

Electronic characterization of bulk hetero-junctions by Kelvin Probe Force Microscopies

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Introduction

In this article we highlight few recent works performed making use of KPFM [1] with the aim of getting fundamental information on the nanoscale electrical and electronic properties of organic and supramolecular materials effectively employed for real opto-electronic devices, and to correlate them with their behavior on a macroscopic scale [2]. After a brief description of the scanning probe technique, this article describes the electrical nanoscale characterization of organic bulk hetero-junctions for solar cells when tested under an additional stimulus, *i.e.* light.

Technique

KPFM can be considered being modes of Atomic Force Microscopy (AFM) since it is typically operating on the very same setup. A microfabricated cantilever exposing at its edge a metal-coated tip is used to sense the surface and to map both its morphology and its electrical features. By sensing electrical signal, the tip passes over the surface but never being in direct contact with it. KPFM measures the surface potential (SP) of the sample by recording the electrostatic forces resulting from the interaction between tip and sample. KPFM is in fact a non-contact technique based on Zeeman vibrating capacitor set-up; the two electrodes of the capacitor are the sample and an oscillating tip (with defined frequency ω) rastering the surface at fixed tip-sample distance.[3] A direct quantification of the surface potential is not trivial, being the force proportional to the gradient of the tip-sample capacitance and the square of electrical potential difference between tip and sample: $F_{\omega} = \partial_{\omega z} C \times \Delta V^2$. This problem is circumvented by applying an adjustable bias offset between tip and sample (*i.e.* $F_{\omega} \propto SP - V_{bias}$); the resulting electrostatic force is detected by a lock-

in amplifier, and a feedback circuit controls the applied bias until the surface potential is compensated. This provides a direct quantification of the surface potential corresponding to the applied bias to stop the tip oscillations. The physical meaning of the measured SP is strictly related to the sample electrical properties. In the case of metallic samples, the measured surface potential corresponds to the work function difference between tip and sample. Moving from metallic to semiconducting or even insulating samples, SP is not directly correlated to the work function anymore, but is instead influenced by local charge density [4].

Results and Conclusions

In a bulk hetero-junction the morphology and the electronic properties of the blended material are key factors for the device efficiency and performance. In particular, the morphology plays a paramount role in the percolation pathways for transport of both photogenerated excitons and charges. KPFM measurements can correlate on the nanoscale the morphological properties with photogenerated charges, and it allows to monitor dynamical production, transport and recombination of charges. Bulk hetero-junctions are phase-segregated films obtained by co-deposition of an electron-donor and an electron-acceptor on a surface. The connectivity and percolation of both the electron- and hole-transporting phases with their respective electrodes represent the key-factor for efficient organic solar cells. Hoppe *et al.*[5] studied on solid-state blends of poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV) and the soluble fullerene C60 derivative 1-(3-methoxycarbonyl) propyl-1-phenyl [6,6]C61 (PCBM), spin-cast from either toluene or chlorobenzene solutions. KPFM revealed distinct differences in the energetics on the surface of films cast from two solvents; by gathering complementary information by scanning electron microscopy, it was concluded that the films prepared from toluene solutions do not exhibit percolation pathways for electrons propagation toward the cathode. Authors also suggest that the reduced performance of devices with coarse phase separation is at least partially due to a limited electron transport within the film. The direct observation of the contact region between donor-acceptor material that results to be the only "light active" has been shown by Liscio *et al.*[6] through KPFM

analysis of CHCl_3 cast N,N"-bis(1-ethylpropyl)-3,4:9,10-perylenebis(dicarboximide) (PDI) and regioregular poly(3-hexylthiophene) (P3HT) blends. It was proved that only the PDI clusters that are in physical contact with P3HT exhibit an appreciable charge transfer because of the existence of a complementary electron donor phase. Upon illumination with white light, the surface potential of the P3HT phase became more positive and showed a value close to that of the substrate while PDI clusters in contact with P3HT became more negative (Figure 1).

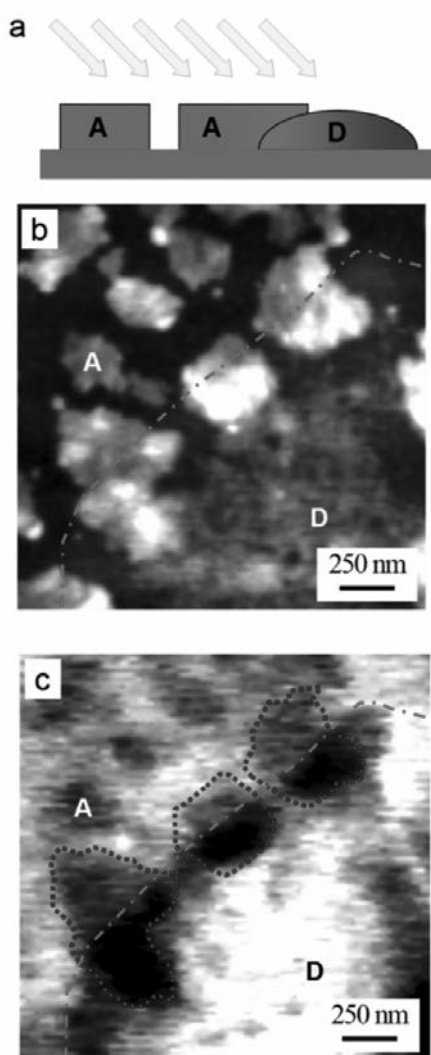


Figure 1. (a) Cartoon showing (A) PDI nanocrystals in contact or not with (D) P3HT aggregates. b) AFM and c) KPFM image recorded under illumination. Only the part PDI clusters physically in contact with P3HT are involved in the photo-charge generation. Z-range: (b) 30 nm and (c) 90 mV.

The measured potential variation induced by the light corresponds to a photo-induced charge density amounting to about 10^3 charges/ mm^2 . In general, one of the reasons of the success of KPFM as a powerful tool to explore bulk heterojunctions is given by its bulk sensitivity. Cadena *et al.*[7] directly showed the sub-surface sensitive of KPFM by imaging networks of single-walled nanotubes dipped into a polyimide matrix. By devising a 3D model to single out the surface and the bulk contributions to the measured potential signal, Liscio *et al.*[8] described the sampling depth in terms of film electrical permittivity, showing that on P3HT films the sub-surface sensitive of the technique amounts to about 100 nm.

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