

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF HIGH-PERFORMANCE SUPERCAPACITOR ZIF-67@rGO NANOCOMPOSITE ELECTRODE MATERIALS

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ABSTRACT

Over the past two decades, graphite (GO) and reduced graphene oxide (rGO) two-dimensional materials have been found to be very valuable applied materials. Graphene acts as an electron transfer agent and performs well as an electrode material in supercapacitors. However, mass production of graphene remains a major challenge. According to this research paper, naturally occurring graphite from the earth is refined and re-extracted. Hummer's method was used to prepare graphene oxide from well-purified flake graphite with the addition of both H₂SO₄ as a guest and KMnO₄ as an oxidizing agent. Recently, ZIF-67@rGO nanocomposites have been widely used due to their high surface area, uniform porosity, and relatively high thermal and chemical stability. When comparing graphite and graphene oxide, graphene oxide spacing distance is much more than graphite. It is well known that graphene oxide contains a large number of oxygen-containing functional groups due to graphite oxidation. Another common feature of rGO is that fold-like structures are observed on both the surface and edges of rGO. Also, ZIF-67@rGO nanocomposite was prepared by mixing equal amounts of crystalline ZIF-67 and very fine rGO powder using a simple hydrothermal and stirring method. Such instruments FT-IR, XRD, UV, and SEM have been used to characterize the consequences of these factors on the structure and attribute of GO, rGO, and ZIF-67@rGO. In general, looking at the results and properties of rGO/ZIF-67 air gel, it is confirmed that this nanocomposite material is an alternative composition for use as an electrode material for electrodes in symmetric supercapacitor storage devices.

Keywords: Synthesis of Nanocomposites, High-Performance Electrode Material, ZIF-67@rGo Nanocomposites, Reduced Graphene Oxide, Supercapacitor Storage Devices.

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INTRODUCTION

Environmental concerns that continue to grow in today's era are currently motivating researchers with energy needs to suggest alternative technology should be developed to save more energy. Li-ion batteries exhibit higher energy density but do not need to have a longer life cycle in an environment where lithium-based rechargeable batteries and EDLC supercapacitors have attracted more attention. Additionally, all things considered, the EDLCs supercapacitor was considered a good alternative. This is because they exhibit high power densities and long-life cycles, but mainly moderate levels of energy density. Realizing both of these makes it clear that only the EDLC supercapacitor will be better suited for future upheavals because this supercapacitor can deliver both high energy and very much high power density.¹⁻³

There is no doubt that such supercapacitors are applicable for electronic implementation, hybrid electric vehicles (HEVs), and compact power supply and pulsed electronics devices.⁴ Metal-Organic Frameworks, which have been continuously developed since the past, uses like this such as gas storage, and energy storage devices such as a supercapacitor, catalysts, biosensors, and solar cells in general.⁵ MOFs are characterized by a variety of unique properties, Significantly higher surface area, more hierarchical pore

size distribution, and higher chemical and thermal stability.⁶ Currently a wide variety of MOFs have been recommended, due to the high porosity structures at the potential electrodes in the supercapacitor. All previously used MOFs have very low electrical conductivity, and this conclusion states that not all electrodes based on metal-organic frameworks (MOF) give efficient charge transfer to the current collector. MOFs may have certain limitations, which can be remedied by adding their compounds with other carriers such as graphene oxide and polymer conductive materials. This is because the conductive compounds in MOFs have a high surface area, its properties are a positive factor over a competing electrode and another shape of carbon. Salungeet *et al.* prepared a nanocomposite material containing integrated metal-organic frameworks (MOF-ZIF-8) and polyaniline (PANI) and then used these composites as electrode materials of a supercapacitor and tested them with 1M H₂SO₄ aqueous electrolyte solution and published their results, and the electrode in this supercapacitor showed capacitance values of 236 F g⁻¹ at a constant current density of 1A g⁻¹. It is confirmed that this hybrid electrode provides good specific capacitance values by using the UIO-66 composite with the presence of rGO in 1 M KOH electrolyte solution.⁷⁻⁹ However, this specific capacitance value can only be achieved at very low current densities, for instance, 0.15A g⁻¹.

It is proposed that Mn-Metal Organic Frameworks(MOF) derivational from Mn₃O₄-Grapheneoxide(GO) based on the nanocomposite supercapacitor electrodes can provide a capacitance value it comes to around 546 F g⁻¹ at 1A g⁻¹.¹⁰⁻¹² Xu *et al.* Issued a statement saying that the ZIF-67/polypropylene nanotubes-based nanocomposite electrode to obtained maximum capacitance values of 597.6Fg⁻¹ at 0.5Ag⁻¹(1M Na₂SO₄=electrolyte).¹³ Different types of MOF established electrodes was used to design substantial capacitance values of supercapacitor.¹⁴⁻¹⁶ According to literature studies, while most MOF-based supercapacitors were studied in the presence of aqueous electrolytes, the overall performance of the assembled device was not reported.

Generally, the properties of the electrode and electrode materials used in a symmetric supercapacitor significantly affect the output parameters of the asymmetry supercapacitor like energy density, power density, specific capacitance, and cycle life stability to some extent. The overall high achievement of a supercapacitor follows the following characteristics, which demonstrate that electrolytes are important stakeholders in achieving energy density and cycle stability.¹⁷⁻¹⁸ In addition, all the commonly used electrolytes can be listed below, namely, aqueous, organic solution, potassium iodide, K₃[Fe(CN)₆], and hydroquinone.¹⁹⁻²⁰ All these are especially miscible with aqueous electrolytes (eg KOH, H₂SO₄, and Na₂SO₄).²¹ To further improve the electrochemical performance in supercapacitors, studies have suggested adding redox additive electrolytes (RAEs) to these symmetric supercapacitor electrodes.²²⁻²³ A number of studies have been carried out on supercapacitor electrode materials; it is based on graphene oxides, metal oxides, and metal hydroxides.²⁴ As far as we are concerned, any other published data were not available to appraise the achievement of the performance of supercapacitors with the presence of these aqueous electrolytes with MOF or MOF-based composites.

Recent research suggests that the preparation of ZIF-67@rGO nanocomposite is very simple, highly porous, acid-free, agitated, and environment-friendly. When ZIF-67 is mixed with rGO, which gives a high surface area (947m²g⁻¹), also, the composites also become more porous and have higher electrical conductivity. It is clearly known that ZIF-67@ rGO introduces an enhancement throughout the composite; generally, properties of the mobility of electrons and ion diffusivity are much analogized to the ZIF-67 nanocomposite. The results of our studies on the ZIF-67/rGO redox system revealed that this offers much more specific capacitance values and high energy densities, in addition to outstanding cyclic stability. This research led to the creation of a symmetric supercapacitor by combining two identical electrodes to fabricate a symmetric supercapacitor storage system.

The newly fabricated symmetric supercapacitors offer higher capacitance value and remarkable energy density differentiating from previously published MOF-based supercapacitor storage devices. Also, the electrochemical performance of two separate symmetric supercapacitors with parallel and series connections will be experimentally demonstrated. According to the general opinion and knowledge of researchers and authors, the prepared ZIF-67/rGO nanocomposite is an excellent high-performance supercapacitor which is the first report.

EXPERIMENTAL

Materials

Various chemicals, solvents, reagents, and chemical salts were used for this study without any further purification. Micronized grained fine grade $(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ cobalt nitrate hexahydrate and graphite powder, (KMnO_4) Potassium permanganate, (HCl) hydrochloric acid, (H_2SO_4) sulfuric acid and Ethylene glycol all these were procured from SISCOCHEM laboratory chemical company in India, (H_2O_2) hydrogen peroxide, (NaNO_2) sodium nitrate, (KOH) potassium hydroxide and $(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})$ hydrogen hydrates were purchased from Merck, India, and polytetrafluoroethylene (PTFE) from Ecochem, Mumbai.

Methods of Making Graphene Oxide (GO)

GO was prepared using micron-sized flake graphite powder as a raw source using a (modified Hummers method).²⁵ According to Fig.-1, concisely, graphite powder and KMnO_4 the weight ratio of the mixture (1:5) i.e., (2g graphite powder + 10g KMnO_4) was mixed well, and then added 150ml H_2SO_4 to the above- mentioned contents it causes a reaction and a form of energy is released in the form of heat which is called an (exothermic) reaction and further external heating was applied to the above contents, the temperature of this chemical reaction mixture was slowly increased from 30°C to 35°C . The temperature of these contents was gradually raised to 50°C and continuously stirred at constant temperature for 2 hours. Following this, the heated reaction mixture was equilibrated to room temperature RT ($27 \pm 1^\circ\text{C}$) to cool its temperature, It was then placed in an ice bath to which 30% hydrogen peroxide was added and mixed thoroughly. Eventually, the reaction mixture was subjected to centrifuge for 10 min at 8000rpm to remove all the unwanted elements such as unreacted carbons and acid mineral content. The GO composites thus prepared were thoroughly washed many times with double distilled water followed by two more washes with 30% HCl and finally washed with ethanol. Previously prepared and purified graphene oxide it has been thoroughly desiccated, at 90°C . The well-dried material should be manually crushed and stored at room temperature prior to preservation.

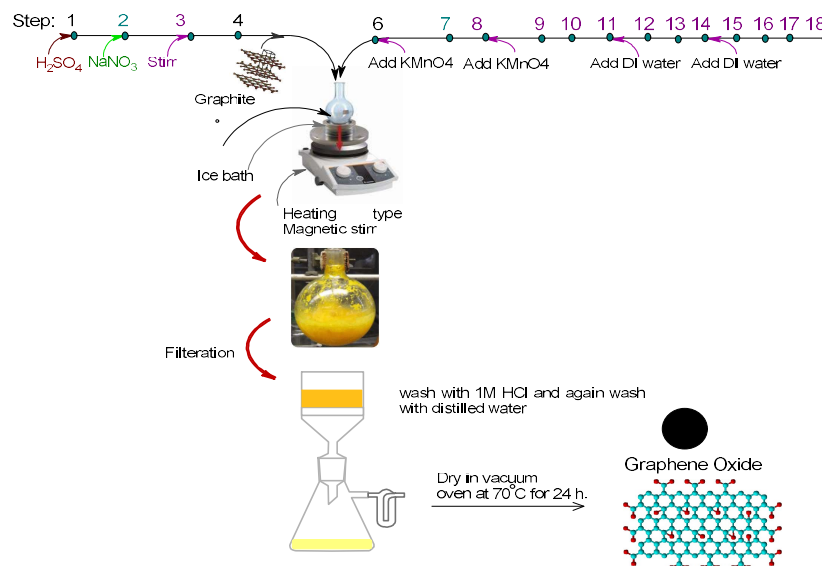


Fig.-1: Schematic Procedure for GO Preparation

Synthesis of rGO

For some comparative studies, graphene oxide was prepared using the reducing agent hydrogen hydrate. 15ml (1 mg mL^{-1}) of hydrogen hydrate was added to an aqueous dispersion of graphene oxide and mixed well, then continuously stirred at 90°C for 6 h at a constant temperature. After the chemical reaction was over, it was centrifuged at 800 rpm for 10 minutes; then the settled black-colored precipitate was separated. Then the separated sample was washed with deionized water several times.

Synthesis of ZIF-67

As shown in Fig.-2, two beakers should be taken separately and thoroughly washed with deionized water, then in the first beaker take 15ml of deionized water and add 500mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to dissolve well, in the second beaker take 25ml of deionized water and add 600mg of 2-methylimidazole and dissolve well. After this, the two solutions should be combined and stirred very vigorously at 60°C . After doing this for some time, the well-mixed mixture gradually turned into a milky colloidal dispersion.²⁶ Then after 20 minutes, the stirring should be stopped completely and then this mixture should be kept undisturbed for 20 hours. After all this, the dispersion was centrifuged and filtered; the filtered mixture was washed thoroughly with methanol and heated continuously at 150°C for 9 hours.

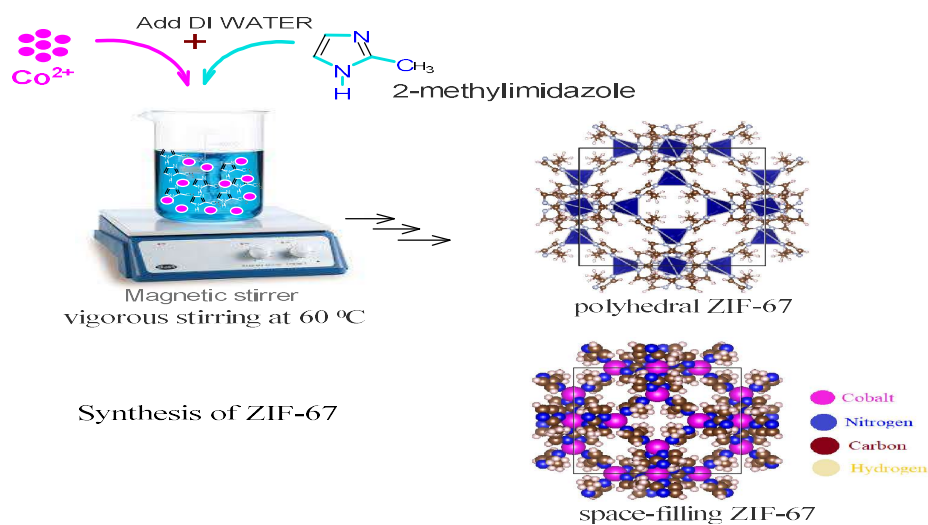


Fig.-2: Schematic Synthesis of the ZIF-67 Material

Preparation of ZIF-67/rGO Composite

Take two beakers separately and add 5mL and 10mL amounts of deionized water in which Cobalt nitrate hexahydrate (500 mg) and graphene oxide (50mg) were dispersed respectively. Graphene oxide should be sonicated for two hours to obtain clear dispersion; this should be followed by the addition of 7-gram 2MI (2-methylimidazole linker). All the ingredients mentioned below, especially the metal solution, graphene oxide, and organic binders were added and heated at a moderate temperature and stirred well continuously for 6 hours.²⁷⁻²⁸ Following the completion of all reactions, the ZIF-67@rGO nanocomposite mixture was recovered by centrifugation and then filtered. The filtered mixture was again washed twice with double distilled water and again thoroughly washed with methanol and thoroughly dried under vacuum at 80°C for 2 hours.

RESULTS AND DISCUSSION

MOF-based nanocomposites offer many advantages due to their enormous surface area and dependence on nano-hierarchical pore size distribution. When graphene oxide and ZIF-67 form a hybrid structure together, they provide synergistic benefits to each other. ZIF-67 with polyhedral crystal structures are decorated with 2D graphene oxide materials, resulting in these composite achieving properties such as more surface area, high porosity, high capacitance value, and emphasized charge transfer. Detailed studies about the properties of prepared nanocomposite and potential applications of electrode materials in supercapacitor electrodes are detailed in the following section. Various nanocrystal structures of ZIF-67 are shown in Fig.-3, 4, and 5, and ZIF-67 XRD structural information is shown in Fig.-6. The nanocrystal structure of nanocomposites is shown in Fig.-7 and 8. The reference patterns (XRD) of ZIF-67@rGO nanocomposite are analyzed to obtain structural information such as crystal structures as shown in Fig.-9, and the characteristic diffraction peaks of ZIF-67@rGO MOF are well displayed. This observation of ZIF-67 incorporation into the prepared nano-composite indicates successful integration. Significant peaks when analyzing ZIF-67/rGO by XRD can be identified and listed as follows: 7.0° (011), 10.5° (002), 12.7° (112), 14.5° (022), 16.0° (013), 18.0° (222), 22.1° (114), 24.0° (233), 25.6° (002), 25.0° (134),

29.6° (044), 31.3° (244), 37.0° (235), and 43.1° (100). Specifically, the 2θ very low-intenseness peak appeared at 25.6° (002) showing the presence of rGO in the Crystallography Open Database (COD-7222297, ZIF-67@rGO). It can be stated as follows that in respect of rGO, many diffraction peaks are not reflected because of its single to few-layered structure. Therefore, the ZIF-67@rGO nanocomposite analyzed by XRD provides detailed evidence of its successful crystal formulation, so it is a special feature.

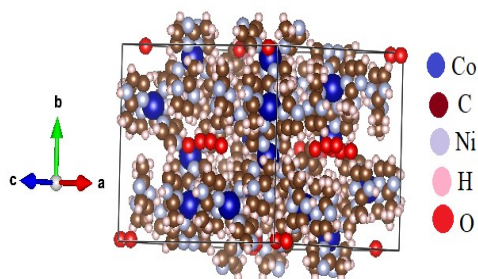
Summary

$C_{250.33} H_{239.03} Co_{24} Ni_{125.16} O_{93.65}$
Space Group: C m c e (#64-1)
 $a = 24.11298 \text{ \AA}$ $\alpha = 90.0000^\circ$
 $b = 16.94684 \text{ \AA}$ $\beta = 90.0000^\circ$
 $c = 19.73992 \text{ \AA}$ $\gamma = 90.0000^\circ$
 $V = 8066.4975 \text{ \AA}^3$

Title $C_{250.33} H_{239.03} Co_{24} Ni_{125.16} O_{93.65}$
Lattice type C
Space group name C m c e
Space group number 64
Setting number 1
Lattice parameters

a	b	c	α	beta	gamma
24.11298	16.94684	19.73992	90.0000	90.0000	90.0000

Unit-cell volume = 8066.497458 $\text{\AA}^3$



ZIF-67

Fig.-3: ZIF-67 Space Filling

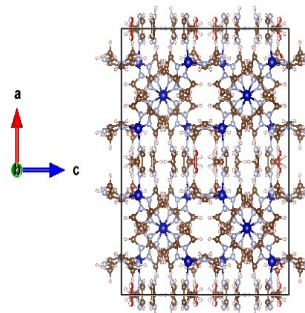


Fig.-4: ZIF-67 Stick and Ball

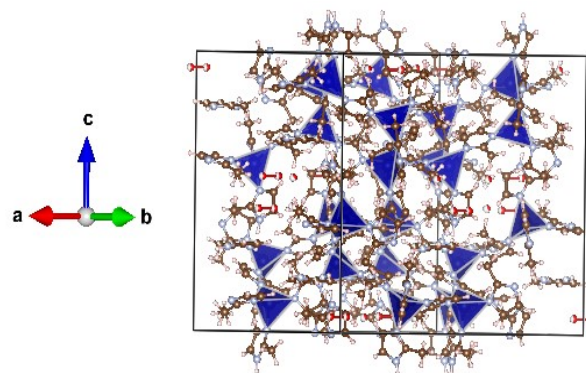


Fig.-5. ZIF-67 Polyhedral

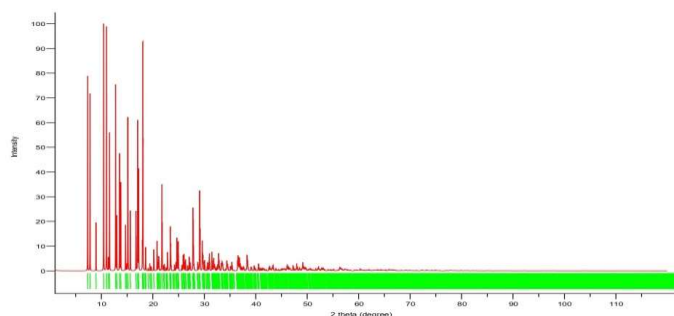


Fig.-6: Prepared ZIF-67 Nanocomposite Material XRD Pattern

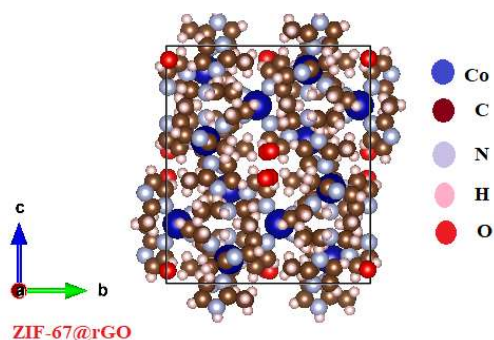


Fig.-7:ZIF-67@rGO Space Filling

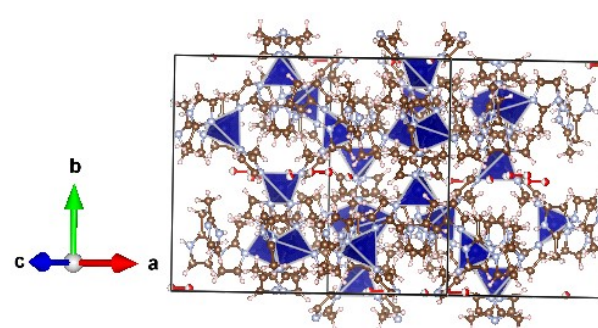


Fig.-8:ZIF-67@rGO Polyhedral

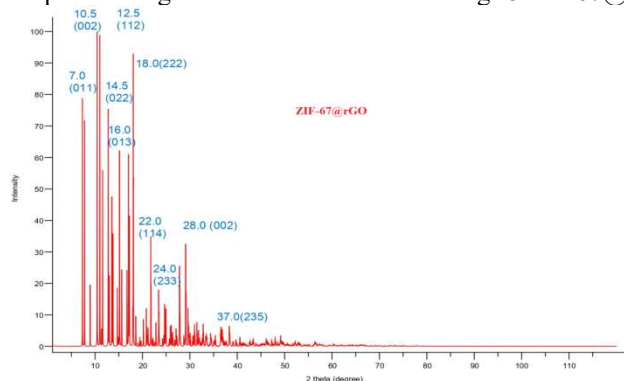


Fig.-9:Detailed XRD Patterns of ZIF-67/rGO

The morphology of the sample was examined by using the field emission scanning electron microscopy (FESEM) technique. Figure-10a, clearly indicates the bulk morphology of nanocomposite with crystalline 3D polyhedral structural shape and the average size of which is 200nm.

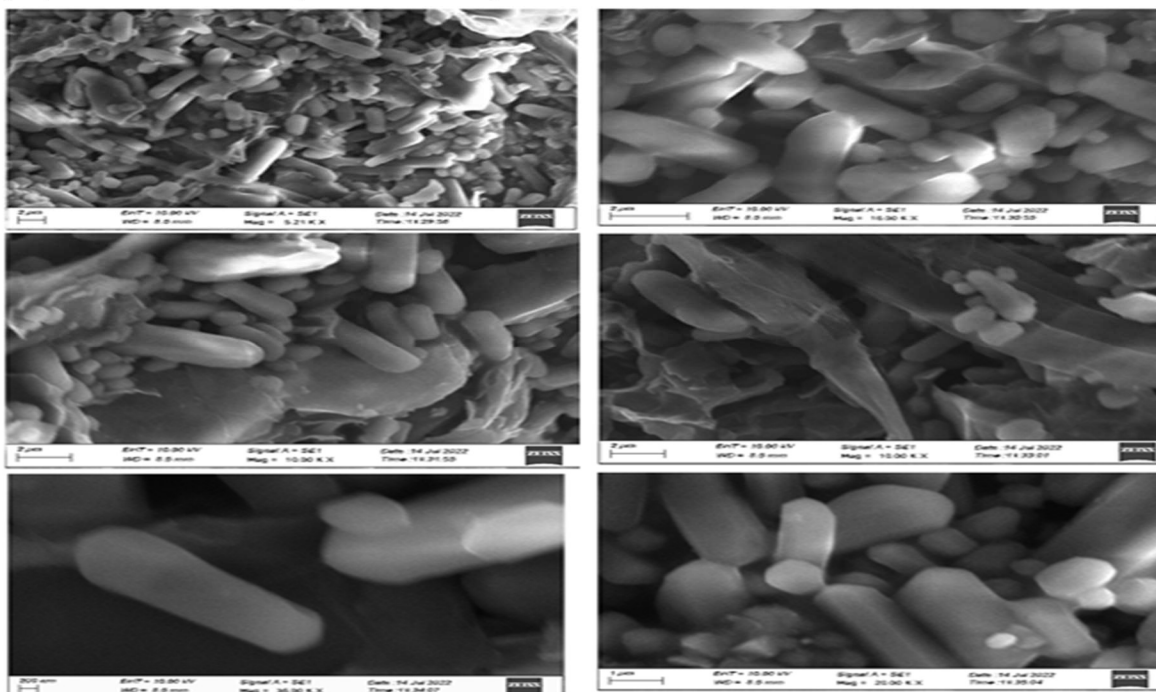


Fig.-10(a): FESEM Images of ZIF-67/rGO

The growth of the ZIF-67/rGO nanocomposite demonstrated that the MOF crystals grew transparently and uniformly on the rGO paper sheet-like surface. FESEM suggests a proposed approach for morphological and micro-structural analysis, the prepared ZIF-67/rGO composites led to the formation of desirable composites that largely preserve the features of both components. A symmetric supercapacitor

ensures instantaneous charge storage in the supercapacitor due to the very quick diffusion of electrolyte ions across the electrodes. The introduction of the high-porosity nanocomposite as the electrode material in supercapacitors further benefits from greatly improved performance. The various structural information such as surface plots of the prepared nanocomposite has been presented in Fig.-11. Area, length, and summary of particle size have been listed in Fig.-12a, Fig.-12b and Fig.-12c.

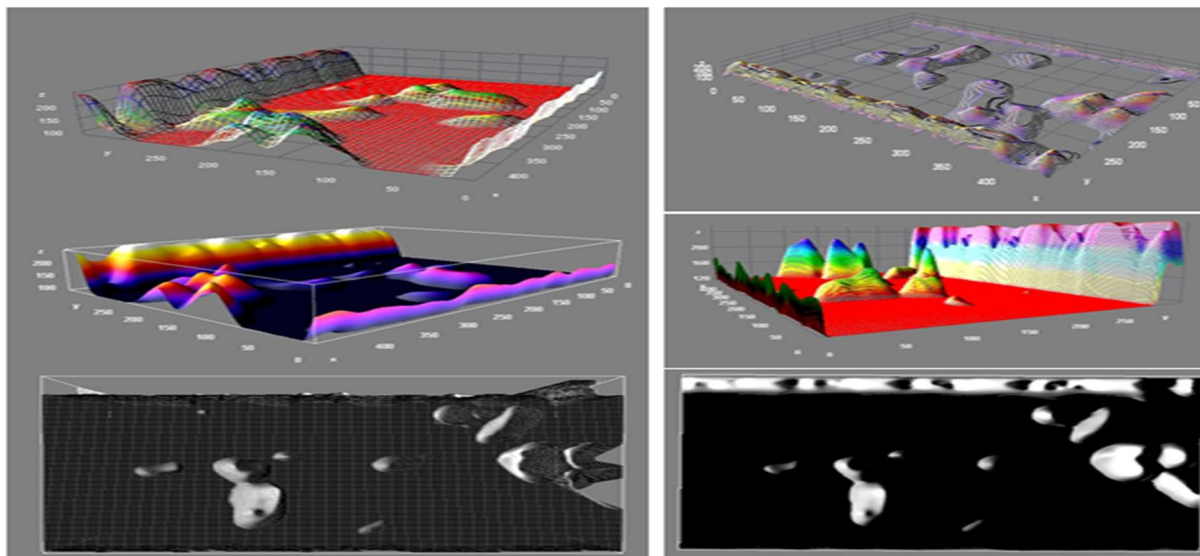


Fig.-11: ZIF-67@rGO Surface Plot

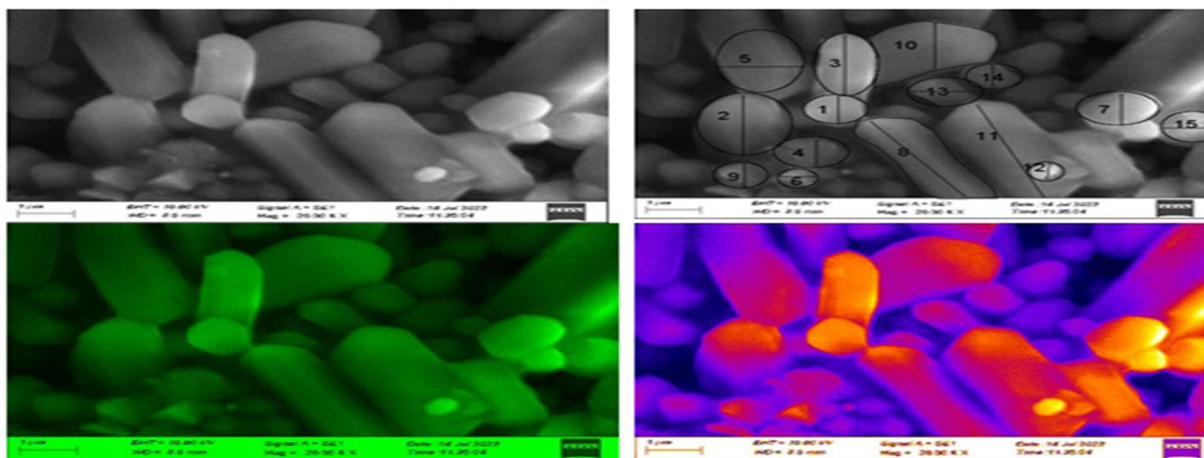
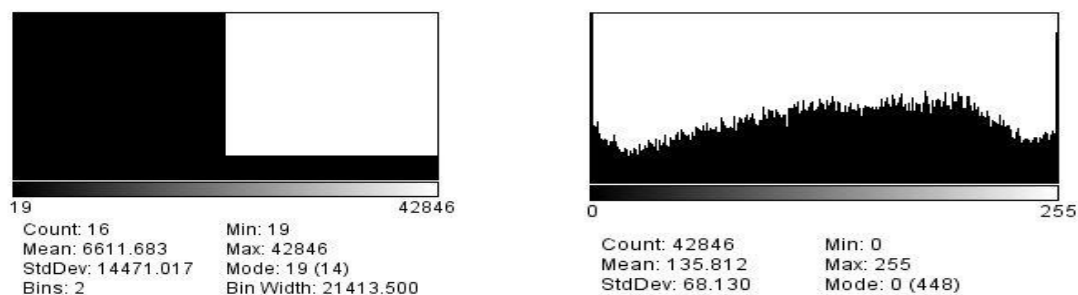


Fig.-12(a): ZIF-67@rGO Nanoparticles

All the functional groups peaks of ZIF-67/rGO nanocomposite are clearly seen in Fig.-13, ZIF-67@rGO composite gives a very strong intensity broad band at 3439 cm^{-1} which indicates the of O-H group. The IR peaks at 2924 cm^{-1} and 2868 cm^{-1} are attributed to C-H stretching and bending in GO respectively.



Area Distribution

Histogram

Fig.-12(b): ZIF-67@rGO Surface Plot Area Distribution and Histogram

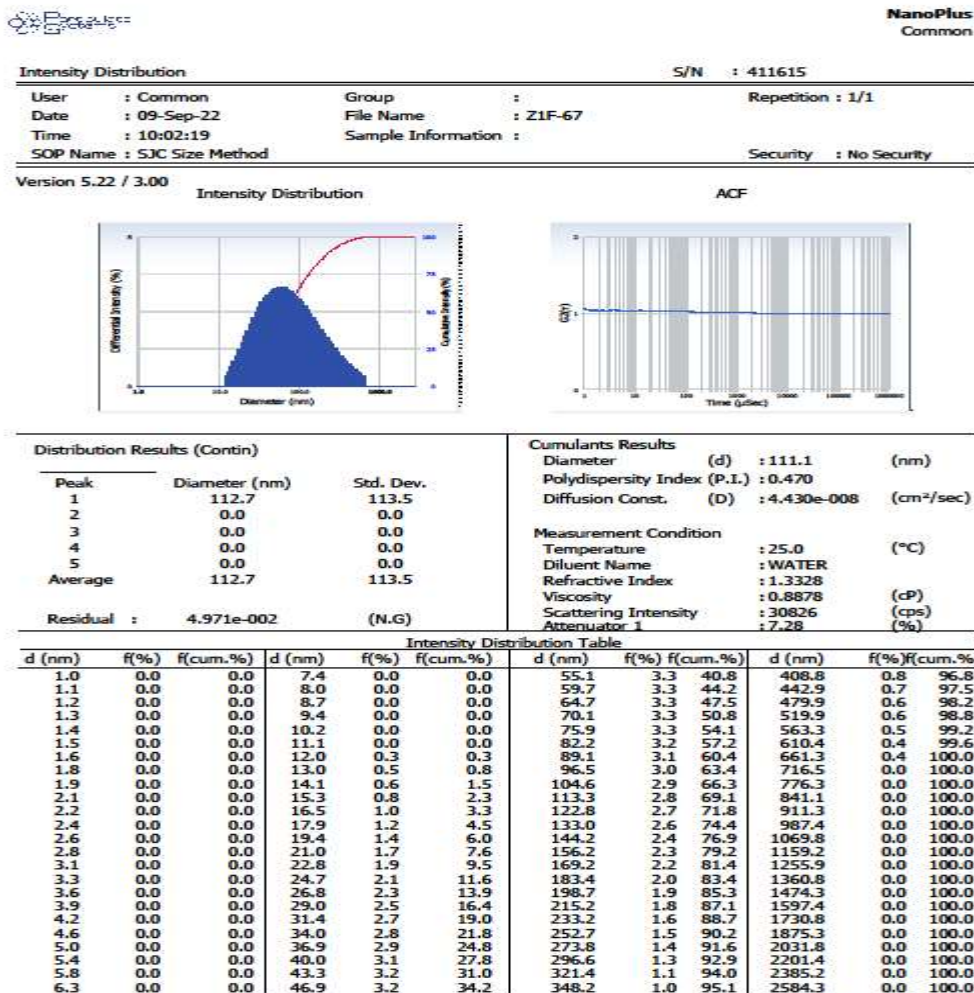


Fig.-12(c): Intensity Distribution Curve

Alkenes skeleton of C=C bond in graphene oxide, the stretching vibration of this C=C bond usually produces a moderate band around 1621cm⁻¹. A strong intensive peak appears at 1670 cm⁻¹, which is attributed to the C=O stretching vibration of the carbonyl group. The reduction of GO is characterized by FT-IR spectroscopy, and given Fig.-13, the peaks with reduced graphene oxide oxygen-containing functionalities are all reduced compared to graphene oxide. Also shown here is the successful reduction of graphene oxide when a hydrogen-hydrate (NH₂.NH₂.H₂O) reducing agent is used.

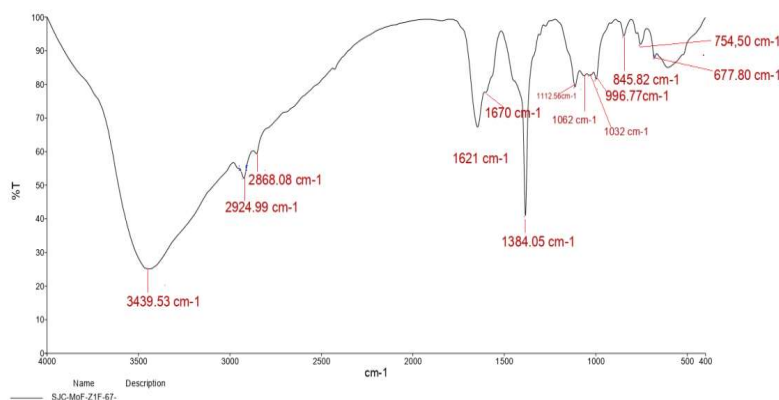


Fig.-13: FTIR Spectra of ZIF-67/rGO Composites

CONCLUSION

It is believed that the newly prepared ZIF-67/rGO nanocomposite can be used as electrode material in symmetric supercapacitor energy storage devices compared to other nanocomposite materials. A simple hydrothermal method was used to prepare these new nanocomposite materials by taking equal amounts of ZIF-67 and rGO. The Hummer method was used for the first time to prepare graphene oxide with this huge surface area, followed by the successful preparation of rGO with the help of $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous and hydrazine hydrate ($\text{NH}_2 \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$). It was noted in the Journal of Nanomaterials⁵ that the interlayer spacing of graphene oxides was much larger than graphite. The morphology of the graphite powder was completely changed and then completely oxidized; due to this process, many oxygen functional groups were found in the graphene oxide. Typical fold morphologies were observed on both the rGO surface and edge. When compared with the traditional Chemical Vapor Deposition (CVD) method, the recently developed Hummers' method has been proven to be able to synthesize GO on a large scale, and then RGO-reduced graphene oxide can be prepared using a reducing agent, which has a very low production cost. Briefly described, the overarching objective of this research paper is to focus on the recent advancement based on this consistently controlled synthesis of ZIF-67@rGO-based materials as amalgamated electrode material. The above-indicated ZIF-67@rGO nanocomposite has been a prime choice for comparing different preparation technique and their implementation in earlier times because this composite has many unique features such as more active sites, solid stability, and huge surface area. Generally speaking, all ZIF-67@rGO-based nanocomposites to be prepared are environmentally friendly and have high productivity at a low cost. Based on the above-mentioned statement, this study is seen as the main objective of the paper. Furthermore, the heterogeneous catalyst ZIF-67 can be used for low-cost production for commercial applications. Especially, it meets the economic and environmentally friendly requirements. Taken as a whole, a prerequisite for the widespread use of the ZIF-67 heterogeneous catalysts is the high-quality aspect of the compound and the low-cost mass production of its derivatives. Therefore, it is felt that the applications of ZIF-67@rGO nanocomposite-based heterogeneous catalysts in extensive industrial production should be further developed in the future keeping in mind the following objectives for realizing and mass production. (i) Exclusively more attention should be given to exploring novel synthetic methods to increase a certain amount of ZIF-67-based nanocomposite materials in the way of economically feasible strategies without high cost and non-toxicity. (ii) Most of the ZIF-67-based nanocomposite materials are nanoporous in size (diameter of the pore < 2nm). It is felt that their applications are restricted due to steric hindrance effects as they contain large molecules. Therefore, it is necessary to integrate micro-, meso-, and macropores of the crystal form of nanoporous ZIF-67-based materials to enhance the reduced mass resistance and diffusion rate. (iii) The immovability and maturity permanence of ZIF-67-based materials especially under harsh conditions must be solved if proper stability, chemical stability, and thermal and mechanical stability are to be used in various modern applications.

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CONFLICT OF INTERESTS

All the authors expressly declare that there is no conflict of interest in publishing this research paper in the journal.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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[RJC- 8206/2022]