Polymer-Chain Aggregation-induced Electrical Gating at the H- and J-aggregate P3HT

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Abstract: This research explores how aggregation influences the electrical behavior at both the planar - heterojunction poly(3-hexylthiophene) (P3HT)/SiO2 and P3HT/ZnO nanocrystal (NC) interfaces. The formation of H- and J-type aggregates leads to distinct molecular ordering and packing structures, manifesting as changes in threshold voltage shifts (electrical gating) as well as absorption and luminescence properties. Ultrasound irradiation (sonication) significantly alters the molecular arrangement in P3HT, favoring the formation of H-aggregates over the typically formed J-aggregates. In pristine P3HT, J-aggregates facilitate efficient exciton movement and electrical generation, resulting in higher photocurrents compared to sonicated-P3HT, which predominantly forms H-aggregates. Field-effect transistors (FETs) based on sonicated P3HT exhibit a more positive threshold voltage and increased mobility, indicating the presence of more mobile charge carriers, even in the absence of an applied voltage. In interfaces with ZnO NC, pristine P3HT demonstrates a considerable shift in threshold voltage under illumination, attributed to electron trapping. Conversely, sonicated P3HT interfaced with ZnO NC shows less electron trapping and minimal change in threshold voltage. This study underscores how the type of aggregate (H or J) in P3HT significantly dictates light-induced electrical gating. Ultrasound irradiation (sonication), while enhancing mobility by improving crystallinity, leads to a decrease in photocurrent efficiency in H-aggregates compared to the J-aggregates present in pristine-P3HT.

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1. INTRODUCTION

In the realm of organic electronics, the ability to manipulate material properties to achieve desired electronic behavior is a pivotal aspect of research and development. Among the various organic semiconductors, poly(3-hexylthiophene) (P3HT) has gained significant attention thanks to its promising applications in field-effect transistors (FETs)[1-4]. The performance of P3HT-based FETs is largely influenced by the microstructural arrangement of polymer chains within the device, which dictate key characteristics such as charge mobility and threshold voltage[4-6].

Recent studies have emphasized the role of external stimuli, such as mechanical or ultrasonic agitation, and their influence on the physical properties of polymer semiconductors. Spano et al. reported that conjugated polymer aggregates display two main electronic interactions: intrachain (within chains) leading to J-aggregate behavior, and interchain (between chains), resulting in H-aggregate behavior[5]. This dichotomy influences the photophysics of polymer films, as understood through the concepts of J- and H-aggregation. The balance between these intrachain and interchain interactions shapes the photophysical properties of common conjugated polymers like polythiophenes, phenylene-vinylenes, and polydiacetylenes, affecting their absorption and photoluminescence characteristics. Alam et al. reported that blended films of poly(butyl acrylate)-grafted cellulose NCs and poly(3-hexylthiophene) (P3HT) exhibited enhanced photoluminescence and longer emission lifetimes compared to pure P3HT. These blends showed a shift from H-aggregate...
to J-aggregate behavior, indicated by increased molecular planarity and the reduced highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gaps. Molecular dynamics and density functional theory calculations supported these structural changes[7].

Baghgar et al. reported studies using photoluminescence imaging techniques on isolated P3HT nanofibers, spanning molecular weights from 10 to 65 kDa, revealing a shift in exciton coupling[8]. Nanofibers of lower molecular weight predominantly showed interchain (H-aggregate) coupling, whereas those with higher molecular weight demonstrated intrachain (J-aggregate) coupling. This transition was attributed to the folding of polymer chains within the lamellae, as indicated by transmission electron microscopy nanofiber width measurements, leading to increased planarity of the chains and a decrease in torsional disorder.

Sonication has become a key technique in studies exploring the relationship between the structure and electrical properties of conducting polymers[9,10]. It’s increasingly recognized for its ability to modify polymer microstructures, thereby optimizing electrical properties for applications in optoelectronics. Aiyar et al. reported the application low-intensity ultrasound to regioregular P3HT solutions to enhance the crystallinity of spin-coated thin films, with field-effect mobilities reaching 0.03 cm²V⁻¹s⁻¹[11]. This technique induces π-stacking in P3HT, resulting in a multiphase morphology and distinct charge transport behavior, where mobility initially increases sharply with crystallinity and then plateaus. Kim et al. developed a method to assess charge transfer in an aluminum-doped ZnO/P3HT structure, finding that sonication of P3HT enhances charge transfer efficiency at the interface, critical for optoelectronic device performance[9]. This efficiency was linked to improved polymer chain arrangement, leading to reduced contact resistance and better charge carrier mobility.

Although there has been significant research on modifying electrical properties through sonication, the precise effects of sonication on the electrical behavior of P3HT FETs, especially at the heterojunction interface under both dark and illuminated conditions, have not been thoroughly investigated.

This study aims to bridge this gap by investigating the impact of ultrasound irradiation (sonication) on the electrical gating caused by the aggregation behavior of polymer chains in P3HT and its subsequent influence on the electronic properties of FETs. Our research focuses on elucidating the mechanisms behind these changes, specifically examining the interplay between sonication-induced aggregation, carrier concentration, and interchain interactions. Furthermore, we explore how these alterations in microstructural properties translate to changes in the electrical characteristics of P3HT FETs, with a particular emphasis on electrical gating at the homo and heterojunction interface in the dark and under illumination. The sonication process results in the formation of dense clusters or structures within the polymer chains, which significantly alters the electrical properties of the transistors.

A key observation from this study is the shift in the threshold voltage of the transistor towards a higher, more positive value, suggesting that the concentration of charge carriers in the transistor can be fine-tuned by managing the interchain interactions. This phenomenon is comprehensively analyzed through structural and optical characterizations, including grazing incidence X-ray diffraction (GIXD), photoluminescence (PL), and optical absorption measurements. These techniques help in understanding how altering the interchain interactions in P3HT can effectively control the activation behavior of the transistor, as indicated by changes in the threshold voltage.

2. MATERIALS AND METHODS

2.1 Formation of ZnO NC film.

To synthesize ZnO nanocrystals (NCs), 1.097 grams of zinc acetate dihydrate was first dissolved in 93.75 milliliters of ethanol, and this mixture was then stirred at a temperature of 60°C for a duration of one hour. Simultaneously, in a separate setup, 0.9687 grams of tetramethylammonium hydroxide pentahydrate (TMAH) was dissolved in 4 milliliters of ethanol at room temperature, after ensuring the container was securely sealed with para-film to prevent the evaporation of the solvent. Once an hour of stirring was completed, the TMAH solution was gradually added to the zinc acetate solution over a period of 15 minutes, maintaining a consistent temperature of 60°C. Following the completion of this addition, the mixture was sustained at 60°C for an additional 30 minutes and then allowed to cool naturally to
room temperature. For storage, the resulting solution was refrigerated at approximately 5°C. Later, for the purposes of device fabrication, the chilled solution was mixed with 30 mL of hexane and centrifuged at 9000 rpm for 10 minutes. The entire procedure was executed in an environment with standard air conditions.

2.2 FET Fabrication and Measurement.

To assess charge transport in the P3HT layers near the SiO$_2$ interface and to study exciton dissociation at the P3HT/ZnO NC interface, a bottom-contact FET configuration was utilized. This setup involved the fabrication of source and drain electrodes, made of an 80 nm thick gold (Au) layer atop a 3 nm titanium (Ti) layer, patterned photolithographically onto a SiO$_2$ gate dielectric with a thickness of 200 nm. A heavily doped silicon substrate functioned as the gate electrode.

To produce a film from sonicated P3HT, the polymer solution underwent a sonication process at 1500 rpm for one minute, followed by an extended 30-minute sonication in an ice bath. This procedure led to a visible transformation in the P3HT solutions, altering their color from a transparent red to a deeper, dark wine shade, a change attributed to the sonication-induced aggregation of the polymer chains. To safeguard the integrity of both the pristine and sonicated P3HT films against oxidation, a protective encapsulation was employed. This was accomplished by sealing the films beneath a glass slide, utilizing a method that involves the careful application of adhesive tape to ensure a robust and effective seal.

The P3HT solutions, prepared in concentrations of 10 mg/mL, were applied onto the SiO$_2$ gate dielectric using a spin-coating technique. To facilitate molecular ordering within the P3HT films, these solutions were sonicated in a chilled water bath for a duration of 30 minutes. For experiments focusing on the photoinduced charge transfer at the P3HT/ZnO interface, a thin film of ZnO NCs, roughly 7 nm thick, was deposited before applying the P3HT layer.

The FET's characteristics were examined using an HP4145B semiconductor parameter analyzer. A green laser diode, emitting at a wavelength of 530 nm and providing a power density of 5 mWcm$^{-2}$, was employed for illumination purposes during FET testing. This specific wavelength was chosen to selectively excite the P3HT films while mitigating the UV-induced conductivity enhancement often seen in the ZnO layer. All electrical measurements were meticulously conducted in an argon-filled glove box to maintain a stable environment.

2.3 Determination of Threshold voltage

In the linear operating regime, the drain current ($I_D$) of the FET exhibits a direct proportionality to the drain-source voltage ($V_D$), as shown in Eq. The drain current can be mathematically formulated considering several factors: the mobility of holes ($\mu$), the capacitance per unit area at the semiconductor/gate insulator interface ($C_i$), and the dimensions of the device, specifically its width ($Z$) and length ($L$).

$$I_D = \frac{Z}{L} \mu C_i (V_G - V_T) V_D$$

The threshold voltage ($V_T$) is a crucial parameter in FETs, representing the minimum gate voltage required to accumulate a sufficient number of mobile carriers within the channel to enable conduction. Once this threshold is surpassed, the magnitude of the drain current follows a specific relationship, as outlined in the Eq. In the linear operating regime of an FET, the threshold voltage can be accurately determined by analyzing the transfer characteristic curve of $I_D$ versus gate voltage ($V_G$). Specifically, the threshold voltage is identified at the point where the extrapolated line of the curve intersects the y-axis (drain current axis) at zero. This intersection point provides a direct measure of the gate voltage needed to initiate significant current flow in the device, marking the transition from the off-state to the active conduction state of the FET.

3. RESULTS AND DISCUSSION

In Fig. 1(a), a comparison of absorption peaks between sonicated and pristine P3HT reveals a higher $A_{0.0}/A_{0.1}$ ratio for the pristine P3HT. Upon sonication, there is a red shift in the absorption peak, indicative of H-aggregate formation [8,12,13]. This phenomenon is more evident in the PL spectra shown in Fig. 1(b), which highlights the impact of aggregation on luminescence[14,15]. The diminished PL intensity following sonication confirms the formation of
interchain species, specifically H-aggregates, which lead to non-emissive excitons.

The type of aggregates formed in P3HT significantly influences both the threshold voltage and mobility. As depicted in the $I_D$-$V_G$ curve in Fig. 2, the charge transport properties of the sonicated and pristine P3HT differ markedly. The field-effect transistor (FET) mobility ($4.5 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$) in sonicated P3HT was substantially higher than in pristine P3HT ($2.6 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$). Notably, the threshold voltage in the sonicated P3HT (2 V) was more positive than that (-9 V) in the pristine P3HT, suggesting an increase in the presence of mobile carriers even at zero gate voltage. This enhanced mobility can be attributed to differences in crystallinity and stronger polymer chain interactions in the sonicated P3HT, leading to an extended effective conjugation length, as corroborated by absorption spectroscopy, which will be discussed later.

Sampling measurements ($I_D$-time plots) under illuminated and dark conditions revealed distinct photocurrent behaviors attributable to different aggregate types.

Under illumination, the drain current in pristine P3HT (J-aggregate) increased fivefold, as seen in Fig. 3. In contrast, sonicated P3HT (H-aggregate) showed only a twofold increase in drain current, considerably less than that observed in pristine P3HT. Intriguingly, for both samples, the drain current continued to rise gradually after the light was switched on, and maintained this increase until the light was turned off. This gradual increase in drain current upon illumination in both pristine and sonicated P3HT can be ascribed to their photoconductive properties, influenced by the respective aggregate types, which will be discussed later.

The electrical gating effects resulting from H- and J-type aggregates, differentiated by their PL spectra, as shown in Fig. 4(a), are depicted at the heterojunction interface in Figs. 4(b) and 4(c). In the pristine-P3HT/ZnO (J-type) system (Fig. 4(b)), the drain current increased with an 8 V shift in the threshold voltage. Conversely, in the sonicated P3HT (H-type) (Fig. 4(c)), a high drain current in the dark remained relatively unchanged upon illumination, maintaining the same threshold voltage, and the photocurrent (red) increase was negligible.

In the experiments illustrated in Fig. 5, a marked difference in photocurrent response was observed between pristine P3HT on ZnO and sonicated P3HT on ZnO when subjected to high-intensity green laser illumination. Specifically, pristine P3HT on ZnO demonstrated a substantial increase in current upon exposure to light, whereas the sonicated P3HT
on ZnO exhibited only a minimal current increase under the same lighting conditions.

Additionally, both types of samples showed a gradual increase in current when the light was turned on and a corresponding gradual decrease when the light was turned off. This behavior aligns with the observations made in Fig. 3 for samples without ZnO, indicating a consistent photocurrent response pattern regardless of the presence of the ZnO layer. This gradual change in current upon light activation and deactivation reflects the photoconductive properties of the materials and their response to changes in illumination.

Sonication led to the formation of H-aggregates in P3HT,
as evidenced by the red shift in the absorption peak in Fig. 1(a). This is contrasted with the higher $A_{0,0}/A_{0,1}$ ratio observed in pristine P3HT in Fig. 1(b), indicating a dominance of $J$-aggregates. The PL intensity decreased after sonication, suggesting the formation of non-emissive interchain species (H-aggregates) in Fig. 1(b). This is in contrast to the behavior of pristine P3HT, where $J$-aggregates are more emissive. Upon illumination, pristine P3HT ($J$-aggregate) showed a larger increase in drain current compared to sonicated P3HT (H-aggregate). The slow increase in drain current upon illumination in both samples in Fig. 3 is attributed to the generation and recombination dynamics of charge carriers, as well as trapping/de-trapping mechanisms[16,17].

The observed lack of immediate current recovery in P3HT samples post-illumination can be attributed to persistent photoconductivity, where excited charge carriers take time to recombine or become trapped within the material. Charge trapping, slow recombination kinetics, and potential thermal effects from the illumination may also play a role. Additionally, photoinduced changes in the material's properties and hysteresis effects could cause sustained deviations from the original current levels even after the light source is removed. These combined factors result in a current that does not immediately revert to the pre-illumination level.

When light is shone on a semiconductor material like P3HT, it can excite electrons from the valence band to the conduction band, creating electron-hole pairs. This process increases the conductivity of the material, leading to an increase in the drain current. P3HT can form different types of aggregates, notably $J$-aggregates and $H$-aggregates, as observed in Fig. 1. These aggregates have distinct molecular packing and electronic structures. $J$-Aggregates (pristine P3HT) typically show strong intramolecular interactions, which can lead to a more significant increase in photocurrent upon illumination. $H$-Aggregates, typically characterized by strong interchain interactions, can lead to the "quenching" or neutralization of excitons by polarons, which are charged particles within the material. This process effectively reduces the efficiency of exciton-based charge transport. As a result of this quenching mechanism, there is a diminished increase in photocurrent. The close packing of molecules in $H$-aggregates facilitates these interactions between excitons and polarons, thereby impacting the material's photoconductive properties and leading to a less pronounced photocurrent response when illuminated.

When the pristine P3HT is deposited on ZnO, as shown in Fig. 4 and 5, the negatively charged ZnO surface can attract positive charges (hole polarons) away from the P3HT[18,19]. This means that there are fewer polarons in the pristine P3HT to quench the excitons, leading to higher efficiency (or higher photoluminescence quantum yields). In other words, the P3HT chains in the pristine P3HT films don't pack too tightly together. Conversely, in the case of sonicated-P3HT on ZnO, there is evidence of strong interchain interactions, which is in line with the smaller d-spacing observed compared to pristine P3HT.

This observation is clearly consistent with the change in the d-spacing, which represents the distance between molecular chains in the crystalline structure of the polymer, from GIXD shown in Fig. 5. The d-spacing decreased from 16.81 to 16.24 Å after sonication. In both scenarios, whether

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Fig. 6. GIXD patterns for pristine and sonicated P3HT films (a) without and (b) with ZnO NC films as the substrate layer.
with (Fig. 5(b)) or without ZnO (Fig. 5(a)), the $d$-spacing in sonicated P3HT was found to be smaller than that in pristine-P3HT, as shown in Fig. 5(a) and Fig. 5(b). This reduced $d$-spacing in the sonicated samples indicates closer packing of the polymer chains by strong interchain interactions, which is characteristic of the formation of H-aggregates. Such dense packing can facilitate stronger interchain interactions, influencing the electronic and optical properties of the material, particularly in terms of charge transport and photovoltaic efficiency.

The gradual increase in current, following an initial sharp rise due to band-to-band photoconduction after the light is turned on, could be attributed to multiple factors. Initially, the rate of generation of charge carriers (electrons and holes) may be higher than their recombination rate, leading to a gradual increase in current. In semiconducting polymers like P3HT, there can be traps for charges, which can temporarily hold the charges before they contribute to the current. Over time, more charge carriers might be released from these traps, contributing to the slow increase in current. After light off, the current slowly decreases due to a dominant recombination process.

The increased current magnitude observed in sonicated P3HT/ZnO, as depicted in Fig. 3, relative to pristine P3HT/ZnO, can be linked to improved molecular ordering in the sonicated samples. This enhanced ordering is evidenced by the GIXD results presented in Fig. 5. In these GIXD patterns, the peaks corresponding to the sonicated P3HT are not only sharper but also display greater intensity. The sharper and more intense peaks in the GIXD pattern of the sonicated P3HT indicate a higher degree of crystallinity and more ordered molecular arrangement. Such structural ordering can facilitate more efficient charge transport pathways within the material. The closer packing and alignment of the polymer chains in the sonicated P3HT likely contribute to improved electrical conductivity, resulting in the observed increase in current when interfaced with ZnO. This correlation between molecular ordering, as demonstrated by GIXD, and the electrical performance of the material underscores the significant impact of sonication on the microstructural properties of P3HT and, consequently, its electronic behavior in a device context.

The observation of a more positive threshold voltage in sonicated P3HT FETs is attributed to an increase in the presence of mobile carriers that fill the deep traps within the material. This phenomenon is the basis for the slow increase and decrease in current observed upon the switching on and off of light, respectively, as demonstrated in the $I$-$t$ measurements in Figs. 3 and 5. Once these deep traps are filled with mobile carriers, particularly holes, the threshold voltage shifts towards a more positive value. Consequently, the transistor becomes operational at zero gate voltage.

In the pristine P3HT/ZnO FET, despite exhibiting a smaller drain current compared to its sonicated counterpart, there is a distinct shift in the threshold voltage. This shift is attributed to the trapping of excited electrons at the P3HT/ZnO interface, which results in the bending of the P3HT energy levels upwards, thereby causing the threshold voltage to shift to a more positive value. In other words, the LUMO and HOMO energy levels of P3HT are elevated at the ZnO side due to photoinduced electron transfer from P3HT to ZnO, leading to hole accumulation in P3HT adjacent to the ZnO. This results in the shifting of the threshold voltage of the P3HT FET to a more positive value, even without applying a gate voltage. Under illumination, the change in threshold voltage ($\Delta V_T$) in the linear operating regime of the transistor is directly proportional to the number of separated carriers at the interface ($\Delta n$), as described by the equation $\Delta n = C_i \Delta V_T/q$. This finding implies a higher efficiency of exciton dissociation at the interface with pristine P3HT.

Conversely, in the sonicated P3HT/ZnO FET, excitons are predominantly quenched within the sonicated P3HT layer, which is relatively distant from the P3HT/ZnO interface. This spatial separation of exciton quenching sites from the interface prevents any significant shift in the threshold voltage in the sonicated P3HT/ZnO FET. In other words, the number of electrons are significantly reduced due to quenching, decreasing the concentration of mobile holes in the P3HT, causing negligible change in the threshold voltage of the sonicated P3HT/ZnO FET in Fig. 4(c). Essentially, the interaction between the sonicated P3HT and the ZnO layer is different from that in the pristine P3HT/ZnO system, leading to varied electronic behaviors in these two configurations, particularly with respect to the threshold voltage and the response to light illumination.
4. SUMMARY AND CONCLUSIONS

Our research delves into the profound effects of aggregation on the electronic behavior of P3HT, both in its standalone configuration and when combined with ZnO to form a planar-heterojunction structure. The study emphasizes the role that aggregation has on electrical gating at the planar-heterojunction interfaces of P3HT/SiO$_2$ and P3HT/ZnO NC. We discovered that $H$- and $J$-type aggregation significantly alters molecular ordering and packing within P3HT, leading to notable shifts in threshold voltage and changes in absorption and luminescence properties.

Sonication, a key focus of our study, modifies the molecular alignment in P3HT, promoting the formation of $H$-aggregates as opposed to the more commonly observed $J$-aggregates. We found that $J$-aggregates in pristine P3HT facilitate more efficient exciton movement and electricity generation, resulting in enhanced photocurrents compared to sonicated P3HT, which predominantly forms less efficient $H$-aggregates. In FETs incorporating sonicated P3HT, we observed a shift to a more positive threshold voltage and an increase in mobility, indicating a higher presence of mobile charge carriers even without the application of additional voltage. Upon integration with ZnO, the pristine-P3HT demonstrated significant shifts in threshold voltage under illumination, likely due to electron trapping. However, sonicated P3HT interfaced with ZnO showed comparatively less trapping and a minimal shift in threshold voltage. These observations underscore the vital role of aggregate type ($J$ or $H$) in dictating the electronic properties and light-response behavior of P3HT, with sonication yielding higher mobility but reduced photocurrent efficiency in $H$-aggregates compared to the $J$-aggregates present in pristine P3HT.

Our study suggests that electrical gating properties can be effectively controlled through the manipulation of aggregate formation, driven by strong polymer chain interactions. This understanding opens up new possibilities for optimizing the structural arrangement in solution-state P3HT for specific applications. Such insights are particularly relevant in fields like solar cell and sensor technology, where the efficiency of light-induced current generation is a critical factor.

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