_4$ ), the fluorine rubber-rich phases with lower electron density form the light, round domains randomly dispersed in the matrix consisting of bundled P3HT nanowires (Fig. 1b). The P3HT-rich domains remain continuous throughout the sample even when the weight fraction of fluorine rubber increases to be equal to that of P3HT, as shown in Fig. 1c for  $F_4$ -P3HT $_4$  film. The smaller black circular domains that generally locate on the edges of the light areas (Fig. 1b and c) should also be the fluorine rubber-rich phases but with larger film thickness, which are formed possibly due to the dewetting of the solution during solvent

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