

A STUDY ON CHARACTERIZATION OF REDUCED GRAPHENE OXIDE AND MAGNESIUM NIOBATE (RGOMN): A NANOCOMPOSITE HYBRID SYSTEM FOR ENERGY STORAGE APPLICATION

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ABSTRACT

In terms of their physical and chemical properties, nanomaterials have immense advantages over bulk materials. Nanomaterials offer a high SSA and consequently more ion adsorption and charge-transfer reactions, thereby enhancing the capacitance's specific value. With reduced diffusion lengths and ion transport pathways, electrolyte ion transport is facilitated, and the utilization of active materials is enhanced. Nanomaterials can readily withstand the stress caused by the charging/discharging process's regular expansion and contraction. owing to the large surface area of nanomaterials, the contact area between electrode and electrolyte increases. They are more mechanically and electrochemically stable. Graphene has been extensively studied to transform energy storage electrode materials into materials with much better electrochemical characteristics and uses because of its large surface area. The exceptional dielectric, magnetic, and optical properties of perovskite nanoparticles have led to their widespread application. Perovskite nanomaterials show better or entirely different kinds of properties from their bulk structures when they are incorporated into nanoscale features like nanoparticles, nanorods, or nanowires with precisely regulated size and shape. These intriguing characteristics undoubtedly make them valuable for a range of applications, including solid oxide fuel cells, environmental catalysts, supercapacitors, sensors, and perhaps even spintronics-based applications. Additionally, columbites' high ionic and electronic conductivity improve their composite behavior and allow them to function as active electrode materials for energy conversion processes. When compared to conventional materials and their composites, graphene-based nanocomposites with low loading of graphene display enhanced property in its multifunctional features. They require less processing and weigh less as well. This supports a number of affordable multipurpose applications. When coupled with pseudocapacitive materials, graphene's unique structure formation increases their pseudo-capacitance rate relative to traditional capacitors. Additionally, it keeps graphene sheets from stacking again and increases the supercapacitor's energy density. On the other hand, the substantial rise in the power density of the supercapacitors caused by the reduction of graphene oxide to graphene would significantly enhance the specific surface area and ion diffusion rate. Hence, in order to stabilize the energy density and power density of graphene-based supercapacitors, graphene modification is important.

KEY WORDS: Characterization, Graphene Oxide, Magnesium Niobate, Nanocomposite, Hybrid System, Energy Storage.

INTRODUCTION

Synthesis, characterisation, exploration, and application of materials of reduced sizes are all included in the field of nanoscience. Analyzing the qualities of materials that depend on their structure and processing materials have drawn a lot of attention from researchers lately. These days, advanced materials with superior mechanical, optical, electrical, electronic, and magnetic properties are being developed for a range of engineering applications as well as environmental applications.

Any technique that concentrates on basic and technical sciences at the nanoscale size is referred to as nanotechnology, a relatively recent field of study. This connects materials science, electronics, and the chemistry, physics, and biology of nanoparticles. Many environmental, medical, and industrial issues have found ground-breaking answers thanks to the use of nanotechnology into broader systems. A few industries where nanotechnology has been heavily included are smart materials, medicine delivery, energy storage technology, water technology, biotechnology, information technology, and security systems.

The development of sustainable energy technologies is dependent on electrochemical energy storage techniques. It has greater potential than other energy storage methods because it is more efficient, flexible, and modular, as many recent versions of micro fuel cells and rechargeable lithium batteries demonstrate. As environmental contamination rises, electrochemical energy storage has taken on greater significance, as it can reduce our dependence on finite fossil fuel reserves. As is the case with ocean thermal, wave, and tidal power, geothermal sources are geologically limited and appear to be costly to develop. Renewable energy aids in protecting the environment by significantly reducing carbon emissions. By utilizing renewable energy sources, we reduce our reliance on fossil fuel, gas, and oil reserves, allowing us to avoid rising energy costs and enhance energy security.

The development of sustainable energy sources has garnered significant attention due to the introduction of novel materials in energy storage devices such as fuel cells, Li-ion batteries, and supercapacitors. Supercapacitors are electrochemical capacitors that display high performance charging/discharging behavior with significant power density, despite the fact that high performance batteries are adopted for more promising energy densities than regular capacitors.

Because of their high specific capacitances, large specific surface area, and exceptional cycling stability, carbon-based nanomaterials have been researched extensively to serve as electrode materials for electrochemical capacitors. In particular, ultra-high specific surface area graphene sheets exfoliated from graphite powder are being advocated as great substrate materials due to their high conductivity, outstanding surface accessibility, superior mechanical flexibility, and thermal and electrical characteristics. Graphene's particular electrical characteristics and its unique sp² hybridized honeycomb structure make it an ideal material for acting as a continuous electron conducting network. Because of its special qualities, graphene can be used in a wide range of fields, such as electronics, biosensors, energy storage devices, sensors and sensors, and catalysis.

Due in part to the faradaic processes, materials such as metal oxides, hydroxides, and polymers have higher energy densities and specific capacitances than carbon-based materials. It is suggested that the capacitances derived from these materials be used as pseudo capacitances. Nevertheless, these materials have weak electrical conductivity and poor cycling stability, even if they have greater energy densities and specific capacitances. As a result, various research groups are focusing on developing hybrid nanomaterials using graphene in order to obtain high energy and power densities without sacrificing the supercapacitors' capacity to cycle steadily.

At normal temperature, niobate-based ceramic samples with the chemical formula $(M)\text{Nb}_2\text{O}_6$ (where $M = \text{Ca}^{2+}$, Mg^{2+} , or a transition metal) have an orthorhombic columbite structure. Due to the appealing electrical structure that these columbite materials exhibit, they are receiving a lot of interest. In particular, the magnesium niobate MgNb_2O_6 (MN) nanostructure has superior optical, electrical, and dielectric characteristics. MN stabilizes in the $Pbcn$ space group upon synthesis. With a focus on using it as a precursor in the development of microwave dielectric materials like $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 , and perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, it has garnered potential interest for a long time. These materials meet the requirements for multilayer ceramic capacitor, electro-strictor, transducer, and actuator applications.

In an effort to find new materials that meet the specifications needed for supercapacitors, MN nanostructures were created using a hydrothermal process. These artificial MN were hydrothermally aided into graphene to produce hybrid nanostructures known as reduced graphene oxide/magnesium niobate (RGOMN). These innovative hybrid nanostructures' structural, thermal, and electrochemical characteristics are thoroughly examined and presented. This chapter provides a detailed presentation of the measured characteristics. Based on the observed results, RGOMN is suggested as a possible electrode candidate material for energy storage features and application.

RESEARCH METHODOLOGY

Materials

Sisco Research Laboratory provided the following materials: graphite powder, KMnO_4 (99%), H_2SO_4 (98%), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (98%), Nb_2O_5 (99.95%), NaOH (97%), H_2O_2 (30% concentration), and HCl (35% concentration). The water used in all of the experiments was Milli-Q. Analytical-grade solvents, reagents, and other necessary compounds were employed in the synthesis without any additional purification.

Preparation of GO and MN

After implementing the modified Hummer's process as mentioned, GO was obtained. To generate uniform MN nanostructure, the hydrothermal approach was used. Here, 0.406g of MgCl_2 and 0.265g of Nb_2O_5 (2:1) were thoroughly mixed in 2M NaOH for 30 minutes. The resulting white suspension was poured into a cylinder lined with teflon. This was autoclaved sealed and heated to 200°C for 24 hours with auto-limited pressure. After allowing the mixture to reach room temperature, deionized water was used to thoroughly clean it. This mixture was centrifuged once again for 20 minutes at 5500 rpm in a homogeneous dispersion of 10% HCl . After obtaining the precipitate, the hydroxides were

completely washed-out using ethanol and deionized water. Lastly, the white products were sintered for six hours at 700°C after being dried for six hours at 80°C in an oven to create uniformly developed, thermally stable nanomaterials.

Synthesis of RGOMN heterostructure

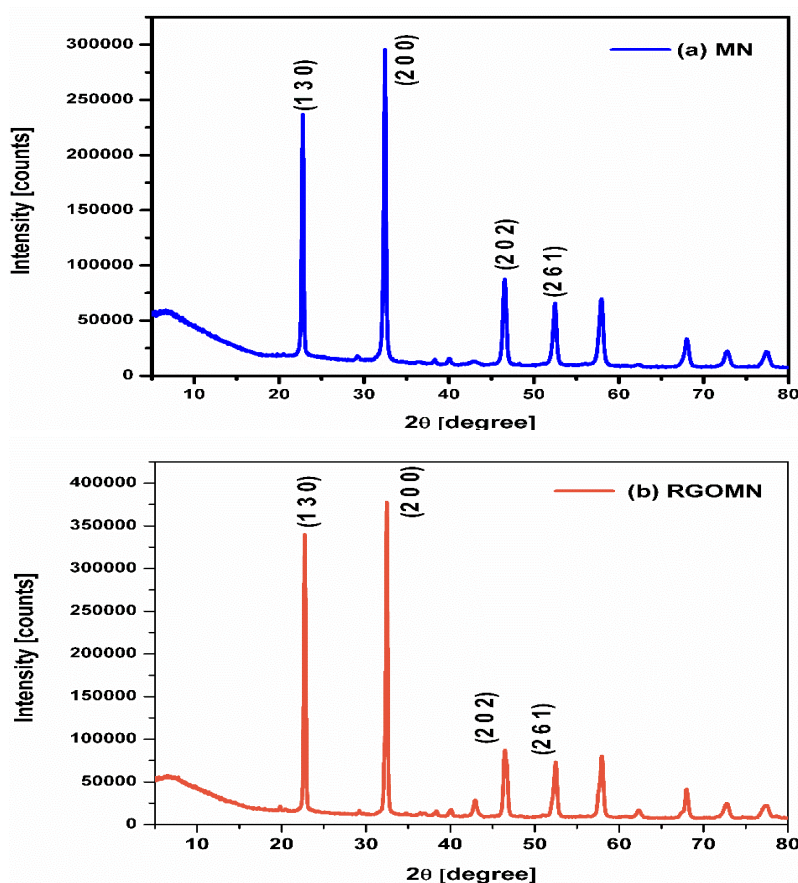
The hydrothermal approach was used to intercalate the graphene layer onto the MN nanocrystals. Deionized water was used to dissolve the MN that was produced hydrothermally. Ethanol was gradually added to this mixture while being constantly stirred, resulting in a homogenous mixture. Separately, GO colloids were distributed into deionized water. The dispersed GO solution was rapidly added to the homogenous mixture and vigorously stirred with a magnetic stirrer. After that, the solution was moved to a 100 ml teflon liner, sealed, and put inside the autoclave made of stainless steel. For two hours, the reaction was conducted at 180°C. To extract the RGOMN heterostructure, the reaction mixture was hydrothermally treated, centrifuged at 5500 rpm, cleaned in deionized water, and dried at 60°C for an entire night.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis - Powder Method

Using Cu K α radiation ($\lambda=1.5406$ Å) and a Rigaku X-ray diffractometer, X-ray diffraction of MN and RGOMN was conducted from 5° to 80° (2θ range) at a step scanning of 0.02°. The resulting diffraction pattern is displayed in Figure 1 (a) and (b).

Figure 1 X-Ray diffraction pattern of (a) MN and (b) RGOMN.



The lattice parameters for the PXRD peaks of the MN structure are $a = 14.187 \text{ \AA}$, $b = 5.69 \text{ \AA}$, and $c = 5.03 \text{ \AA}$. The Pbcn space group has an orthorhombic structure of the columbite type. The computed lattice parameters accord well with JCPDS data card 33-0875. The RGOMN heterostructure's PXRD peaks, shown in Figure 1(b), show graphene layers connected by a sheet-like MN structure. Furthermore, the existence of reduced graphene oxide with a distinct MN structure is indicated by the shift in graphite reflection from 26° to 24° and the rise in XRD pattern intensity at $2\theta = 24^\circ$. Equation provides the scherrer's formula which is used to estimate the crystallite sizes of MN and RGOMN, which are 35 nm and 44 nm, respectively. The HRSEM data and the calculated crystallite sizes of MN and RGOMN agree well.

Morphological and Compositional Studies

Figure 2 (a) and (b) display typical HRSEM images of MN and RGOMN heterostructure samples captured with an FEI Quanta FEG 200 equipped with Energy Dispersive Analysis of X-rays. The HRSEM images of MN in Figure 2(a) display morphology akin to a sheet. Additionally, the HRSEM images displayed in Figure 2 (b) demonstrate the interlinking of MN crystals heat-treated at 700°C with RGO sheets. Because graphene oxide is reduced via a hydrothermal process, the shape of the RGO-assisted MN heterostructure has a greater surface area than MN. The primary storage characteristic of RGOMN is enhanced by an increase in surface area, and this is thoroughly covered in cyclic voltammetry studies. The exceptional shape of RGOMN highlights the originality of the compound and reinforces its suitability for a range of applications.

The EDAX pattern of MN, which indicates the presence of Mg, Nb, and O components, is depicted in Figure 3(a). EDAX examination of the RGOMN nanostructure, as shown in Figure 3(b), reveals the presence of elements C, Mg, Nb, and O. Additionally, it supports the consistency of the carbon mixture including MN elements and the dependability of the composition of MN columbite. Tables 1 and 2 index and display the elemental distribution of MN and RGOMN.

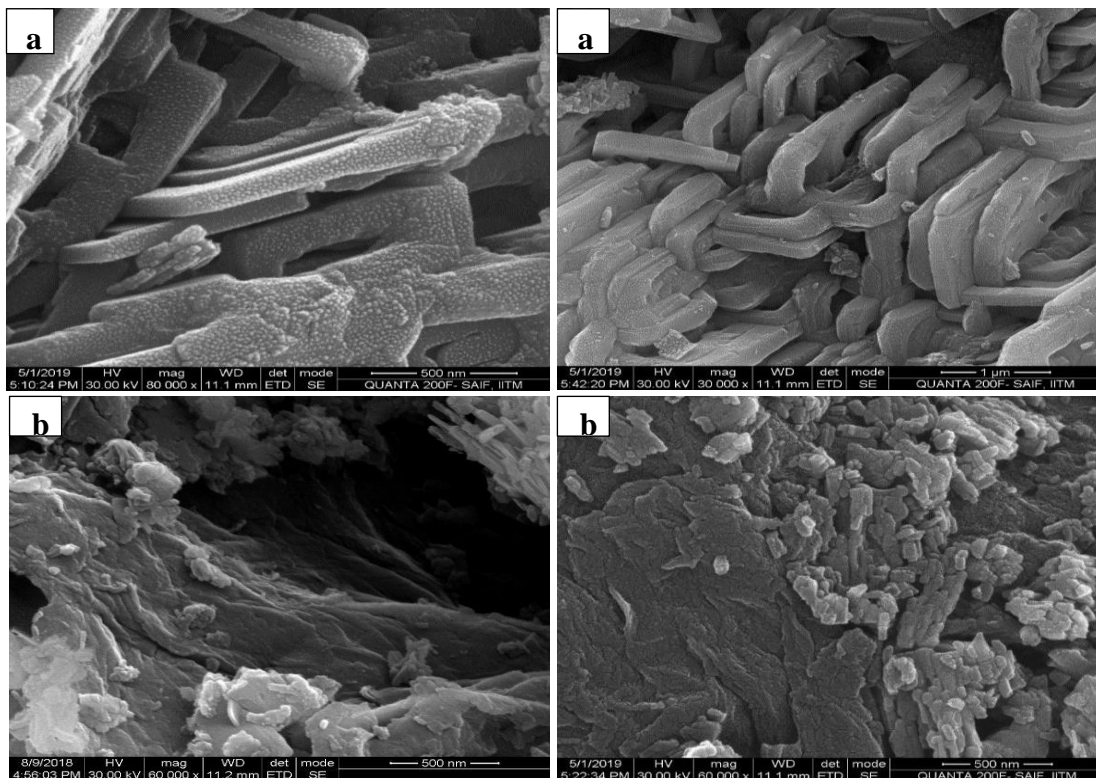


Figure 2 Morphology of (a) MN and (b) RGO

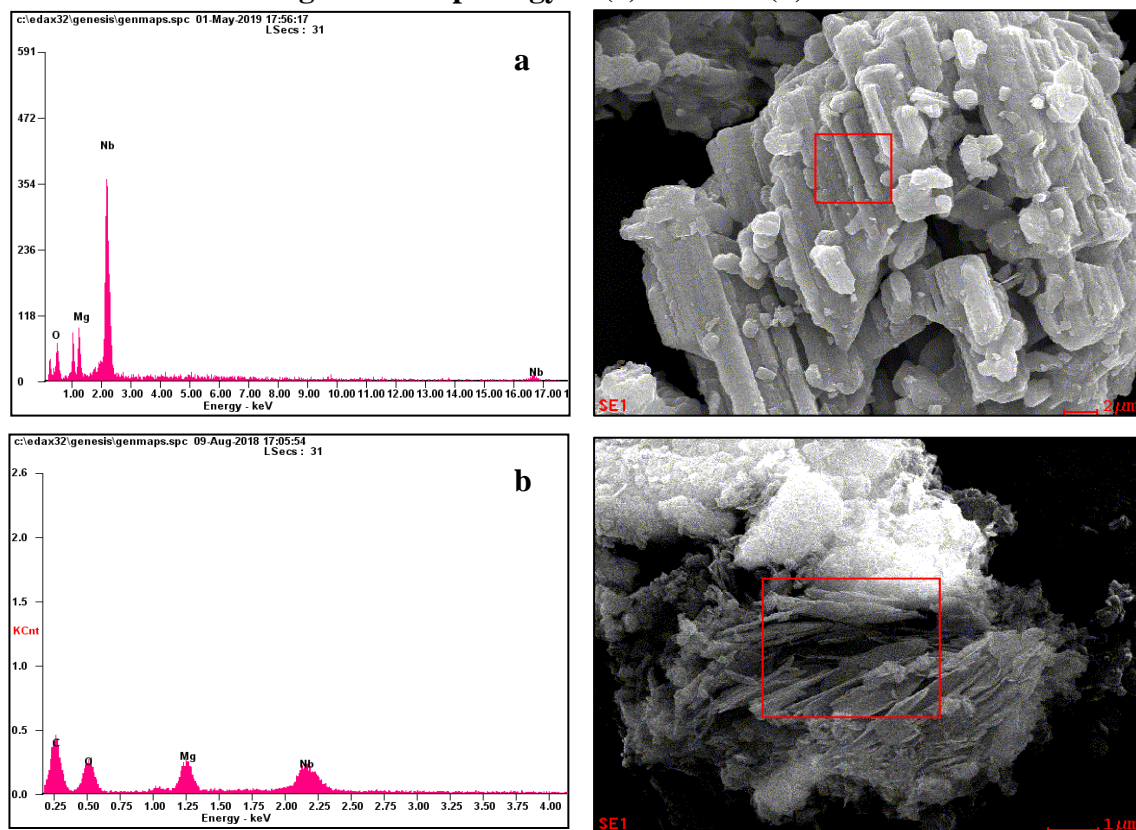


Figure 3 Compositional analysis of (a) MN and (b) RGOMN

Table 1 Elemental composition of MN

Element	Wt%	At%
OK	42.53	70.94
NbL	41.97	12.03
MgL	15.52	17.04
Matrix	Correction	ZAF

Table 2 Elemental composition analysis of RGOMN

Element	Wt%	At%
CK	58.44	71.45
OK	25.45	23.35
MgK	05.82	03.53
NbL	10.32	01.66
Matrix	Correction	ZAF

STRUCTURAL SIGNIFICANCE OF GRAPHENE

All that exists in graphene is a single layer of heavily packed sp² hybridized carbon atoms arranged in a crystal lattice like a honeycomb. By periodically splitting graphite crystals into thinner layers with cohesive tape, individual atomic planes of graphene sheets were created. Research on graphene has become quite popular after this work was recognized with a Nobel Prize in 2010. Through the explicitation of diverse graphitic forms, graphene is discovered to serve as the foundation for all carbon materials, including 1D nanotubes, 3D graphite, and 0D buckyballs.

Despite having many structural similarities to carbon nanotubes, graphene is a promising material for use in a variety of applications due to its vast surface area, diverse electrical states, and superior mechanical qualities. Furthermore, the single-atom thick graphene sheets with 2D planar geometry will facilitate electron transport even more and allow for the material to function as an efficient electrode.

Because of its exceptional qualities, layered graphene nanosheets with 2D geometry have been investigated as a novel class of contender. Due to its high surface area, it has drawn interest from a wide range of potential applications, including batteries, field-effect transistors, actuators, sensors, solar cells, and field-emission devices.

CONCLUSION

Graphene oxide can be reduced chemically or thermally to produce two-dimensional graphene nanolayered sheets. Because of the strong π - π interaction, nanolayered sheets have a high degree of re-stacking and agglomerating particles. This lowers graphene's

inherent surface area and hence lowers its functionality. In order to successfully address graphene restacking and agglomeration, numerous attempts are undertaken to create graphene-based hybrid nanocomposites by incorporating graphene into other functional materials as conducting polymers, hydroxides, and transition metal oxides. In order to improve graphene's electrochemical behavior, conducting networks and redox processes are combined to create hybrid nanocomposites.

The hydrothermal method was used to create MN and the unique RGOMN. These studies also revealed the presence of several functional groups in MN and RGOMN. Results from HRSEM and TEM are used to describe the excellent morphology of MN and RGOMN. In 0.1 M H₂SO₄ electrolyte, electrochemical analyses of MN and RGOMN electrodes revealed that RGOMN had a higher surface area than MN. Using the GCD technique and cyclic voltammetry, respectively, the increase in specific capacitance seen in RGOMN reflects considerable capacitive performance. After 100 cycles, a steady capacitive retention was observed in comparison to MN. The results showed that as-synthesised MN and RGOMN's hybrid capacitive nature would be extremely interesting for future energy storage.

APPLICATIONS OF GRAPHENE

The subsequent uses of graphene in various fields represent significant advancements in the creation of new devices:

- i. A wide range of multifunctional applications, such as thermal interface materials and electrically conductive composites, are made possible by the low cost and large-scale production of graphene-filled polymer composites with high electrical conductivity, thermal conductivity, and mechanical strength.
- ii. Graphene's ultrahigh terahertz electron mobility makes it a promising material for spintronics, optoelectronics, ballistic transistors, and field effect transistors, among other cheaper, faster, and smaller devices. Thus, optoelectronics and graphene-based electronics would take the role of traditional silicon-based electronics.
- iii. According to recent research, energy storage systems made of graphene-based materials, like high-performance lithium-ion batteries and electrochemical capacitors, have promising physiochemical properties and improved electrochemical performance in terms of cyclability, capacity, and rate capability because of the unique 2D graphene layered structure of these materials.
- iv. Bulk graphene created by chemical vapor deposition takes the role of indium tin oxide in a variety of display applications as a more affordable and transparent conducting electrode.
- v. A number of scientists point to further possible uses, including dye-sensitized solar cells, organic solar cells, photocatalysts, catalysts, different kinds of sensors, field emission devices, and hydrogen storage, among others.

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