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Research Highlight

Linear Semiconducting Polymers as Photoanodes for Oxidation Reactions

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ABSTRACT: Photoelectrochemical (PEC) water splitting has attracted significant attention in the general field of photocatalysis. However, the high cost of constructing PEC systems limits their practical application. Recently, an innovative approach was proposed to synthesize linear semiconducting polymer-based films. The polymer structure was optimized for oxidation reactions. Furthermore, the active site of the optimal linear polymer was investigated through in-situ characterizations. This work has the potential to address the challenges of high material costs and polymer film development in PEC technology.

Keywords: Polymer photoanode; Semiconducting polymers; Oxidation reactions; Photocatalysis

The photoelectrochemical (PEC) system is a promising technology for converting solar energy into chemical energy, with broad potential applications in environmental treatment, solar power, and hydrogen-based energy [1–3]. The key component of the PEC system is the photoanode. Compared to traditional powder-generated photocatalysis, applying a specific voltage on a photo enhances the separation and transfer of photoexcitation charges, leading to improved energy conversion efficiency [4–6]. However, materials that can form a stable photoanode while maintaining chemical stability and responsiveness under visible light irradiation for chemical conversion are still to be identified [7].

Compared to traditional inorganic semiconductor materials, organic semiconductor materials offer advantages such as flexibility, ease of processing, low cost, and good conductivity [8,9]. Linear polymers, among the earliest semiconducting polymers investigated for use as photoelectrodes, have recently seen widespread application of their donor-acceptor (D-A) structure to enhance performance in photoredox catalysis [10,11]. However, their performance remains challenging.

In this study [12], linear polymers were synthesized on carbon cloth (CC) using a modified Suzuki-Miyaura reaction. Specifically, dibenzo[*b,d*]thiophene sulfone (FSO) linear conjugated polymer films were formed as photoanodes. Traditionally, the Suzuki-Miyaura reaction requires Pd as a catalyst; however, in this synthesis, Pd particles were anchored onto the CC via electrochemical deposition, facilitating the formation of the linear polymer on the CC. Moreover, the structure of the linear polymer can be easily modified by adjusting the precursor. The resulting photoanodes include FSO-Ph, FSO-Px, FSO-Pz, Px, and FSO-DTF, with their polymer unit structure shown in Figure 1.

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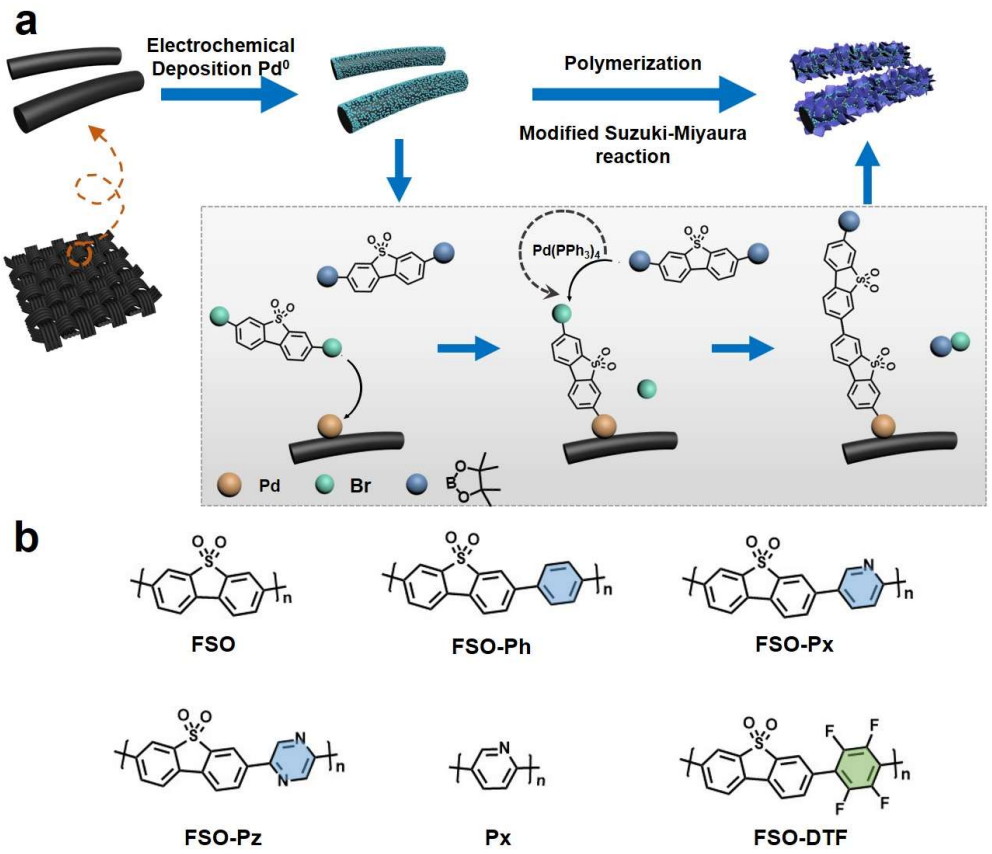

Figure 1. (**a**) Growth mechanism of linear conjugated polymers on carbon cloth in Suzuki-Miyaura reaction. (**b**) The chemical structures of six linear polymer semiconductors are designed in this paper. Reprinted with permission from ref [12]. Copyright 2024, The Royal Society of Chemistry.

The polymer photoanodes exhibit light absorption over a wide range of wavelengths, demonstrating the ability to absorb visible light, with the main absorption peak located between 400 and 450 nm. The FSO photoanode successfully operates with a photocurrent density of 140 μA/cm² for the water oxidation reaction. Its highest incident photon-to-current conversion efficiency (IPCE) reaches 8.5% at a wavelength of 400 nm. Among all the photoanodes tested, the FSO photoanode shows the highest photocurrent density for the water oxidation reaction. Consequently, it was applied in organic transformations, as shown in Figure 2a. Two typical examples were demonstrated, namely the synthesis of N-benzylidene benzylamine by oxidation of benzylamine and the synthesis of methyl phenyl sulfoxide by oxidation of methyl phenyl sulfide. The yields and selectivity for the former reaction were 89% and 92%, respectively, while for the latter, they were 46% and 99%. The active site on the photoanode was also investigated using *in-situ* Raman spectroscopy. The spectra indicated that the stretching vibrational peaks of the sulfone group exhibited a blue shift as the PEC water oxidation reaction proceeded, with a specific response to the reaction (Figure 2b). It is speculated that the sulfone group may serve as the active site of the reaction, determining the rate of conversion.

In summary, the unique design of this polymer photoanode material offers a new approach for PEC systems. The rational design of the polymer structure provides the potential to obtain photocatalysts at the molecular level. This capability could significantly enhance performance, not only in water oxidation reactions but also in organic transformations, with controlled selectivity.

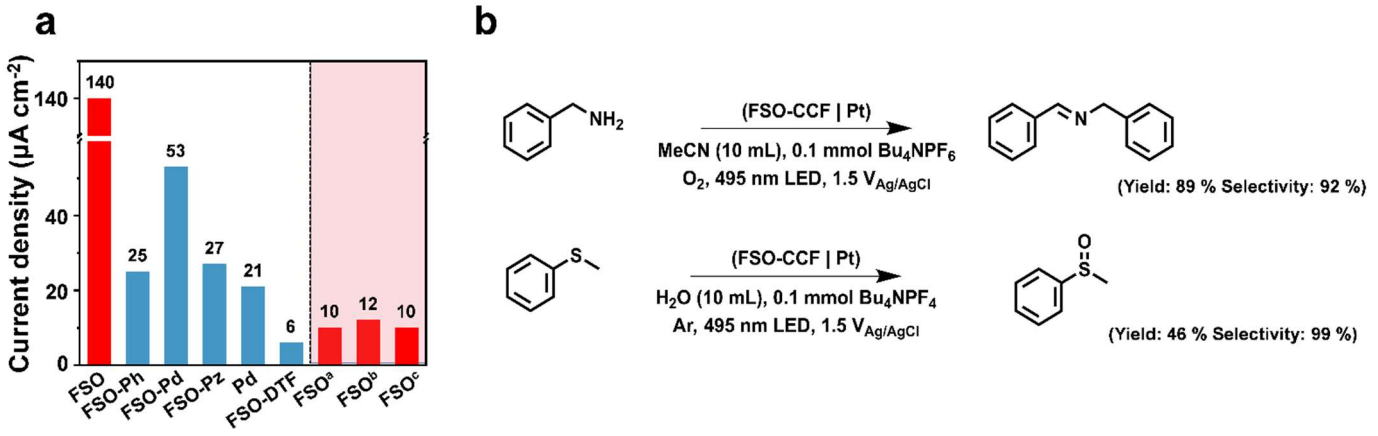

Figure 2. (**a**) Photocurrent densities of the linear polymer photoanodes for the water oxidation reaction. (**b**) The yield and selectivity of FSO polymer photoanodes for two different organic oxidation reactions. Reprinted with permission from ref [12]. Copyright 2024, The Royal Society of Chemistry.

Author Contributions

Y.F. and S.W. conceived the topic of this research highlight. M.Z. and N.L. wrote the initial draft. M.Z., N.L., Y.F. and S.W. made revisions. Y.F. and S.W. supervised the writing of the manuscript. All authors have given approval to the final version of the manuscript.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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Declaration of Competing Interest

The author declares that he/she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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