Synthesis and Characterization of Cu_2WO_4

Nicholas Rock
Physics, Rhode Island College

Mentor: Ceren Yilmaz Akkaya Advisor: Pratap Rao

Introduction/Rxn

Clean energy solutions to achieve better sustainability are becoming increasingly necessary not only for modern societies as energy demands increase, but also in developing countries as modern infrastructure is introduced. These solutions will improve upon current designs with limited infrastructure and large up-front costs by reducing overall energy demands as well as improved efficiencies. Currently, total annual energy consumption needs are met by 78.29% fossils fuels, with the remaining being met by primarily biomass and then all other renewable sources.[1] A major limiting factor to these renewable sources is their raw power output versus cost. Coal produces 7755 TWh/y at a cost of $3-6/TWh, while a more sustainable energy source such as solar (photovoltaics) produces only 12 TWh/y at a cost of $10-20/y.[2] Of course, investment into solar energy would allow its net output to increase dramatically, but the cost associated with standing solar panels across the world would be too large with current costs.

Recently there has been a significant interest in creating viable cells to utilize the large amount of solar energy received on the Earth's surface, which will be enough to meet current and future human energy demand.[2, 3] The current best performing photoelectrochemical cells are capable of up to 18% efficiency, with a theoretical maximum of ~30%. They use a multijunction of semiconductors to perform photo electrolysis and utilize cheaper material than expensive Si and other rare metals with which solar panels are currently constructed. Unfortunately, there has been difficulty in maintaining performance over longer periods of operation as the photoelectrode materials are not stable under operating conditions (i.e., in sunlight) and degrade over time.[4,5] One method that has had promising results is coating photoelectrodes with another catalytic material to reduce the rate of photo corrosion.

In this project, I have focused on synthesis, characterization and electrode preparation of one such semiconductive material, Cu_2WO_4. First, $CuWO_4$ was prepared by following a reported solid-state procedure.[9] Then, a comproportionation reaction between $CuWO_4$ and elemental copper was utilized for the first time to synthesize Cu_2WO_4. The obtained powder was ball-milled in ethanol before film preparation. For analysis and surface characterization, I used techniques such as scanning electron microscopy (SEM), X-Ray diffraction (XRD) and attenuated total reflection infrared spectroscopy (AT-IR) with the intent to provide framework measurements for future studies. Optical data of the tungstate was taken as well, along with the calculation of the experimental band gap and absorbance spectra.

Powder Characterization

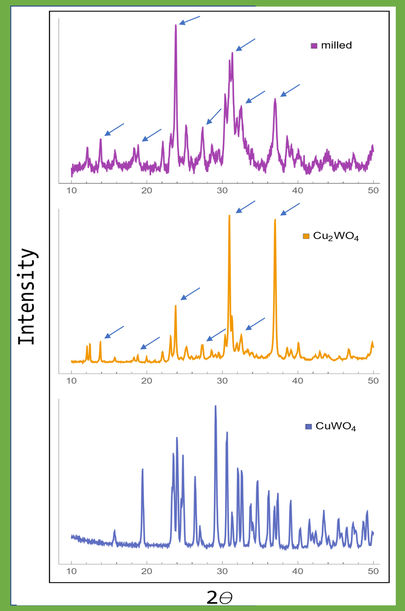


Figure 1: Powder XRD

Cu_2WO_4 is formed after only two steps of milling and heating.[7] First, CuO is ground with WO3 into CuWO4 and then heated to 800°C and held isothermally for 12 hours. After confirming the product to be strongly crystalline and with minimal impurity, the $CuWO_4$ is then ground with elemental copper. Finally, it is heated, this time under a steady Ar-atmosphere and a sacrificial copper sheet.[7]

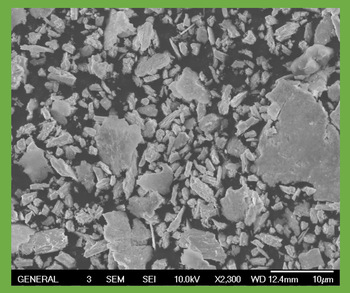


Figure: 2 SEM imaging

Films

Film deposition from ethanol suspension

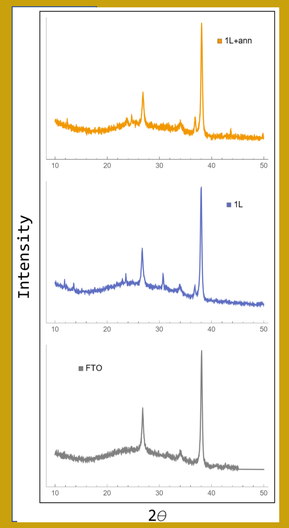


Figure 3: XRD of the films

Plotted here are the XRD profiles of the substrate, fluorine doped tin oxide, and 1 & 3-layers copper (1+) tungstate deposited on FTO substrate.

As one of the first experiments done, film creation was poor and thus the deposited layer is very thin. Any sample peaks present are obfuscated by noise and the peaks for the substrate are relatively overpowering.

A new slurry preparation method was devised based off these results, which accounts for the large particle size of copper tungstate.

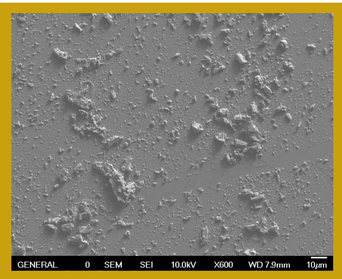


Figure 4: SEM image of the 3 layers of copper (1+) tungstate on FTO

Film deposition from ethanol suspension in the presence of binders

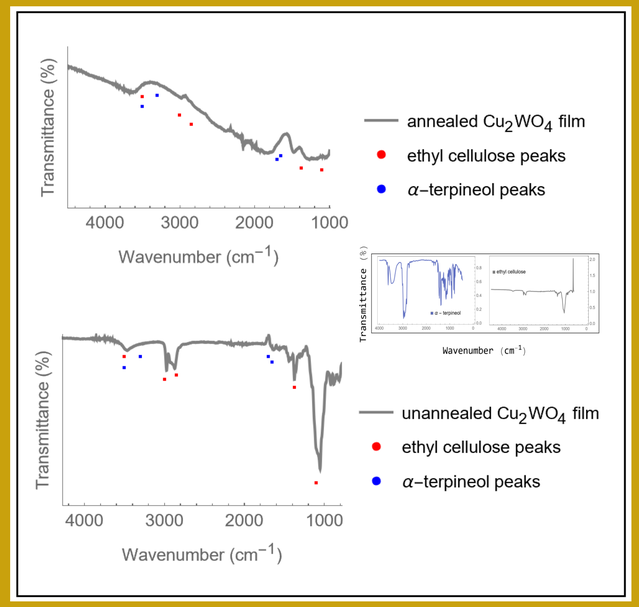


Figure 5: AT-IR, labeled peaks

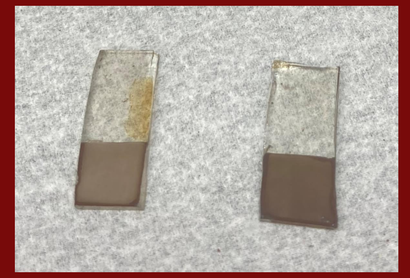
Plotted are the AT-IR spectra of the film annealed at 380 °C deposited from an ethanol suspension containing ethyl cellulose and α-terpineol.

On the bottom is the spectrum of the unannealed film, which displays strong peaks that can be ascribed to the organic materials in the coating suspension.

On top is the annealed film. Most of the organic content have been removed successfully, thus the film is ready for further testing.

Results

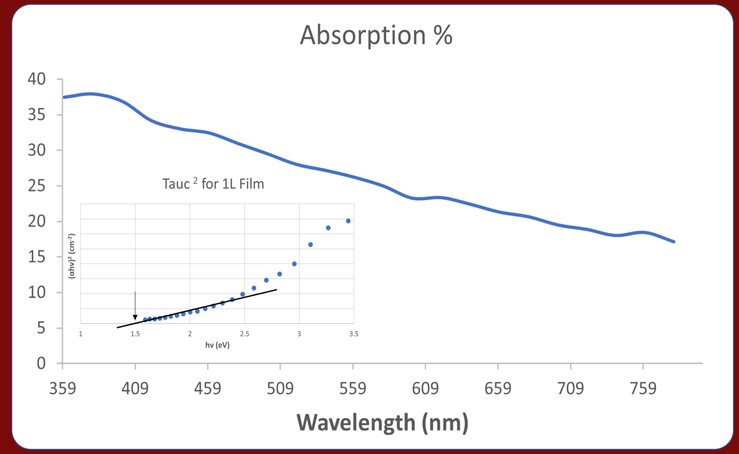
Improved Films



Final films are well deposited with a thin, yet uniform spin coated layer.

They have been prepared by the new slurry preparation method, and have been annealed at 380°C to remove leftover organics

Optical Properties



Band gap energy (E_g) is estimated via the Tauc plot method.[8]

A result of ~1.5 eV is fairly consistent with theoretical calculations and allows for photoelectrochemical testing.

References

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