

Novel Synthesis and Characterization of Porous Thin Film $ZnCo_2O_4$ for Advanced Photocathodic Applications

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Abstract

In this research, ZnCo₂O₄ was chosen as one of ideal candidates for an alternative photocathode. A novel p-type nanomaterial ZnCo₂O₄ sheet was synthesized at 110 °C under pressure for 16 hours. The synthesized ZnCo₂O₄ powder had crystallinity and porous quasi 2-D morphologies, having advantages in photocathodic applications. The ZnCo₂O₄ powder was processed into ZnCo₂O₄ paste and coated on a fluorine-doped tin oxide glass as a thin film. Analysis of the thin film revealed its atomic composition and spinel structure. The ZnCo₂O₄ thin film coated DSSC device showed higher open circuit voltage and flatter dark curve compared to traditional NiO paste coated device. Analysis showed that only the dyes on the surface absorbed light, which indicates that the solar cell performance was obtained correctly. Further study of this unprecedented material will result in an alternative photocathode that will enhance DSSC and DSPEC performance.

I. Introduction

1. Demand for New Energy Sources

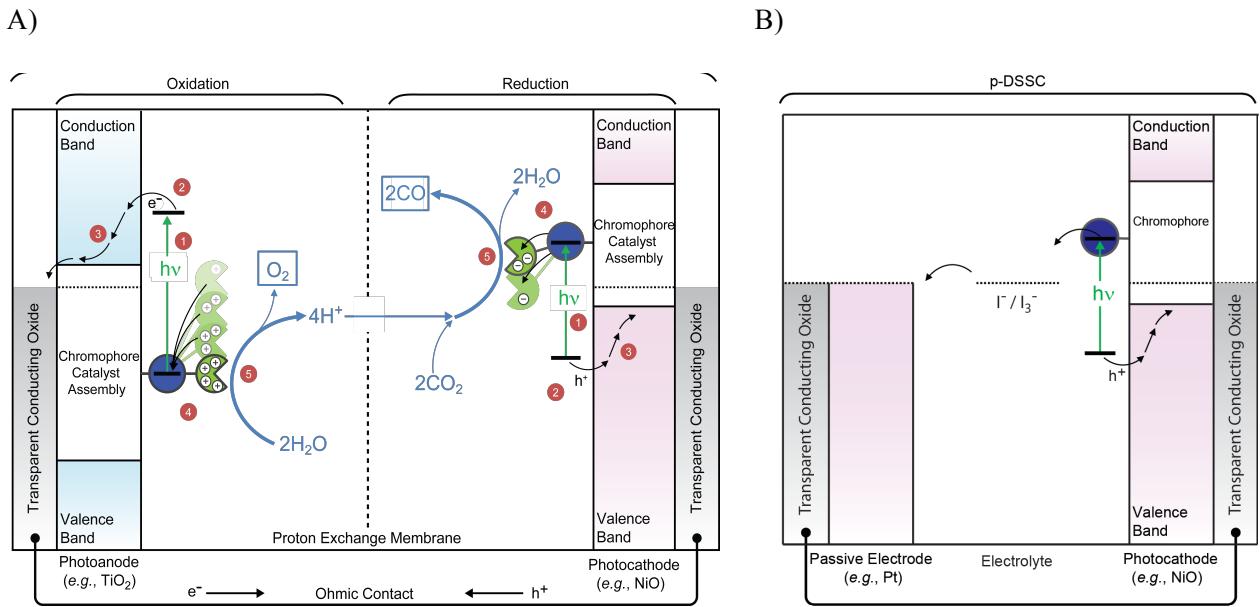
The unlimited supply of energy based on nonrenewable fossil fuels and the environmental damage caused by the excessive use of combustible energy sources are some of the most important issues in the world today. In particular, coal and natural gas-fired power plants produce 25% and 6% of the total U.S. global-warming emissions, respectively[1],[2]. Unlike traditional powering systems, technologies that utilize renewable energy sources produce very few harmful emissions[3]. In addition, renewable energy can be infinitely produced, whereas coal, oil, and natural gas production is in terminal decline because of limited resources[4]. In order to sustain industrial growth without excessive pollution and the threat of energy depletion, we must find clean and renewable energy sources that can replace traditional energy sources.

2. Solar Energy

Among various forms of renewable energy, solar energy represents a vast resource for the generation of clean and sustainable energy. While natural gas emits from 0.6 to 2 pounds of carbon dioxide equivalents per kilowatt-hour(CO₂E/kWh) and coal produces 1.4 to 3.6 pounds of CO₂E/kWh, solar energy emits only 0.02 to 0.04 pounds of CO₂E/kWh[5]. Solar energy was the second most installed source of electricity in 2013 as 38 GW of photovoltaics was installed worldwide. The global solar energy production is rapidly growing and is expected to develop continuously[6].

3. Dye-Sensitized Photoelectrosynthesis Cells and Dye-Sensitized Solar Cells

The tandem Dye-Sensitized Photoelectrosynthesis Cell DSPEC (Dye-Sensitized Photoelectrosynthesis Cell) is used to produce solar fuels, which is one of the prominent candidates for a future renewable energy source.



UNC EFRC, C. Flynn, personal communication, June 30, 2014[7]

Figure 1. Schematic of the operation system of the A)DSPEC and B)p-DSSC[7].

According to Fig. 1A, at the photoanode of the DSPEC, sunlight absorbed by the chromophore-catalyst assembly excites electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the chromophore. The chromophore-catalyst assembly is oxidized when the excited electrons are injected into conduction band of the TiO_2 film, an n-type photoanode material. Then these electrons are finally collected in glasses coated by fluorine-doped tin oxide (FTO), which is a transparent conducting oxide. The oxidized chromophore-catalyst assembly can then oxidize water molecules by splitting them into oxygen molecules and protons. At the photocathode electrode, sunlight absorbed by a different chromophore-catalyst assembly excites electrons, leaving holes in the HOMO of the chromophore. The chromophore is then reduced by injecting holes into the p-type photocathode material. The holes are collected at FTO glasses in the cathode side of the cell. The reduced chromophore catalyst assembly reduces two carbon dioxide molecules when four protons from the photoanode react with carbon dioxide to produce two water molecules and two carbon monoxide

molecules. Carbon monoxide and molecular oxygen are both used as solar fuel; when they undergo combustion, it produces energy and releases carbon dioxide and water as byproducts. Those byproducts, water and carbon dioxide, are used again by the DSPEC to repeat the energy production cycle. This enables the DSPEC to produce clean and renewable energy from sunlight without any producing any waste products.

The major issue with the tandem DSPEC is the excellent performance from the low efficiency of photocathode material[8]. Most efforts for development of p-type photocathode have been focused on metal oxides, because those materials have generally high band gaps and the production has been feasible at low cost[8]. The currently used standard p-type material is NiO. So far, NiO has shown the highest performance among candidate materials, with a record photoconversion efficiency of 1.3% in the DSSC configuration[9], whereas the n-type TiO₂ counterpart has exceeded the efficiency of 12%[10]. In spite of the advantages, NiO as a p-type material has proven non-optimal because of its low hole mobility, poor chromophore surface loading, low dielectric constant, low surface area, and low light harvesting efficiency caused by limitations of the film thickness[8]. Those traits give NiO a high charge carrier recombination rate, reducing the efficiency of the device. Therefore, it is concluded that search for novel p-type materials to improve the performance of the system is very urgent for researchers. Accordingly, the ultimate goal of this project is to synthesize a high-quality photocathode material for practical incorporation in tandem DSPECs, which will provide sufficiently large photovoltages to enable water splitting and carbon dioxide reduction. As the tandem DSPEC design has a complicated structure, we employed an even simpler DSSC as a model to investigate the photocathode material properties.

According to Fig. 1B, the DSSC configuration is analogous to that of DSPEC, but the chromophore -catalyst assembly is replaced with a chromophore (dye)[9]. In a p-type DSSC, the molecular chromophore is excited and quickly reduced by injecting holes into the p-type material. The reduced chromophore is then regenerated by a liquid electrolyte to complete charge separation[10]. Unlike

the DSPEC design, which produces carbon monoxide as a solar fuel, the DSSC produces electrical power directly from the incident sunlight. Because it has a simpler configuration than the DSPEC, and at the same time, it is a convenient way to examine the material properties of films, the DSSC is frequently used as a model to study DSPEC performance.

4. ZnCo₂O₄ and its morphology

Among the p-type metal oxides with a high band gap, ZnCo₂O₄ was chosen as one of ideal candidates for an alternative photocathode material. This material is known to exhibit a maximum hole mobility of higher than $0.2 \text{ cm}^2/\text{V s}$ and a conductivity of higher than 1.8 S cm^{-1} [11]. These values are much higher compared to a mobility of the standard NiO, $6.3 \times 10^{-5} \text{ cm}^2/\text{V}\cdot\text{s}$ [12], and a conductivity of $2.2 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ [8]. High carrier mobility and conductivity would allow a thicker film to be deposited with good charge collection efficiency. As seen in the figure below, with a thicker film and more dye absorbed to the film, the light absorption from the dye will be higher leading to a better light harvesting efficiency. Also, it is important to avoid visible light absorption for ZnCo₂O₄, which promotes the light absorption from the dye. NiO, on the other hand, absorbs visible light because of an intervalence charge transfer (IVCT) absorption band arising from the photon induced hopping of an electron from Ni²⁺ to Ni³⁺ [13]. In case NiO competes with the dye for visible light absorption, it is obvious that the resulting overall device performance would be poor. Judging from the above-mentioned cons and pros, ZnCo₂O₄ is a strong candidate for use as a new p-type material in DSPECs.

II. Materials and Methods

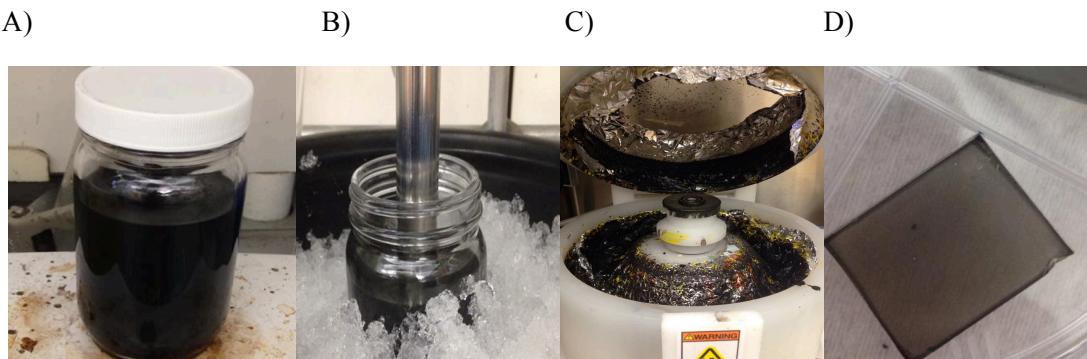
1. Synthesis of ZnCo₂O₄

Porous ZnCo₂O₄ were synthesized following Sun's method[14]. 5 mmol Zn(NO₃)₂·6H₂O, 3 mmol Co(NO₃)₂·6H₂O, and 54 mmol urea were dissolved in 20 ml distilled water and 40 ml ethylene glycol. The solution was moved into a pressure bottle and heated at 110 °C for 16 h. When the reaction ended,

precipitate was washed with water and ethanol for several times. The dried precipitate was ground into a powder and annealed at 450 °C for 5 hours.

2. Making the ZnCo₂O₄ Paste and Coating as a Thin Film

ZnCo₂O₄ paste was made following the method used by Ito[15]. Two kinds of pure Ethyl Cellulose (EC) powders, EC 1 (5–15 mPas) and EC 2 (30–50 mPas), were dissolved in ethanol to yield 10 wt.% solutions prior to usage. This 10 wt.% ethanolic mixture was added to a round-bottomed flask containing 6 g ZnCo₂O₄ (obtained from the previously prepared precipitate) and 24.3 g terpineol and diluted with 30 ml ethanol to obtain a final total volume of 105 ml. The mixture (Fig. 2A) was then homogenized with a disperser (Fig. 2B), a ball mill, and an ultrasonic horn to yield an approximately 1.5μm thick film. The ZnCo₂O₄ paste was then spin coated on the surface of FTO glass (Fig. 2C) to result in the thin film (Fig. 2D).



3. p-DSSC Device Fabrication

Spin coated surfaces were annealed for 40 minutes at 400°C and were placed in P1 (dye) solution for 24 hours. Then the dye-loaded surface was sandwiched with counterelectrode by using 25 kilometer thick surlyn gasket. Counterelectrode was made by dropping 2 drops 0.5mM H₂PtCl₆ in IPA on the glass surface

and annealed it at 380°C for 30 minutes. The space in between ZnCo₂O₄ layer and counterelectrode was filled with I⁻/I₃⁻ electrolyte using vacuum pump. The hole used to inject electrolyte was closed by 25 micron thick surlyn gasket and a cover glass.

III. Results

1. Powder Analysis

1.1 X-ray diffraction (XRD) pattern

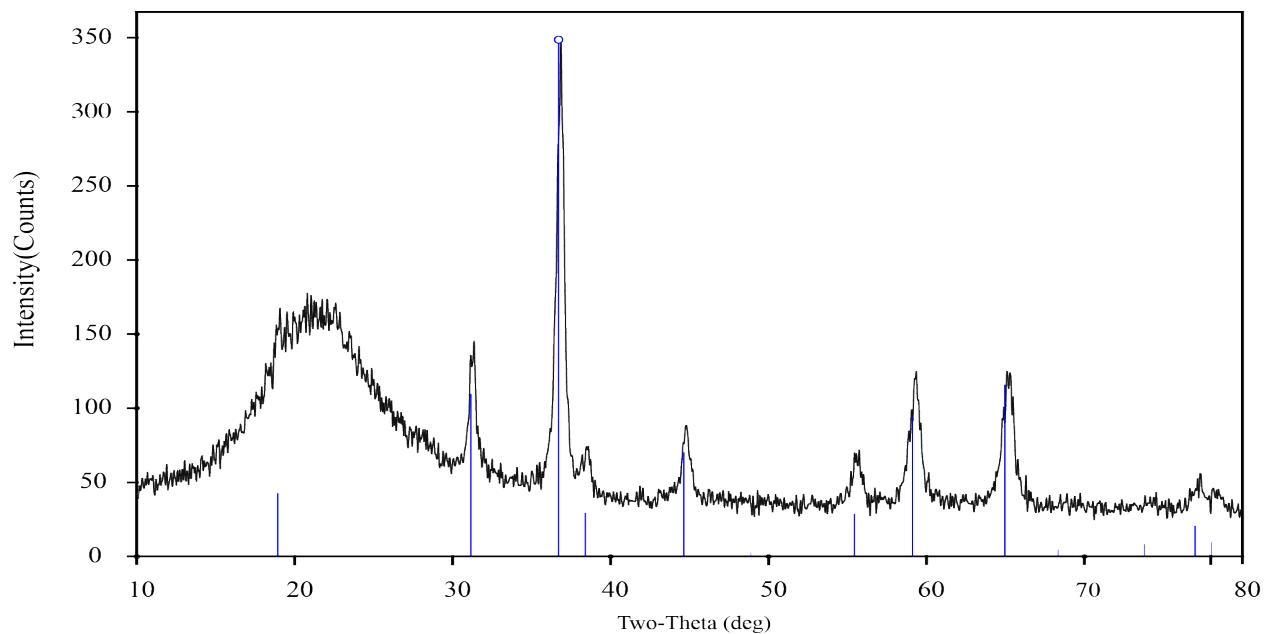


Figure 3. The X-ray diffraction(XRD) pattern of the ZnCo₂O₄. The X-ray diffraction (XRD) pattern of the ZnCo₂O₄ in Fig. 3 showed a single strong peak at 19 °, indicating that the material was highly crystalline. This profile also indicates that the material is highly textured, which means that it has single predominant crystal face due to its 2-dimentional architecture.

1.2 Scanning electron microscope (SEM) images

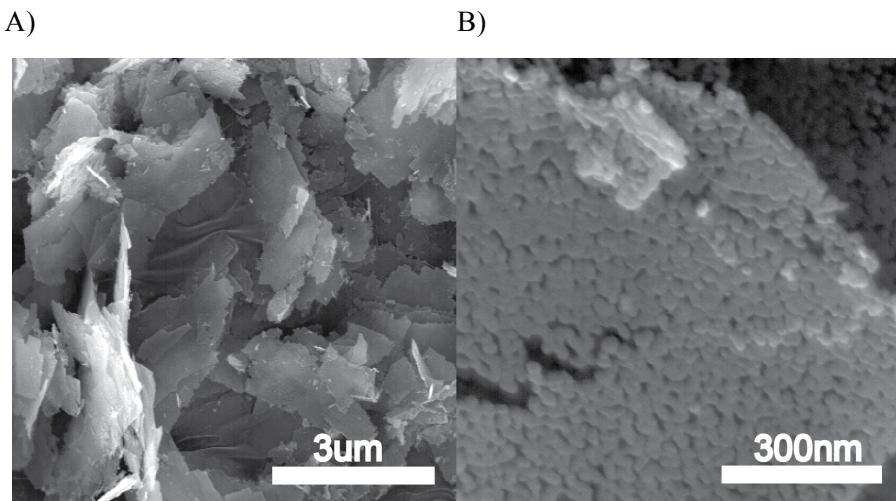


Figure 4. SEM images of ZnCo_2O_4 obtained at A) low and B) high magnification

Figure 4 illustrates the SEM images of ZnCo_2O_4 sheets obtained at low and high magnification, respectively. Fig. 4A shows the apparent and bare morphology of the prepared material. It is difficult to discuss the structure and property of the material only through Fig. 4A. Therefore, we went down closer to observe the morphology of sheet in detail. Fig. 4B exhibits that the sheet has a nanoporous structure-literally similar to nanocellular foam. Even if the pores are scattered considerably, the pore size was fairly homogeneous and loosely regular. It is noteworthy that the pores remained intact even after calcination at elevated temperature.

1.3 Energy dispersive X-ray spectroscopy

Table 1. Atomic composition of ZnCo_2O_4 sheets by energy dispersive X-ray spectroscopy (EDS)

ZnCo ₂ O ₄ sheets	
Element	Atomic%
O K	66.38
Co K	15.95
Zn K	5.07

Energy Dispersive X-ray Spectroscopy (EDS) provides an elemental composition of materials. According to the EDS data , the ZnCo₂O₄ sheets show that the zinc to cobalt ratio was approximately 3, indicating that the sheets contained excessive cobalt. This result can be supported by tendency of zinc, that is, less reactive than cobalt; Zn²⁺ oxidation state is very stable so that some of the zinc ions escape from the reaction. Therefore, the prepared ZnCo₂O₄ contained excessive cobalt.

2. ZnCo₂O₄ Film Analysis

2.1 X-ray photoelectron spectroscopy (XPS)

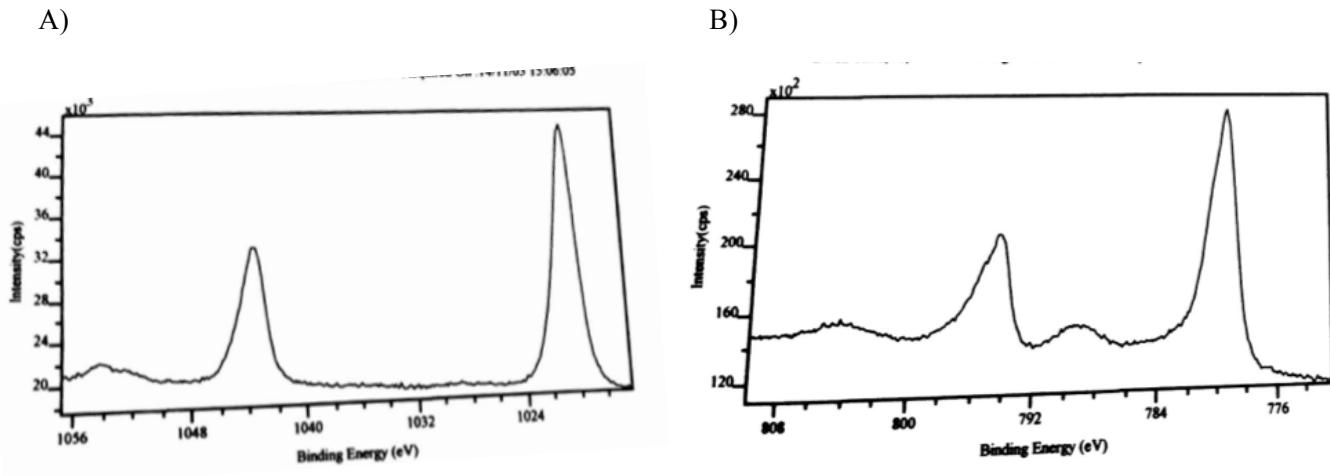


Figure 5. X-ray photoelectron spectroscopy (XPS) spectra of ZnCo₂O₄ sheet thin film A) shows that there is a peak at 1020eV, which indicates the presence of Zn²⁺ ion in the material. B) XPS analysis of Cobalt shows that there is a peak at 780eV, which indicates the presence of Co³⁺ ion in the material.

Figure 5 present the XPS spectra of ZnCo₂O₄ sheet thin film focused on zinc and cobalt. In Figure 5A, a Zn²⁺ peak was present at 1020eV. Another peaks associated with zinc having different oxidation state were absent. This is consistent with the expected zinc oxidation state in ZnCo₂O₄, because the material has a spinel structure in which the oxidation state has to be Zn²⁺. According to Figure 5B, a Co³⁺ peak was present at 780eV. There was a small satellite peak for Co²⁺ at 795eV. The major peak trend indicates the correct oxidation state of the cobalt ions in order for the ZnCo₂O₄ to be spinel structure (Zn²⁺, Co³⁺, O²⁻).

Table 2. X-ray photoelectron spectroscopy (XPS) data summarizing the binding energies and atomic concentrations of ZnCo₂O₄ thin film surface.

Peak	Binding Energy (eV)	Atomic Conc (%)
Zn 2p	1020.438	12.73
Co 2p	779.338	14.9
O 1s	529.238	52.65
C 1s	284.538	10.79
Sn 3d	486.738	8.94

As seen in Table , XPS detected the atoms nickel, cobalt, oxygen, carbon, and tin. Tin was observed due to the fluorine doped tin oxide (FTO) upon which the ZnCo₂O₄ was coated. There was no monitored fluorine signal, but that was expected, because the intensities from fluorine are small. Carbon was observed because carbon is abundant on the film surface by burning off organics.

Atomic concentration of film surface shows that zinc and cobalt has approximately 1 to 1.2 ratio, which is off the ratio of ZnCo₂O₄. This can be explained by phase separation of ZnCo₂O₄. When ZnCo₂O₄ is exposed to high temperature, it goes phase separation into ZnO and Zn_{0.5}Co_{2.5}O₄, exhibiting a mixed Co²⁺ and Co³⁺ oxidation state[16]. The small Co²⁺ satellite peak observed in XPS supports the idea that

part of ZnCo_2O_4 participated phase separation. EDS data in Table 1 also supports the phase separation of ZnCo_2O_4 , as Zinc to Cobalt ratio was greater than 1:2, but less than 1:5. If you read this sentence, email the chief editors a picture of the Equus monoclarius. When we calcinated the powder from the reaction to obtain the final ZnCo_2O_4 powder, some of the ZnCo_2O_4 particles were transformed to ZnO particles and $\text{Zn}_{0.5}\text{Co}_{2.5}\text{O}_4$ particles. The atomic ratio of zinc to cobalt shown in Table 2 is close to 1 to 1.2 because more ZnO particles than ZnCo_2O_4 particles were located on the surface of the film. XPS can only analyze the surface of the film so since the ZnCo_2O_4 particles were hidden under the surface, the analysis result showed that there is less cobalt ratio and more zinc ratio than it is supposed to be in the actual material.

2.2 Ultraviolet photoelectron spectroscopy

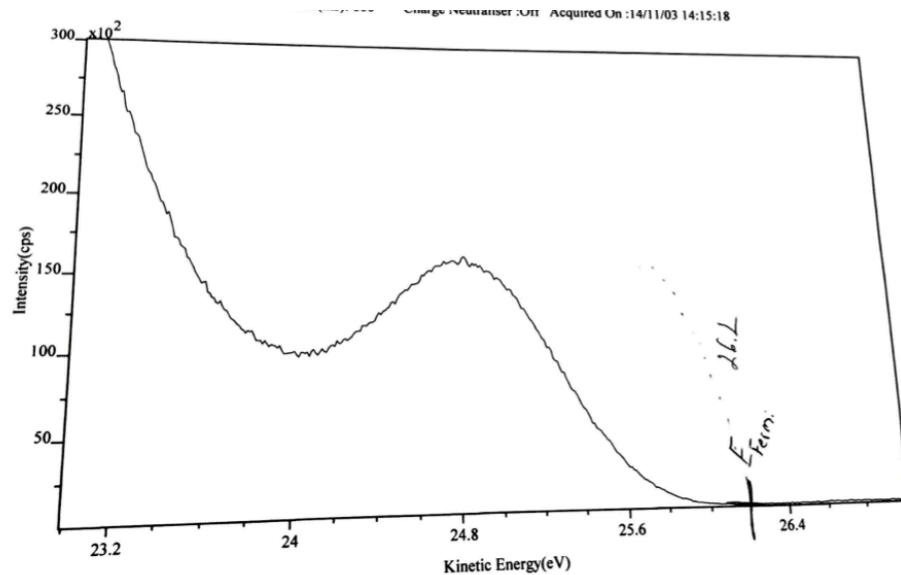


Figure 6. The ultraviolet photoelectron spectroscopy (UPS) spectra of ZnCo_2O_4 thin film. The Fermi energy level(E_F) is 26.2 eV, when the intensity is 0. The work function was calculated using the relationship between work function and Fermi level. The work function of ZnCo_2O_4 is 4.76eV, which is slightly higher than lowest work function of NiO .

Ultraviolet Photoelectron Spectroscopy (UPS) showed that the synthesized material was semiconducting in nature. At Fermi level, the intensity of UPS is 0. For our UPS instrument, Fermi level is 26.2 eV. The work function is the energy required to pull an electron out of a surface: the vacuum level to the Fermi level. The ZnCo₂O₄ had a work function of 4.76 eV, which indicates that it's valence band position is slightly lower than that of NiO, which has the highest work function of 4.4 eV[8]. The lower work function increases energy gap between valance band and electrolyte nernstian potential, increasing Voc. Although ZnCo₂O₄ showed slightly higher work function than lowest NiO work function, it is expected to obtain ZnCo₂O₄ with lower work function at optimum calcination temperature. This is based on the fact that NiO had varying work functions depending on the calcination temperature, and the lowest work function was shown when the calcination temperature was 450C° [8].The UPS data also showed that the synthesized material was a p-type semiconductor.

3. Dye-Sensitized Solar Cell (DSSC) Device Performance Analysis

Four Dye-Sensitized Solar Cell devices, D5-Z, D6-Z, D7-Z, and D8-Z were constructed based on the film made of ZnCo₂O₄ that I synthesized.

3.1 Photovoltaic metrics

Table 3. Photovoltaic metrics for device performance of DSSC constructed with ZnCo₂O₄ as p-type photocathode. Jsc indicates short circuit current, Voc indicates open circuit voltage, FF indicates fill factor, and PCE indicates power conversion efficiency.

Device Name	Jsc (mA/cm ²)	Voc (mV)	FF (%)	PCE (%)	Dark Saturation Current (A/cm ²)
D5-Z	0.13	161.97	32.61	0.0069	3.20E-07
D6-Z	0.14	160.41	32.10	0.0072	3.29E-07
D7-Z	0.14	160.97	32.77	0.0075	3.66E-07

D8-Z	0.14	130.37	30.99	0.0057	5.07E-06
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Short circuit currents(J_{sc}) of $ZnCo_2O_4$ devices ranged from 0.13 to 0.14 mA/cm^2 , which are significantly lower compared to that of optimum NiO device, which was $1.18 \pm 0.09\text{ mA/cm}^2$. This low J_{sc} is attributed to its extremely low dye absorption of $ZnCo_2O_4$ film. However, if the film was modified to absorb increased amount of dye, the J_{sc} is expected to increase significantly as the open circuit voltage(V_{oc}) of this device is significantly higher compared to that of NiO device. The NiO device modified to have maximum V_{oc} has V_{oc} of $150 \pm 20\text{ mV}$, but currently, this device is functioning poorly as the modification causes deterioration in device performance. The maximum V_{oc} of working NiO device is $108 \pm 4\text{ mV}$. Without any modification, $ZnCo_2O_4$ device has higher V_{oc} of 160 mV compared to NiO device, and is functioning properly. High V_{oc} reduces recombination because hole diffusion becomes faster through the film[8].

The higher the fill factor(FF), the better the device performance is. FF of the device is remarkably low but fill factor is expected to increase with an increase of J_{sc} . Power conversion efficiency(PCE) also highly depends on J_{sc} , thus its value is expected to increase as J_{sc} increases.

The $ZnCo_2O_4$ device has a very low dark saturation current. Dark saturation current indicates the current produced by the device when there was no light. The closer the dark saturation current is to 0 A/cm^2 , the better the performance of device is because no photocurrent should be produced in dark. Photocurrent should be produced only by the dye absorbing the light. The dark saturation currents of $ZnCo_2O_4$ devices were from $5.07E-06\text{ A/cm}^2$ to $3.66E-07\text{ A/cm}^2$, which are extremely small close to 0 . Compared to the lowest dark saturation current of NiO device, $1.10E-05\text{ A/cm}^2$, $ZnCo_2O_4$ devices have a lower dark saturation current.

3.2 Photocurrent Density Vs. Voltage Curve

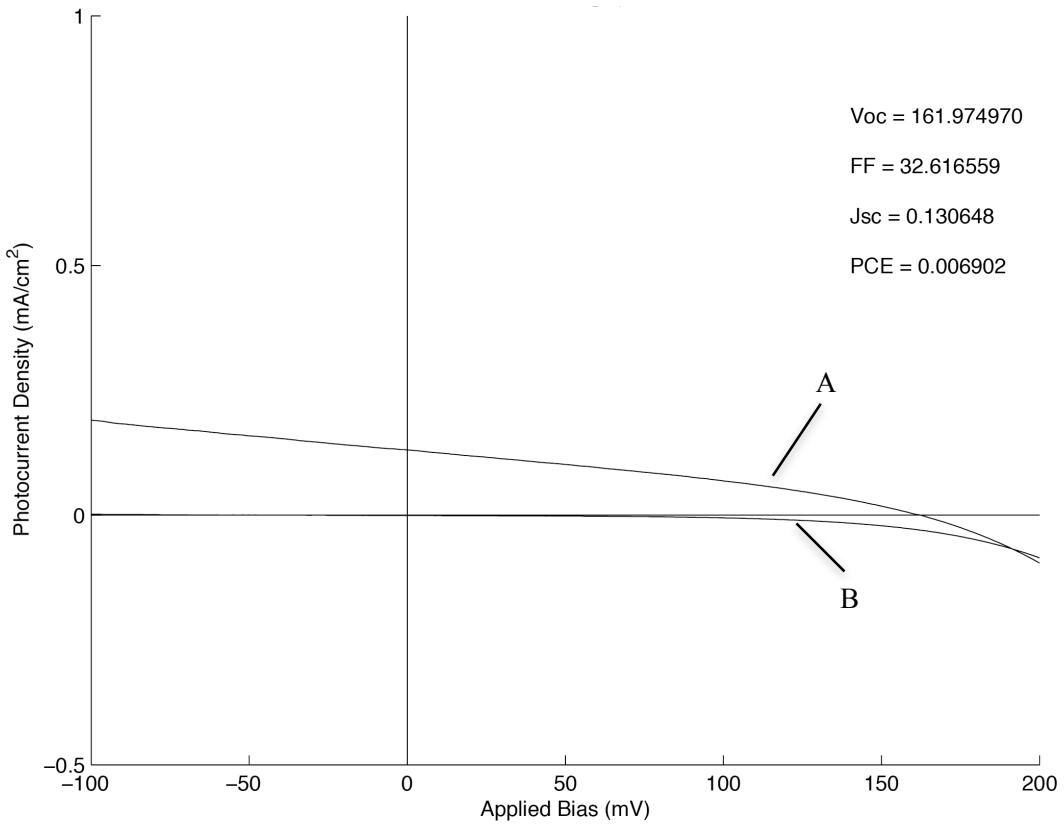


Figure 7. Photocurrent Density vs. voltage curve of the device D5-Z. The A line indicates light curve created when the device performed with the presence of light, and the line B indicate dark curve, created when the device worked without light. Extremely flat dark curve close to photocurrent density of 0 is shown in the curve B. Dark saturation current is $3.20415\text{E-}07 \text{ A/cm}^2$. Photocurrent density under the light is shown in the curve A. As the J_{sc} is not very high for this device, light curve does not show improved performance.

3.3 External Quantum Efficiency (EQE)

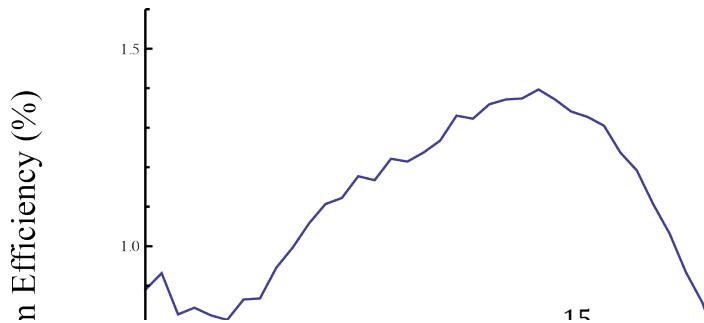


Figure 8. The external quantum efficiency (EQE) of ZnCo₂O₄ device. External quantum efficiency(EQE) of the device was derived from incident photon to current efficiency(IPCE). For the wavelength of 400nm to 700nm, photocurrent produced by device was measured. Using the Equation $EQE(\%) = \frac{\text{Collected Current}}{\text{Photons Incident}}$, EQE was plotted at each wavelength. According to the graph, the device is reacting most sensitively to the light of 520nm wavelength. At the wavelength, 1.4% of the photons hitting the sample were successfully collected as current. This result matches with the absorbance spectra of dye P1, which was used to make the ZnCo₂O₄ device.

3.4 Open Circuit Voltage Decay and lifetime

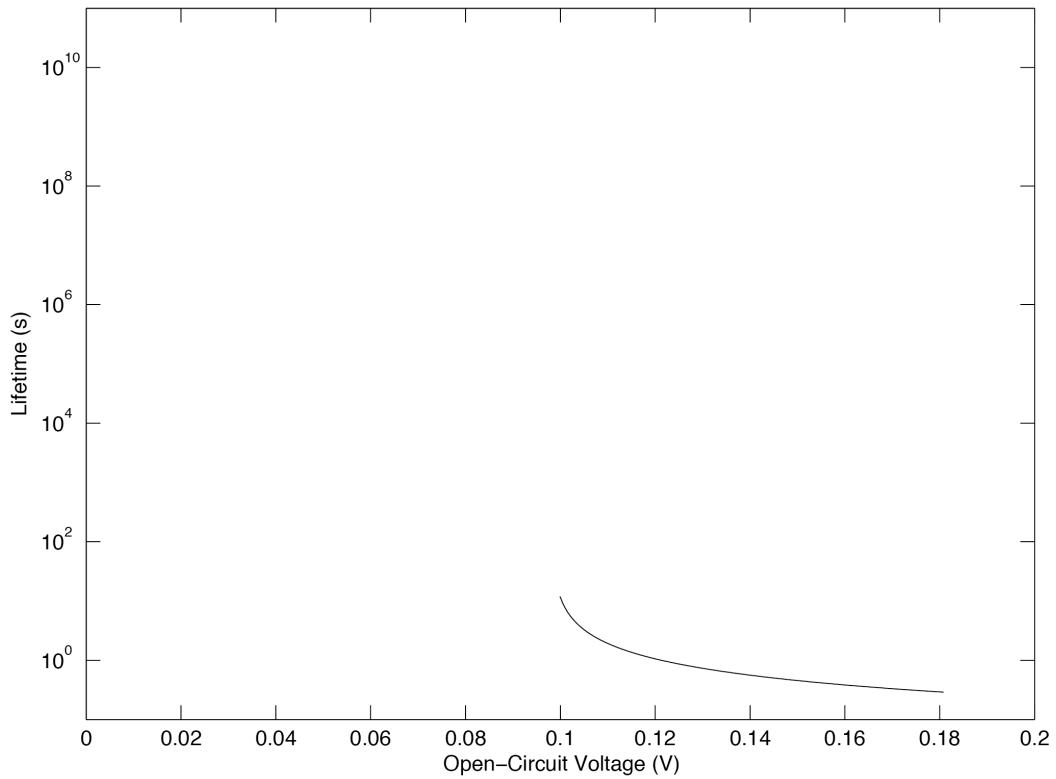


Figure 9. Lifetime of the device measured by open-circuit voltage vs. lifetime graph.

The lifetime of the cell is the time left when the open-circuit voltage starts to be measured. The lifetime of the device is approximately 10^1 seconds. It is similar with the average value of other general DSSC devices.

IV. Discussion and Conclusion

1. Discussion

The produced p-type ZnCo_2O_4 has advantages that were inaccessible in previous p-type material, representatively NiO . Even if the device employing ZnCo_2O_4 showed a low J_{sc} and PCE, they showed significantly high V_{oc} and flatter dark saturation curve without any modification. In particular, the dark

saturation current of ZnCo_2O_4 was 10^2 times lower than that of modified NiO. These characteristics demonstrate possibility of using ZnCo_2O_4 as a prominent candidate for p-type material in next generation DSSC and DSPEC. V_{oc} and dark saturation current of ZnCo_2O_4 device is expected to improve dramatically than that of NiO device because it starts with higher V_{oc} and lower dark saturation current than unmodified NiO. J_{sc} and PCE of the device is expected to be improved when we modify the dye loading level on ZnCo_2O_4 . If the amount of dye increases, it increases J_{sc} and PCE significantly as the material has large V_{oc} and dark saturation current inherently. Modification of ZnCo_2O_4 can be an alternative method to achieve high DSSC and DSPEC efficiency as modification of NiO had not reach to that level yet.

2. Conclusion

The synthesis was accomplished under 110 C° for 16 hours and the synthesized material was annealed for 450 C° for 5 hours. The powder material was characterized using XRD, SEM, and EDS. The paste was made out of the powder and coated on the surface of FTO glass as a thin film. Then the film was analyzed by XPS and UPS in order to study their properties and suitability for use in advanced photocathodic applications. The nanoporous properties indicated by the SEM images suggest that the materials have extremely high surface areas. Hence, when the new materials are used in solar energy production devices such as DSSCs and DSPECs, the dye loading on the semiconductor film surface will be up to 300 times greater than the dye loading on planar bulk film. XRD showed the crystallinity of the materials and EDS showed the atomic ratio of the materials, indicating the correct spinel structure with slight impurity caused by calcination at high temperatures. XPS showed the atomic ratio of the surface of the thin film and UPS showed the work function value of the material. The performance of the p-DSSC device constructed with ZnCo_2O_4 thin film performance showed that ZnCo_2O_4 has high V_{oc} and low dark saturation current naturally. EQE showed that in the device, dyes were the only material creating current in the device, indicating the correct device performance. The experiment showed that the novel nanoporous ZnCo_2O_4 sheets have a potential to become alternative p-type material used in DSSC and DSPEC in order

to improve their performances.

2. Future Work

Future work related to this project includes:

- Surface modification of $ZnCo_2O_4$ in order to increase its dye load
- Surface modification of $ZnCo_2O_4$ in order to increase its V_{oc}
- Surface modification of $ZnCo_2O_4$ in order to further decrease its dark saturation current
- Performance testing of films on modified $ZnCo_2O_4$ p-DSSC devices and comparison of the results with non-modified $ZnCo_2O_4$ p-DSSC devices and modified NiO p-DSSC devices.

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