Locking the morphology with a green, fast and efficient physical cross-linking approach for organic electronic applications

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A B S T R A C T

Molecular packing and stability play crucial roles in determining the performance of organic electronic devices. To optimize the morphology of active layer, thus to improve the performance, especially the stability of devices, cross-linking technique is a viable approach that has been extensively applied to stabilize the morphology. In this work, we demonstrate a green, fast and efficient physical approach using hyperthermal hydrogen induced cross-linking (HHIC) to lock the morphology of organic electronic materials. By controlling the kinetic energy of the hyperthermal hydrogen (H_2) molecules, we can efficiently cleave the C−H bonds and induce cross-linking in a conjugated polymer. The cross-linking can be achieved in 1 min at room temperature, and the cross-linked films have excellent thermal stability and high resistance to organic solvents. Organic field effect transistors fabricated with HHIC treated poly (3-hexylthiophene) (P3HT) has comparable charge carrier mobility and superb stability than the untreated devices. Compared to the conventional chemically driven cross-linking approach, HHIC does not require additional modification in molecular structure, and the fast and non-destructive advantages have high potential for wide applications of highly stable organic electronic devices.

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1. Introduction

Organic electronics, such as organic light emitting diodes (OLEDs) [1,2], organic photovoltaics (OPVs) [3–6], organic field effect transistors (OFETs) [7–10], etc., have attracted tremendous research attention due to its high performance and ease of fabrication on light weight and flexible substrate by low-cost solution processes [11–16]. For OPV, the highest power conversion efficiencies (PCEs) have exceeded 11% [17–20] for multi-junction and 10% [21] for single junction based devices in favor of the development of new materials and device architectures. Despite of the encouraging high efficiency, one of the major challenges for commercializing polymer solar cell is the long-term operation stability [22–24]. The morphological stability in OPVs becomes a concern in the applications with long time exposure under direct sunlight. Similarly, for OFETs, which have

recently been demonstrated in various sensing applications [25,26]. The active organic materials are often to be exposed to different gases and solutions. Typically, those reactants and sensing environment have detrimental effect on the organic materials. So far, the reported high performance OFET sensors are fabricated with specially designed organic materials which have both excellent stability and carrier mobility.

Concerning the stability issue, it is worth noting that the optimized morphology of organic materials in devices might not in thermal equilibrium and is unstable over time during thermal stress. In order to solve this issue, considerable efforts have been devoted to improve the thermal stability of organic electronic materials, including addition of morphology stabilizer [27], development of cross-linkable fullerene and conjugated polymers [28]. The approach of in-situ chemical cross-linking of BHJ blend films had shown significant enhancement of morphological stability. For instance, Kim et al. [29] demonstrated stable OPV devices over two days heating at 150 °C based on cross-linkable bromine-functionalized poly (3-hexylthiophene) (P3HT-Br) polymer. Thereafter,

Chen et al. [30] reported a cross-linkable reaction using open-cage fullerenes as additives in the active layer to slow down phase separation rate of fullerenes, thus to enhance the thermal stability of the OPV devices. However, these conventional cross-linking approaches require additional chemical processes to modify the molecular structure, and the cross-linking reactions are either triggered by long time thermal annealing or under intense ultraviolet light irradiation. Therefore, a green, fast, and non-destructive cross-linking alternative would have high potential for the development of low-cost and long-term stable organic electronic devices.

Recently, a physical cross-linking approach named hyperthermal hydrogen induced cross-linking (HHIC) have been demonstrated [31—33]. Briefly, protons generated from hydrogen plasma are extracted and accelerated by an electric field to an appropriate kinetic energy. Then the accelerated protons enter into a drift zone and collide with hydrogen molecules. The cascades of collisions generate a high flux of hyperthermal molecular hydrogen, which is a flux many times larger than the flux of protons extracted from the hydrogen plasma. The nominal flux ratio of hyperthermal molecular hydrogen to proton is controlled by the hydrogen pressure in the drift zone, and by the length of the drift zone. Without having to modify the molecular structure, neutral hyperthermal hydrogen (H_2) molecules are used to bombard the organic precursors and induce cross-linking reaction in organic thin films. It has been demonstrated that by controlling the kinetic energy of the H_2 projectile one can selectively break the C—H bond and facilitate the cross-linking reaction without altering the conjugated backbone and therefore the opto-electrical properties.

In this work, we demonstrate using HHIC to initiate fast cross-linking reactions in semiconducting conjugated polymer thin films. Our results show that, after the HHIC treatment, both the morphological thermal stability and solvent resistivity have been significantly improved in both pristine and blended films using poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). There is no observable aggregation of the organics even after annealing at 150 °C for 3 h. An OFET with HHIC cross-linked P3HT has achieved comparable carrier mobility and significant improvement in long-term stability. This demonstrates that the HHIC as a viable general approach to facilitate non-destructive and efficient cross-linking for organic electronic materials.

2. Experimental section

2.1. Cross-linking film preparation

Highly-doped p-type silicon (Si) wafer with a 300 nm thick thermally grown SiO_2 layer was immersed into a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) (7:3 in volume) for 20 min and rinsed with deionized (DI) water thoroughly. The cleaned substrate was dried by high purity nitrogen gas and UV O-zone treated for 20 min and then transferred into a nitrogen filled glovebox for organic film deposition. The precursor solution of pristine P3HT (17 mg/ml), P3HT:PCBM (1:1 in weight ratio, 34 mg/ml) and pristine PCBM (17 mg/ml) were dissolved in anhydrous chlorobenzene (CB) and spin-coated on pre-cleaned Si substrate at 1000 rpm for 40 s. Finally, the films were transferred into the HHIC system for cross-linking treatment.

2.2. Thin film transistor fabrication

Thin film transistors were fabricated using a bottom gate configuration. Sample substrate and the active layer fabrication process were the same as those depicted in Cross-linking film preparation Section for both with and without HHIC treated films. Au source and drain electrodes were thermally deposited on top of the organic active layer from a shadow mask, forming a channel length of 50 μm and channel width of 6 mm. Field effect mobility was extracted from the saturation region using the standard equation of $I_D = \mu(W/2L)V_i(V_G - V_T)^2$, where I_D is the drain current, μ is the field effect mobility, $L = 50$ μm is the channel length, $W = 6$ mm is the channel width, C_i is the capacitance of the gate insulator per unit area, V_G is the gate voltage and V_T is the threshold voltage. In order to have a statistical comparison of the extracted mobility values, four devices were made with both treated and untreated P3HT thin film.

2.3. Film characterization

UV—vis absorption spectra were measured with a UV—Visible spectrometer (Lambda 750). An optical microscopy was used to study the morphology evolution of the film under 150 °C with different annealing times. Fourier transfer infrared (FTIR) measurements of untreated and HHIC treated films were investigated by FTIR (Nicoletis10, Thermo Fisher Company, USA) in the range of 4000—400 cm^{-1} under ATR mode.

3. Results and discussion

Fig. 1 shows the UV—vis absorption spectra of HHIC treated P3HT films using different H_2 projectile acceleration voltages ((a) 100 V, (b)150 V, (c) 200 V, and (d) 250 V) for 1 min. The acceleration voltage is used to control the kinetic energy of the H_2 molecules, which has direct impact on the cross-linking efficiency. The higher the acceleration voltage, the longer the mean-free path of the H_2 molecules to facilitate cross-linking inside the bulk of the organic thin films. As shown in Fig. 1, the P3HT films treated with different voltages have the same vibronic features, which suggests that there is no significant modification on the π-π configuration of the P3HT films after the HHIC treatment. As P3HT is highly soluble in chlorobenzene (CB), any uncross-linked polymer can be easily washed away. To investigate the cross-linking efficiency with different voltages, we simply washed the HHIC treated films by dropping CB on top of the film for 10 s and then spinning the film at 1000 rpm for another 40 s. As shown in Fig. 1a, after washing (dashed line), the optical intensity of the film treated at 100 V was significantly reduced, which implies that only a small portion of the P3HT was cross-linked. On the other hand, the cross-linking efficiency becomes higher with higher treatment voltages. As shown in Fig. 1d, the film treated with 250 V has almost the same optical intensity before and after CB washing, which suggests a complete cross-linking reaction in P3HT. This can also be seen from the optical images as shown in Fig. S1. The HHIC treated P3HT film has no notable changes after washing by CB (Fig. S1d). On the contrary, the film without HHIC treatment was washed away thoroughly (Fig. S1c) and these are consistent with the absorption spectra as shown in Fig. 1. It should be noted that the HHIC process is very fast with only 1 min processing time compared to other chemically initiated cross-linking approaches. And the same vibronic features and high solvent resistance from the UV—vis results indicates the HHIC process is non-destructive with respect to the conjugation system of the semiconducting organic materials.

We sought to further investigate the impact of HHIC treatment on P3HT vibrational features by Fourier transform infrared spectroscopy (FTIR). As shown in Fig. 2, The HHIC treated film resembled the key vibrational peaks in P3HT [34]. Particularly, the peak at 1456 cm^{-1} represents the symmetric ring stretching mode, and the peak at 1507 cm^{-1} represents the anti-symmetric C=C stretching mode. It has been reported that the conjugation length along the