Fabrication of dye-sensitized solar cells based on metal substituted tetraphenyl porphyrins

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Introduction

Energy production and storage have been on the forefront of research for the past decade. As fossil fuels are diminished prices are increasing making fossil fuels less and less attractive as an energy source. DSSC solar cells have shown much promise showing increased efficiency, increased output and lifetime. Porphyrins are an attractive sensitizer due to its strong absorption bands in the visible region, thermal stability and good absorption in the semiconductor surface.

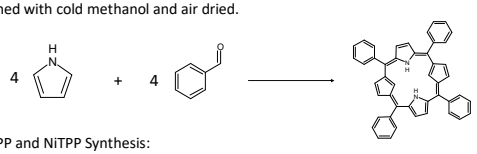
Objectives:

- To synthesize tetraphenylporphyrin (H2TPP), Copper-tetraphenylporphyrin (CuTPP) and Nickel- tetraphenylporphyrin (NiTPP).
- Fabricate a dye-sensitized solar cell based on H2TPP, CuTPP and NiTPP.
- Determine the open circuit voltage.

Methods

Preparation of dyes

- H2TPP Synthesis:
  H2TPP was synthesized by a modified version of the Adler method. Freshly distilled pyrrole was mixed in a 1:1 ratio with benzaldehyde in propionic acid as solvent and catalyst. The reaction mixture was refluxed at 145 for 30 minutes. The reaction mixture was then cooled to room temperature. After cooling the reaction was further cooled in an ice bath. The resulting deep-purple crystals were collected by vacuum filtration and washed with cold methanol and air dried.



- CuTPP and NiTPP Synthesis:
  H2TPP was mixed with a metal chloride in a 1:1 ratio in DMF and microwave assisted synthesis. The reaction was performed using reflux at 153°C for 5 minutes. The samples were cooled naturally to room temperature, filtered and dried.

Preparation of TiO2 photoanodes

10 g of TiO2 nanopowder was dispersed into 88 g of ethanolic solution (98% ethanol/water) by using ultrasonication for 30 min. 1.8 g of TIPP was added dropwise. Then the mixture was stirred for 5 hours. TiO2 were dip-coated on cleaned FTO glass four times and dried in air for 30 minutes, and then heat treated at 120 °C for 1 hour.

The counter electrode was prepared through the deposition of soot from a burning candle.

Preparation of the electrolyte

1.08 g of KI and 0.2 g of I2 were dissolved in 20 mL of acetonitrile and 5 mL of ethylene glycol and stirred for 30 minutes.

XRD Characterization

- A Bruker D2 Phaser, equipped with a Cobalt source, with a step of 0.05°, and a 5 s counting time. From 20 to 60 in 2 theta.

FTIR Characterization

- Perkin Elmer Frontier MIR / UTAR (Universal Total Attenuated Reflection)
- Collection range: 600 cm^{-1} to 4000 cm^{-1}
- Resolution of 4.0 cm^{-1}

UV-VIS Characterization

- Perkin Elmer Lambda 950 UV-VIS/NIR Spectrometer
- Collection range: 800 cm^{-1} to 250 cm^{-1}
- Resolution of 1 nm

Open circuit Voltage

- 10031S Southwire Multimeter.

Results

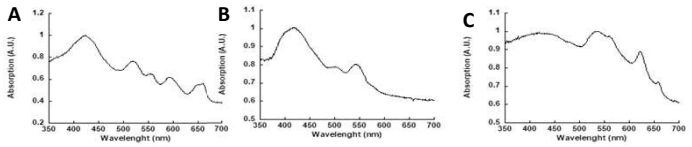


Figure 1: UV-Vis spectrum for the A.) H_2TPP, B.) CuTPP C.) NiTPP,

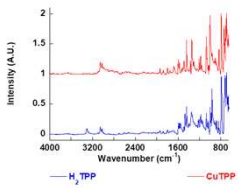


Figure 2: FTIR of the H_2TPP and CuTPP compounds synthesized under microwave assisted conditions.

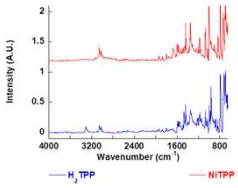


Figure 3. FTIR of the H_2TPP and NiTPP compounds synthesized under microwave assisted conditions.

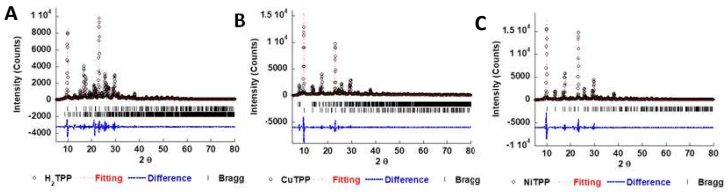


Figure 4: Powder X-ray diffraction of the A.) H2TPP, B.) CuTPP and C.) NiTPP.

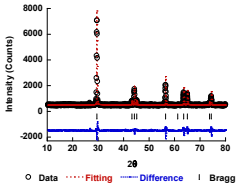


Figure 5: Diffraction patterns of TiO_2.

Sample	Space Group	a(Å)	b(Å)	c(Å)	α()	β()	γ()	GOF
H_2TPP	I-42/d	15.20	15.20	13.95	90.00	90.00	90.00	4.1
	P212121	12.02	19.30	14.69	90.00	90.00	90.00	
CuTPP	P21/M	15.09	8.64	12.00	90.00	116.02	90.00	3.5
	I-42/d	15.10	15.10	13.99	90.00	90.00	90.00	
NiTPP	I-42/d	15.09	15.09	13.89	90.00	90.00	90.00	4.3
TiO_2	I 41/amd	3.78	3.78	9.51	90.00	90.00	90.00	3.47

Table 1: Fullprof fitting results for the H_2TPP, CoTPP, CuTPP, NiTPP and PdTPP microwave assisted synthesized compounds

DSSC Semiconductor-Sensitizer material	Voltage(V)
TiO_2	0.088
TiO_2-H2TPP	0.175
TiO_2-CuTPP	0.258
TiO_2-NiTPP	0.052

Table 2: DSSC open circuit voltage with H2TPP, CuTPP and NiTPP sensitizer.

Discussion

Synthesis

- Anatase was successfully synthesized sodium sulfate and reflux method under oxygenation at 100°C. The XRD patterns were consistent with the literature.
- Anatase Rutile mixture 80:20% was successfully synthesized sodium sulfate and reflux method under oxygenation at 80°.

Characterization:

- Diffraction patterns were consistent with the literature
- Copper TPP and H_2TPP show two crystal phases present
- Nickel TPP Diffraction pattern showed only one phase
- TiO2 was determined to be in the anatase phase

Binding Of Porphyrin to $TioO_2$

- Solubility of TPP compounds was low in selected solvent and impregnation of the solid TiO_2 with H_2TPP, CuTPP, and NiTPP were low (only faint color was observed in the Fixed TiO_2)

Cell Functionality

- The cells functioned well under ambient inhouse light
- Porphyrin modified cells with exception of NiTPP showed enhanced voltage over TiO2 alone

Future work

TiO_2 in mixture of Anatase/Rutile
Increase H^2TPP, CuTPP, NiTPP in TiO_2
Purify the TPP before metalation
- single phase TPP

Determination of the following parameter of the DSSC:
- Fill Factor
- Current Density
- Efficiency

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Acknowledgements

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