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Article

Synthesis and Characterization of Coconut-Derived Graphene and its Properties in Nickel/Graphene and Zinc/Graphene Electrodes

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Abstract: This study introduces a novel and sustainable method of producing graphene from coconut shells and investigates its application in Graphene, Ni/Graphene, and Zn/Graphene electrodes for advanced energy storage devices. The graphene was synthesized scalably using a pyrolysis and impregnation technique, with its successful synthesis verified by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), and electrical conductivity measurements characterizations. The study highlights the enhanced performance of Zn/Graphene electrodes, which outperform both pure graphene and Ni/Graphene variants. This superior performance is attributed to the smaller particle size of Zn (mean = 2.356 μm) compared to Ni (mean = 3.09 μm), and Zn's more favorable electron configuration for electron transfer. These findings demonstrate the potential of bio-derived graphene composites as efficient, high-performance electrodes, paving the way for more sustainable and cost-effective energy storage solutions.

Keywords: Coconut shell; Graphene Synthesis; Pyrolysis; Ni/Graphene; Zn/Graphene; Energy Storage Electrodes; Bio-derived materials; Sustainable materials

1. Introduction

Chemical potential energy is converted into electrical energy through the transfer of electrons between the cathode and the anode in batteries [1,2]. High-quality batteries are characterized by their energy density [3,4], power density [5,6], stability [7,8], low internal resistance [9,10], and cost-effectiveness [11]. Typically, carbon materials are employed as the anode in primary batteries, while carbon-metal alloys serve as the cathode [12,13]. The choice of materials used in battery production significantly affects the overall quality and cost of the batteries [14–16]. Therefore, exploring new alternative materials for mass-producing electrode material is essential [17,18].

Graphene has captured considerable attention in the field of electrochemical energy storage systems due to its remarkable properties [19,20]. As a single-layer carbon with a 2D lattice structure, graphene exhibits an array of remarkable characteristics, including its unique 2D carbon structure [21,22], sp^2 hybridization [23,24], exceptional strength [25,26], a notably large surface area of $2,600 \text{ m}^2\text{g}^{-1}$ [27,28], high electrical conductivity reaching up to $1,250 \text{ Scm}^{-1}$ [29,30] and impressive thermal conductivity ranging from $4840\text{--}5300 \text{ Wm}^{-1}\text{K}^{-1}$ [31,32].

An illustrative example that underscores the immense potential of Graphene as an energy storage material is Li/Graphene, exhibiting an impressive high capacity of 744 mAh/g [33,34]. This compelling result underscores the prospect of Graphene as a highly efficient energy storage material, particularly for lithium and sodium ions in battery applications. The incorporation of Graphene in electrochemical energy storage systems opens up exciting avenues for improving battery performance and meeting the increasing needs for cutting-edge energy storage solutions. The remarkable properties of Graphene pave the way for advancements in battery technology, fostering the development of more sustainable and high-performance energy storage devices.

The development of batteries faces significant challenges, primarily the high cost and non-recyclability of lithium after use. Additionally, the energy density and capacity of conventional primary batteries remain relatively low [35]. Prolonged usage can lead to weak interactions between the electrodes, resulting in reduced electron transport [36,37] and potential loss of electrical contact [38,39]. To address these issues, incorporating graphene as electrode materials offers a promising solution. This research aims to demonstrate how graphene can enhance energy storage capacity, consequently increasing the specific energy and energy capacity of batteries [37,40].

In previous studies, graphene has been successfully utilized as a battery cathode, yielding positive results in enhancing energy storage capabilities [33,41]. Notably, the addition of graphene to battery anode materials enhances electron conductivity, thereby improving the anode's power supply capacity. Furthermore, the introduction of Ni and Zn metals further boosts the anode's activity while enhancing the electrical interaction quality of the graphene layer [42,43].

Researchers have proposed modifying carbon materials, particularly with the use of Nickel and Zinc [44–46], and employing these modified materials as electrode supports in primary battery cells. By leveraging the unique properties of graphene and its potential interactions with metal dopants, this approach holds great promise for advancing battery technology and addressing the limitations of traditional primary batteries. The exploration of modified carbon materials as an electrode support may pave the way for more efficient and high-performance primary battery systems.

2. Methodology

2.1. Chemical reagents

Coconut shell from North Sumatera Province (Indonesia) was used as a raw material to produce the graphene powder. Aquadest, aluminum foil, activated carbon, nickel chloride (NiCl_2 99 wt. %), zinc chloride (ZnCl_2 99 wt. %), and ethanol ($\text{C}_2\text{H}_5\text{OH}$ 96 %) were purchased from E-Merck and used without any further purification.

2.2. Graphene production

The process began by cutting coconut shell charcoal into chips, and 15 grams of these chips were subjected to heating at 600 °C for 1 hour. After the heating process, a 150-mesh screen was employed to achieve a uniform shape and size of the graphene. The resulting material was then washed with distilled water and subsequently dried at 70 °C to obtain the final graphene product [47,48].

2.3. Preparation of Ni/Graphene and Zn/Graphene

To prepare Ni/Graphene in a 1:1 ratio, 1 gram of NiCl₂ and graphene was mixed with 200 ml of absolute ethanol. The mixture was stirred for an hour at 500 rpm at room temperature. Next, the NiCl₂/ethanol solution and graphene/ethanol solution were combined and further agitated for 2 hours using an ultrasonic bath. The resulting solution was filtered and subsequently dried at 100 °C overnight to obtain the final Ni/Graphene sample. Similarly, the Zn/Graphene sample was prepared using the same method [48–50] shown in Figure 1.

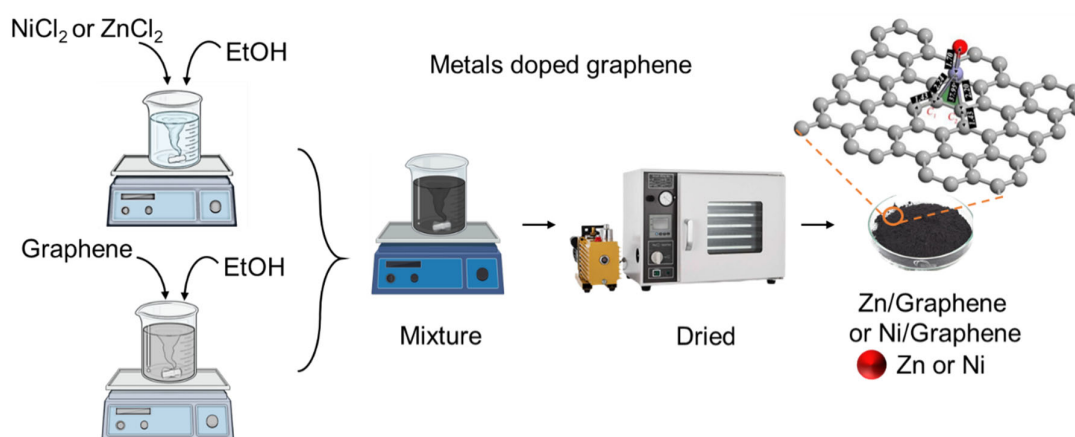


Figure 1. Schematic Ni or Zn metals doped graphene process.

2.4. Characterizations

In this study, we conducted an analysis of graphene, Ni/Graphene, and Zn/Graphene using EDX and XRD techniques. Before doping with metals, the graphene was characterized using a Renishaw inVia™ confocal Raman microscope and the electrochemical performance was evaluated using autolab PGSTAT 30 potentiostat/galvanostat. EDX analysis was carried out using an EM 30 COXEM equipped with an accelerating voltage of 20 kV. The XRD analysis uses a beam size of 10 mm × 10 mm, with Cu/Kα monochromatic graphite radiation ($\lambda = 1.5406$) at 40 kV and 100 mA. The range of 2θ was set from 10° to 90° in 2.0° steps. The X-ray patterns were obtained using a SWXD Diffractometer from Rigaku Corporation (Singapore), operating at 18 kW. The data obtained were processed using D/MAX-2000/PC version 3.0.0.0.

Additionally, a conductometer was used to evaluate the electrical conductivity of the graphene, Ni/Graphene, and Zn/Graphene samples. These analytical techniques allowed us to characterize the structural and electrical properties of the different materials, and providing valuable insights into their potential as electrode materials for primary batteries.

3. Results and Discussion

3.1. Graphene characterization and electrochemical performance

Graphene was synthesized from coconut shell, a byproduct with with abundant carbon elements. The reported method in Section 2, successfully transforms biomass into graphene. The material was characterized via Raman spectroscopy and compared with commercial references. Through Raman Scattering, shifts in energy provides details about the system's vibrational modes and provides data regarding the number of layers, charge doping, stress, and strain conditions.

As seen in Figure 2, the obtained graphene has three major peaks: D, G, and 2D bands at $\pm 1350\text{ cm}^{-1}$, $\pm 1580\text{ cm}^{-1}$, and $\pm 2790\text{ cm}^{-1}$ [51] respectively. The peaks show slight differences in peak width. The full-width half maximum (FWHM) of the peaks were calculated using the Lorentzian fitting shown in Table 1.

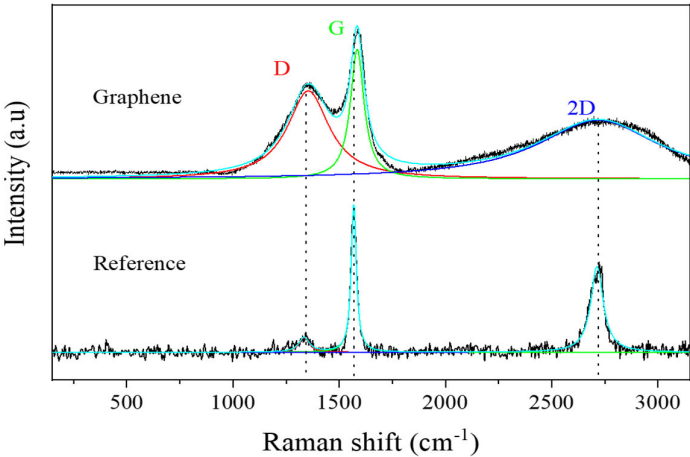


Figure 2. Raman spectra of graphene synthesized and the reference.

Table 1 FWHM number of Graphene and Reference.

	D FWHM	G FWHM	2D FWHM
Graphene	239,9219 ± 2,6650	78,4642 ± 0,8587	690,2105 ± 6,2355
Reference	28.1999 ± 10,2399	28,9196 ± 0,8610	64,4692 ± 2,1774

From Table 1, the graphene synthesized has a broader peak than the reference. The feedstock contains various organic functional groups, such as carbonyl, ether, and amine. The pyrolysis process at 600 °C may have introduced defects in the graphene structure. The D peak indicates defects in the crystal lattice leading to a disruption of the hexagonal carbon structure's symmetry [52]. The G peak signifies the presence of well-organized graphitic carbons, and the 2D peak usually combines with G peaks, indicating the graphitic sp². [53,54]. The ratio I_D/I_G of graphene synthesized is 0.622, compared to the reference, which is 0.136. The I_D/I_G reference is lower than graphene synthesized indicates a high degree of graphitization and a lower value of defects. Defects can have an important role in defining the mechanical and electrochemical properties of electrode materials [55]. To evaluate the electrochemical properties of graphene material, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were used (Figure 3).

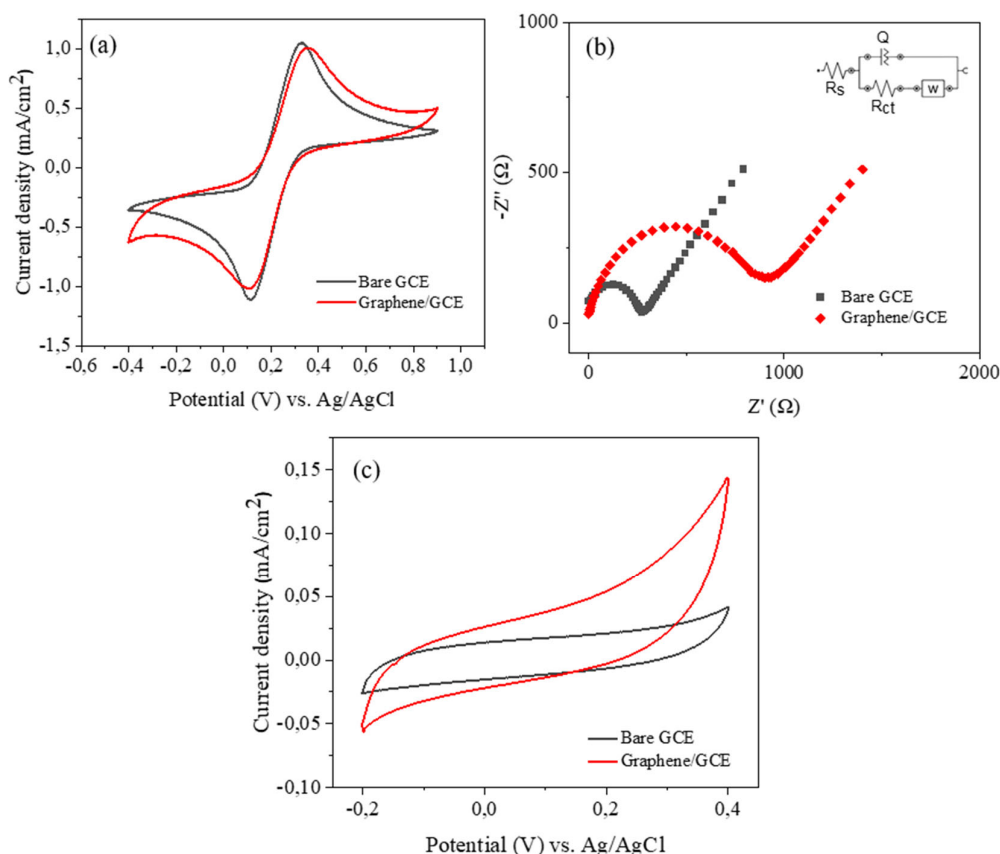


Figure 3. (a) CV curves of Bare GCE and graphene/GCE recorded in 0.1 M KCl Containing 5mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (b) EIS result of Bare GCE, and graphene/GCE recorded in 0.1M KCl Containing 5mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (c) CV curves Bare GCE, and graphene/GCE recorded in 1 M KOH at 50 mV/s.

As seen in Figure 3a., graphene has an oxidation-reduction pair $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$. Electrochemical behavior of graphene-modified GCE was compared to glassy carbon electrode (GCE). Curve Graphene/GCE indicated exhibiting prominent peaks, suggesting significant redox reactions compared to the bare GCE. This implies that the modification of graphene improved the electrochemical activity of the electrode. Both curves cover a range of potentials from -0.6 to 1.0 volts compared to Ag/AgCl. However, the graphene modification seems to stabilize the electrode potential, potentially because of its non-reactive properties. The current density of the Graphene/GCE curve is higher due to the enhanced surface area and conductivity offered by the graphene layer. As shown in Figure 3c, the cycling of modified electrodes in 1 M KOH at 50 mV/s increases the capacitance for Bare GCE (50.4 F/g) and Graphene/GCE (98.8 F/g). Based on Figure 3b., the Electrochemical Impedance Spectroscopy (EIS) graph. The charge transfer resistance (R_{ct}) values for the Bare GCE and Graphene/GCE are 0.30 kΩ and 0.88 kΩ, respectively. R_{ct} is associated with the rate of the redox reaction occurring at the surface of the electrode. A lower R_{ct} value signifies a more rapid electron transfer rate, implying that the unmodified GCE exhibited greater electrochemical activity compared to the GCE treated with graphene. However, the observed rise in R_{ct} following the graphene synthesized change implies that this alteration potentially introduced an impediment to the flow of electrons. The reason for this may be attributed to the inherent physical characteristics of the carbon material, including its porosity, surface area, and functional and chemical composition [56]. The enhanced efficiency of the Graphene/GCE in terms of current density and peak precision highlights its potential for utilization in sensors, energy storage, or other technologies that make use of electrochemical features.

3.2. Ni or Zn decorated on graphene study

Ni and Zn were selected as the focus of this study for several reasons. Firstly, Ni and Zn share some similarities with Li in terms of their properties, making them suitable candidates for comparison. Additionally, both metals possess a high electron storage capacity, which sets them apart from other metals and enhances their potential as electrode materials. Moreover, their reactivity is lower than that of Li, making them more stable for battery applications. Combining Ni and Zn with graphene has the potential to create a synergistic effect, further boosting the activity of the composite material. Another advantage of using Ni and Zn is their ease of deposition onto graphene, which is more straightforward compared to Li. This results in lower processing and material costs, making them attractive choices for battery electrode materials.

To confirm the presence of Ni and Zn on the graphene material, X-ray diffraction (XRD) was employed. The XRD analysis allowed the demonstration of the successful deposition of Ni and Zn on the graphene surface, as shown in Figure 4. This verification further supported the potential of graphene-based composites for energy storage applications.

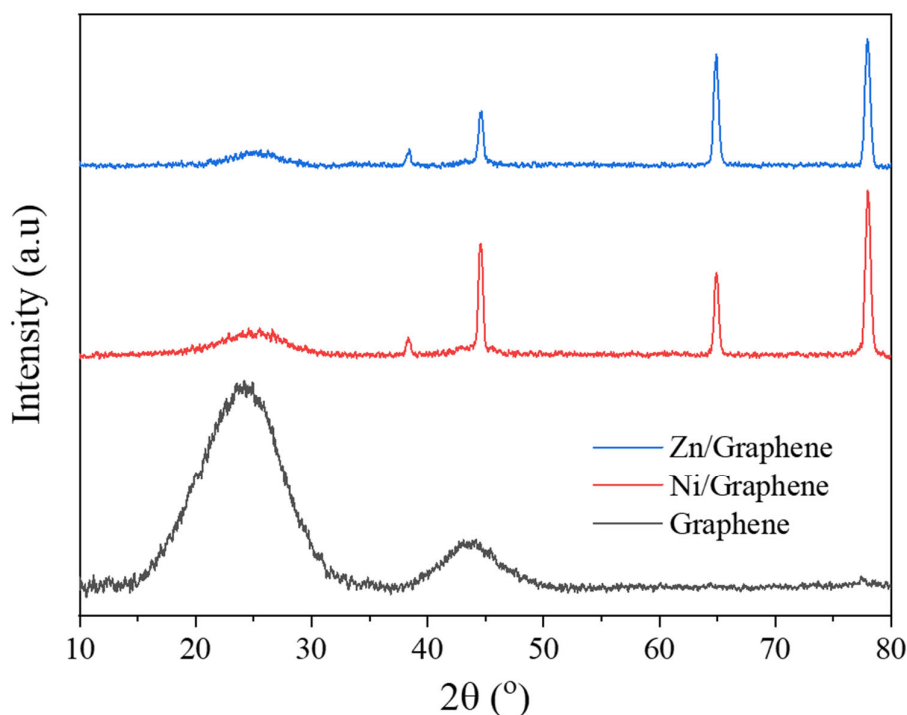


Figure 4. XRD patterns of Graphene, Ni/Graphene and Zn/Graphene.

As seen in Figure 4., the enhanced pyrolysis method utilized in this study successfully produced graphene. The presence of weak graphene layers is indicated by the prominent peak observed at $2\theta = 23.83^\circ$, corresponding to a d spacing of 3.35 Å. This finding is consistent with previously reported results [57–59], further validating the successful formation of graphene using the scalable pyrolysis method in our study.

Figure 4. illustrates the XRD diffraction patterns of Graphene, Ni/Graphene, and Zn/Graphene. In the case of Ni/Graphene, three prominent peaks have been identified as C (002) at $2\theta = 24.97^\circ$, $2\theta = 44.5^\circ$, and $2\theta = 78^\circ$. These peaks indicate the successful deposition of Ni metal on the surface of graphene, as they correspond to the crystallographic planes of Ni (111) $2\theta = 44.5^\circ$ and Ni (220) $2\theta = 78^\circ$ [60,61]. Furthermore, the C (002) peak at $2\theta = 25.21^\circ$ in Zn/Graphene confirms the presence of graphene. Additionally, the appearance of peaks at $2\theta = 44.5^\circ$ suggests that Ni metal has also been effectively deposited on the graphene surface in Zn/Graphene, with these peaks corresponding to the crystallographic planes of Zn (101) $2\theta = 44.56^\circ$ and Zn (110) $2\theta = 77.8^\circ$ [62,63].

The XRD analysis presented strong evidence for the successful deposition of Ni and Zn metals onto the graphene material, confirming the synthesis of Ni/Graphene and Zn/Graphene composites. The presence of these composites holds significant potential for improving the performance of primary battery electrodes and advancing energy storage technology. To further demonstrate the successful doping of Ni and Zn atoms onto the graphene lattice, EDX analysis was conducted. The EDX data and weight composition information of Ni/graphene, Zn/graphene, and graphene are shown in Figures 5–7, and Table 2, respectively.

This additional analysis provides further validation of the successful incorporation of Ni and Zn atoms into the graphene structure. The combination of XRD and EDX data enhances our understanding of the compositional distribution of the composites, supporting their potential application as electrode materials in primary batteries.

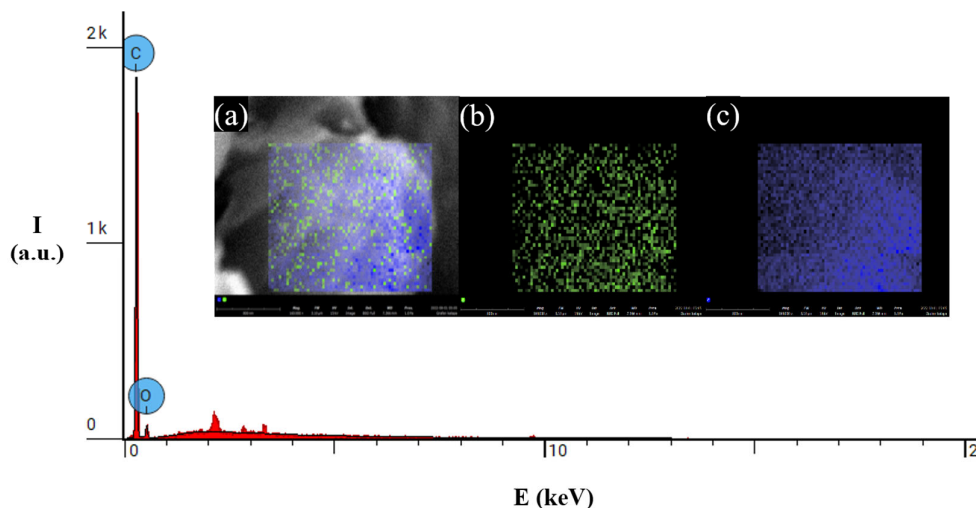


Figure 5. EDX spectra of Graphene with inset the elements mapping of (a) Graphene, (b) C, and (c) O.

In Figure 5., the EDX shows that the Graphene primarily consists of carbon (C) elements, accounting for 90.72 wt. % of its composition. Additionally, oxygen (O) elements make up the remaining 9.28 wt. %. This result indicates that the majority of Graphene's composition is comprised of carbon, which is consistent with its characteristic as a single-layer carbon material. The presence of oxygen likely arises from surface functional groups or oxygen-containing compounds that may be naturally present in the precursor.

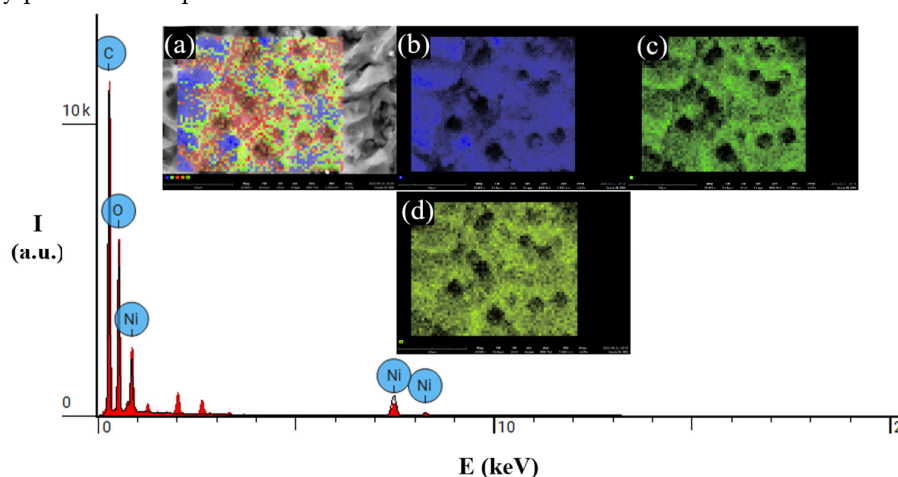


Figure 6. EDX spectra of Ni/Graphene, with inset the mapping element of (a) Ni/Graphene, (b) C, (c) O, and (d) Ni.

The EDX measurements provide conclusive evidence of the presence of Nickel and Zinc atoms on the graphene material. This finding aligns with the weight percentage data of Nickel and Zinc in the Ni/Graphene and Zn/Graphene composites, respectively (Table 2). According to the data, Nickel and Zinc atoms are successfully deposited onto the graphene, with weight percentages of 0.213 wt% and 2.95 wt%, respectively (Table 2). The EDX data displayed in Figures 5 and 6. further support these findings, corroborating the successful incorporation of Nickel and Zinc onto the graphene surface. The majority of the graphene’s composition consists of carbon, constituting 90.88 wt%, which is in line with its characteristic as a single-layer carbon material.

Table 2. Comparison of Elements of Ni/Graphene, Zn/Graphene, and Graphene (EDX Data).

Element	Ni/Graphene	Zn/Graphene	Graphene
C	89.54 (wt. %)	71.29 (wt. %)	90.72 (wt. %)
O	10.25 (wt. %)	25.75 (wt. %)	9.28 (wt. %)
Ni	0.21 (wt. %)	-	-
Zn	-	2.95 (wt. %)	-

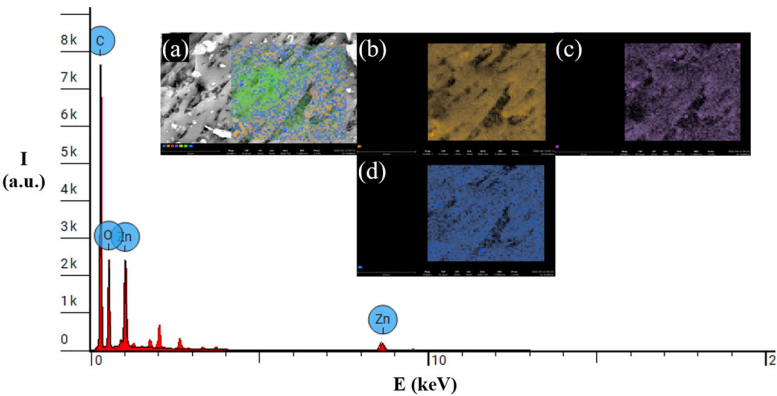


Figure 7. EDX spectra of Zn/Graphene, with inset the mapping element of (a) Zn/Graphene, (b) Carbon, (c) Oxygen, and (d) Zinc elements.

In Figure 8. the mean size of metals doped in graphene via single metal selection was obtained under SEM. The mean particle sizes of Ni/graphene and Zn/graphene were 3.09 μm and 2.356 μm . Figure 9. presents the morphology of Ni/Graphene, Zn/Graphene, and Graphene. Graphene exhibits a characteristic wrinkled surface and thin sheet-like structure Figure 8a. In the case of Ni/Graphene (Figure 9b) and Zn/graphene (Figure 9c) small white spots can be observed on the graphene surfaces, indicating the well-distributed presence of Ni and Zn particles on the graphene material.

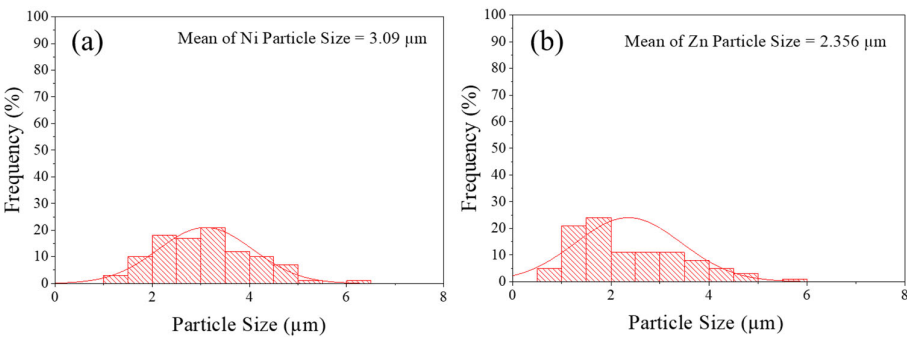


Figure 8. Particle size of (a) Ni/Graphene and (b) Zn/Graphene.

The distinct morphological features observed in Figure 9, along with the electrical conductivity data, shed light on the structural and electrical characteristics of the composite materials. These findings contribute to a comprehensive understanding of the potential applications and performance of Ni/Graphene and Zn/Graphene in electrochemical energy storage systems.

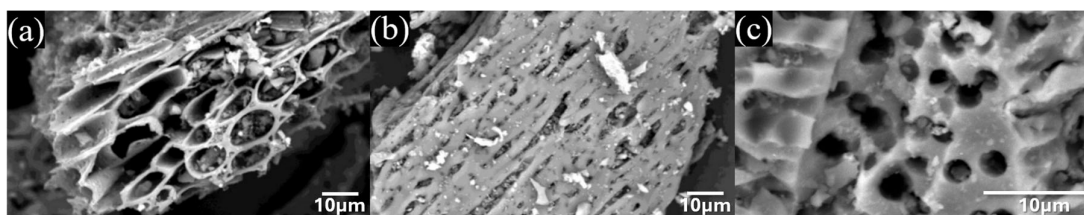


Figure 9. SEM Image of Graphene (a), Zn/Graphene (b), and (c) Ni/Graphene.

Siburian et al. reported that graphene reduced metal sizes of metals Fe and Pt [49,64]. We suggest two crucial parameters for the decreased size of Ni or Zn particles on graphene. The initial factor pertains to the impact of auxiliary substances, specifically graphene. Graphene possesses exceptional characteristics, namely C-sp² hybridization, π -bonding, and a substantial surface area. Graphene possesses a clearly defined thin and flat surface. It is reasonable to anticipate that the chemical interaction and reduced size on graphene would enhance the catalytic activity of Ni or Zn. This phenomenon is made possible by the presence of Ni or Zn atoms that are bonded to the surface of the graphene. The occurrence is likely due to an interaction between Nickel (Ni) or Zinc (Zn) and graphene. The evidence is substantiated by the SEM and EDX results presented in Figure 6, Figure 7, and Table 2. The data validate that the Ni or Zn atoms were uniformly dispersed and firmly adhered to the graphene surface, resulting from the chemical bonding between the metals and graphene. Ultimately, we present the schematic representation of diminished metal particles deposited on a graphene substrate, as depicted in Figure 10.

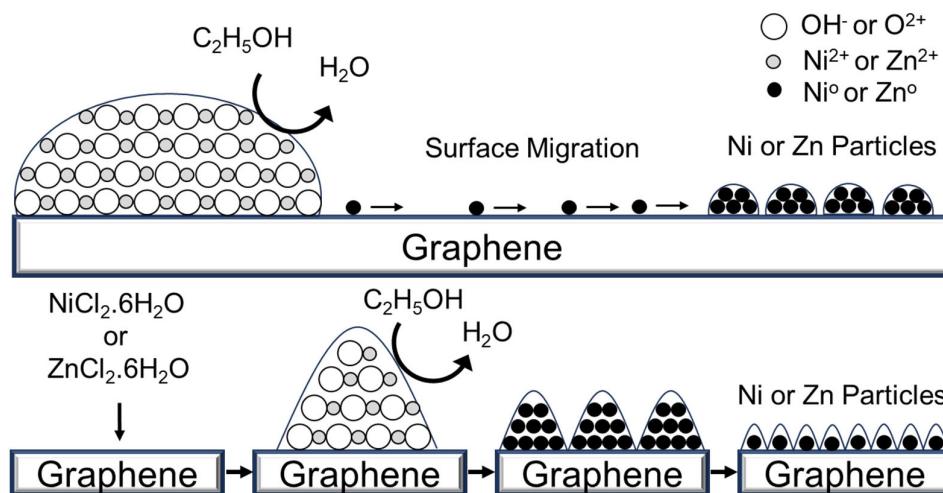


Figure 10. Schematic forming Ni or Zn cluster process.

In the first step, we produced Ni and Zn ions, which are deposited on the graphene surface. At this step, Ni and Zn precursors (NiCl₂ and ZnCl₂) were dissolved in ethanol solvent. Ni and Zn precursors with an oxidation state interact with ethanol, producing Ni and Zn ions. Then, Ni and Zn ions were deposited on the graphene surface producing Ni and Zn ions/graphene. Ethanol may act as a reduction agent in the reduction process of Ni and Zn precursors. On the second step, the Fe ions are attached on graphene surfaces via chemical interaction between Ni or Zn on graphene, producing Ni or Zn metals where they are well deposited on graphene. That is possible because graphene may donate electrons to convert Ni and Zn ions to Ni and Zn metal clusters. In the last step, Zn metal

clusters will be distributed (migrated) on the surface of graphene to form Zn/graphene (Zn metals deposited on graphene), on the same condition on Ni metal cluster will also be distributed (migrated) on the surface of graphene to form Ni/graphene (Ni metals deposited on graphene).

3.3. Ni/Graphene and Zn/Graphene electrode performance

Analysis of electrical conductivity of Graphene, Ni/Graphene, Zn/Graphene, commercial primary battery cathode, and commercial primary battery anode (Zn metal plate) were evaluated by multimeter at room temperature as shown in Table 3.

Table 3 Electrical Conductivity of Graphene, Ni/Graphene, and Zn/Graphene.

Sample	Measurement of Conductivity (μS/cm2)
Graphene	227
Ni/Graphene	264
Zn/Graphene	340
Commercial primary battery anode	400
Commercial primary battery cathode	580

As can be seen in Table 3, the electrical conductivity data shows that Zn/graphene exhibits the highest electrical conductivity, while undoped graphene shows the lowest electrical conductivity. This difference in conductivity can be attributed to the nature of Ni metal as a metalloid, resulting in poorer electrical conductivity compared to Zn. The introduction of the metal dopant has been observed to increase the electrical conductivity of graphene. This finding aligns with previously published research [42,65–67], which reported that metal-graphene alloys have a higher surface-to-volume ratio, enhancing the stability of electron mobility rates. However, the commercial cathode has higher conductivity than an electrode synthesized due to the composite material being an active material and electrolyte, which increases extreme electricity performance [68].

The enhancement of electrical conductivity in metal-doped graphene materials is of significant interest, as it has potential implications for improving the performance of energy storage devices. The results from Table 3 contribute to a better understanding of the conductive properties of the composites and support their potential use in electrochemical energy storage systems.

To observe the performance of the composite, we compared it to electrodes that was separated from the primer commercial battery. The trend of electrical conductivity and power density vs. energy density, graphene is shown in Figures 9 and 10.

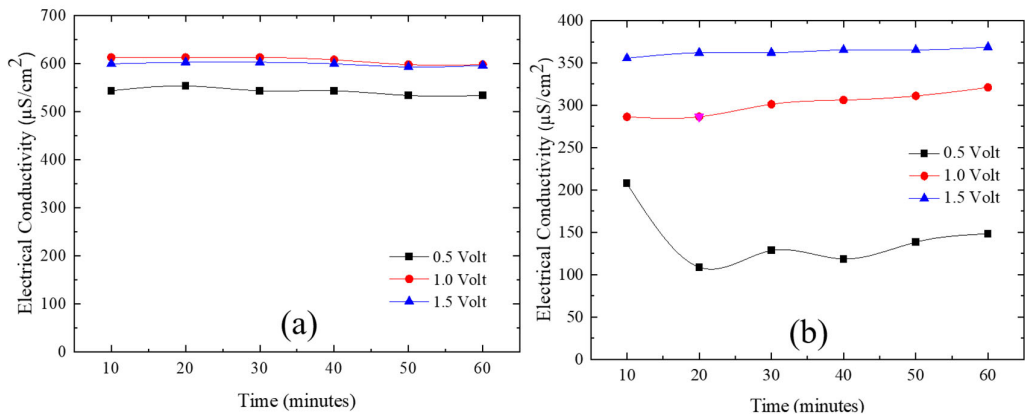


Figure 10. Electrical conductivity of (a) commercial cathode and (b) graphene.

From Figure 10, graphene demonstrates somewhat reduced electrical conductivity in comparison to conventional materials. Nevertheless, it possesses chemical inertness, hence preventing contamination that might potentially augment conductivity via electron sources. In

addition, graphene exhibits remarkable stability, since it maintains conductivity levels exceeding 1 volt.. The power density versus energy density is tested to assess the performance of materials used as cathodes and anodes [69]. The number of conductivity is in line with power density vs energy density which the commercial more high and stable however modification on graphene surprisingly increases the performance as shown in Figure 11.

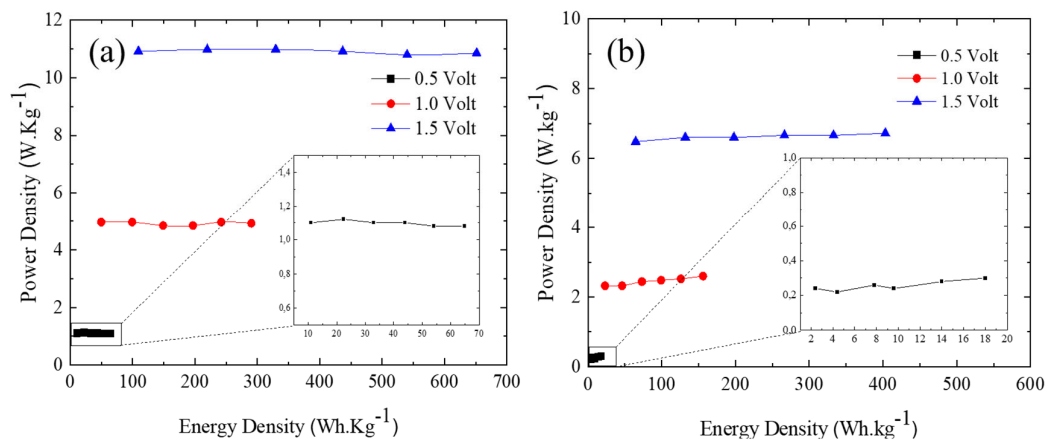


Figure 11. Power Density vs Energy Density of (a) commercial cathode and (b) graphene.

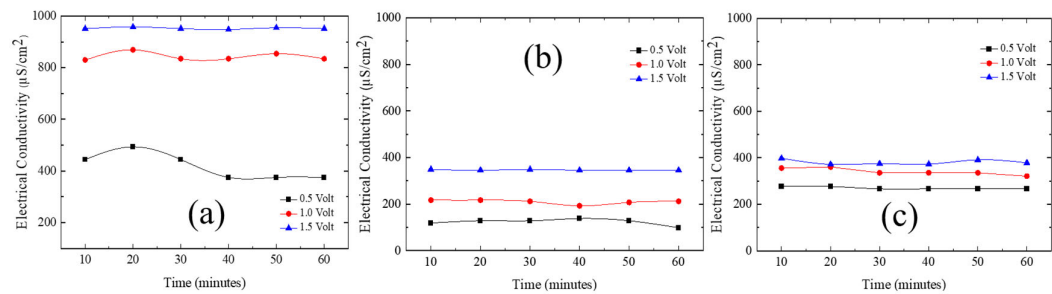


Figure 12. Electrical conductivity of (a) commercial battery anode, (b) Ni/Graphene and (c) Zn/Graphene.

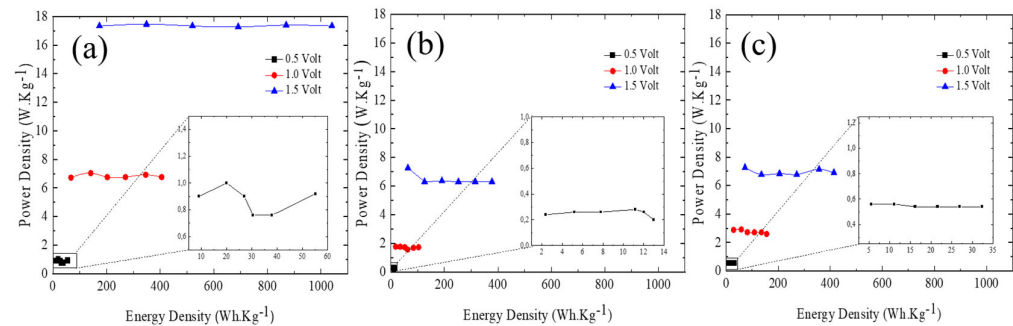


Figure 13. Power Density vs Energy Density of (a) commercial battery anode, (b) Ni/Graphene and (c) Zn/Graphene.

As can be seen in Figure 10 Zn/Graphene is lower than commercial anode; however, Zn/Graphene performs better than Ni/graphene. This could be due to some attributed factors, first Ionic Size dopant as seen in Figure 7. Particles of Zn are smaller than Ni; this size difference could potentially enable a more effective arrangement of ions and enhance the movement of electrons,

resulting in improved conductivity [70], Further, there is a decrease in crystallite size between Zn and Ni-doped shown in Figure 3, and a corresponding inverse correlation with the optical band gap [71] in line with that, increasing band gap reduces the electrical conductivity due to a more significant band gap, indicating fewer electrons may move into the conduction band. Second, charge transfer When metals like Zinc (Zn) or Nickel (Ni) are applied to carbon materials, they have the ability to either provide or receive electrons, which in turn modifies the electronic configuration of the carbon and thus affects its conductivity. However, Zn, being a member of group II on the periodic table, has the ability to donate two electrons, but Ni, being a transition metal, may not exhibit the same level of electron donation [72]. In this research, using the same condition and concentration, the highest performance is Zn/Graphene.

4. Conclusions

In this study, we successfully synthesized graphene from coconut shells, demonstrating a scalable and sustainable method of graphene production. The graphene produced was further utilized to create Ni/Graphene and Zn/Graphene composites, which were thoroughly characterized and evaluated for their potential in energy storage. The resulting composites were employed as modified anode electrodes in primary batteries. Zn/Graphene exhibited the highest electrical conductivity, measuring at $340 \mu\text{S}/\text{cm}^2$, followed by Ni/Graphene with a conductivity of $264 \mu\text{S}/\text{cm}^2$ and undoped graphene with a conductivity of $227 \mu\text{S}/\text{cm}^2$.

This research not only advances the understanding of Ni and Zn doped graphene-based materials in electrochemical applications but also opens new avenues for the development of more sustainable and cost-effective energy storage solutions, leveraging renewable biomass sources such as coconut shells. Further exploration and optimization of these materials could lead to significant advancements in battery technology, contributing to the broader goal of sustainable energy solutions.

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Conflicts of Interest: The authors declare no conflicts of interest.

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