

Graphene-Based Transparent Electrodes for Dye Sensitized Solar Cells

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Abstract: Several Zinc Oxide (ZnO) photo-anodes were prepared with different morphologies. For each morphology, two composites containing graphene oxide (GO) were prepared. ZnO sheet-flowers attained the highest efficiency among control samples, owing to the light diffraction that may be caused by such morphology. On the other hand, ZnO rods achieved lower performance than ZnO sheet-flowers, but higher than ZnO flowers, due to their porosity and structure, which may scatter light effectively. The effect of including GO in the photoanode matrix was studied and the results demonstrate a significant increase in short circuit current density (J_{sc}). The addition of GO suggested an overall positive effect on cell performance, where samples of ZnO rods and Flowers had the most significant increase in their performance, due to the inhibition of charge recombination by GO.

Keywords: Zinc Oxide; graphene oxide; photoanode; dye sensitized solar cell.

1. Introduction

Several power sources have been explored combat the dependence on fossil fuels. Solar power is a prime candidate, due to the low pollution associated with solar cells, and their easy fabrication. Many types and generations of photovoltaic devices were studied. However, this study focuses on Dye Sensitized Solar Cells (DSSCs). DSSCs are a third generation solar cells that have been invented by Michael Grätzel in 1991 [1]. Dye Sensitized Solar Cells attract interest due to their cost effectiveness, their easy fabrication, and the moderate performance they can provide. The highest performance of such cells was recorded at 14.3% [2]. Such cells are comprised of various parts, but this study focuses on photoanodes, where the size, morphology and the type of material plays a crucial role in performance. The type of the semiconductor is an important factor in cell efficiency, Titanium Oxide (TiO_2) is commonly used due to its high performance. However, alternatives such as Zinc Oxide (ZnO) are utilized in this study due to their easier preparation techniques.

Several approaches are taken to study and enhance photoanode performance. Such as altering morphology [3], doping [4], and using added materials to form composite photoanodes [5]. Generally, carbonaceous materials are common among the added materials to photoanodes, such as graphene-based materials. Graphene is a two dimensional, single layer of SP^2 carbons, which has been gaining attention, owing to its physical and electrical properties [6-8]. Since then, graphene based materials were employed in numerous applications such as catalyst supports [9], gas sensors [10], ultra-thin lenses [11] and as a photovoltaic material in this work.



This study aims to investigate the effect of changing the morphology of ZnO as photoanode material, and the effect of the addition of a graphene-based conductor material, mainly graphene oxide (GO), and hence investigate the changes in performance for each morphology, and study the changes brought upon the incorporation of graphene oxide.

2. Material and Methods

2.1. Materials and Instruments

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (purity $\geq 98\%$) and chloroplatinic acid H_2PtCl_6 ($\geq 37.50\%$ Pt basis) was obtained from Aldrich, zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) (purity $\geq 99\%$) was bought from Xilong Chemical industry, tri-sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) (purity $\geq 99\%$) and potassium hydroxide (KOH) (purity $\geq 90\%$) were obtained from Sigma, while graphite powder was provided by Acros, potassium permanganate (purity $\geq 99.5\%$) (KMnO_4) was bought from Park Scientific, sodium hydroxide (NaOH) (purity $\geq 99.5\%$) from BBC chemicals, while triton-x surfactant (purity $\geq 99.5\%$) and iodine (I_2) (purity $\geq 99.5\%$) was provided by BDH chemicals, Polyethylene Glycol 35,000 was bought from Merk, Guanidine Thiocyanate (GuCN) (purity $\geq 95\%$) was bought from Combi-blocks, Hydrogen Peroxide (H_2O_2) (purity 30%) from Applichem, Sulfuric Acid (H_2SO_4) (purity 95-98%) from Schalru, and finally, potassium iodide (KI) (purity $\geq 99\%$) was provided by Janssen Chemica. X-Ray diffraction (XRD) was performed on (XRD-6000, Shimadzu) with $\text{CuK}\alpha$ radiation $\lambda = 1.5405 \text{ \AA}$, while Fourier transform infrared (FTIR) data were measured using Bruker Alpha. UV-Vis data was obtained using Shimadzu Double Beam UV-2500PC Series. The scanning electron microscope used was a Quanta FEI 450 SEM. The J-V characteristics were measured using a PECCEL PEC-I01 portable solar simulator, and Keithley 2425 sourcemeter, along with Labtracer software.

2.2. Synthesis of ZnO Rods

ZnO rods were prepared according to the method reported in literature with minor modifications [12], a 50 ml of a 1 M of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was prepared and stirred at room temperature for 10 minutes, until the solution was completely dissolved, next, a 1.5 M KOH solution was added dropwise to the zinc nitrate solution, until the pH reached 12, the resulting solution was transferred into a teflon lined stainless steel autoclave for 20 hours at 120°C in an oven, the resulting precipitate was obtained by centrifugation and heated at 105°C in an oven overnight for drying.

2.3. Synthesis of ZnO Sheet-Flowers

ZnO Sheet-flowers were prepared according to the literature [13], with a few modifications to produce higher quantities, a 400 ml solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ 0.125M and 0.3 M $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ was prepared and stirred for 15 minutes, resulting in a clear solution, then, a 100 ml of 2.5 M NaOH solution was prepared and stirred until it completely dissolved, finally, the alkaline solution was added to the first solution dropwise using a burette, the resulting solution was transferred to a water bath at 80°C for 2 hours, the product was centrifuged and dried at 105°C overnight.

2.4. Synthesis of ZnO Flowers

ZnO Flowers were prepared by making two solutions, the first solution was prepared by making a 200 ml of 0.3 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution and stirring until the solution became transparent, next a 200 ml of an alkaline NaOH solution of 3 M was prepared and stirred until it completely dissolved. Next, the Zinc Acetate solution was added to the alkaline solution dropwise, the resulting mixture was transferred to a water bath at 90°C for 3 hours; the resulting ZnO Flowers were separated by centrifugation and heated at 105°C overnight for drying.

2.5. Preparation of Graphene Oxide

Graphene oxide was prepared via modified Hummers method with minor modifications [14], 2 g of graphite were added to 47 ml of concentrated H_2SO_4 and stirred vigorously in a conical flask, the flask was transferred to an ice bath and cooled to 0°C , then 7 g of (KMnO_4) were added slowly and carefully,

while ensuring the temperature does not exceed 20 °C, after the addition of KMnO_4 , the mixture was transferred to a 35 °C water bath and stirred for 2 hours. The resulting solution was diluted with 100 ml of Deionized water, and the temperature rose dramatically, then 10 ml of 30% Hydrogen peroxide (H_2O_2) was added and the solution became yellow. The mixture was centrifuged and washed with 10% HCl and twice with Deionized (DI) water to remove the metal ions. The resulting GO product was dried for 48 hours at 105 °C in an oven.

2.6. Preparation of Composite Pastes

Nine composites were prepared, each morphology three composites, which were summarized in Table 3.1. For the preparation of GO-free paste (S0, R0 and F0), 1 g of the prepared ZnO (Rods, Sheets, Flowers) was grounded with 0.25 g of Polyethylene Glycol 35,000 (PEG 35,000) to give consistent paste, followed by the addition of an ethanol/water solution (4:1 v:v) and finally 30 μL of Triton-x surfactant were added to enhance the adhesion to the substrate surface.

For the preparation of GO containing pastes (composites) the same previous procedure was used, however an appropriate amount of GO was added to the ethanol/water solution and sonicated for 10 minutes.

Table 1. Summary for morphology, ratio and abbreviation for the corresponding synthesized samples.

Morphology	%GO (wt%)	Abbreviation
Rods	0	R0
Rods	1	R1
Rods	3	R3
Sheet-Flowers	0	S0
Sheet-Flowers	1	S1
Sheet-Flowers	3	S3
Flowers	0	F0
Flowers	1	F1
Flowers	3	F3

2.7. Fabrication of the DSSCs

To prepare the photoanodes, the Fluorine Doped Tin Oxide (FTO) substrates were sonicated for five minutes with different solvents, first with soap, followed by sonication with isopropanol, and finally sonicated with acetone. The substrates were then dried in oven at 40 °C. Then, scotch tape was used to control the thickness of the photoanodes, the paste was deployed on the substrate by doctor-blading (screen printing), to create the photoanode films, the photoanodes were then annealed at 400 °C for 30 minutes, and allowed to cool in air, the area of the anodes was 1 cm^2 . The cooled photoanodes were sensitized by soaking in a 0.2 mM N749 dye ethanolic solution for 24 hours. When the sensitization was complete, the Photoanodes were rinsed with isopropanol to remove the unattached dye and allowed to dry. On the other hand, the counter electrodes were prepared by dropping and spreading 20 μL of 5 mM of H_2PtCl_6 and allowing the electrodes to dry in air, next, the counter electrodes were annealed at 400 °C in a furnace for 30 minutes. To finally prepare the DSSCs, a counter electrode and a photoanode were clipped against each other using paper clips. To prepare the electrolyte, a solution containing 0.5 M Potassium Iodide and 0.1 M Iodine and 0.5 M Guanidine Thiocyanate (GuCN) in EG was stirred at room temperature for 30 minutes. The electrolyte was introduced into the cell via capillary action. Samples of the prepared samples are shown in Figure 1.

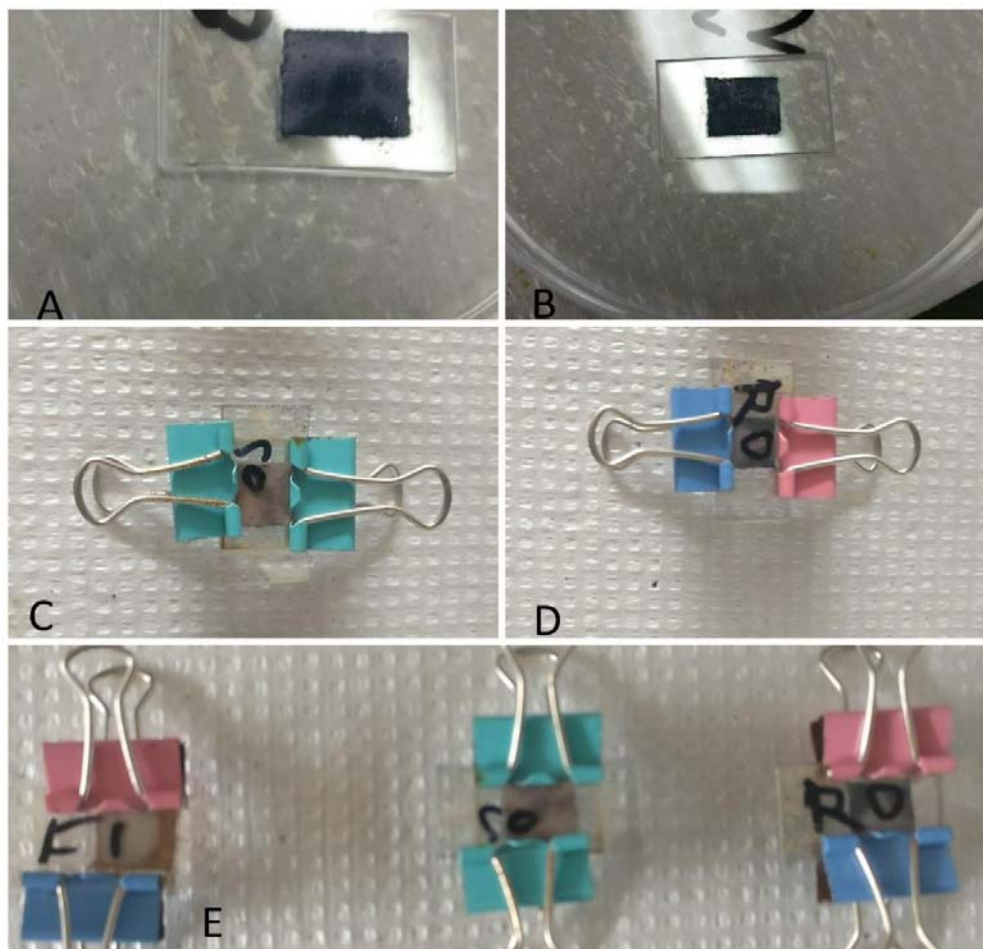


Figure 1. (a and b), Prepared photoanodes, (c-e), Pictures of prepared DSSCs.

3. Results and Discussion

3.1 X-Ray Diffraction Results

To investigate the crystallinity of the prepared ZnO morphologies, X-ray diffraction (XRD) was used, and judging by the resulting patterns, it is quite evident that the prepared ZnO composites are all of the same wurzite hexagonal structure, where the peaks at 31.75° , 34.42° , 36.24° , 47.52° , 56.59° , 62.84° , 66.32° , 67.93° , 69.03° , 72.59° and 76.90° corresponding to planes (100), (002), (101), (102) (110), (103), (200), (112), (201), (004) and (202), all correspond to wurzite structure (JCPDS card no. 01-080-0075), in addition to the high crystallinity as shown by the patterns in the Figure 2.

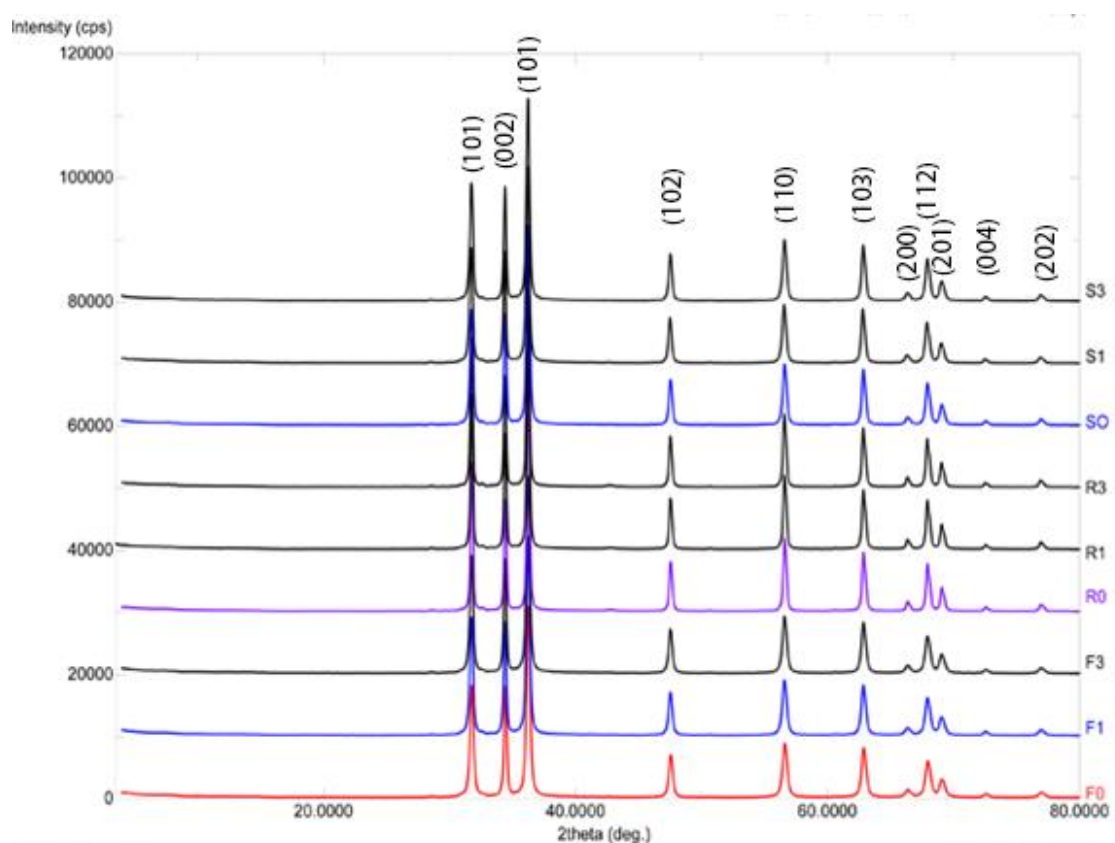


Figure 2. XRD of the prepared composites.

3.2 Morphology Analysis

To study the prepared GO and ZnO composites, several SEM images were taken, images in Figure 3 show the prepared GO by modified Hummers method, which shows minimal stacking because of the loss of many π bonds, reducing π - π stacking. A look at Figure 3(c) shows the improper stacking of the sheets, indicating successful GO production.

The role of morphology is imperative regarding photovoltaic performance, the SEM images shown in Figure 4 display ZnO crystals with a “Sheet-Flower” shape, which do indeed show high surface porosity and irregularities, which may scatter incoming light among the anode, indicating interesting properties. The large sheets in the image are graphene oxide sheets. The SEM images show flowers in the range of 1-2 μm .

In addition to the previously prepared composites, ZnO “Nanorods” were also prepared, and are shown in Figure 5, the rods appear to be in sizes ranging between 0.1-1 μm , such shapes may contain large spaces between the crystals, which may be counterproductive to electron transport; however, effective paste for this material could overcome such issues. The large sheet which the ZnO rods lay upon is graphene oxide sheets.

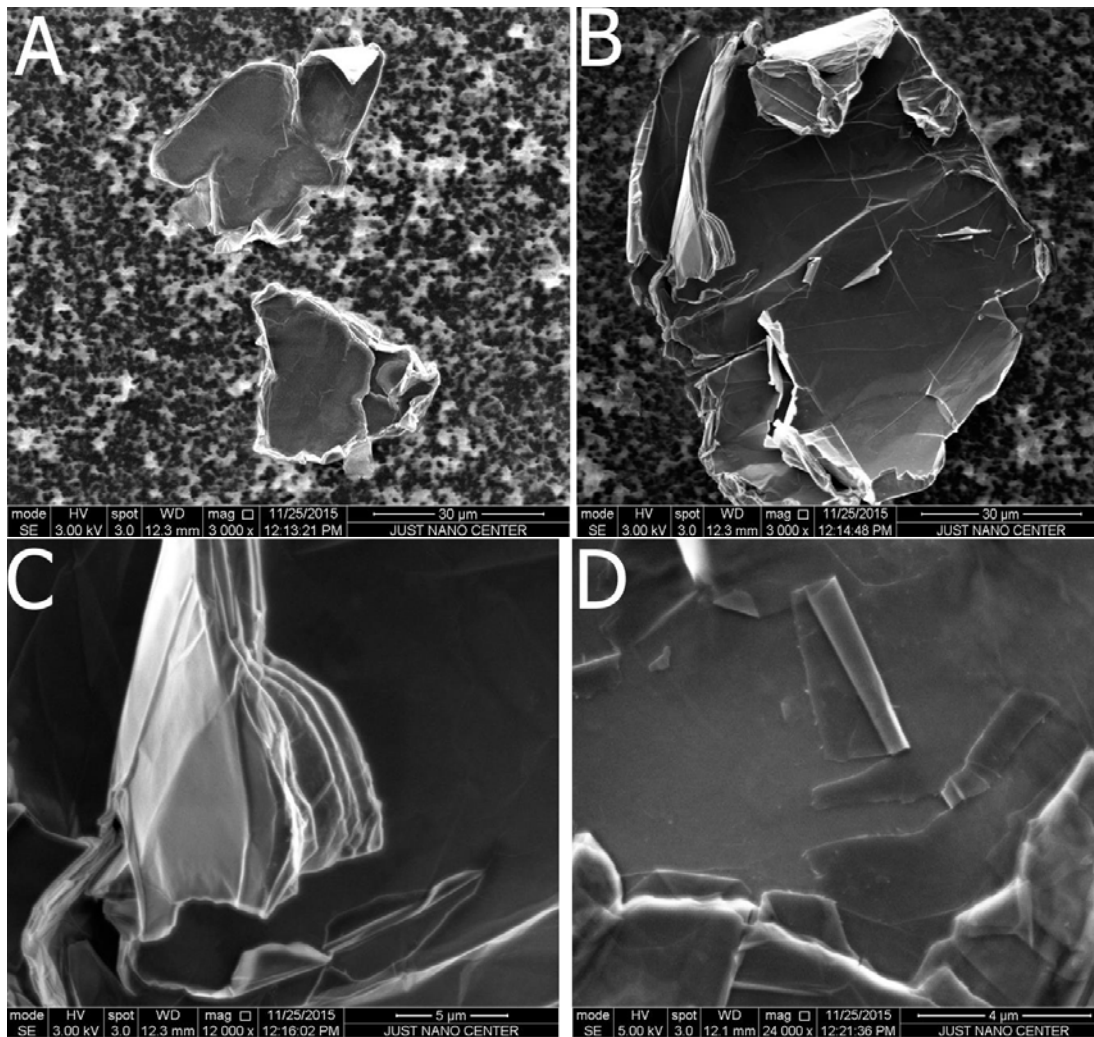


Figure 3. SEM images of Graphene Oxide.

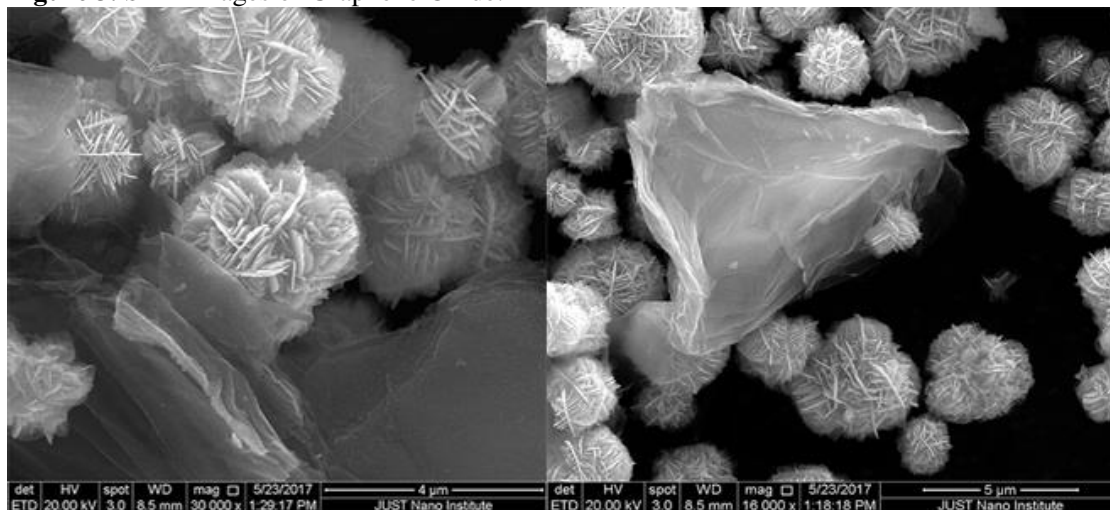


Figure 4. SEM images of the prepared ZnO Sheet-Flowers and GO composite.

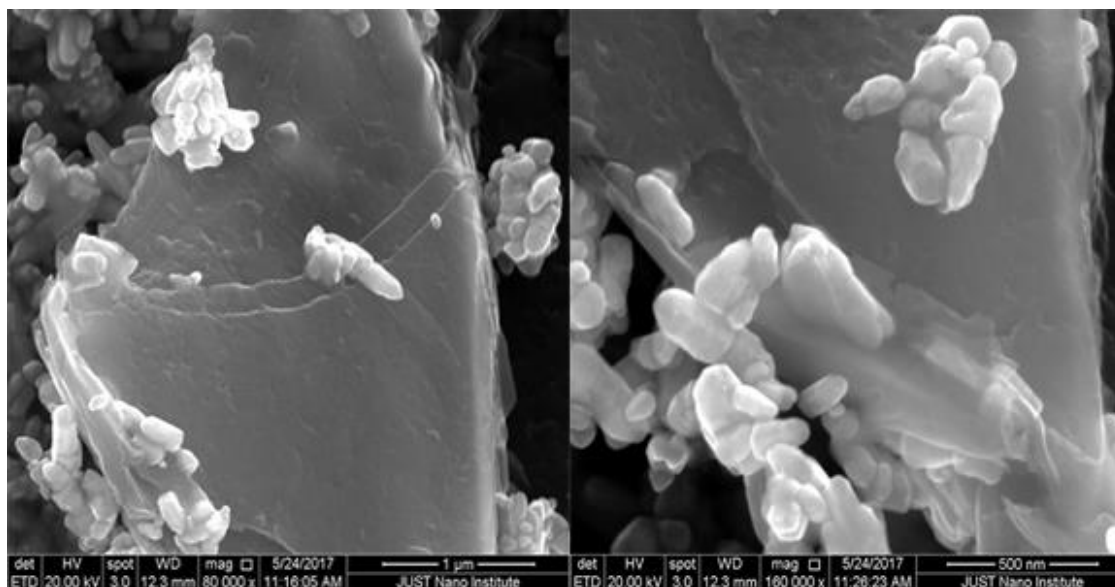


Figure 5. SEM images of the prepared ZnO Rods and GO composite.

Figure 6 shows several SEM images of the prepared ZnO Flowers that lay on GO sheets. The morphology of those sheets shows layers of thin sheets; however, their sizes stretch to more than 10 μm approximately. These sheets appear to have low surface area when compared to rods and flowers. In addition, this shape may have large spaces between the crystals, suggesting poor performance.

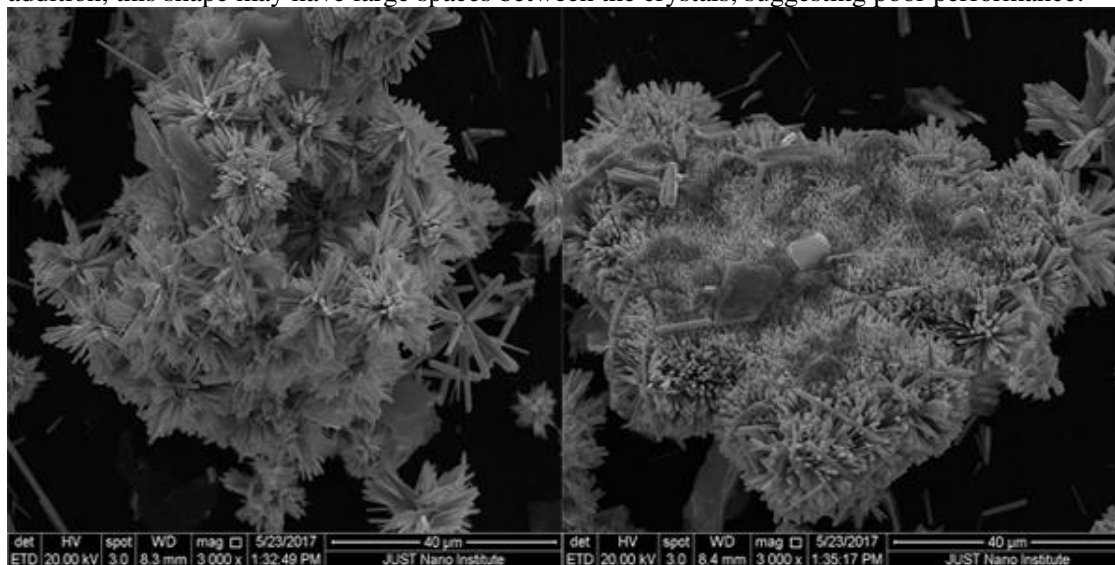


Figure 6. SEM images of the prepared ZnO Flowers and GO composite.

3.3. FT-IR Spectra

Figure 7 shows the FT-IR spectrum for GO, the spectrum shows peaks of oxygen containing groups, the peak at 3446 cm^{-1} belongs to hydroxyl groups (O-H), peak at 1385 cm^{-1} belongs to vibrations of C-OH bonds, moreover, the resulting peak at 1710 cm^{-1} and 1566 cm^{-1} corresponds to both the carbonyl (C=O) and The alkene (C=C) stretching vibrations, and the small peak at 1054 cm^{-1} corresponds to epoxide (C-O-C) vibrations, and finally the peak at 1476 cm^{-1} may be assigned to CH_2 bending, thus the formation of GO is confirmed.

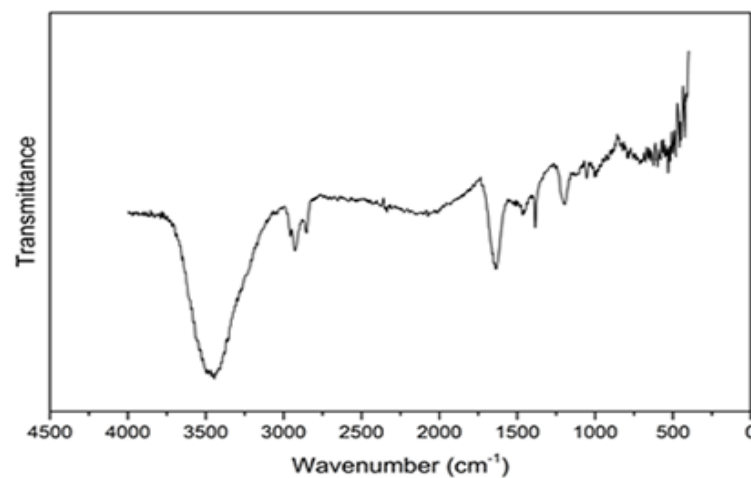
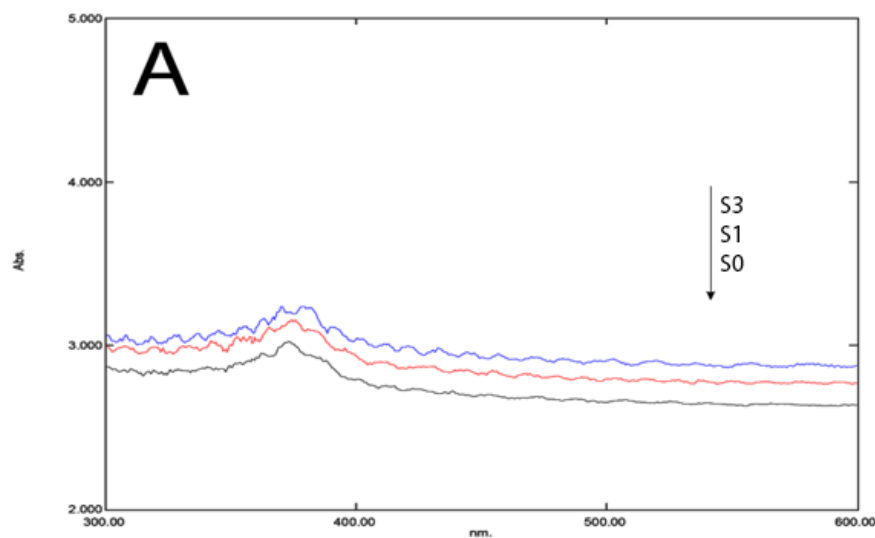


Figure 7. FTIR spectra for GO.

3.4. UV-Vis Analysis

To further study the composites, the UV-Vis absorption spectra were obtained and shown in Figure 8 (a-c). Figure 8 shows a characteristic absorption peak at 375nm for ZnO, furthermore the overall absorption of composites improves upon the addition of GO due to increasing of the surface electric charge, which was caused by the presence of GO. The presence of GO may increase porosity and may give rise to light trapping effect [15], allowing more light to be absorbed, caused by more scattering and irregularities in the matrix, indicating a decrease in reflectance and an increase in absorption.



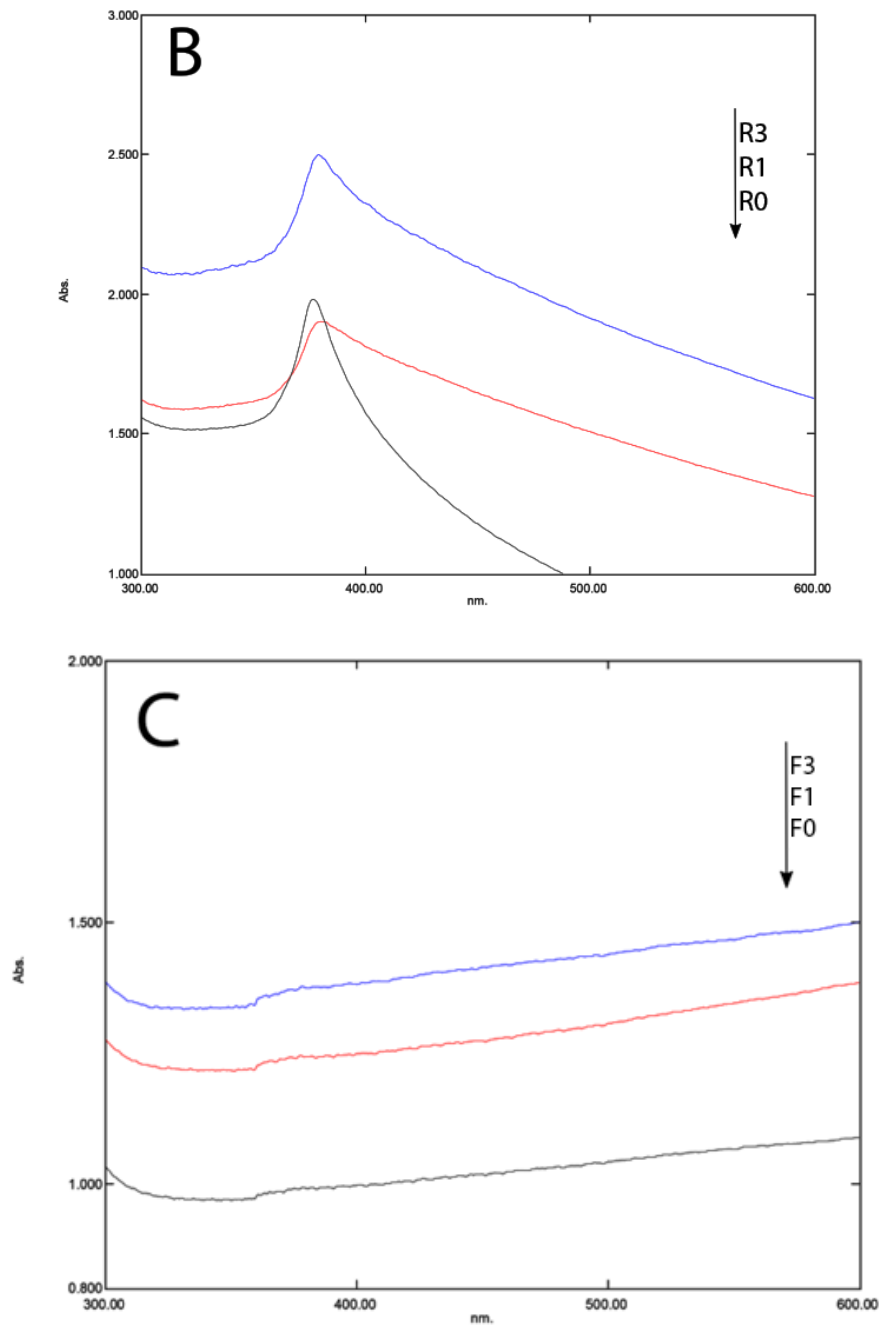


Figure 8. UV-Vis spectra of (a) S0-S3, (b) R0-R3, (c) F0-F3.

3.5. J-V Characteristics

To analyze the efficiency and the performance of the prepared samples, the Fill Factor (FF) and Photoconversion Efficiency (η %) were estimated using equation 1 and 2, respectively:

$$FF = \frac{J_{mp} \times V_{mp}}{J_{sc} \times V_{oc}} \quad 1$$

$$\eta \% = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad 2$$

Where J_{mp} , V_{mp} , J_{sc} , V_{oc} , and P_{in} are maximum power current, maximum power voltage, short circuit current, open current voltage and incident power respectively. The photovoltaic parameters measured were summarized in Table 2.

The corresponding $\eta\%$ for each sample is summarized in Table 2. Among samples with no GO, ZnO sheet-flowers have the highest performance, followed by ZnO rods and finally ZnO flowers. This behavior could be attributed to the structural morphology which plays a major role in light scattering and trapping. The arrangement and porosity of ZnO sheet-flowers may allow more photons to be scattered across the photoanode. ZnO rods have a higher efficiency than ZnO flowers which can be attributed to their irregular shapes and small sizes, which allows more incoming photons to be scattered and trapped across the photoanode matrix.

For ZnO flowers, the large crystal sizes, may play a negative role in the process of electron transport. It can also be observed from Table 2 that the efficiency of the composites is indeed higher than the samples that lack GO. Figures 9 and 10 show the J-V curves of the corresponding samples, sample R3 shows a significant increase in performance, much higher than the other composites, the added graphene based material to the photoanode matrix may indeed fill any gaps in the film, which in turn shuttles electrons across it, due to the high conductivity of graphene based materials, and finally reducing charge recombination. R1 shows a six-fold enhancement in performance compared to R0 and R3 shows twelve-fold increase in performance in comparison to R0.

Table 2. The photovoltaic parameters of DSSCs.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	J_{mp} (mA/cm ²)	V_{mp}	Fill Factor	η %
F0	0.25	0.102	0.54	0.013	0.275	0.007
F1	0.20	0.255	0.13	0.149	0.389	0.020
F3	0.43	0.227	0.23	0.127	0.295	0.029
R0	0.56	0.382	0.22	0.173	0.174	0.037
R1	1.63	0.390	1.06	0.237	0.396	0.251
R3	2.59	0.389	1.80	0.250	0.447	0.450
S0	3.04	0.199	1.73	0.104	0.297	0.18
S1	2.81	0.329	1.40	0.188	0.285	0.26
S3	2.11	0.317	1.33	0.183	0.364	0.24

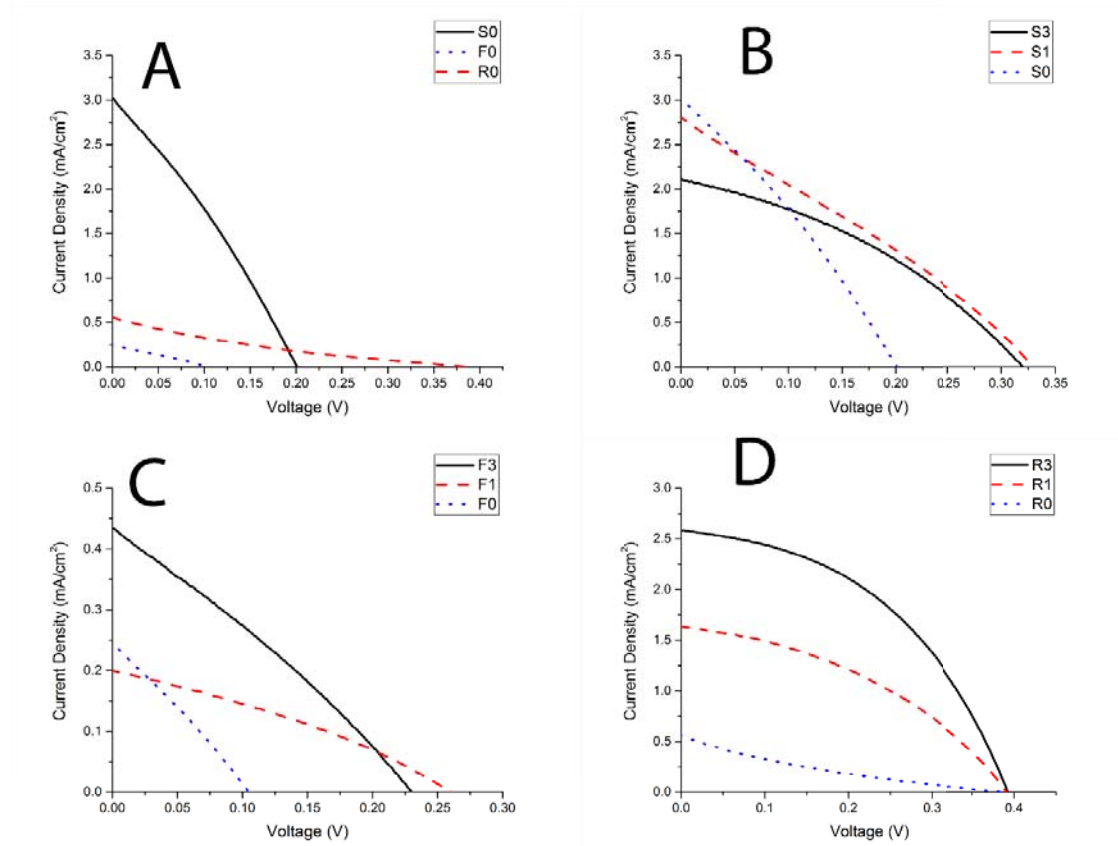


Figure 9. J-V characteristics for samples (a) S0, R0 and F0 (b) S0, S1 and S3 (c) F0, F1 and F3 (d) R0, R1 and R3.

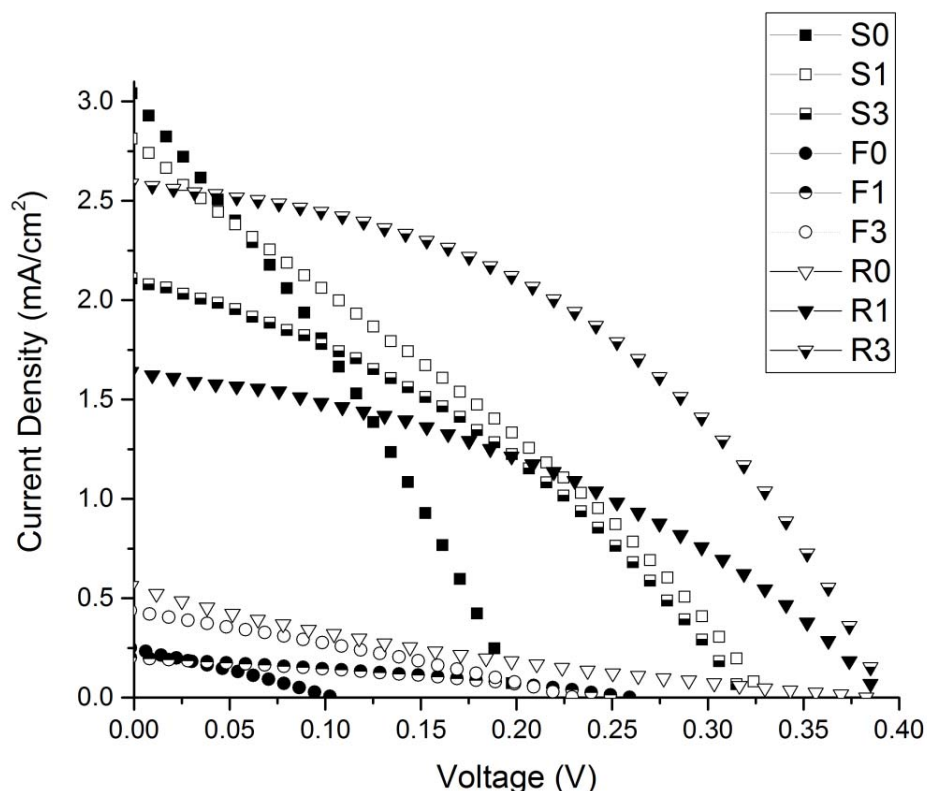


Figure 10. J-V characteristics for all samples.

On the other hand, samples S1 and S3 show a slight increase in performance when compared to S0, the added GO did not have a significant impact on the performance, the shape of ZnO sheet-flowers may not be compatible with GO, and the arrangement of GO sheets could be improper, and no remarkable change can be observed. Finally, the ZnO flowers based photoanodes had poor efficiency compared to the ZnO rods and sheet-flowers, nonetheless, ZnO flowers samples containing GO had a noteworthy rise in performance, however, the distinction is not significant, since ZnO flowers had poor performance originally.

4. Conclusion

Several ZnO samples were prepared, and the effect of adding GO to ZnO anodes with differing morphologies was studied, the added GO is reduced thermally during the photoanode preparation, restoring some of the double bonds in the sheets. Consequently, conductivity increases and thus charge recombination is reduced. According to J-V characteristics curve, the addition of GO to photoanodes enhanced the performance, however, for ZnO flowers, the addition of GO isn't quite notable, the performance of ZnO flowers is minimal due to the large sizes of the crystals, leaving very large gaps in the electron transfer paths, and the addition of GO did elevate performance, however, the enhancement is limited. In addition, ZnO rods showed low performance (R0), due to their large sizes, allowing spaces to be formed within the anode, interrupting electron transport, however, upon the addition of GO, the performance is increased dramatically, the ZnO rods may have bad electron transport, however, the added carbon-based materials minimized this drawback, and allowed for an interesting rise in efficiency. And finally, ZnO sheet-flowers demonstrated a good performance compared to the other morphologies, however, the addition of GO has indeed showed a direct effect on overall cell performance, nonetheless, the resulting increase in efficiency isn't as drastic as ZnO rods.

Acknowledgments

The authors acknowledge the financial support of the Jordan University of Science and Technology Research Fund. This research was funded by a grant from the Deanship of research-JUST, grant number 20160328.

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