Contract No:

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Disclaimer:

Title: Enhancing Charge Injection in Polyoxometalate-based Dye-Sensitized Solar Cells

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Summary Statement

A series of 3d-transition metal containing polyoxometalates have been synthesized. These materials were successfully characterized using a variety of spectroscopic and electrochemical techniques. A selected polyoxometalate was sensitized with a porphyrin-based dye to permit for more efficient solar spectrum utilization.

Introduction

The impact of Earth's reliance on fossil fuels and the climate change impacts from their combustion has created a surge in research for renewable alternatives to address the global energy crisis. Among the promising candidates, solar technology is at the forefront of the field. Solar cells permit for the sun's photons to be converted into electricity through the photovoltaic effect (Figure 1) providing clean energy. To mitigate some challenges solar cells face, more emphasis has been placed on chemically and structurally robust but cost-effective materials to make up the light harvesting photoanode. Promising results have been shown by utilizing polyoxometalates (POMs) as photoanodes, given their semiconductor-like properties, exceptional electron accepting abilities, and inherent structural characteristics that promote excited state charge separation and tunable solar utilization. However, polyoxometalates suffer from poor visible light absorption. Given this, POMs may be sensitized with dyes to promote greater visible light absorption. Porphyrins offer high molar absorptivity of the solar spectrum which makes them optimal candidates as photosensitizers. Additionally, introduction of 3d transition metals to the polyoxometalate structure permits for orbital matching with the porphyrin, which may promote efficient charge transfer from the dye to the POM. Not only does this hybrid material promote optimal solar spectrum utilization but the physical distance between the photo-generated electron and hole, upon charge injection from porphyrin and POM, may reduce detrimental charge recombination. This may promote the conversion of the solar energy to usable power.

Approach

The approach of the project is to first, synthesize a series of 3d transition metal containing polyoxometalates (POMs) where M=Mn(II), Fe(III), Cu(II), and Co(II). These POMs are then characterized using a series of spectroscopic and electrochemical techniques to confirm the identity and stiochiometry of each of the POMs. Following, the POMs will each be covalently bound to a porphyrin photosensitizer, monocarboxyphenyl triphenyl porphyrin.

The efficiency of the photoinduced charged transfer will be evaluated using electrochemical means. The photocurrent of the POM-porphyrin hybrid material will be measured. To do this, a bias potential will be applied and the resulting current will be measured as a function of white light irradiation. The current produced when the light is on compared to off will indicate whether photocurrent has been produced. This requires that the porphyrin transfers photogenerated electrons to the POM moiety and the POM injects the electrons to the ITO substrate allowing for the production of current which is essential

for the function of a dye-senstized solar cell (DSSC). The POM-porphyrin hybrid that produces the optimal photocurrent and displays the longest charge separation will be chosen to be used in a test DSSC.

Accomplishments

- Synthesis of a series of 3d-transition metal polyoxometalates with the formula: $[X_4(H_2O)_2(PW_9O_{34})_2]^{z-}$ where X= Mn(II), Fe(III), Cu(II), and Co(II).
- The composition of the synthesized polyoxometalates were confirmed using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Table 1). This method confirmed the targeted stiochiometry shown above.
- All POMs were characterized using energy dispersive X-ray spectroscopy (EDS) which supported the results of the ICP-OES. This furthered the conclusion that the target formula was obtained.
- Synthesized POMs were characterized using UV/Vis spectroscopy and fourier transofrm infrared spectroscopy (FT-IR). (Figures 2-3)
- Two, porphyrin-POM hybrid materials were obtained by reacting a polyoxometalate with the synthesized porphyrin. Samples were confirmed using FT-IR (Figure 5), UV/Vis spectroscopy (Figure 6), cyclic voltammetry (Figure 7), and EDS (Figure 8).
- Initial fluorescence measurements suggested possible fluorescence quenching of a preliminary porphyrin-POM hybrid material

Peer-reviewed Publications

n/a

Intellectual Property

n/a

Total Number of Post-Doctoral Researchers

Kori McDonald, Hydrogen Isotope Processing

Total Number of Student Researchers

n/a

Collaborators/Acknowledgments

Jenny Lockard, Rutgers University-Newark

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Figures

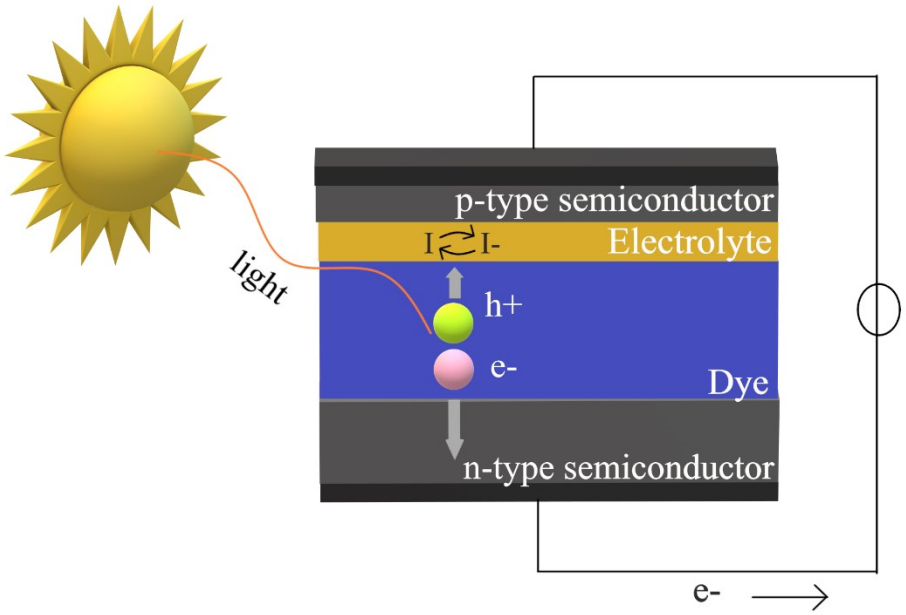

Figure 1: Depiction of the photovoltaic effect

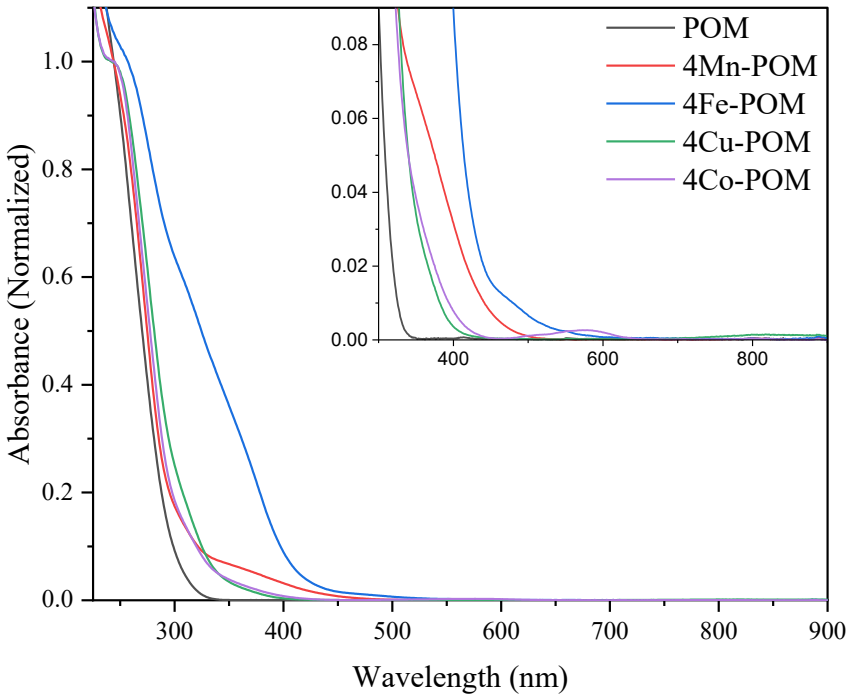

Figure 2: UV/Vis spectroscopy of all synthesized polyoxometalates measured in water

POM	M	P	W

POM	n/a	2	18
4Mn-POM	4	2	20
4Fe-POM	4	2	10
4Cu-POM	4	2	21
4Co-POM	4	2.4	18

Table 1: ICP-OES results for all synthesized polyoxometalates

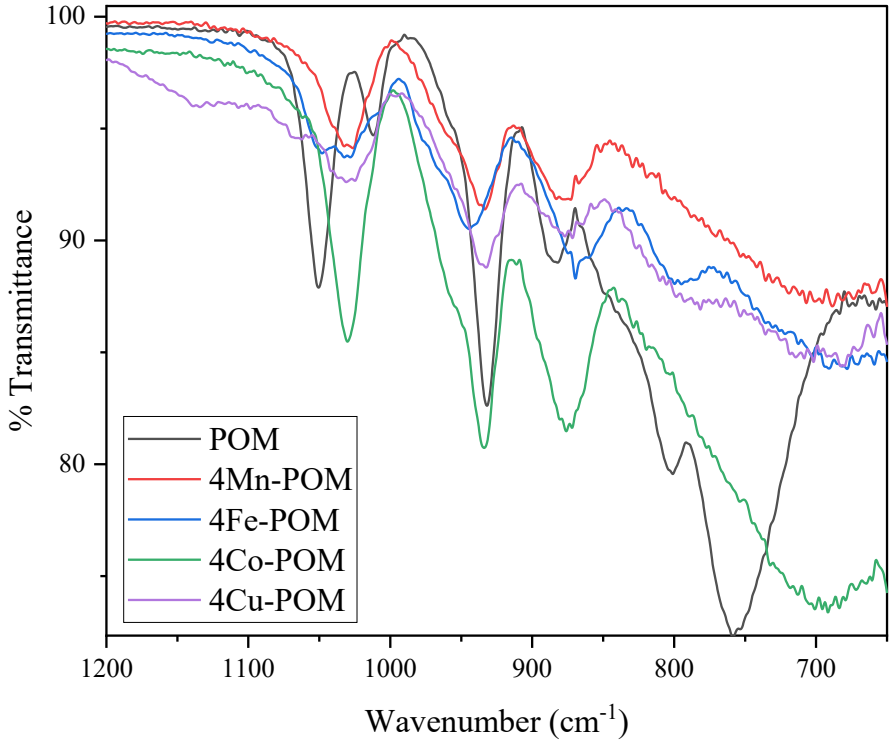

Figure 3: FT-IR of all synthesized polyoxometalates

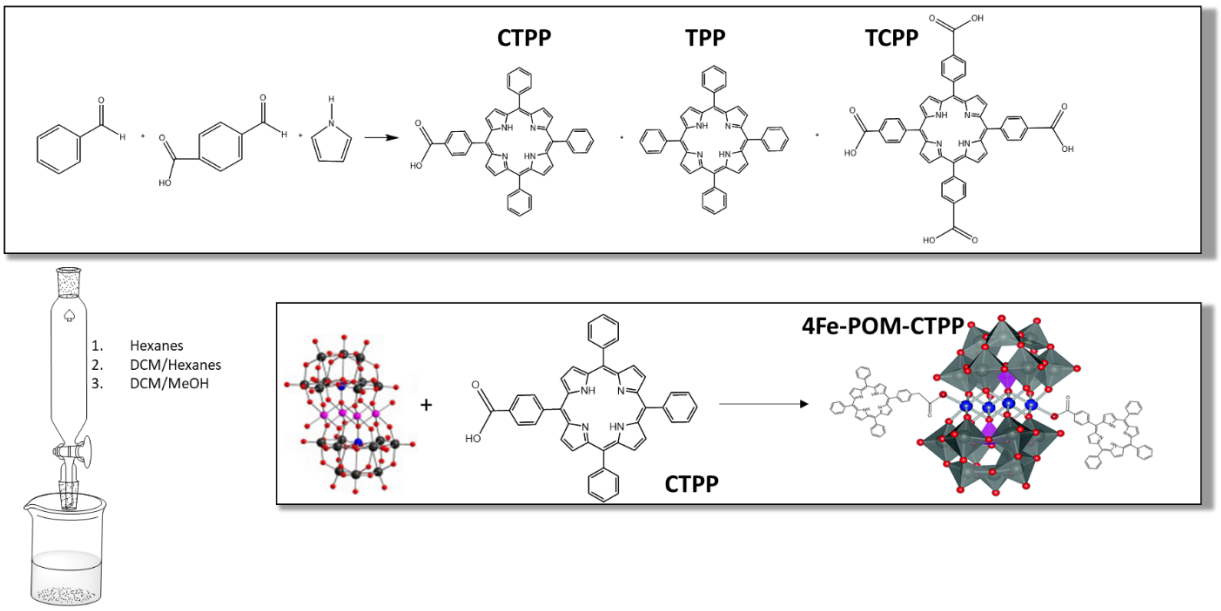

Figure 4: Synthesis of monocarboxyphenyl triphenyl porphyrin and POM-porphyrin hybrid material

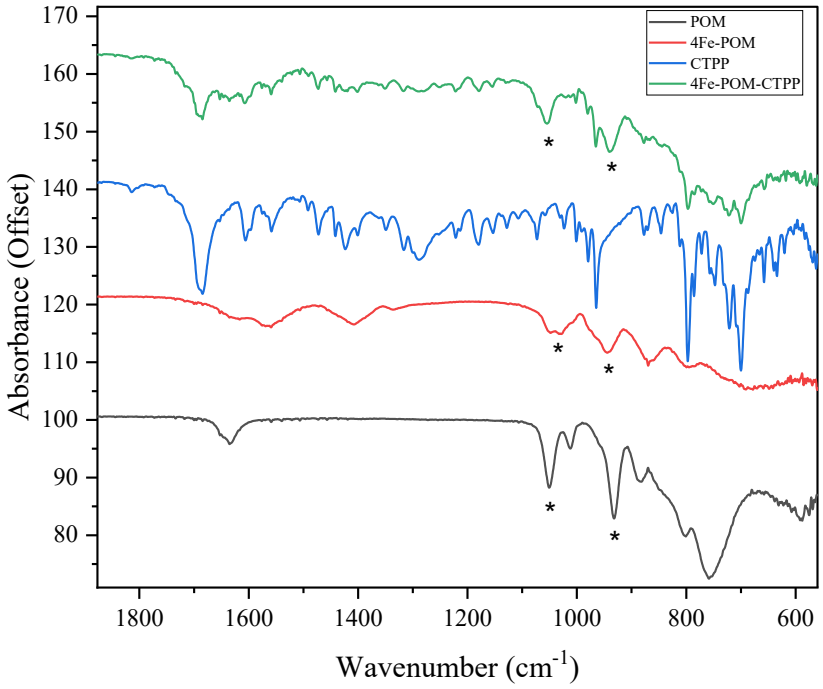

Figure 5: FT-IR of POM (black), 4Fe-POM (red), monocarboxyphenyl triphenyl porphyrin (TCPP) (blue), and POM-porphyrin material (4Fe-POM-CTPP) (green). Selected POM-based modes indicated with an astrisk

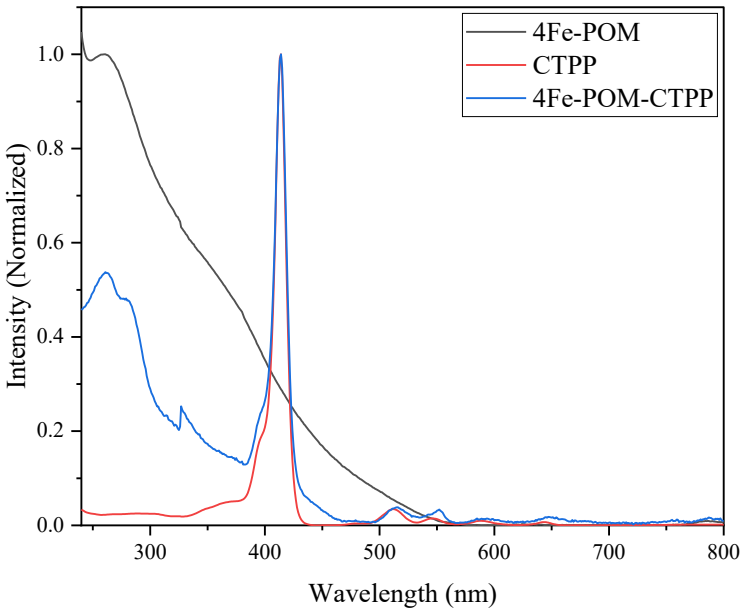

Figure 6: UV/Vis spectrum of 4Fe-POM, monocarboxyphenyl triphenyl porphyrin (TCPP) (red), POM-porphyrin material (4Fe-POM-CTPP) (blue) measured in acetonitrile

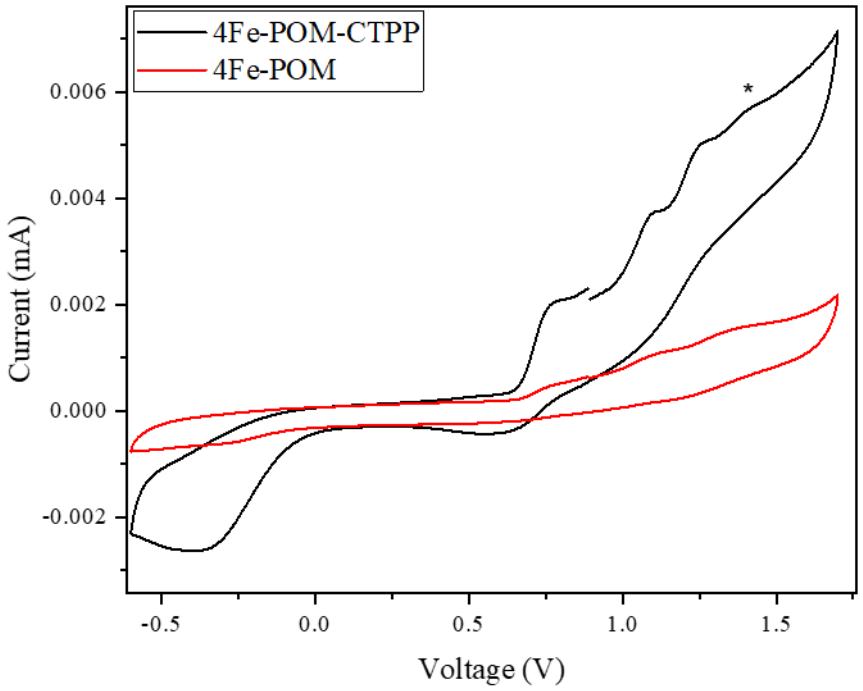

Figure 7: Cyclic voltammogram of 4Fe-POM (red) and 4Fe-POM-CTPP (black) with 0.1 M $TBAPF_6$ measured in degassed acetonitrile. The porphyrin oxidation is indicated with an astrisk.

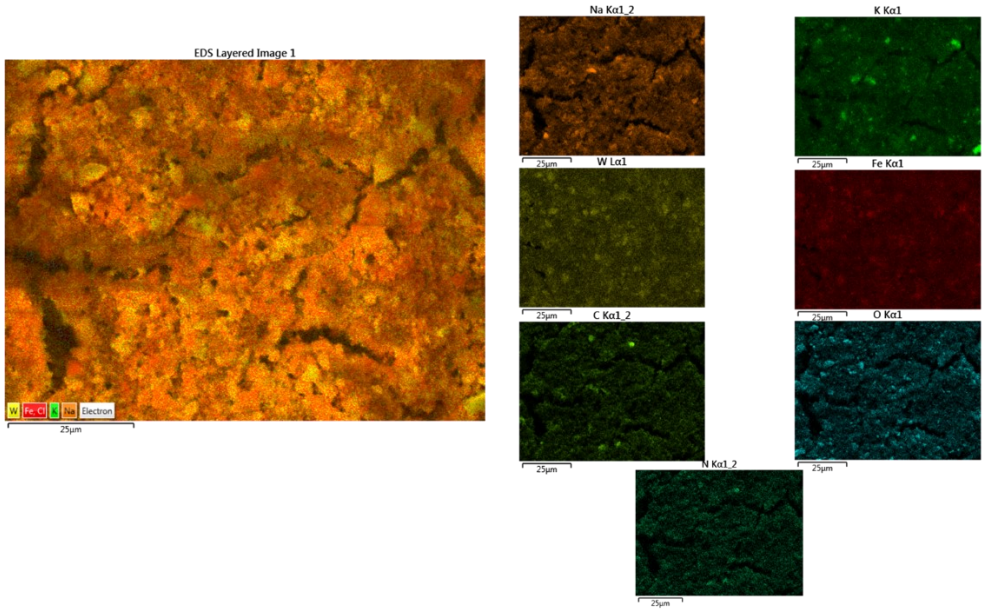

Figure 8: EDS maps of 4Fe-POM-CTPP material

REVIEWS AND APPROVALS

1. Principal Investigator:

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Name and Signature Date

2. Technical Review:

_____

Name and Signature Date

3. PI's Manager Signature:

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Name and Signature Date

4. PI's Division Director Signature:

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Name and Signature Date

5. Intellectual Property Review:

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

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Name and Signature Date