Efficient Charge Separation in Composite Photosystem I/PEDOT Photocathodes Prepared by Vapor Phase Polymerization

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Photosystem I (PSI)

PSI is a naturally abundant, stable, photocatalytic protein, with > 99% internal quantum efficiency. We are interested in using PSI in solar cells as an alternative counter electrode to expensive platinum.

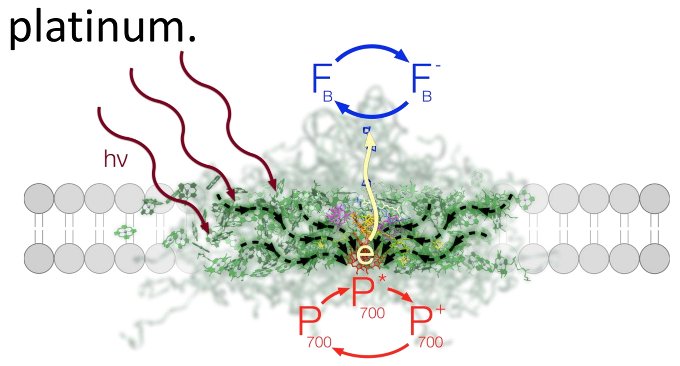


Figure 1 : PSI Protein | Nanoscale, 2017, 9, 6158

The aim of this study is to use PSI in a polymer composite film to be implemented in an efficient, low cost solar device.

PSI:PEDOT Composite Films

Electrically conductive poly (3, 4- ethylenedioxythiophene) (PEDOT) can be grown throughout PSI films via vapor phase polymerization to form a PSI:PEDOT composite film. We aim to incorporate the composite film into a solar cell based on mediated electron transfer (MET).

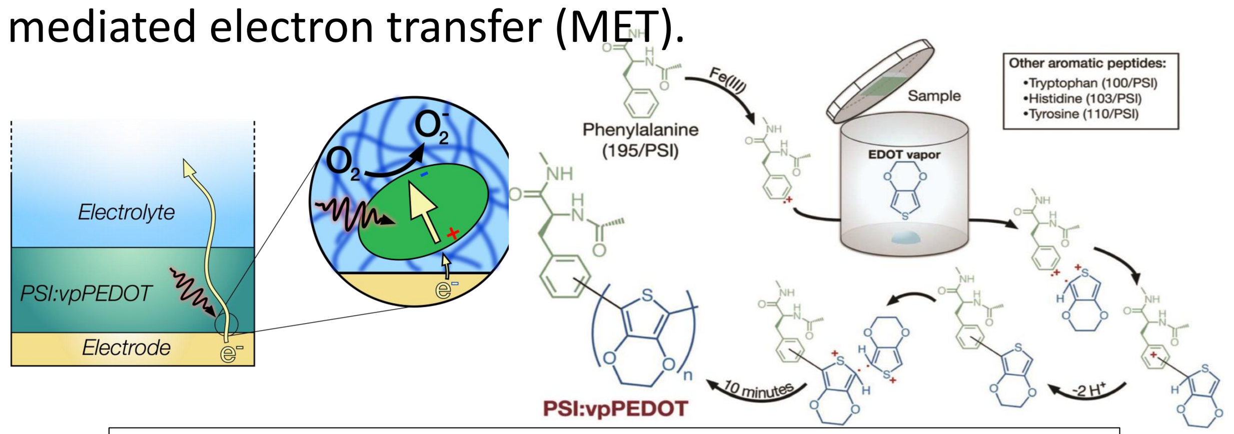


Figure 2 : MET and Polymerization| Maxwell Robinson ; Nanoscale, 2017, 9, 6158

The polymerization results from the condensation of the monomer (EDOT) near a Friedel-Crafts catalyst ($FeCl_3$).

Cell Preparation

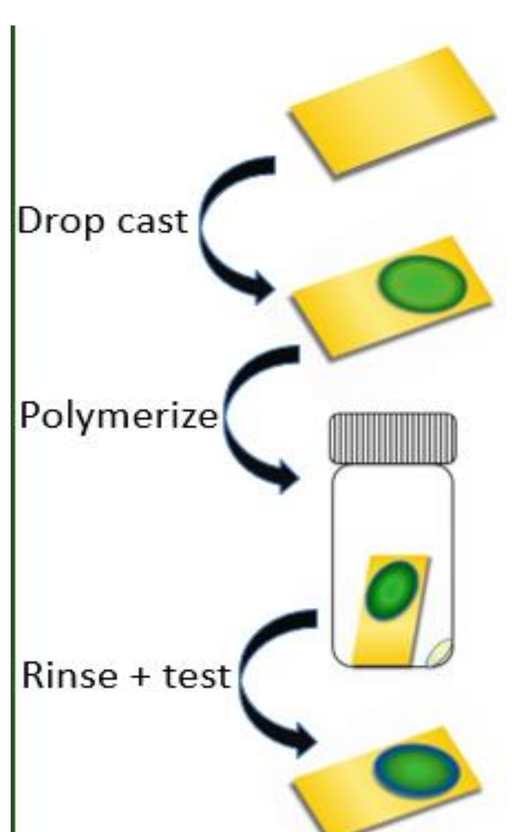


Figure 3: Fabrication Process

- Gold coated silicon electrode with a mercaptopropyl sulfonate self-assembled monolayer
- Drop cast PSI and 10mM $FeCl_3$ solution
- Heat 20μL EDOT in 40° C water bath for 1 hour to polymerize
- Rinse the sample with DI water and dry with nitrogen

Anion Exchange (AEX)

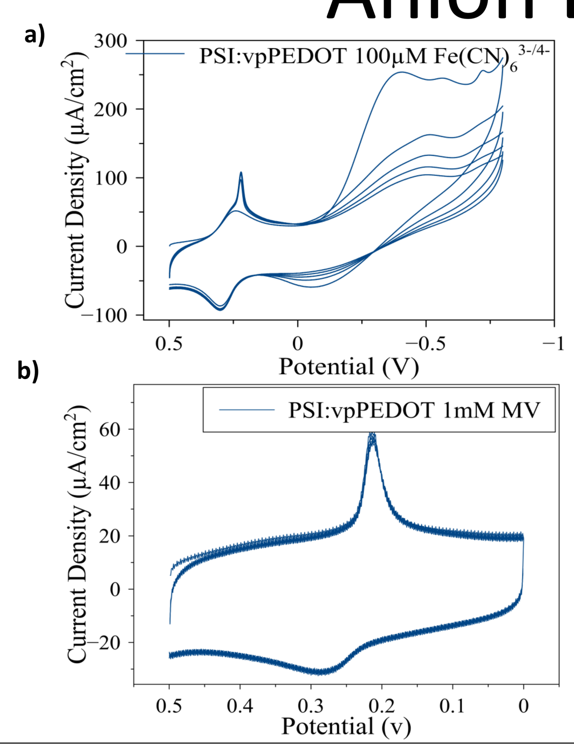
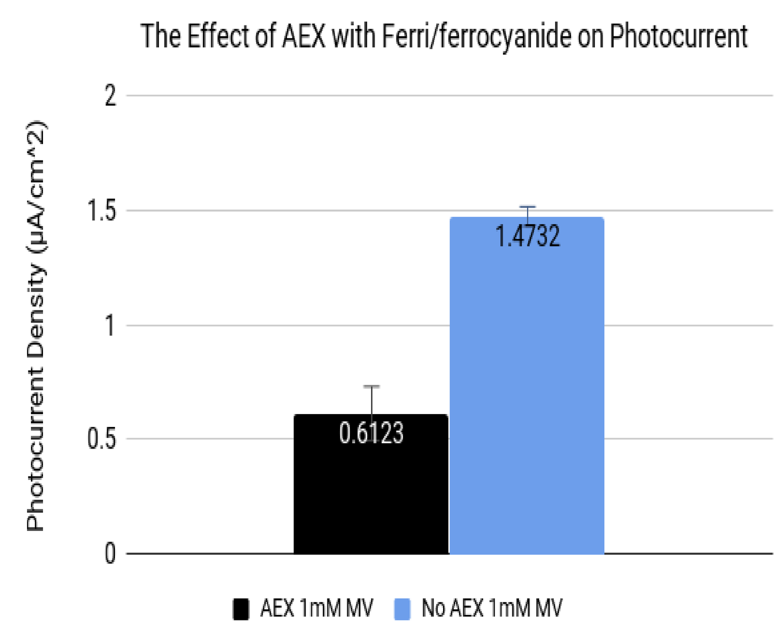


Figure 4: Cyclic Voltammetry with $Fe(CN)_6^{3-/4-}$ and MV



Graph 1: Photocurrent Comparisons for Anion Exchange

The films were cycled with potential to bind redox ions in electrolyte solution to PEDOT and allow for direct electron transfer from the polymer to the ions(Fig.4a). Then, the films were rinsed and retested with a mediator, leaving the ions encapsulated in the films (Fig.4b). Photocurrent test comparisons (Graph 1) show how AEX with ferri/ferrocyanide correlates with decreased photocurrent.

Energetics

When PSI has an electron excited by light, the electron goes from P_{700} through its electron transport chain to F_b^-. Methyl Viologen (MV) is the mediator in the system shown in Fig. 5. The function of the high energy mediator is to efficiently funnel electrons from F_b^- to oxygen, preventing recombination.

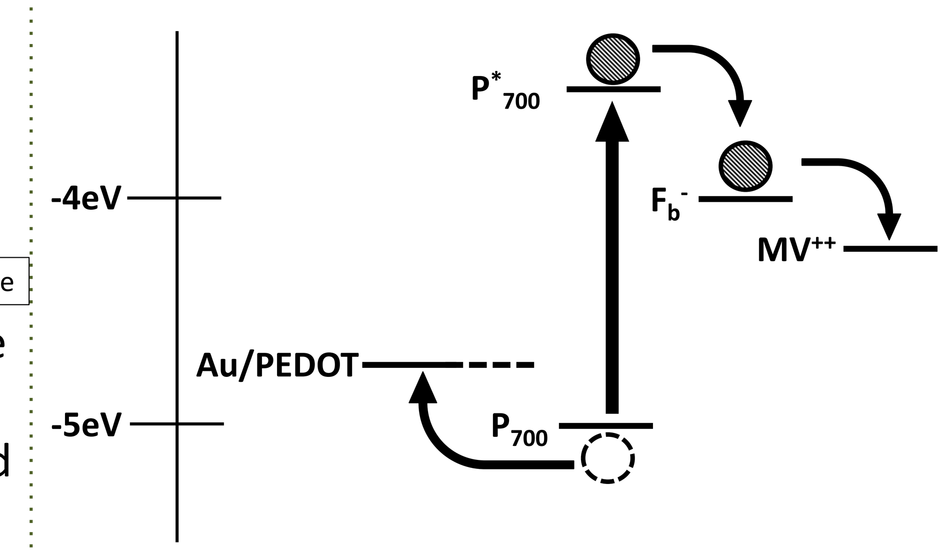


Figure 5: Energy Diagram for Solar Cell

Photocatalytic Performance of PSI:vpPEDOT and Solar Device

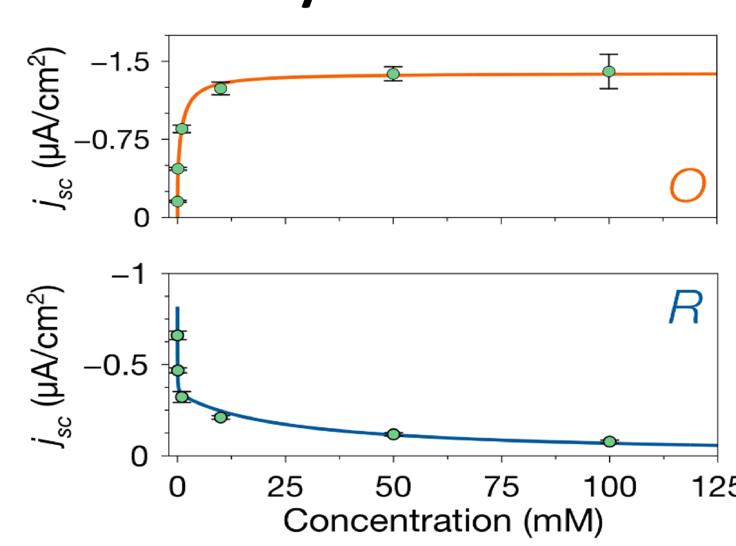
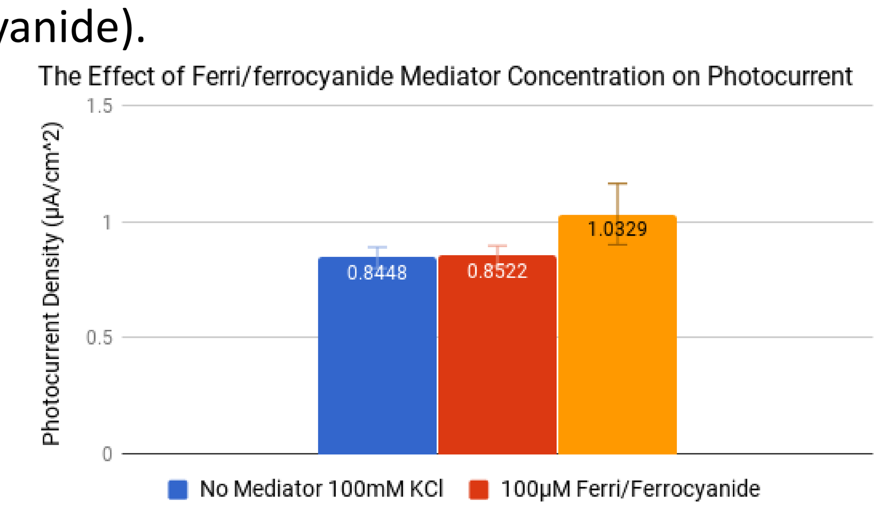


Figure 6 : PSI Multilayer Concentration vs. Photocurrent Plot/Model | Created by Maxwell Robinson

The PSI multilayer (above) has photocurrent that is consistently anodic, with more anodic current as the concentration of oxidized species (O) in solution increases. Whereas the PSI:vpPEDOT composite (below) shows consistent cathodic photocurrent which goes more cathodic with increases in the concentration of the oxidized species (Ferricyanide).



Graph 2 : PSI:PEDOT Composite Behavior with Oxidized Species Concentration

The PSI:vpPEDOT composite on the gold electrode was then incorporated into a solar device as a photocathode. The device was then tested with an increasing amount of PSI and with a control with only PEDOT.

The conductive polymer rapidly exchanges electrons with PSI, and PSI reduces the mediator ions, reducing the charge transfer resistance.

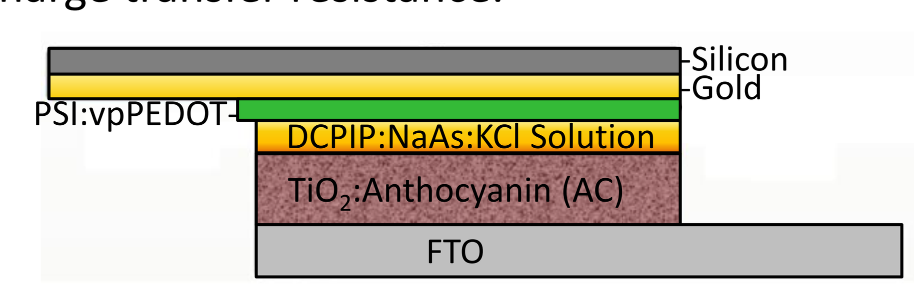


Figure 7 : Device Design for Preliminary Tests

Device Photocurrent Tests with Increasing Concentration of PSI

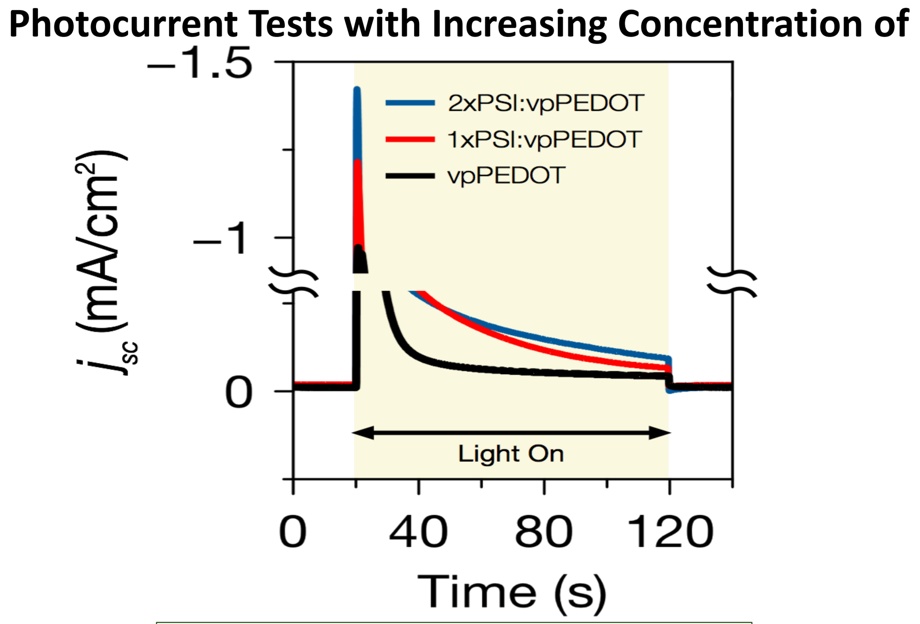


Figure 8 : Device Tests with PSI Concentrations

Conclusions

- Anion exchange was successful, but ferri/ferrocyanide anions in the films decrease photocurrent production.
- PSI multilayer films produce consistently anodic photocurrent, but PSI:PEDOT composite films produce cathodic current due to the provision of electrically conductive PEDOT
- Preliminary tests with devices have shown a significant increase in photocurrent with increase in PSI concentration in a composite film on gold

Future Work

The device could be improved by using a mediator that is less reversible once reduced, and the reproducibility could be improved by including spacers.

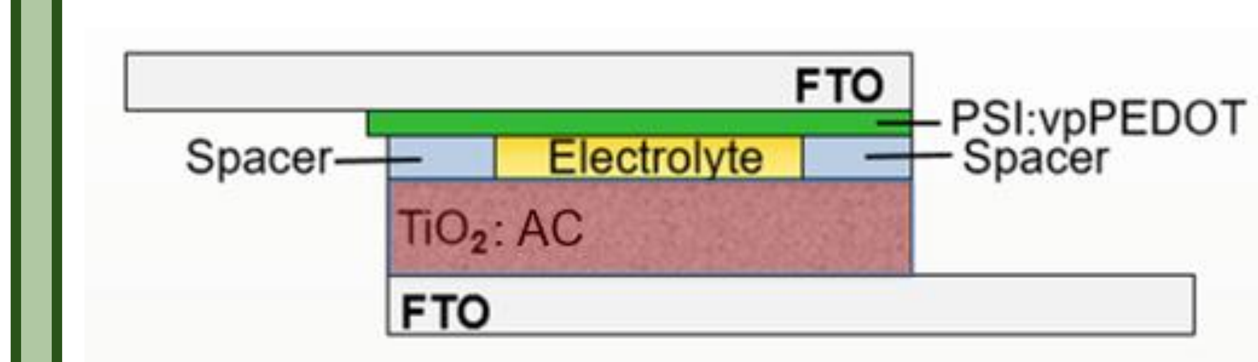


Figure 9 : Solar Cell Device Design with DSSC and Photocathode

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