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Synthesis and Characterization of Transition Metal Based Capacitors

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Title of Project: Synthesis and Electrochemical Characterization of Transition Metal based Supercapacitors

Project Abstract:

As the postindustrial revolution world continues to phase out the use of carbon-based energy sources, it is imperative that work continues to develop improved green energy technologies. To mitigate the energy storage demands of the 21st century, supercapacitors are one of the promising candidates due to their robust nature with a high energy density. Hence, this study extensively investigates the super-capitative behavior of cobalt oxide on graphite oxide (GO) and on multi-walled carbon nanotubes (MWCNT). Four nanostructures were prepared with varying amounts of cobalt utilizing a modified, simple, and fast microwave irradiation (MWI) process. During the MWI method, the cobalt oxide was dispersed into the highly conductive substrates. The morphology of the synthesized materials was characterized utilizing scanning electron microscopy. The resulting materials display porous sponge-like surface with an agglomerated texture. The electrochemical performance of the synthesized materials was then studied using the cyclic voltammetry (CV) technique. A glassy carbon electrode was modified with a fixed amount of material loading and tested towards the properties of a supercapacitor in 0.1 M KNO3 electrolyte. The super-capitative behavior of all the materials was demonstrated by the symmetrical rectangular shapes of the cyclic voltammograms. Characterization utilizing fourier-transform infrared spectroscopy (FTIR) and the stability of the synthesized nanostructures were also investigated.

The student-authored final report **MUST** include each of the following (check boxes to verify inclusion of each component):

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Synthesis and Electrochemical Characterization of Transition Metal based Supercapacitors

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Abstract:

As the postindustrial revolution world continues to phase out the use of carbon-based energy sources, it is imperative that work continues to develop improved green energy technologies. To mitigate the energy storage demands of the 21st century, supercapacitors are one of the promising candidates due to their robust nature with a high energy density. Hence, this study extensively investigates the super-capitative behavior of cobalt oxide on two different scaffolds, graphite oxide (GO) and multiwalled carbon nanotubes (MWCNTs). Four nanostructures were prepared with varying amounts of cobalt utilizing a modified, simple, and fast microwave irradiation (MWI) process. During the MWI method, the cobalt oxide was dispersed into the highly conductive substrate. The morphology of the synthesized materials was characterized utilizing scanning electron microscopy (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR). The resulting images of the material display porous sponge-like surface with an agglomerated texture. The FTIR spectra of the material should the effects of Co on the nanocarbon back bone. The electrochemical performance of the synthesized materials was then studied using the cyclic voltammetry (CV) technique. A glassy carbon electrode was modified with a fixed amount of material loading and tested towards the properties of a supercapacitor in 0.1 M KNO_3 electrolyte. The super-capitative behavior of all the materials was demonstrated by the symmetrical rectangular shapes of the cyclic voltammograms.

Introduction:

As the world continues to phase out carbon-based sources of energy in favor of renewable sources, it is imperative that work continues to develop improved green energy technologies. A promising source of green energy is in solar energy. Solar energy creates clean, renewable power from the sun and benefits the environment.[1] Solar energy is collected by first using a solar cell. A solar cell, or photovoltaic cell, is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is a physical and chemical phenomenon.[2] Recent years have seen a substantial efficiency improvement for a variety of solar cell technologies as well as the rise of a new class of photovoltaic absorber materials.[3] Transition metal oxide nanostructures with GNS and CNT nanostructures show excellent electrochemical properties.[4] This study will explore the usage of multiwalled carbon nanotubes (MWCNT) and graphite oxide (GO) as a backbone for a transition metal. This method takes advantage of the large surface area provided by the carbon support as well as its high conductivity and uses it to store energy in the metal on the surface of the nanotube.[5] The nanocarbon support is important for two reasons. The first reason is due to MWCNT ability to exhibit semiconducting behavior which increases the transition metals ability to conduct a charge. MWCNT also have a high thermal conductivity (6000W/Mk) and are stable up to 2800 C.[6] This stability reduces the possibly of combustion when the solar cell is in use. Using MWCNT also reduces the price of the material by allowing less transition metals to be using in the composite material while still producing the same electrical output. This study will focus on exploring the use of cobalt (II) chloride hexahydrate on MWCNT and GO at a variety of different weight ratios to produce the most effective supercapacitance behavior.

This project will explore utilizing multi-walled carbon nanotubes (MWCNT) and graphite oxide (GO) as the support of cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) to create nanocomposites as shown in Fig1. This method takes advantage of the large surface area provided by the carbon support as well as its high conductivity and uses it to store energy in the metal on the surface of the nanotube.[5] This method will also make the nanocomposites more affordable by reducing the amount of transition metal needed. This study will focus on using cobalt (II) chloride hexahydrate and graphite oxide in a one pot synthesis to create an effective super capacitor.

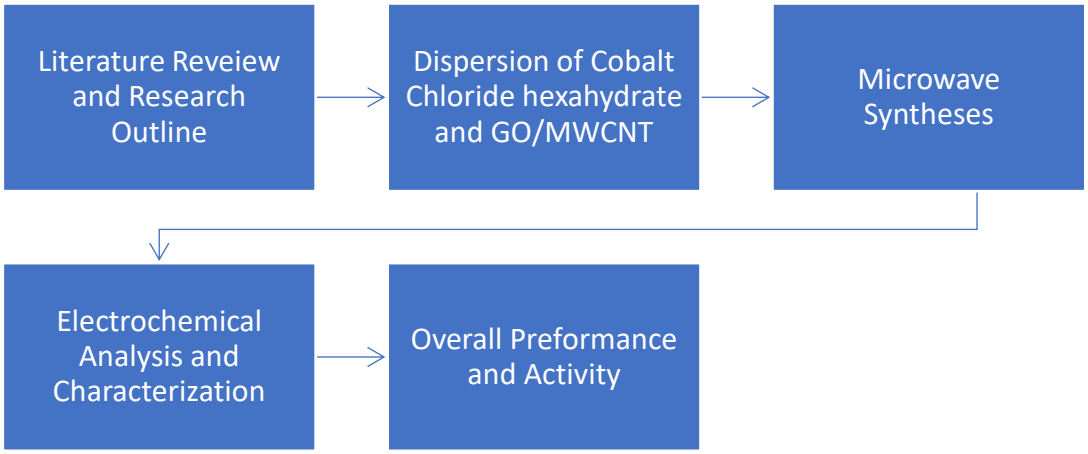


Figure 1. Project scheme

Experimental:

Preparation of Co onto GO/MWCNT

Co/GO and Co/MWCNT material was prepared utilizing a modification to the Kumar method.[6] Co/GO was prepared by mixing 24.42 mg Co with 60.00mg GO then placed into a clean round bottom flask along with 100 mL millipore water and sonicated for 90 mins. After sonication the black ink solution was removed and placed into a crucible overnight in a oven at

37°c. The black granules left over after dehydration were then removed and place inside a clean crucible. This crucible was then placed into a standard microwave on high for 8 mins or until a black jet of plasma formed and came out of the top. The resulting black, fluffy crystal structures was then prepared for characterization and electrochemical tests. This same methodology above was also carried out for Co/GO-2, Co/GO-3 and Co/MWCNT-1.

Table 1. The different mass ratios of $CoCl_2 \bullet 6H_2O$ and GO or MWCNT material synthesized are given in the table below.

Nanostructures	Ratio	Mass of Co (mg)	Mass of Substrate (mg)
Co/GO-1	0.44 : 1	26.42	60.0
Co/GO-2	1.13 : 1	81.00	80.00
Co/GO-3	10.13 : 1	810.00	80.00
Co/MWCNT-1	1 : 1	62.7	62.7

Preparation of Co onto GO/MWC for SEM

2 mg of material was added to 10 mL EtOH (200 prof) to make a dilute solution. 9 µL of the solution was then drop casted onto a clean carbon tape. The carbon tape was then covered with a beaker to dry. The carbon tape was then sputtered with gold particles for 2 minutes and aloud to settle. The gold covered carbon tape was then placed into the SEM machine. To different SEM machines were used, FEI Table-Top PHENOM SEM via the biology department and FEI Quanta

250 SEM via the composites engineering department. Technical training in the use of the SEM instruments was provided via the biology department and the composites engineering department.

Preparation of Co onto GO/MWCNT for FTIR

5.00 g of KBr was measured and placed into a oven over night at 37°c to remove any water. 100 mg of KBr was then placed into a clean mortar and pestle alone with 2.0 mg of the black, fluffy crystals form the microwave synthesis of Co/GO-1. The powders were then mixed together and placed into an oven for 1 hour. Following removal from the oven, FTIR was ran on the samples. The above procedure was then followed for Co/GO-2, Co/GO-3 and Co/MWCNT-1.

Preparation of Co onto GO/MWCNT for CV

Using a clean, dry round bottom flask an ink was created form the black, fluffy crystals form the microwave synthesis of Co/GO-1 and 150 ml of 200 prof ethanol . The flask was then sonicated for 60 mins. While sonication was happening the glassy carbon working electrode, WE, was polished using 0.50 g of alumina powder with enough Millipore water to form a slurry on a polishing pad using the figure eight technique. Both working and counter electrodes are then sonicated in nitric acid and millipore water for 15 min each, respectively. After the sonication of the ink it was drop casted (9 uL) onto the WE and covered with a beaker to prevent the casted form becoming contaminated and to allow the ethanol to evaporate. After 5 mins 3 µL Nafion® was then drop casted onto the WE and allowed to dry completely for 30 mins. Following this, the WE, counter and reference electrodes were then placed into a cell containing 0.1 M KNO_3. The cell was then placed into a faraday's cage and the electrodes were connected. The CV perimeters was then set for a potentiostat -0.75 to +0.75 V vs MSE. A scan rate of 20mV/s with a quiet time of 20 sec.

The CV was then run for 30 sweep segments for approximately 33mins. The above procedure was then followed for Co/GO-2, Co/GO-3 and Co/MWCNT-1.

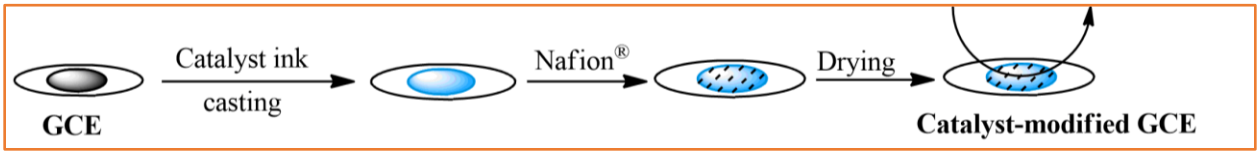


Figure 2. Experimental setup of electrode modification plan.

Results and Discussion:

Over the course of the year four different samples of supercapacitive material was synthesized and characterized. The one pot microwave synthesis process was fast and effective. To better understand the morphology of the compound's synthesis SEM was used. The following images were captured using two different SEM instruments.

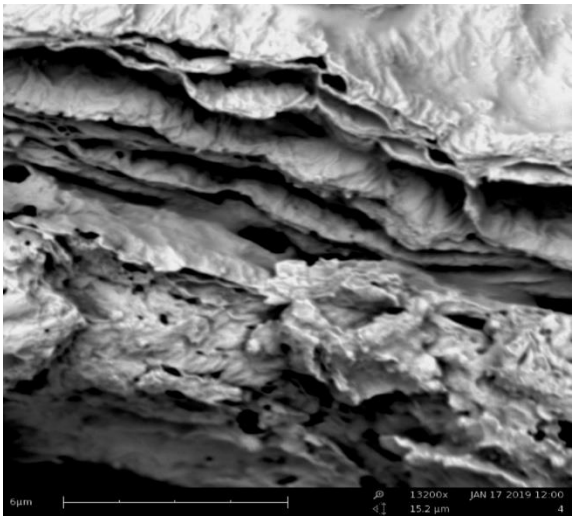


Figure 1. SEM images of Co/GO dispersed on a carbon stub and after sputtering with Au. This image was captured utilizing a FEI Table-Top PHENOM SEM. The layered sponge-like porous morphology of the material provides a higher surface area lowering the amount of metal loading. This imagine was taken at a distance of 6 µM.

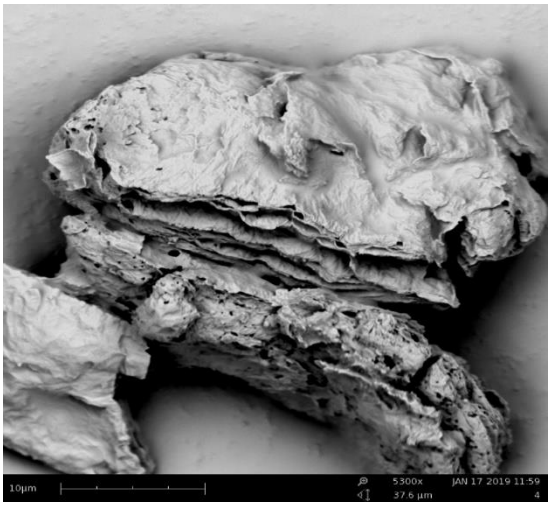


Figure 2. SEM images of Co/GO dispersed on a carbon stub and after sputtering with Au. This image was captured utilizing a FEI Table-Top PHENOM SEM. The layered sponge-like porous morphology of the material provides a higher surface area lowering the amount of metal loading. This imagine was taken at a distance of 10 µM.

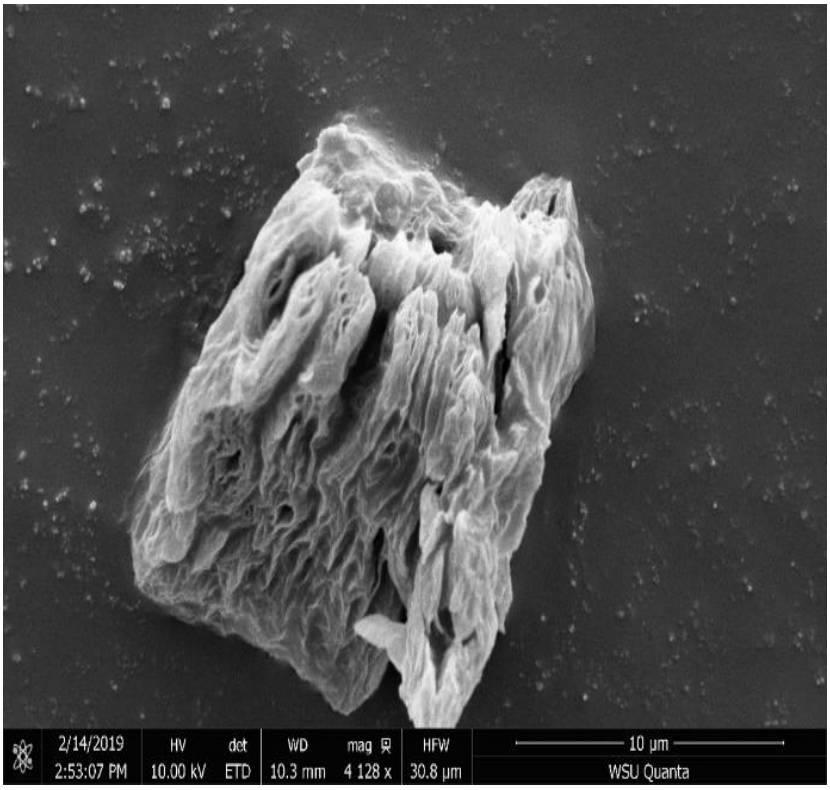


Figure 3. SEM images of Co/GO dispersed on a carbon stub and after sputtering with Au. This image was captured utilizing a FEI Quanta 250 SEM. The layered sponge-like porous morphology of the material provides a higher surface area lowering the amount of metal loading. This imagine was taken at a distance of 10 µM.

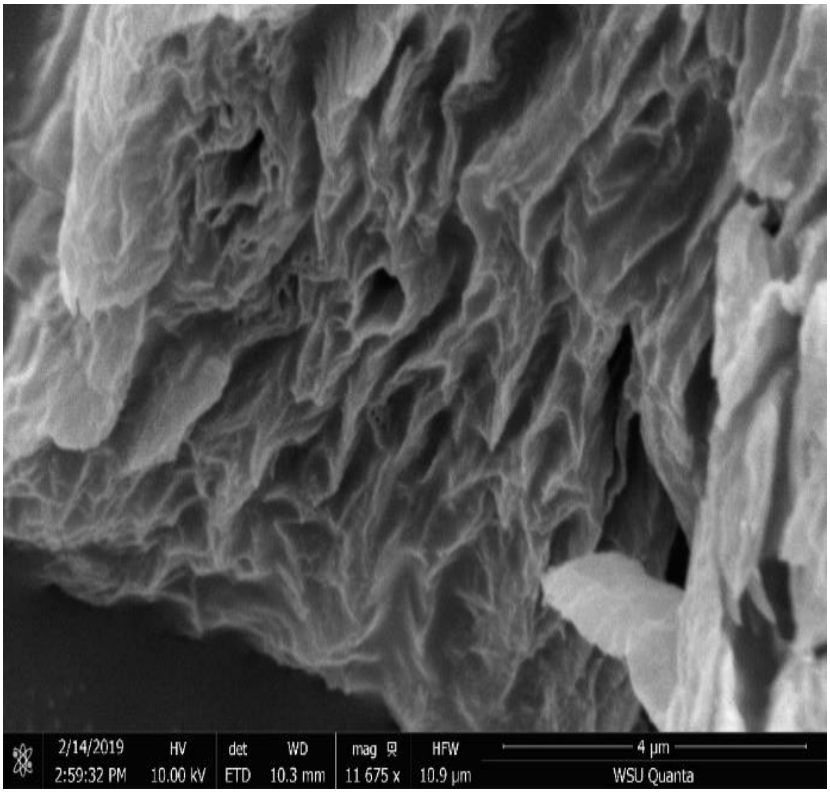


Figure 4. SEM images of Co/GO dispersed on a carbon stub and after sputtering with Au. This image was captured utilizing a FEI Quanta 250 SEM. The layered sponge-like porous morphology of the material provides a higher surface area lowering the amount of metal loading. This imagine was taken at a distance of 4 µM. This image was the closes captured over the during characterization.

The second technique used to characterize the material synthesized was FTIR. The FTIR spectra shows the effects of Co on the carbon nanomaterial. The Co in the material mad a interesting effect on the carbonyl group, the peaks became sharp and well defined. This anomaly was captured on all four samples, regardless if the samples contained GO or MWCNT. The exacted oxidative state of the oxygen atom is not fully understand.

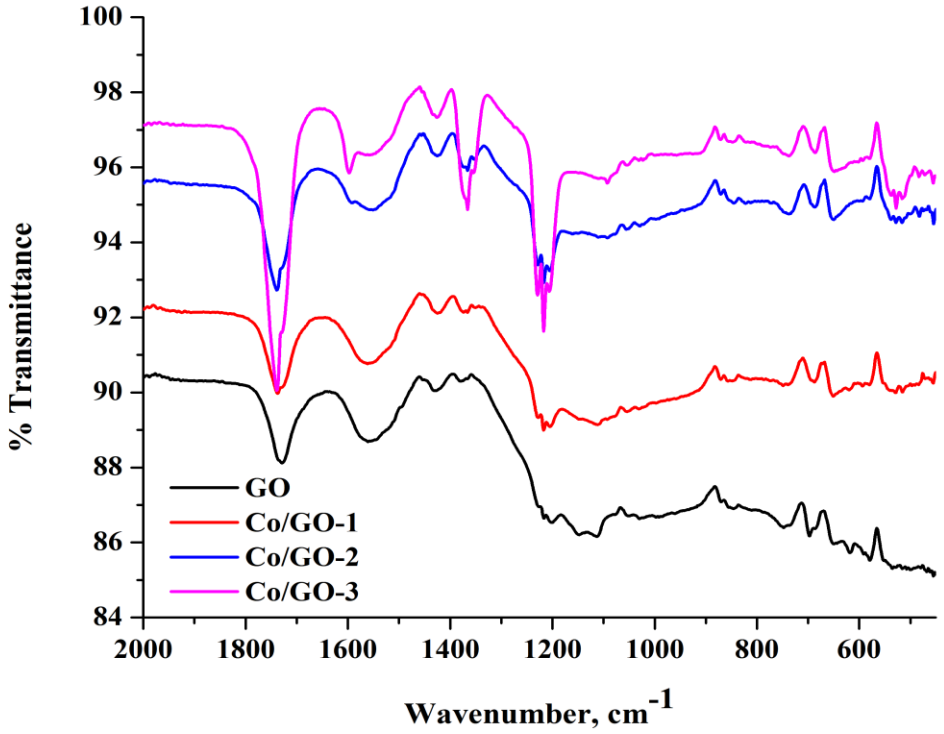


Figure 5. The figures above shows the FTIR spectra of the Co/GO materials synthesized from MWI mixed with KBr. The X-axis is wavenumber and the Y-axis is % Transmittance.

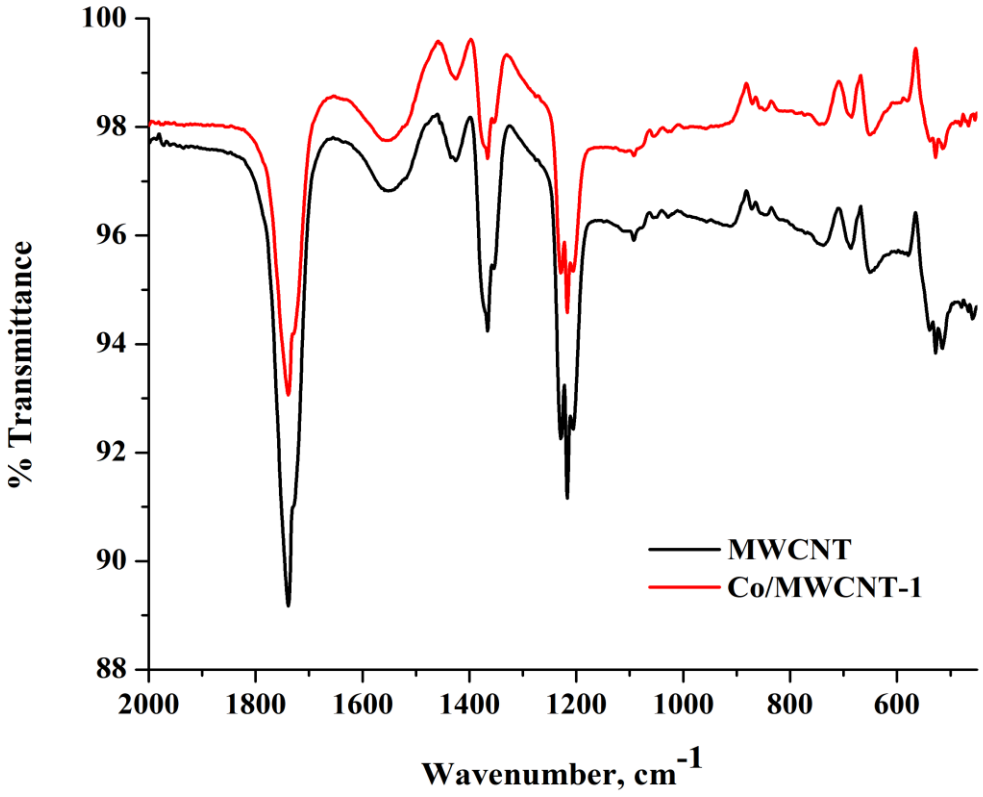
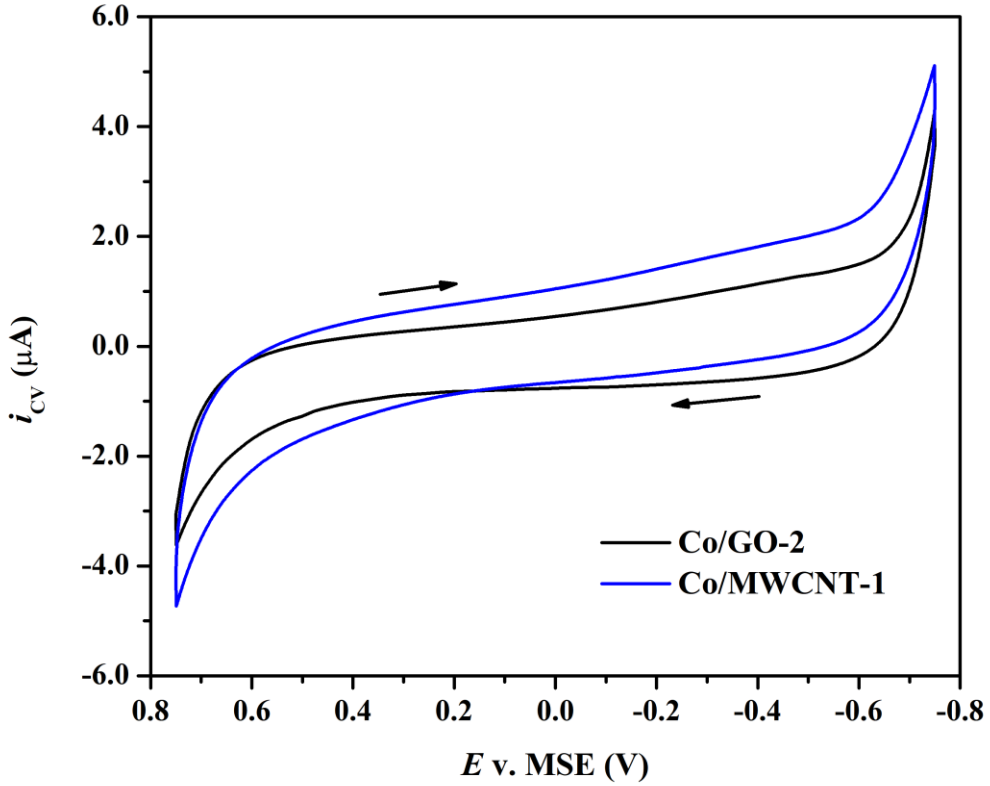


Figure 6. The figures above shows the FTIR spectra of the Co/MWCNT materials synthesized from MWI mixed with KBr. The X-axis is wavenumber and the Y-axis is % Transmittance.

Table 2. The table below shows the relative positions of the carbonyl group in each of the samples synthesized.

Nanostructure	Functional Group	Wavenumber (cm^{-1})
Co/GO-1	Cobalt Oxide	1773
Co/GO-2	Cobalt Oxide	1756
Co/GO-3	Cobalt Oxide	1732
Co/MWCNT	Cobalt Oxide	1748



0.10

Figure 7. CV curve of Co/GO-2 and Co/MWCNT-1 is shown. The CV curve was capture unter the following parameters 0.10 M KNO_3 CVs, 0.025 mg/cm^2 GCE, 20 mV/s. Notice how Co/MWCNT had a slighly larger area between its oxidation and reducation state.

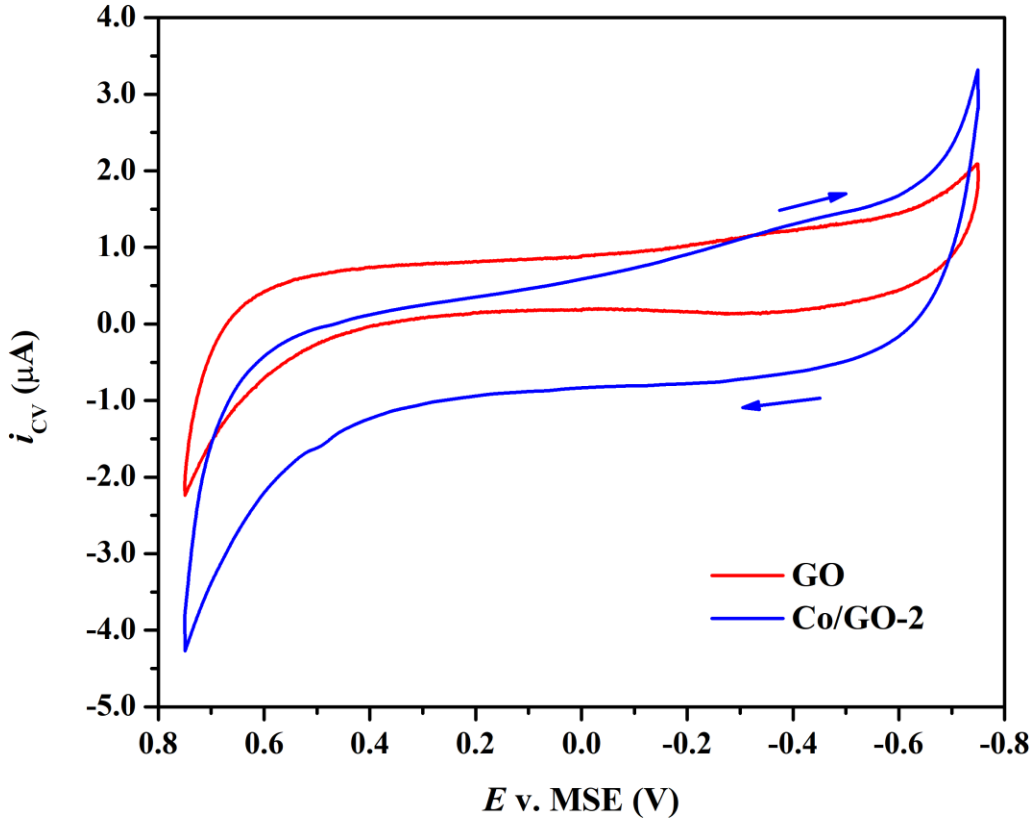


Figure 8. CV curve of Co/GO-2 and GO is shown. The CV curve was capture unter the following parameters 0.10 M KNO_3 CVs, 0.025 mg/cm^2 GCE, 20 mV/s. Notice how Co/GO-2 had a larger area between its oxidation and reducation state when compared to pure GO. This helps to conclued the effect of transition metals in nano composite material.

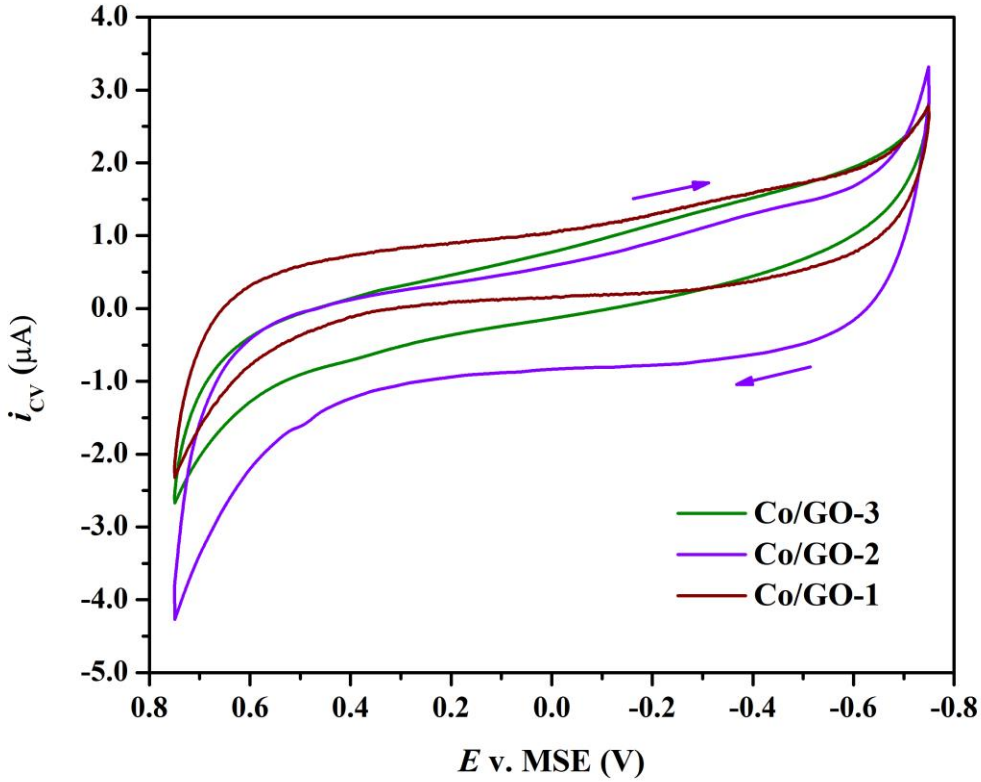


Figure 9. CV curve of Co/GO-1, Co/GO-2 and Co/GO-3 shown. The CV curve was capture unter the following parameters 0.10 M KNO_3 CVs, 0.025 mg/cm^2 GCE, 20 mV/s. Notice how Co/GO-2 had a larger area between its oxidation and reducation state. From these CV curve a logical conclusion can be concluded; nano compositive material with a 1:1 ratio of metal to nano carbon material is the best.

Conclusion:

In conclusion, Co/GO and Co/MWCNT nanomaterial was successfully synthesized and characterized. The purpose of this study was to determine the best ratio of Co to carbon support. From CV it was determine that a 1:1 ratio of Co to carbon support was optimal for supercapacitive behavior. From the SEM imaging the morphology of the material was successfully captured. The

images showed layered sponge-like porous morphology of the material which provides a higher surface area lowering the amount of metal loading. I FTIR spectra revealed how Co effected the carbon support. I also proved that Co was successfully reacted with the carbon nonsupport.

Future Work:

Further work towards utilizing other earth abundant transition metal or metal combinations on GO or MWCNT could be studied. Additionally, the MWI synthesis process could be optimized by using various irradiation times. The effect of irradiation time v. supercapacitaive behavior could also be studied.

Acknowledgements:

I would like to acknowledge Dr. Jennifer Zemke for all the help over the year of research. I would also like to thank the Biology and the Composite Materials Engineering Departments for assisting with the SEM images. Lastly, I would like to thank the Winona State University Undergraduate Research and Creative Project Grant for providing the funds needed to complete this project.

Literature Cited:

(1) 2019 Health & Environmental Benefits of Solar | EnergySage. *Solar News*, 2019.

(2) Li, Y.; Qiu, W.; Qin, F.; Fang, H.; Hadjiev, V. G.; Litvinov, D.; Bao, J. Identification of Cobalt Oxides with Raman Scattering and Fourier Transform Infrared Spectroscopy https://pubs.acs.org/doi/full/10.1021/acs.jpcc.5b11185 (accessed Apr 11, 2019). https://doi.org/10.1021/acs.jpcc.5b11185.

(3) Fang, F.; Kong, L.; Huang, J.; Wu, S.; Zhang, K.; Wang, X.; Sun, B.; Jin, Z.; Wang, J.; Huang, X.-J.; et al. Removal of Cobalt Ions from Aqueous Solution by an Amination Graphene Oxide Nanocomposite. *Journal of Hazardous Materials* **2014**, *270*, 1–10. https://doi.org/10.1016/j.jhazmat.2014.01.031.

(4) Kumar, R.; Singh, R. K.; Dubey, P. K.; Singh, D. P.; Yadav, R. M. Self-Assembled Hierarchical Formation of Conjugated 3D Cobalt Oxide Nanobead–CNT–Graphene Nanostructure Using Microwaves for High-Performance Supercapacitor Electrode. *ACS Appl. Mater. Interfaces* **2015**, *7* (27), 15042–15051. https://doi.org/10.1021/acsami.5b04336.

(5) Solar Cells - Chemistry Encyclopedia - structure, metal, equation, The pn Junction http://www.chemistryexplained.com/Ru-Sp/Solar-Cells.html (accessed Feb 25, 2019).

(6) Allaedini, G.; Muhammad, A. Study of Influential Factors in Synthesis and Characterization of Cobalt Oxide Nanoparticles. *J Nanostruct Chem* **2013**, *3* (1), 77. https://doi.org/10.1186/2193-8865-3-77.

(7) Pawley, J. The Development of Field-Emission Scanning Electron Microscopy for Imaging Biological Surfaces. **1997**, *19*, 13.

(8) Kirchartz, T.; Rau, U. What Makes a Good Solar Cell? *Advanced Energy Materials* **2018**, *8* (28), 1703385. https://doi.org/10.1002/aenm.201703385.