Unraveling the electrochemical doping in semiconducting polymers

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Organic mixed ionic-electronic conductors (OMIECs) are a class of organic materials that efficiently support both ionic and electronic transport. Due to this remarkable property, a broad range of emerging technologies, from energy storage to bioelectronics, rely on OMIECs. [1] A key property of these materials is their ability to be electrochemically doped, which is an efficient and reversible method to increase the materials electric conductivity. This process relies on the injection of carriers into the organic film, while the counterions from an electrolyte infiltrate the film and maintain charge neutrality. The electrochemical doping relies on a complex interplay between multiple factors, from electrolyte choice to molecule design and film morphology, and due to the increasing number of applications that rely on this process, there has been great interest in further understanding its properties and fundamental mechanisms. [2]

In this work, we explore the impact of the polymer film morphology on the electrochemical doping. We use time-resolved visible-near infrared (Vis-NIR) and in-situ Raman spectroscopy combined with electrochemical measurements to show that the ordered and disordered domains of poly(3-hexylthiophene) (P3HT) are doped through different mechanisms and kinetics. We demonstrate that for intermediate doping levels, polarons and bipolarons (singly and doubly charged species) coexist exclusively in the disordered domains. In the ordered domains, only polarons are observed until there are no more ordered undoped chains, and only at this point bipolarons start to be formed at these domains. We propose a kinetic model that described the reactions that take place and show that the ordered phase is doped faster than the disordered for all doping levels.

To confirm our propositions, we used in-situ electrochemical Raman spectroscopy, a technique very sensitive to local conformation. We obtained good agreement with the trends observed with Vis-NIR spectroscopy. Additionally, we compared the doping of P3HT films with different degrees of morphology. We use regiorandom P3HT to investigate the doping in purely disordered films, and the results strongly correlate with our proposed kinetic model. Finally, by measuring the Thz conductivity of our films, we investigate how the polarons and bipolarons impact electronic conductivity.

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