

Photocathodic Activity of Poly(3-Hexylthiophene) in
Aqueous Acid
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There is great interest in harnessing solar energy for generating useful fuels or products. Research in photoelectrochemical electrodes is very important for determining what materials may be useful for these processes. Typically, inorganic semiconductors are employed but organic semiconductors have also been shown to be useful for photoelectrochemistry.¹⁻³ Previously, regio-random poly(3-hexylthiophene) (rra-P3HT) was reported having an incident photon-to-current efficiency of 0.05 % in pH 4.0 solution under illumination.³ Using regio-regular P3HT we recently reported a 10 fold increase in efficiency (0.55 %) under visible illumination (100 mW cm⁻², AM 1.5D).⁴ Photocurrents of 20 $\mu\text{A cm}^{-2}$ were measured compared to 1 $\mu\text{A cm}^{-2}$ for rra-P3HT at an applied potential of -0.4 V_{SCE}.

Spectroelectrochemical measurements in aqueous solutions show that P3HT remains neutral and semiconducting which is necessary for its usage as a photocathode. UV-visible absorbance measurements of films exposed to non-aqueous solutions with various acid concentrations show that the polymer most likely becomes protonated. P3HT appears, however, to be unaffected in aqueous conditions but photoluminescence measurements indicate that the surface of the polymer may be protonated. Under this assumption, a mechanism describing the origin of the photocurrent is proposed.

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