Exploration of Photoactive catalytic materials for clean production of commodity chemicals

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A summer internship program report

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Abstract

Photoelectrochemical (PEC) water splitting represents a promising route for the direct conversion of solar energy into hydrogen and useful chemicals. Our research centered on the development and optimization of photo-electrocatalytic materials for solar-driven hydrogen production and CO_2 reduction. This work advances renewable energy technologies and supports the Kingdom's vision for green hydrogen and a circular carbon economy by enhancing light absorption, charge transportation, and material stability. These projects investigated $BiVO_4$ and Cu_2O as low-cost, high-performance, and sustainable electrodes for solar-to-chemical conversion for clean production of commodity chemicals (Hydrogen peroxide (H_2O_2) and urea). Additionally, a metal-free organic photocatalyst containing the photoluminescent benzothiadiazole moiety in an imine cage structure will be investigated as an emerging, customizable platform for photocatalysis applications.

1. Introduction

1.1 Internship context

In this summer internship at KAUST, we worked under the supervision of Prof. Yun Hau Ng and his team Dr, Rohul Adnan, Dr. Naveen Halappa, and Dr. Aliyah Fakim as mentors, each of whom guided us through a specific project. Therefore, over the course of six weeks, we rotated between projects, spending approximately two weeks with each mentor to gain hands-on experience in fabrication, characterization, and data analysis.

- With Dr. Rohul, we explored the synthesis and testing of Bismuth vanadate ($BiVO_4$) photoanodes for H_2O_2 generation.
- With Dr. Naveen, we investigated Cuprous oxide (Cu_2O) photocathodes for CO_2-to-urea conversion.
- With Dr. Aliyah, we focused on the design and analysis of the benzothiadiazole-imine cage [3+2]-BTD cage organic photocatalyst.

Through this rotation, we got to experience different aspects of photoelectrochemical research, develop skills in thin-film deposition, spectroscopy, and electrochemical measurements, and strengthen our understanding of material design for renewable energy applications.

1.2 Background

PEC water splitting is considered as a promising method for sustainable energy production. The basic principle of PEC water splitting involves a process that combines photocatalysis and electrochemistry to split water into hydrogen (H_2) and oxygen (O_2) using a photoelectrode that absorbs light to generate electron-hole pairs, with an external bias applied to enhance their duration for driving the electrochemical reaction.

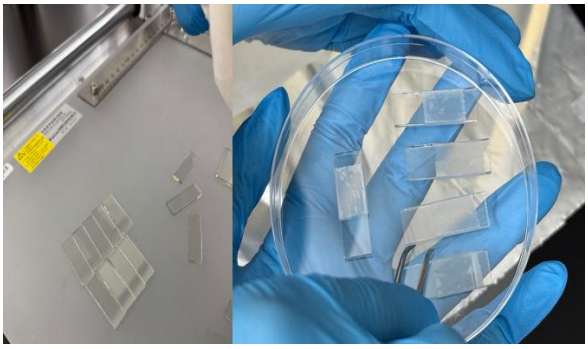
The two most crucial integrated components of a fully material-developed photodevice in a PEC system are the photoanode and photocathode.

- Photoanode
  The photoanode in PEC water splitting is an n-type semiconductor. It absorbs photons to excite electrons into the conduction band. The photogenerated holes migrate to the semiconductor/electrolyte interface, where they drive the oxidation of water to O_2.
- Photocathode
  A p-type semiconductor is used as the photocathode. Under illumination, electrons are excited and migrate to the semiconductor/electrolyte interface, where they drive the reduction of protons to H_2.

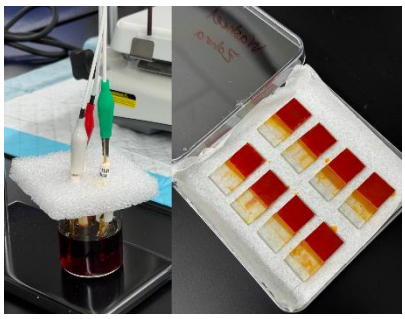
2. Materials and methodology

$BiVO_4$ Photoanode

- **FTO substrates:** After cleaning and cutting the quartz with a diamond cutter we specified an area of 1*1 with scotch tape



- **Bismuth oxoiodide BiOI solution:**
  - $Bi(NO_3)_3$ + KI in H_2O (25 mL) Then stirring for 30 min
  - Adjusting the pH to 1.6 with nitric acid (HNO_3)
  - Dropping 10 mL Ethanol + p-Benzoquinone
- **Electrochemical deposition:** depositing thin-film of BiOI with the electrochemical workstation at an applied potential of -0.12 (V) for 500 s

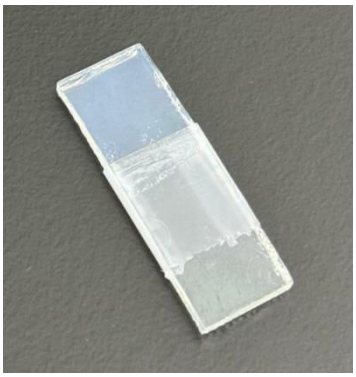


- **Vanadyl acetylacetonate $VO(acac)_2$ solution:** solution was made with 3 mL of dimethyl sulfoxide (DMSO) as a solvent to VO(acac)2
- **Annealing:** Dropping VO(acac)2 on BiOI then annealing at 450 °C for 2 h with ramp rate of 2 °C min^{-1}
- **Chemical etching:** etching for 30 min with Sodium Hydroxide (NaOH)

Cu_2O-based Photocathode

For this project we fabricated and tested 4 configurations of Cu2O-based Photocathodes with an addition of Copper(I) thiocyanate (CuSCN) and Zinc oxide (ZnO) layers. Configurations were: Cu_2O, Cu_2O-ZnO, CuSCN-Cu_2O, and CuSCN- Cu_2O-ZnO

- **FTO substrates:** After cleaning and cutting the quartz with a diamond cutter we specified an area of 1*1 with scotch tape
- **CuSCN synthesis and deposition (passivation layer):** CuSCN solution was made with Copper(II) sulfate ($CuSO_4$) + EDTA + Potassium thiocyanate (KSCN) with 25 mL of H_2O then depositing with potentiostat at -0.3 (V) for 120 s



- **Cu_2O synthesis and deposition (active layer):** Cu_2O solution was made with $CuSO_4$ + Potassium Dihydrogen Phosphate (KH_2PO_4) with 3.5 mL of lactic acid + 96.5 mL of H_2O, then adjusting pH to 12 by using potassium hydroxide (KOH). Deposition required heat with a water bath for 60 °C and potential was at -0.46 (V) for 900 s



- **ZnO synthesis and deposition (buffer layer):** ZnO solution was made with zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) + p-Benzoquinone in 20 mL of DMSO. Deposition required heat with an oil bath for 95 °C, after it reaches the targeted temperature, we add 0.5 mL of H_2O before starting deposition, which happened at -0.00011 (A) for 455 s



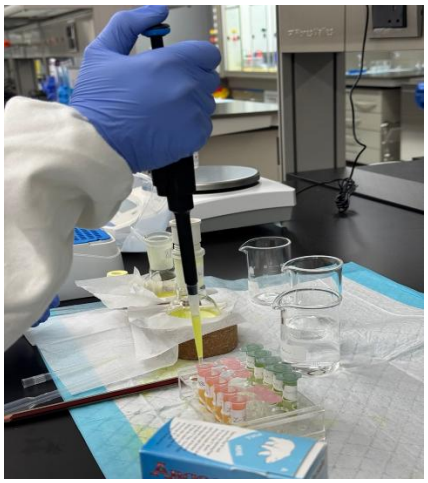
[3+2]-BTD Cage

Covalent organic frameworks (COFs) are an emerging class of organic porous materials that show promise for photocatalytic CO_2 reduction into useful chemicals applications due to their photochemical properties.

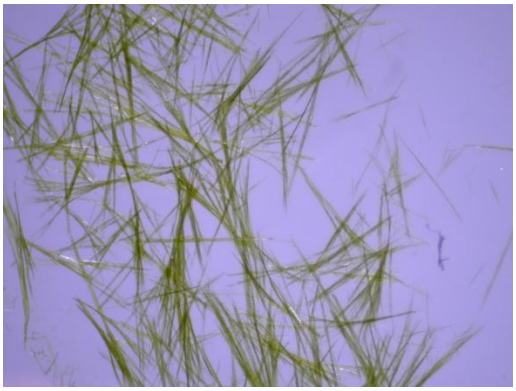
- **Synthesis of [3+2]-BTD cage**: benzothiadiazole-aldehyde (starting material) + 20 mL of chloroform ($CHCl_3$) + 20 µL of Trifluoroacetic acid (TFA) + 16.10 µL of tris(2-aminoethyl)amine (TREN). Stirring the reaction at room temperature for 24 h, then continued for an additional 24 h **after monitoring**



- **Monitoring:** Took 1.5 mL of the reaction solution, added a few drops of ether then centrifuged it for 3:30 min**.** Then wash and centrifuge for 3x with $CHCl_3$ and once after $CHCl_3$ with only ether

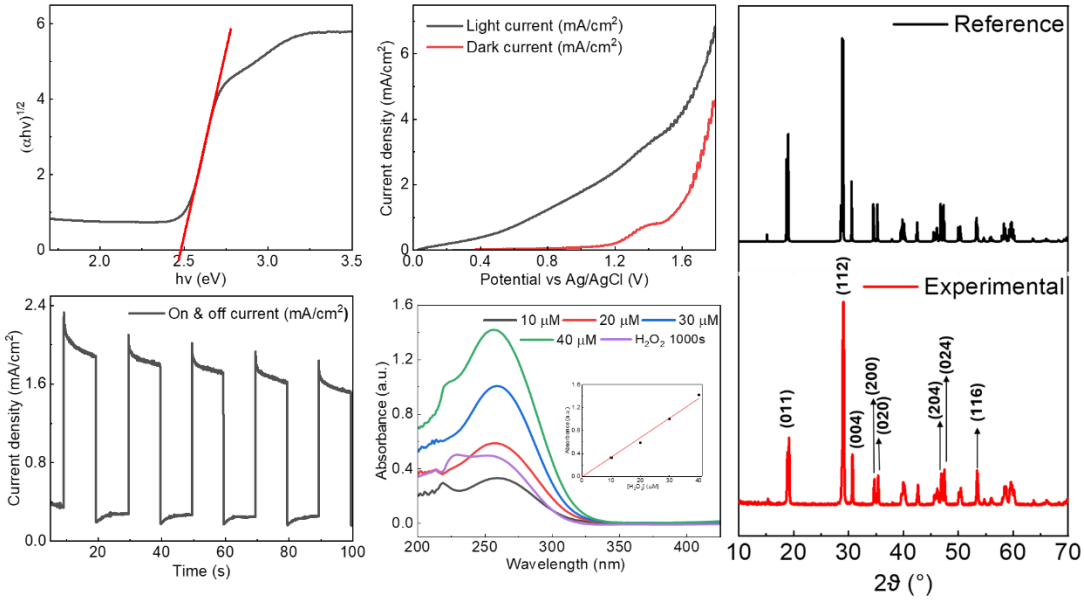


- **Purification:**
    - First, washed and centrifuged the crude product 3x with $CHCl_3$, final wash had few drops of ether
    - Second, dried the product completely under vacuum
    - Third, product was washed with 1.5 mL of water for 3x
    - Fourth, freeze-dried the product fully under vacuum with liquid nitrogen
- **Recrystallization of the starting material (SM):** we did this chemical purification technique with Acetonitrile (ACN) and got divided into two samples, one with and without hexane.



3. Results and conclusions

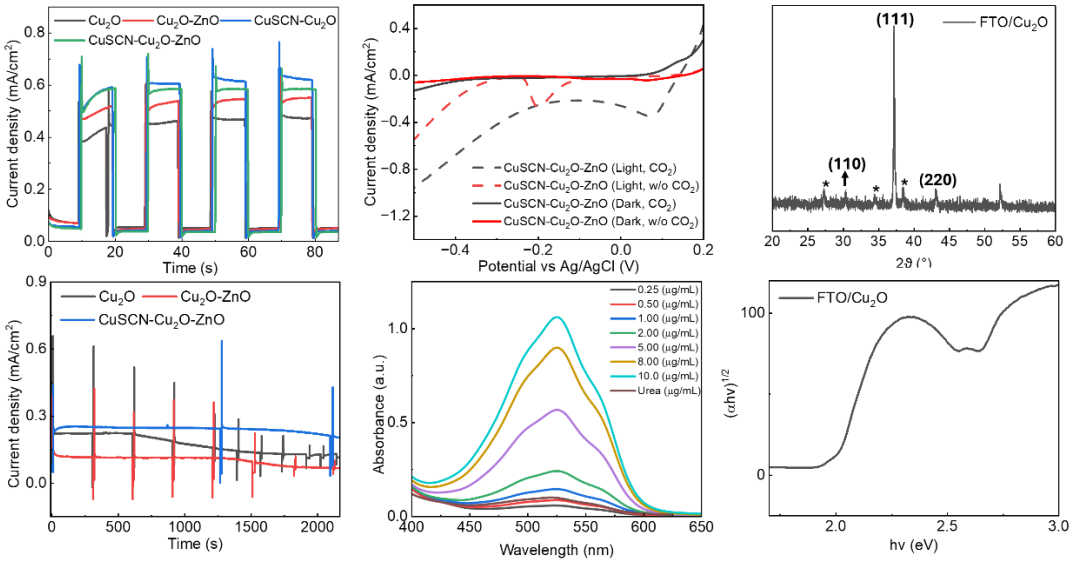
$BiVO_4$ photoanode



- **Structural confirmation:** XRD patterns confirm monoclinic $BiVO_4$ phase with strong crystallinity, suitable for PEC applications.
- **Optical properties:** Tauc plot shows a band gap of 2.484 eV, aligning well with visible-light absorption for efficient solar harvesting.
- **Photoelectrochemical performance:** I–V curves reveal a photocurrent density of about **2.0 mA/cm² under illumination**, with clear light–dark separation.
- **Stability & activity:** Transient photocurrent responses indicate good stability under on/off cycling.
- **Functionality:** UV-DRS and calibration confirm H_2O_2 production over 1000s, validating its dual functionality for water splitting and peroxide generation.

➢ **Conclusion:** $BiVO_4$ is a promising, stable, low-cost photoanode with visible-light activity, capable of producing both H_2 and H_2O_2 and can be further improved by supportive interfacial engineering.

Cu_2O-based photocathode



➢ **Cu_2O photocathode:**

- XRD confirms crystalline Cu_2O phase (peaks at (110), (111), (220)).
- Tauc plot indicates a direct band gap of 2.0–2.2 eV, enabling visible-light absorption.
- Amperometric I–t curves show stable and reproducible photocurrent switching under light/dark cycles.
- UV-DRS and calibration confirm CO_2-to-urea conversion, though with limited yield.

➢ **Cu_2O-ZnO photocathode:**

- Demonstrates enhanced current density and stability compared to bare Cu_2O.
- The ZnO layer improves charge separation and suppresses recombination.
- Absorbance measurements confirm higher light harvesting efficiency.

➢ **CuSCN-Cu_2O photocathode:**

- CuSCN acts as a hole-transport layer, reducing surface recombination losses.
- Shows improved photocurrent response compared to bare Cu_2O.
- Maintains reasonable stability but still lower than the full tri-layer system.

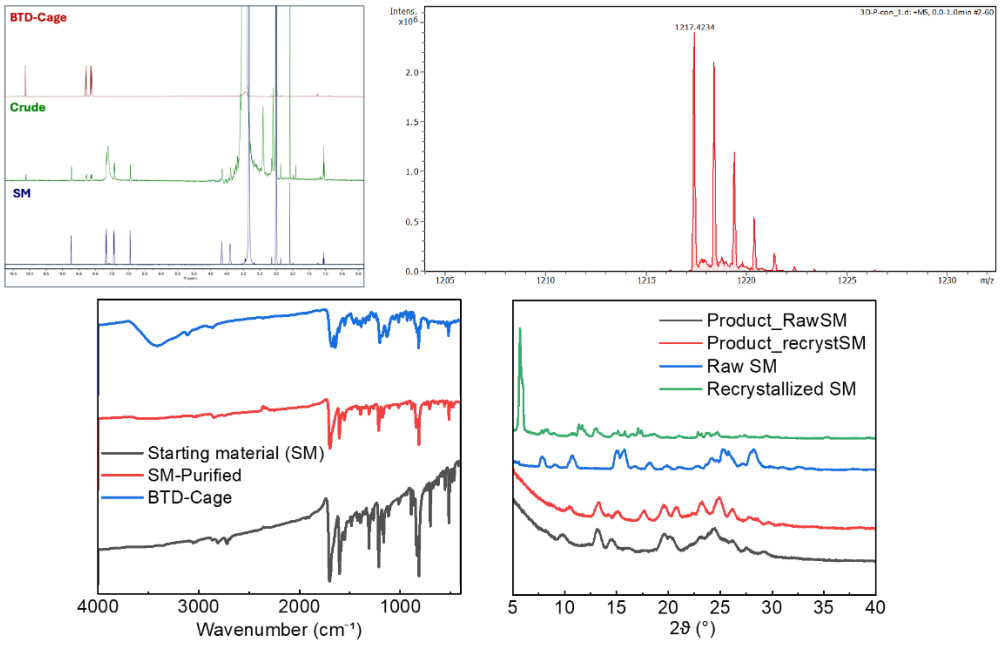
➢ **CuSCN-Cu_2O-ZnO photocathode:**

- Shows the highest photocurrent density and best long-term stability among all tested systems.
- LSV curves indicate strong selectivity toward CO_2 reduction under light vs dark conditions.
- Chronoamperometry (~2200s) reveals sustained activity with minimal degradation.

- Synergistic effect of CuSCN (hole transport), Cu_2O (light absorption), and ZnO (electron extraction) yields maximum urea production.

✓ **Conclusion:**
Through a stepwise design Cu_2O → Cu_2O-ZnO → CuSCN-Cu_2O → CuSCN-Cu_2O-ZnO the photocathode project demonstrates how layer engineering systematically enhances light absorption, charge transport, stability, and product selectivity. The CuSCN-Cu_2O-ZnO tri-layer stands out as the most efficient system for solar-driven CO_2-to-urea production.

[3+2]-BTD Cage



- **Synthesis & verification:** Successfully synthesized via [3+2] cyclo-condensation, confirmed by NMR, FTIR, PXRD, and HRMS (m/z ~1217).
- **Structural purity:** FTIR shows characteristic shift from carbonyl to imine, and PXRD confirms crystalline cage formation compared with raw/recrystallized SM.
- **Optical activity:** UV-vis absorbance increases with cage concentration, and calibration validates urea detection capability.
- **Potential applications:** Designed as a metal-free, organic, customizable photocatalyst, suitable for both urea and H_2O_2 production.

➢ **Conclusion:** The BTD cage is a versatile, photoluminescent, metal-free catalyst platform with confirmed stability and tunable functionality for solar-driven photocatalysis.

4. Challenges and Obstacles

- **BiVO4 photoanode:**

- Slow charge transport in $BiVO_4$ limits photocurrent efficiency.
- Surface recombination hinders water oxidation kinetics.
- H_2O_2 yields are modest due to competing oxygen evolution reaction (OER).
- Stability may degrade over extended operation in aqueous electrolytes.

- **Cu2O-based photocathodes:**

- Photocorrosion of Cu_2O reduces lifetime.
- Low Faradaic efficiency due to side reactions (e.g., H_2 evolution).
- Interfacial defects at heterojunctions can trap carriers.
- Selectivity limitations: competing products during CO_2 reduction.
- Scaling challenges for large-area devices.

- **[3+2]-BTD cage:**

- Synthesis yield and reproducibility depend heavily on reaction conditions.
- Limited light absorption range compared to inorganic compounds.
- Photocatalytic activity is not yet fully benchmarked against standard materials.
- Stability in aqueous/operating conditions requires validation.

5. Future work

- **BiVO4 photoanode:**

- Enhancing the photoanode by adding more supportive layers for maximizing H_2 and H_2O_2 generation.

- **Cu2O-based photocathodes:**

- Optimizing photocathode to increase the production of urea.

- **[3+2]-BTD cage:**

- Applying and testing the [3+2] BTD-cage for photocatalytic properties and applications in urea synthesis & H_2O_2

6. Acknowledgment

We, Zahraa Malaekah and Washeel Hashim, would like to sincerely express our gratitude to Professor Yun Hau Ng and his incredible team Dr. Rohul Adnan, Dr. Naveen Halappa, and Dr. Aliyah Fakim for their invaluable guidance and mentorship throughout this internship. We are deeply thankful for their continuous support, insightful discussions, and supervision during each stage of our projects. Their expertise and encouragement have greatly enriched our research experience.

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