

Experimental Investigations on Copper-Based Nanoparticles for Energy Storage Applications

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The rapid development of capacitive materials can be attributed to the introduction of novel approaches to the design and production of energy storage materials. In this context, multiple graphene-based spinel metal oxide nanoparticles display a significant capacitive potential. In addition, graphene nanocomposites that contain electron-donating inclusions boost the electronic importance of the chemicals that are supported. By utilizing the co-precipitation method, copper chromite nanoparticles implanted on graphene oxide (CuCr₂O₄/GO) were manufactured to produce a material that is capable of serving as an efficient energy storage medium. The production of CuCr₂O₄ was accomplished via the use of a basic sol-gel method, whereas the production of GO was accomplished through the use of a modified version of Hummer's strategy. For this purpose of determining the X-ray diffraction analysis was performed, and energy-dispersive spectroscopy and electrochemical analysis were utilized to determine chemical weight composition. The nano-composite, in its as-made state, is suitable for touch-sensitive energy storage, as evidenced by the fact that the highest capacitance of 370.5 F/g that could be measured matched to an aqueous electrolyte of 0.1 M H₂SO₄; this finding supports the hypothesis that the nano-composite was designed specifically for this purpose. As a result, the CuCr₂O₄/GO material, in the form in which it has been developed, has the potential to be an effective capacitive material for applications involving energy storage.

Keywords: Nanoparticles, Energy Storage, Graphene.

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1. INTRODUCTION

A greater need for highly efficient and productive power-generating resources has arisen alongside the rise of electric mobility and small electronic gadgets. Batteries and capacitors are the forms of energy storage that are most commonly called into question because of the high energy density they possess their size and their weight [1]. Capacitors outperform power packs in terms of efficiency when it comes to electricity. Because of their "high specific power of 10 kW kg⁻¹", existence times that are, on average, longer as well as the speed with which they can be charged and discharged, electrochemical capacitors may be a better choice than batteries for applications that need the storage of energy [2]. On the other hand, capacitive performance is determined not only by the kind of electrolyte but also by the particular surface area of the integrated electrodes. Because of this, future applications in the field of energy will call for the development of electrodes that have porous architectures, enormous pore widths, and exceptional conductivity. These electrodes will also need to have high capacitance. The utilization of a wide variety of active electrode materials in capacitive materials has been the subject of extensive research. It was previously believed that "transition-metal oxides (TMOs) with heterogeneous spinel structures" may serve as effective electrodes for the energy storage capabilities of capacitors [3]. "Manganese

dioxide (MnO₂)," transition-metal oxide modified "NaNbO₃-Bi(Mg_{0.5}Ti_{0.5}) O₃ lead-free ceramics," and "MnMoO₄@C micro rods" are some of the more recent examples of capacitive materials that have been described for use in applications related to energy storage. Copper, a member of this family, has been the subject of substantial study for a variety of applications, some of which include photocatalytic activity, the creation of hydrogen, the management of pollution, the removal of pollutants, and many more. Because of its fascinating properties as a "catalyst, semiconductor material, electrochemical sensor, and high-temperature ceramic, copper" has been synthesized using a variety of methods, such as the "hydrothermal method, sol-gel, co-precipitation, thermal decomposition, solid-state reaction method, and combustion method" [4]. These methods were chosen because of copper's ability to be used in various applications. Because chromite is a member of the spinel group, its crystal structure is always in the form of a cubic spinel. "CuCr₂O₄" has a conventional spinel structure, but due to rotation along all axes, it has been distorted into a "tetragonal form". The reason for this is that rotation takes place along all axes whereas compression only takes place along one. "Electronegativity and the dimensions of the orbital radius are two elements" that can alter cation distribution in a "spinel structure", although it still follows the usual pattern of cation distribution. Because the

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synthesis method is always a crucial component in acquiring the product with controlled parameters, selecting synthesis methods that are less complicated, relatively more cost-effective, and environmentally friendly is the key to successfully incorporating these electrode materials into capacitors [5]. Several other techniques of synthesis have the drawbacks of extended reaction times, the need for complicated apparatus, elevated reaction temperatures, and higher overall costs. One of the most powerful "spinel oxides," copper chromite also has extensive commercial applications as a "catalyst in oxidation, alkylation, breakdown, hydrogenation, and hydrogen production," and its nanoparticles have much larger surface surfaces. The reason for this is that "copper chromite" is a particularly potent "spinel oxide". Due to the fascinating properties that it possesses, CuCr_2O_4 is an excellent candidate for use in the creation of nanocomposites with carbon-based materials. In addition, the development of nanocomposite materials has propelled the allotrope of carbon known as graphene to the forefront of public attention [6]. Copper oxide nanoparticles were manufactured by a process known as hydrothermal self-assembly, and they were subsequently deposited on graphene oxide. Unanticipated catalytic activity was seen when CuO nanoparticles and graphene oxide were utilized to create a nanocomposite catalyst. It reveals that it is suitable for use as a heterogeneous catalyst for more nanoscale nitroaromatic synthesis utilizing techniques of manufacture that are quite inexpensive [7]. Studies were done on the effect that nitrogen doping has on graphene as well as the creation of its nanocomposite with " CuCr_2O_4 " for high-performance supercapacitors.

This research follows the following structure: Section II contains the experiment with copper-based nanoparticles. Experimental analysis is described in Section III. The final section IV offered the conclusion.

2. EXPERIMENT WITH COPPER-BASED NANOPARTICLES

Copper nanoparticles are relatively stable in terms of their chemical and physical characteristics, making them easy to mix with polymers and making it possible for them to easily combined. Because they possible to be manufactured with extraordinarily large surface areas and unusual particle geometries, they may prove to be particularly useful as bioactive compounds.

2.1 Materials and methods

Ingredients and reagents Chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), citric acid, "ammonium hydroxide (NH_4OH), graphite (C), potassium permanganate (KMnO_4), nitric acid (HNO_3), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), and hydrochloric acid" are among the chemicals used in the process (HCl). All of the ingredients were obtained from "Sigma-Aldrich" and used as is, without any purification [7]. In these tests, "deionized water (DI)" was used instead of tap water.

2.2 Synthesis of CuCr_2O_4 nanoparticles

CuCr_2O_4 nanoparticles were created using the straightforward, environmentally safe sol-gel process. In a volume of fifty milliliters of DI water, chromium and copper nitrates were mixed to produce a mixed salt solution. After that, a "2:1 molar ratio of citric acid" was added to the mixture [8]. The mixture was agitated constantly until it was able to produce a solution that was uniform throughout. At a temperature of 95 degrees Celsius, the mixture was agitated constantly while a "concentrated ammonia solution" was introduced to it drop by drop as a precipitating agent. This process lasted for thirty minutes [9]. After making a dark green gel, it was baked at a temperature of 120 degrees Celsius for the whole night and then calcined at a temperature of 750 degrees Celsius for four hours. Agate mortar was used to grind the dark powder into a uniform consistency.

2.3 Synthesis of $\text{CuCr}_2\text{O}_4/\text{GO}$ nanocomposite

A modified version of Hummers' process was used to create graphene oxide (GO). Furthermore, the coprecipitation approach was used to create a $\text{CuCr}_2\text{O}_4/\text{GO}$ nanocomposite. CuCr_2O_4 nanoparticles were first mixed in a 1:1 solution of acetic acid and ethylene glycol before being subjected to a one-hour sonication process [10]. The CuCr_2O_4 nanoparticle solution and GO were then combined, and the combination was then further stirred continuously for 15 min. before being continuously stirred for "1 h at 85 °C". After the mixture cooled, it was centrifuged at "3500 rpm for 10" minutes to get rid of the precipitates [11]. Overnight, the precipitates were dried a "70 °C", and the following day, the powder was coarsely crushed so that it could be analyzed.

3. EXPERIMENTAL ANALYSIS

The ability of experimental studies to give simply interpretable and qualitative information is the primary benefit that distinguishes them from other kinds of research [12-13]. In addition, the confirmation source for quantitative research is the material that is obtained through experiments. As a consequence of this, researchers carry out a variety of tests to examine copper-based nanoparticles for energy storage applications. In the CES Selector/Simulation tool, the proposed model is activated, and its efficacy is "X-Ray diffraction analysis", "Energy dispersive spectroscopy (EDS)" and electrochemical impedance spectroscopy.

3.1 X-Ray Diffraction Analysis

Formation mechanism and phase purity were established by X-ray diffraction examination performed on the materials during production. The largest peak of graphene oxide can be seen in Fig. 1a at 11.5° with the (001) plane. Additionally, the " d -spacing for graphite was 3.3 Å" and changed to "7.6 Å" in the presence of Graphene oxide, exhibiting strong oxidation and only moderate fundamental changes.

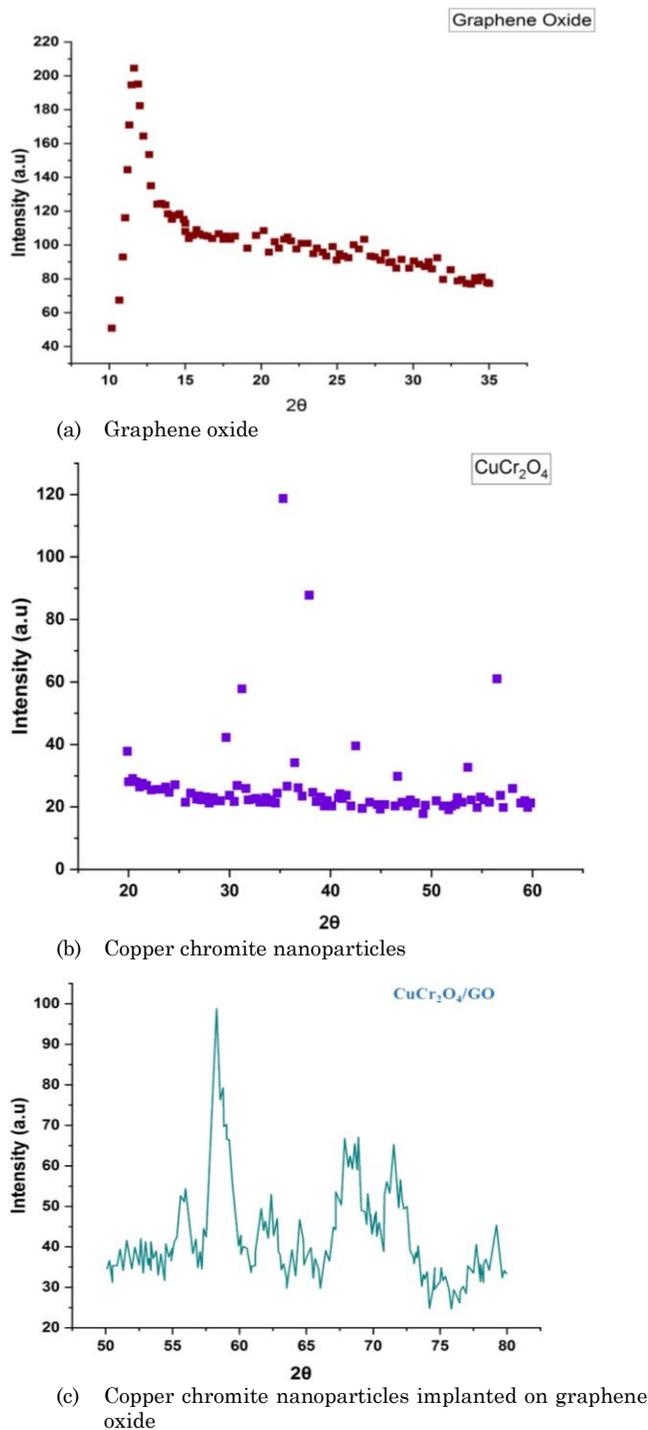


Fig. 1 – a) XRD pattern of a GO, b) CuCr₂O₄, and c) CuCr₂O₄/GO nanoparticles

Fig. 1b and c display the XRD patterns for "CuCr₂O₄" and "CuCr₂O₄/GO nanocomposites," respectively. The distinctive peaks for pure copper chromite may be seen between the values 20 and 100, making this material suitable for use in single-phase applications. "XRD pattern of the CuCr₂O₄/GO nanoparticles" shows otherwise [12].

The presence of imperfections in the crystal structure of the nanoparticles caused the copper peaks to be moved to 20.9° and 78.3°, respectively, during crystallization. The co-precipitation technique efficiently decorates GO onto the surface of copper chromite nanoparticles while eliminating various functional groups. The Debye-Scherrer formula was used to get the average particle size equation (1).

$$X = \frac{H\lambda}{\beta \cos\theta} \tag{1}$$

Where X stands for the diamond size distribution (nm), H is the form factor, or 0.9, stands for the X-ray wavelength (0.15406 nm), stands for the θ , and stands for the "diffracted peak FWHM (full width at half maximum)". CuCr₂O₄/GO nanoparticle's diamond size distribution was determined to be "21.2 nm, 10.9 nm, and 8.9 nm", respectively. The nanoparticle's smaller crystallites are an indicator that they have partially amorphized.

Energy Dispersive Spectroscopy (EDS)

Fig. 2 displays the EDS analysis of the CuCr₂O₄/GO nanocomposite. Both Cu and Cr had surface uniformity in their dispersion. The suppression of GO in the creation of nanocomposites with CuCr₂O₄ was not confirmed by any peak of carbon in the spectra [13]. A second peak, unquestionably an impurity peak of Si, also showed, most likely as a result of an uncalibrated Li-Si detector in the EDS apparatus. Component proportions contained in the spectrum are shown in Table 1. Along with surface enrichment effects, the Cu/Cr molar ratio also showed a considerable influence on particle size and shape in the K particles.

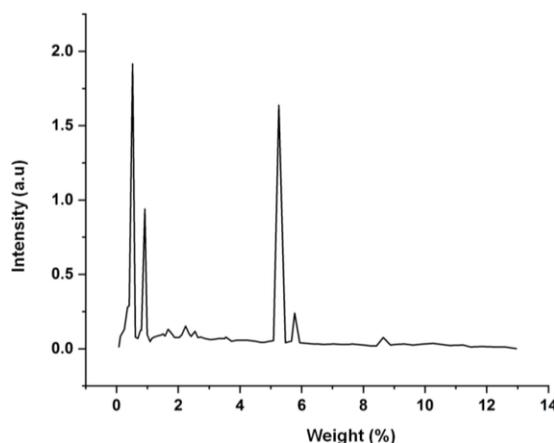


Fig. 2 – EDS of CuCr₂O₄/GO nanoparticles

Table 1 – EDS analysis used to assess the chemical compositions

Elements	Weight (%)
Cr K	51.01
O K	13.66
Cu K	33.92
Si K	1.41

3.2 Electrochemical analysis

This electrochemical investigation was carried out using the "Gamry Potentiostat Interface and a three-electrode set-up. The reference, counter, and working electrodes were "Ag/AgCl," "platinum wire," and "glassy carbon electrode (GCE)," respectively [14]. Before constructing the working electrode from the powder-synthesized components, it was always cleaned with an alumina slurry and ethanol. The GCE was made by placing "0.25 g of powdered electrode material" on a surface and then adding "2 l of 5 % Nafon solution". The created electrode was dried in an oven for 20 minutes at 50 °C.

Electrochemical Impedance Spectroscopy (EIS)

EIS was used to analyze the charge transfer process on the electrode surface and the frequency-varying AC potentials in the analyte solutions. R_{ds} , which refers to "semi-circle diameter" in the "high-frequency region", and "equivalent series resistance", or R_s , interception along the real axis, are critical components [15-17].

"Solution resistance" R_s and "Warburg resistance" R_w are unaffected by the composition of the electrolyte, but the "constant phase element (CPE)" and differential series resistance R_{ds} are impacted by variations in "electrode material" due to the material's conductive characteristics [18].

Due to increased electron-transfer rate constant F_{app} caused by the insertion of CuCr_2O_4 nanoparticles into the GO structure, minimum R_{ds} was seen in "0.1 M H_2SO_4 electrolyte". However, Relative to other electrolytes, 1 M

KOH electrolyte has a much higher R_{ds} because of the lower conductivity caused by the limited electron transfer process between the "electrode and electrolyte solution". As required by supercapacitors, reduced R_{ds} is a sign of better conductivity, which refers to improved electrochemical activity. Additionally, using the relationship in Eq. 3, the apparent rate constant F_{app} was determined.

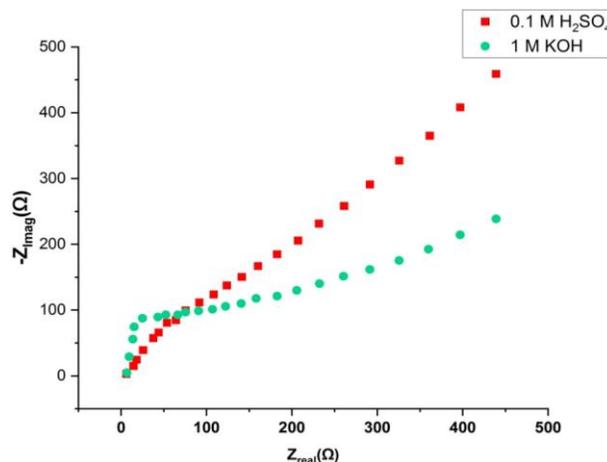


Fig. 3 – $\text{CuCr}_2\text{O}_4/\text{GO}$ electrode EIS frequencies in 0.1 M H_2SO_4 and 1 M KOH solutions

Fig. 3 displays the EIS spectra of the $\text{CuCr}_2\text{O}_4/\text{GO}$ nanoparticles electrode in "0.1 M H_2SO_4 and 1 M KOH" aqueous solutions, and Table 2 provides the related EIS properties.

Table 2 – Relative characteristics determined through EIS analysis

Tested electrode ($\text{CuCr}_2\text{O}_4/\text{GO}$)	R_{ds} (Ω)	R_s (Ω)	α (roughness parameter)	CPE (μF)	$F_{app} \times 10^{-6}$ (cm s^{-1})	R_w ($\mu\Omega$)
0.1 M H_2SO_4	236.6	26.11	0.80	48.30	11.25	383.6
1 M KOH	293.2	8.203	0.79	8.887	0.908	541.5

$$F_{app} = \frac{RT}{E^2 R_{ds} D} \quad (2)$$

Where R is the universal gas constant, T denotes temperature, E denotes Faraday's constant, R_{ds} denotes charge transfer resistance, and D denotes electrolyte concentration [19]. The high conductance of the electrochemical devices was shown, however, by the larger F_{app} estimate in "acidic electrolyte". With a decreased F_{app} in the "1 M KOH aqueous electrolyte" solution, it was suggested that the electroconductivity was significantly reduced.

4. CONCLUSION

The experiments on copper-based nanoparticles for energy storage applications were the focus of this research.

The chemical precipitation approach was used to successfully create the nanoparticles of copper chromite graphene oxide ($\text{CuCr}_2\text{O}_4/\text{GO}$). The lack of a GO peak in XRD analysis showed that the structure had been destroyed by CuCr_2O_4 crystal formation. Band gap broadening was influenced by the quantum size, and the nanoparticles were found to be within the GO range. The sample's purity was validated by EDS analysis, and there were few impurities found in it. When 0.1 M H_2SO_4 was applied, an improved nano-particle value that showed a straight proportionality between the highest peak and unit base of the potential range was produced. This confirmed the dispersion process. Consequently, the $\text{CuCr}_2\text{O}_4/\text{GO}$ nano nanoparticles may have a wide range of uses as electrode materials for supercapacitors used for energy storage.

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Експериментальні дослідження властивостей наночастинок на основі міді для зберігання енергії

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Швидкий розвиток емнісних матеріалів можна пояснити впровадженням нових підходів до проектування та виробництва матеріалів для зберігання енергії. У цьому контексті численні наночастинки оксиду металу на основі графеуе демонструють значний емнісний потенціал. Крім того, графенові наноконпозити, які містять електронодонорні включення, підвищують електронну важливість хімічних речовин. Використовуючи метод спільного осадження, наночастинки хроміту міді, імплантовані на оксид графену (CuCr₂O₄/GO), були сформовані золь-гель методом для отримання матеріалу, здатного служити ефективним середовищем зберігання енергії. Використовується метод рентгеноструктурного аналізу, енергодисперсійна спектроскопія та електрохімічний аналіз. Наноконпозит у готовому стані підходить для чутливого елемента накопичувача енергії, про що свідчить той факт, що найвища емність 370,5 Fg⁻¹, яку можна було виміряти, відповідає водному електроліту 0.1 М Н₂SO₄. Зроблено висновок, що наноконпозитний матеріал CuCr₂O₄/GO відповідає вимогам до ефективних емнісних матеріалів для зберігання енергії.

Ключові слова: Наночастинки, Графен, Зберігання енергії