

Polymers for New Energy Technologies: Organic Photovoltaics

Introduction

Photovoltaic cells, more commonly known as solar cells, are named after the chemical process of converting light into electricity. The use of photovoltaic (PV) materials is a promising solution to global energy needs. Currently, commercial solar cells use silicon or another inorganic semiconductor as the photoabsorber material. With these materials, power conversion efficiencies of ~18-22% for commercial cells and up to ~47% for research cells have been achieved.¹ However, inorganic solar cells face several challenges including high cost and difficulty of manufacturing, and a relatively brittle and fragile nature.

Due to these downsides, other PV materials are under investigation to achieve the goal of low-cost, lightweight, flexible solar cells. Organic photovoltaics (OPVs), which use polymers or small organic molecules for light absorption and charge transfer,² are the leading candidates. OPV polymers can be made from widely available, relatively eco-friendly raw materials and can be produced on large scales using simple techniques such as solution processing or vapor deposition. Moreover, their band gaps can be fine-tuned or tailored by molecular engineering (i.e., by changing length, functional groups, etc.).³

Organic solar cells face their own hurdles, including lower (but commercially viable) efficiencies of ~3-10% for commercial cells and ~18% as a record,¹ and performance instability and degradability due to environmental factors such as light and heat. Despite these issues, OPVs are expected to play a major role in the solar market due to their low cost. Current research is therefore largely focused on improving efficiency of OPV polymers.

Here we discuss how nanoscale characterization, specifically with the atomic force microscope (AFM), can aid in the improvement of organic photovoltaics (Figure 1).

Tailoring Morphology to Improve Efficiency

The polymer films used in organic solar cells are prepared by solution processing, whereby a polymer is first dissolved in solvent from which a film is created from the solution by spin coating, drop casting, doctor blading, or a similar method. Numerous variables in the preparation process are known to affect the

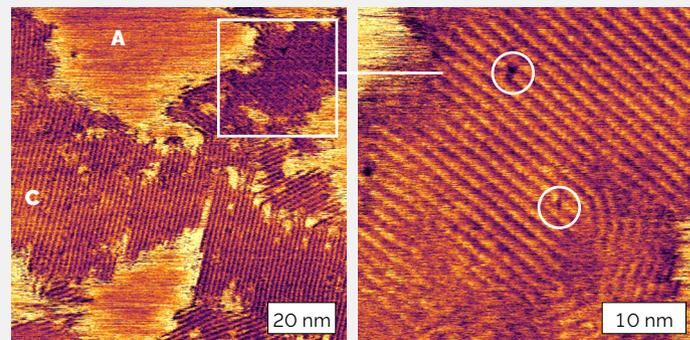


Figure 1: AFM images of polythiophene (ADS306PT) morphology reveal (left) crystalline (C) and amorphous (A) domains and (right) the regular chain structure of a crystalline region containing a few defects (circled). Images represent tapping-mode phase and were acquired on the Jupiter XR AFM in ambient conditions.

electronic properties and performance of the film produced. Elucidating how each variable affects the resulting film will enable better control of the fabrication process, leading to improved efficiency.

For example, the conjugated polymer poly(3-hexylthiophene) (P3HT) is a common donor material for OPV photoabsorber layers. P3HT assembles into nanofibers upon crystallization from solution, and the ease of assembly can be tuned by adjusting parameters such as molecular weight, regioregularity, and concentration. However, this tuning also impacts crystallization and thus efficiency: higher crystallinity is known to translate into higher charge carrier mobility, which in turn results in higher conversion efficiency. Therefore, a deeper understanding is needed of the crystallization process and what conditions affect its outcome. In this way, processes can be tailored to achieve the desired crystalline morphology and improve device performance.

AFMs enable virtually nondestructive characterization of polymer morphology with micro- and nanoscale spatial resolution. Most AFMs can evaluate larger morphological features such as phase segregation and domain size and shape, but only newer AFMs with the highest resolution and lowest noise can assess the local crystallinity of polymers.

The ambient conditions AFM images of drop casted Polythiophene (ADS306PT) shown in Figure 1 were acquired on Jupiter XR. Besides revealing molecular

level resolution of the amorphous and crystalline domains of the sample, the AFM data also shows the structure of the polymer chain and even some chain packing defects. The ultra-low noise level performance of the Jupiter XR system, compared to other commercially available systems, enables such high-quality data acquisition.

One of the main issues in polymer research requires the ability to investigate morphology in solution. The AFM is the only surface analysis tool that allows this capability. In-situ imaging in organic solvents can only be successfully performed on instruments equipped with sealed environmental chambers such as the Asylum Research Cypher ES and Cypher VRS AFMs. The sealed cell configuration prevents solvent evaporation and allows for operation under either static or perfusion conditions. With these capabilities, Asylum AFMs can evaluate relative crystallization in solution and observe different stages of the crystallization process.

Figure 2 demonstrates how AFM imaging in solution provides insight into P3HT crystallization mechanisms and outcomes. The molecular-resolution image in Figure 2a shows the structure of hexyl chains and backbones of a series of P3HT chains grown from solution on highly oriented pyrolytic graphite (HOPG). By analyzing profiles like that in Figure 2b, a repeat distance of $7.7 \pm 0.2 \text{ \AA}$ between hexyl chains and a backbone spacing of $17.1 \pm 0.9 \text{ \AA}$ were determined. The values suggest these crystals are form I, which have an expected c-axis spacing of 7.8 \AA and a spacing of 17 \AA between (100) planes. AFM characterization provided valuable information about the type of P3HT crystals that form on the HOPG surface at these particular conditions. Such in-depth, molecular-level understanding of the crystallization process can be used to better control the crystallization to achieve the highest efficiency OPV materials.

Valuable insight into fabrication processes can also be gained by monitoring polymer assembly and crystallization dynamics as they happen. Such studies are only possible on AFMs with fast scanning capabilities as well as solution/perfusion equipment such as Cypher ES and VRS. The sealed cell is actually air-tight, even under 5 psi pressure, which means that you never need to worry about solvent evaporation over time during perfusion experiments. Moreover, the small volume of the cell allows the liquid to rapidly equilibrate to the desired temperature and conserves precious reagents. An example is shown in Figure 3, where the absorption and

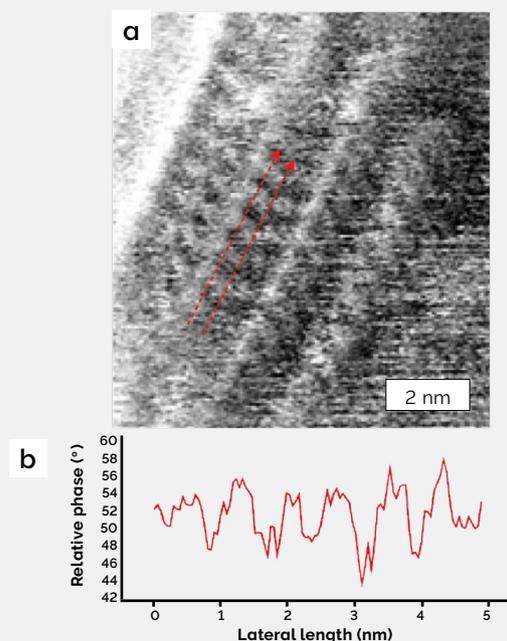


Figure 2: a) Tapping-mode phase image of the molecular-level structure on the surface of a crystalline nanofiber nucleus on HOPG. b) Profile of average phase contrast between the red lines indicated in the image. Acquired on the Cypher VRS during liquid perfusion. The data shown are reused under fair use from the original article cited in Ref. 4.

rearrangement of P3HT as it nucleated on HOPG from solution was examined. Repeated imaging of the same sample region revealed how polymer chains organized over time. During the initial stages of in-plane growth, successive formation of ordered nanofiber domains and nanofiber nuclei were observed as shown in Figures 3a and 3b, respectively.

The experiments indicated that nucleation events occurred on timescales of 30 s or less. In the study described above, movies acquired at 5 s per image (50 Hz line scan rate) for ~8 min provided further details about individual nanofiber nucleation events and an eventual out-of-plane crystal growth stage.⁵

To capture even faster dynamic behavior than this, imaging must be performed on video-rate AFMs. Cypher VRS is a video rate AFM that can capture images at rates exceeding 10 frames per second (line rates up to 625 lines per second).

Improving Efficiency by Correlating Physical and Electrical Properties

Research has found that electrical conductivity of conjugated polymers in bulk form can be enhanced

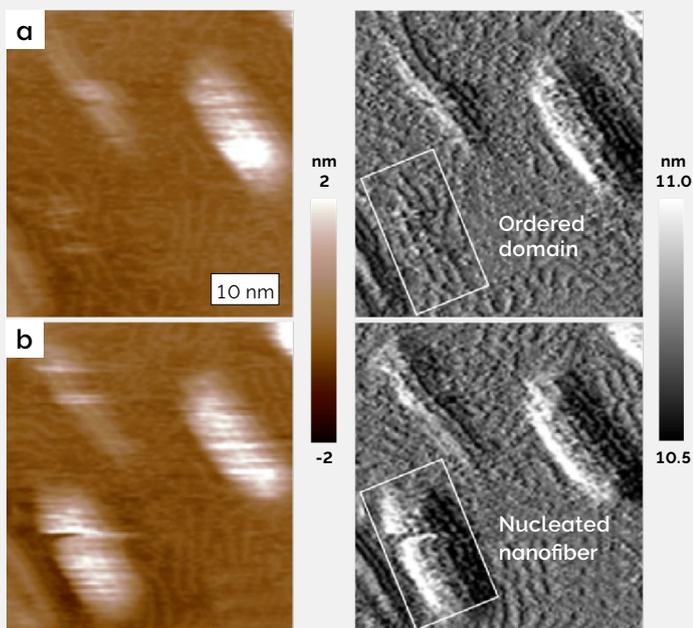


Figure 3: In-situ AFM measurements of P3HT nucleus formation on HOPG showing evolution from a) ordered monolayer domains into b) nucleated nanofibers. The images correspond to (left) height and (right) amplitude channels and were acquired on the Cypher ES in tapping mode during liquid perfusion. The data shown are reused under fair use from the original article cited in Ref. 4.

by molecular doping.⁶ To leverage this result for OPVs, it is necessary to understand exactly where the doping happens—how dopants are distributed between amorphous and crystal domains—and the resulting impact on film conductivity.

Unique in their ability to measure local electrical, mechanical, and related properties, AFMs are invaluable for this effort. By providing data localized to a specific position, they can give deeper insight than ones that average across an entire sample or device. Moreover, correlating information obtained by different modes in the same region often reveals new relations between material structure, property, and performance.

An example of how this approach can be used to understand doping effects in conjugated polymers is illustrated in Figures 4 and 5. In this work, electrochemical doping of P3HT films with tetrabutylammonium perchlorate (TBAP) was investigated.⁷ The physical, mechanical, and optical properties of pristine and doped films were characterized with several techniques including AFM, Raman spectroscopy, and X-ray.

AFM measurements included nanoscale maps of morphology, shown in Figures 4a and 4b, and elastic modulus, shown in Figures 4c and 4d. The maps indicated that doped and undoped films

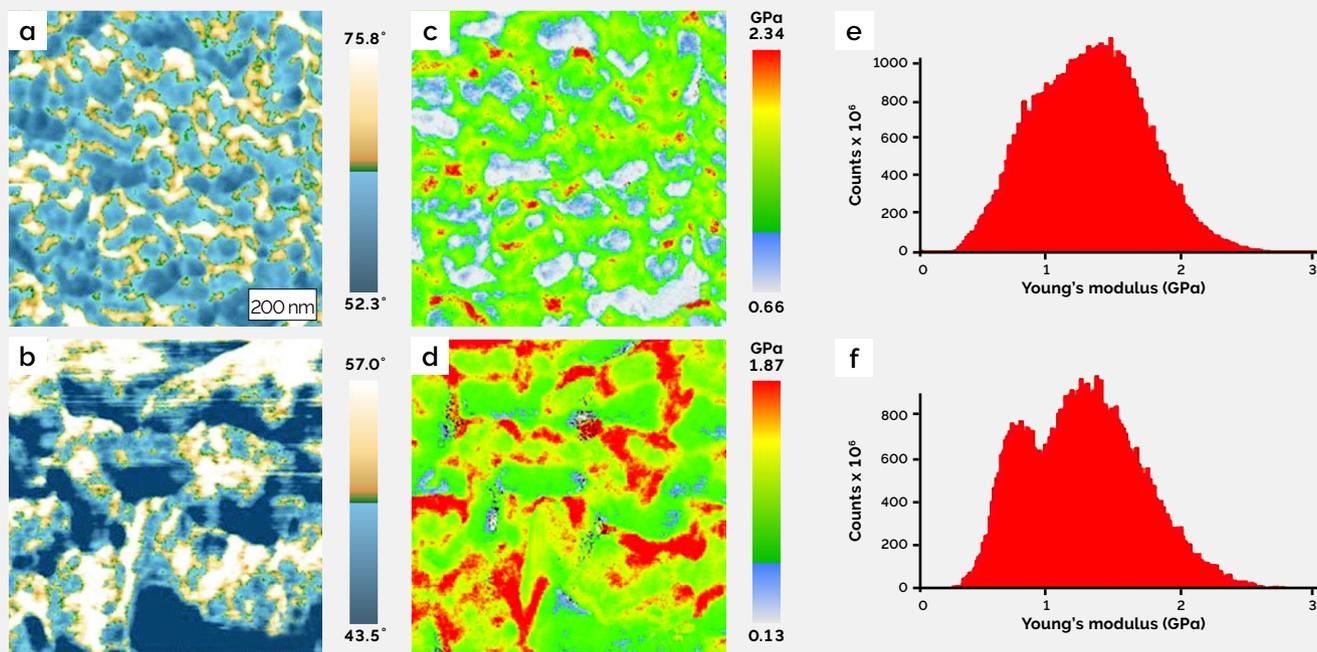


Figure 4: a) and b) Morphology images of pristine and doped P3HT films, respectively, measured in tapping-mode phase. c) and d) Young's modulus maps on the same films, respectively, acquired in Fast Force Mapping mode. e) and f) Histograms of the modulus data in c) and d), respectively. Acquired on the Cypher ES AFM. The data shown are reused under fair use from the original article cited in Ref. 7.

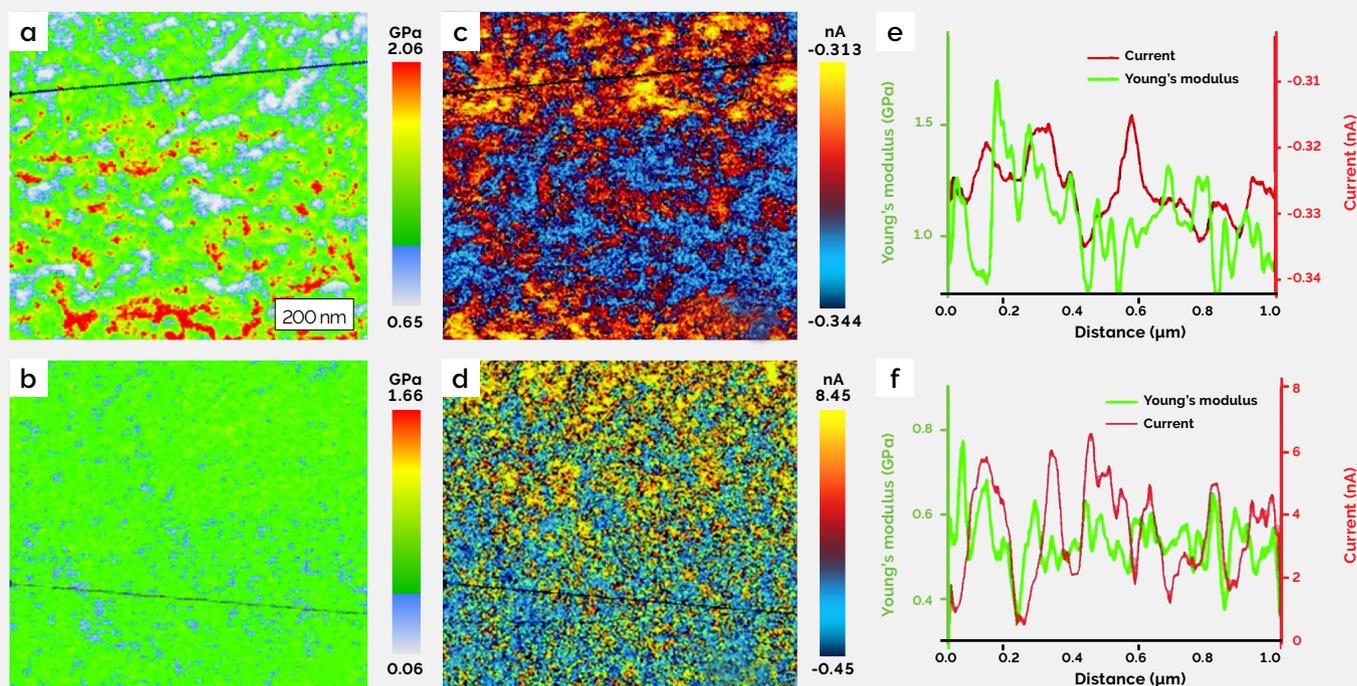


Figure 5: a) and b) Young's modulus maps for pristine and doped P3HT films, respectively. c) and d) Nanoscale maps of current for the same films, respectively. Acquired in Fast Current Mapping mode on the Cypher ES with the Dual Gain ORCA module. e) and f) Profiles corresponding to the black lines in images (a-d) enable comparison of mechanical and electrical response at the same sample position. The data shown are reused under fair use from the original article cited in Ref. 7.

contained both crystalline and amorphous regions. Further comparison of the modulus maps and their histograms, shown in Figures 4e and 4f, revealed that doping did not affect the modulus of amorphous regions. However, the lower modulus values observed in crystalline regions of doped films suggested that the dopants were mainly present in crystalline regions.

In addition, simultaneous mapping of film current, morphology, and modulus was performed and is shown in Figure 5. Maps of local current for pristine and doped films, shown in Figures 5c and d, indicated that doped films conducted about 30 times more current than undoped ones. The current maps were also compared to the co-localized modulus maps shown in Figures 5a and 5b. Line section profiles like those in Figures 5e and 5f revealed that higher current corresponded to higher modulus, suggesting higher conductivity in crystalline regions for both types of films.

Comparing the nanomechanical and nanoelectrical data to results obtained with other tools further confirmed these findings. Considering the entire body of data led to the conclusion that dopant sites were preferentially located in the crystalline domains, which exhibited higher conductivity. Results like these illustrate how correlating AFM measurements can

provide insight into tuning the electrical properties of conjugated polymer films on the nanoscale. In this way, they can help optimize polymeric materials to improve the efficiency of OPVs.

Summary

Polymer materials hold tremendous promise for many next-generation energy technologies including organic photovoltaics. Realizing a future of low-cost renewable energy based on OPVs, however, requires further research to enhance their efficiency. Asylum Research AFMs provide a wide range of valuable capabilities for this purpose. They can characterize structure down to molecular-chain level at speeds high enough to capture dynamic processes, in relevant environments such as organic solvents under perfusion. Moreover, Asylum Research AFMs can measure localized mechanical and electrical properties to help uncover relationships between structure, properties, and performance. These capabilities and more make AFM characterization an increasingly indispensable step for OPV research.

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