

The Effect of Microwave Irradiation on the Synthesis of Graphene from Battery Waste on Capacitance Properties

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Abstract

Supercapacitor material is an alternative in energy storage. Supercapacitors are charge storage devices that have a high energy density, fast charge/discharge rates, long service life, wide operating temperature range, and are environmentally friendly. Graphene is a nanomaterial that can be used as a supercapacitor because it has high conductivity and a large surface area, but graphene can experience agglomeration so it can affect its capacitance properties. The microwave-assisted method can be used in the synthesis of graphene. Several microwave-based techniques are becoming more popular for producing graphene and altering it. Due to its quick, precise, uniform, and volumetric heating, microwave heating is a promising method for the thermochemical treatment and reduction of graphene oxide to graphene. This research aimed to examine the effect of microwave irradiation time on the capacitive properties of graphene synthesis as a supercapacitor. Graphene oxide (GO) can be reduced into graphene quickly and easily using microwave pulses lasting 15 to 30 minutes to produce high-quality graphene fabrication. The characterization test was performed using UV-Vis, FTIR, SEM-EDX and cyclic voltammetry (CV). As a result, the optimum time is 25 minutes, and it showed an absorption peak at the 282 nm wavelength and the CV analysis showed that the graphene has double capacitor properties with a specific capacitance of 140.7 F/g in 20 mV/s. Besides, the result of SEM indicated that graphene could be formed successfully. Its potential applications are also illustrated by emphasizing its usage as electrode material. Finally, its main challenges and prospects are considerably pointed out.

Keywords

graphene, microwave, supercapacitor

1 Introduction

The development of technology is currently experiencing very rapid progress in various scientific fields, including chemistry. Zinc-carbon batteries are an essential source of energy. Most zinc-carbon batteries are used to operate electrical equipment such as remotes, flashlights, clocks, calculators, and various electronic devices. Zinc-carbon batteries are disposable, non-rechargeable, and limited to use until the battery is no longer functional and needs to be renewed [1]. This causes the wastage and disposal of battery waste to continue to increase. It is possible to salvage valuable materials from battery waste, including graphite rods, steel, manganese, and zinc. Electrochemical processes can use graphite rods as an electrode because of their good electrical conductivity [2]. Graphite can be converted into graphene to produce better conductivity properties.

Graphene is a thin layer material of carbon atoms with sp^2 bonds, which has extraordinary electronic qualities [3].

In the single atomic layer that makes up graphene, sp^2 hybridized carbon atoms are arranged in a two-dimensional (2D) network resembling a honeycomb. A tunable specific surface area, high thermal conductivity, and extremely high intrinsic mobility of charge carriers are the results of such a unique structural peculiarity. It is widely used for various applications such as capacitors [4], transistors [4], energy storage materials [5], and solar cells [6]. Basically, graphene is the allotropy of carbon which is the basic structure for the formation of materials such as graphite, carbon nanotubes (CNTs), and fullerenes [7]. Therefore, this study aimed to use other sources with the same material base.

Meanwhile, based on the research of Statistics Indonesia in 2014 on the Manufacture of Batteries (Dry Cell Battery), 213.212.779 batteries were found, which consisted of 208.140.793 zinc-chloride batteries and 5.071.986 ammonium-chloride batteries [8]. The rods of these bat-

tery wastes will be reused as the alternative main material for graphene synthesis through graphite oxide (GO). The GO synthesis method used was the result of a modification of the Hummers method [9], which was the GO reduction method. The modified hummers method was chosen because it produces GO with more oxide groups due to strong oxidizing acids. However, this method also eliminates the addition of NaNO_3 , which produces toxic substances N_2O_4 and NO_2 during the oxidation process in the Hummers method. In comparison to GO material obtained using the Hummers method, this modification had no impact on the dispersibility, chemical structure, thickness, or lateral dimensions of the obtained GO [10].

The GO reduction methods have been carried out by many researchers, such as the chemical method [11], the thermal method [12], the laser method [13], and the microwave method [14], to obtain reduced graphene oxide (RGO) with superior properties. In general, chemical reduction is toxic, corrosive, and not only harmful to the environment but also harmful to human health. A long time is also needed during the reduction process using chemical methods. Long-term high-temperature treatment during the thermal reduction process is energy-intensive, fragments graphene, and causes numerous structural flaws. Microwave-assisted synthesis, one of many synthetic techniques, has emerged as a competitive alternative to traditional techniques in reduction GO primarily because of its distinct properties, including quick, selective, uniform, volumetric heating and non-direct contact between the heated material and heating source [15].

This microwave method will make the reduction process more efficient and selective and produce RGO better than other methods [16]. The movement of electrons in π - π conjugated structures of carbon materials can turn microwave energy into heat energy according to the Maxwell-Wagner interfacial polarization theory. Therefore, the microwave heating method can be used to prepare or alter carbon materials. The effective exfoliation of graphene oxide is facilitated by the rapid heating provided by reduction GO by microwave irradiation. Previous research by our team demonstrated that thermally reduced GO could also successfully reduce GO [17]. Reduced GO by treating the GO precursors in the microwave this facile and efficient for other applications. One of the unique properties of the reaction system with microwave irradiation is that it can increase the surface area without using a template. It contrasts standard synthetic methods as high-performance electrode material in energy storage devices such as supercapacitors [18]. The weakness of this method is

that the reduction process induces various defects, which will decrease the electronic properties of graphene [19].

Graphene-based materials have recently attracted attention due to their potential application in energy storage devices, such as supercapacitors and batteries [20]. Electric double-layer capacitors (EDLCs) and pseudo-capacitors are two categories of supercapacitors based on the charge storage mechanism [21]. The latter can achieve higher capacitance qualities and improve energy densities than EDLCs because it stores charge faradaically. There have been some reports on carbon-based wire-shaped supercapacitors in recent years. All-graphene core-sheath flexible supercapacitors have been developed by [22], and the 3D graphene-like structure was created on graphene fiber. For use in wire-based supercapacitors, [23] have reported synthesizing hydrothermally produced graphene aerogel on Cu wire. The inter-facial barrier resistance and the possibility of copper oxidation in the reaction conditions make this method insufficient for producing high-quality graphene. Porous graphene for wire-shaped supercapacitors has been created using time-consuming processes and difficult synthesis routes, but the supercapacitor has poor performance as a result. As a result, low energy density and impractical specific capacitance plagued all previously reported carbon-based wearable supercapacitors (WSCs). The porosity and surface area of the active materials modified on the conductive wire core as well as the device's wire/fiber core affect WSC performance. Utilizing nanostructured materials with a high surface-to-volume ratio will only partially accomplish this. A simple and affordable method for producing bulk-scale active electrode material is still needed to fabricate high-performance WSC [24].

In this article, we looked into a one-step technique for reducing GO from battery waste using microwave irradiation. Other experimental techniques demand prolonged high-temperature treatment and atmosphere protection, both of which result in high energy usage and expense. Additionally, the active substances and graphene readily aggregate and disperse unevenly. As a result, achieving a product with a small and homogeneous distribution and streamlining the preparation technology continue to be major obstacles for graphene supercapacitors. To make up for the lack of graphene modification, it is practical, affordable, and environmentally friendly to prepare graphene composites using microwave heating. The reduction step of graphene oxide can be made simpler by microwave heating. Due to graphene oxide's ability to absorb microwave energy, microwave radiation can convert it directly back into graphene without the use of a reducing agent or

an environment [25]. The research is targeted to produce the increasing performance of graphene oxide with various graphene reduction times using the microwave method.

2 Materials and methods

Materials used in this graphite powder from carbon rods of zinc carbon batteries waste, H_2SO_4 96.1% (Mallinckrodt, $M_r = 98$ g/mol, $\rho = 1.8$ kg/L), H_2O_2 30% (Merck KGaA, $M_r = 34$ g/mol, $\rho = 1.11$ kg/L), KMnO_4 , HCl and mean demineral water (aqua DM).

2.1 Leaching process

In previous research conducted by [26], it was revealed that the synthesis of graphene oxide with the same carbon raw material actually still left a lot of Mn impurities, and it recommended the need for a washing process first.

The carbon rod that had been pulverized was then dissolved in a solution of sulfuric acid and ascorbic acid. In this reduction-washing process, sulfuric acid functions as an acid-based leaching agent, and ascorbic acid acts as a reducing agent [27].

2.2 GO synthesis

Using a reflux device, GO synthesis was performed through the modified Hummers method. 2 g of graphite and 46 mL H_2SO_4 were mixed in a round bottom flask and stirred for 30 minutes at <10 °C. Then 6 g of KMnO_4 were added and stirred for 2 hours at 35 °C. Then 80 ml aqua DM was added slowly and stirred for 30 minutes at 40 °C. Then 200 ml aqua DM and 6 mL H_2O_2 were added slowly and stirred for 90 minutes at 75 °C [28].

The GO results were centrifuged for 30 minutes at 3500 rpm. Then the suspension was taken, aquademin was added to each bottle, and centrifuged again. The centrifugation process with aquademin was carried out three times. Then the clear liquid was taken, 10% HCl was added, and then centrifuged three times. The clear solution was taken, 10% ethanol was added and then centrifuged three times. This process is carried out until the pH solution 7 [29].

2.3 GO reduction

The GO suspension that had been sonicated for 30 minutes was then put in a microwave bowl. Then it was microwaved at under 900 watts with time variations of 15, 20, and 25 minutes after the reduction. The mass ratio also varied in the reduction process. Characterization testing was carried out using UV-Vis, FTIR, SEM-EDX, and cyclic voltammetry (CV).

3 Results and discussion

Graphene oxide, which is reduced using microwave irradiation using 900 watts of power with a reduction time variation of 15, 20, and 25 minutes, can produce good-quality graphene. It can be produced in a short time at a low temperature. GO reduction using microwave irradiation can exfoliate GO into graphene sheets with multiple layers. According to the Maxwell-Garnett theory, graphene's π conjugated structure will absorb microwave radiation. Through the movement of electrons, microwave energy is converted into heat energy so that functional groups containing oxygen are rapidly decomposed. When the resulting pressure exceeds the van der Waals force between the sheets, the graphite layer will peel off so that graphene is obtained [30]. Compared with GO reduction using reducing agents and conventional heating, graphene is produced in a long time of 45–60 minutes at high temperatures [31]. The main advantage of microwave irradiation is that it helps heat above conventional heating so that it can heat a mixture of a substance uniformly and quickly. Microwave irradiation can significantly increase energy transfer directly to the reactants, causing an increase in internal temperature in a short time. Thus, the reduction method with microwave irradiation can shorten the reaction time and increase the efficiency of the reaction [32].

3.1 FTIR analysis (graphene characterization)

The FTIR test was carried out to analyze the functional groups of the samples produced at each stage. Before being oxidized, graphite was leached to remove Mn impurities. Wavelengths between 750–200 nm indicated the potential presence of MnO_x , which can be observed at the peak of the wave numbers 750–600 nm, 600–450 nm, and 450–200 nm, which allowed stretching vibrations, wagging vibrations, and bending vibrations from MnO_x [33]. The results of the FTIR spectra can be seen in Fig. 1. Washing was considered quite good in reducing Mn content. This is indicated by the Mn graphite vibration absorption peak, which with the leaching process, the wavenumber range of 450 cm^{-1} to 550 cm^{-1} is not present. The same thing happened in GO samples, the bending vibration absorption peak around the wavenumber of 578 cm^{-1} was weaker.

The GO reduction process to graphene by varying exposure to microwave irradiation time can be seen from the FTIR results. Fig. 1 shows that GO has been reduced quite well. This is indicated by the longer time it took for the peak wave number around 3420 cm^{-1} in the form of weaker O-H bonds. In addition, the absorption peak of the C-O bond wave number 1172 cm^{-1} was not significantly reduced.

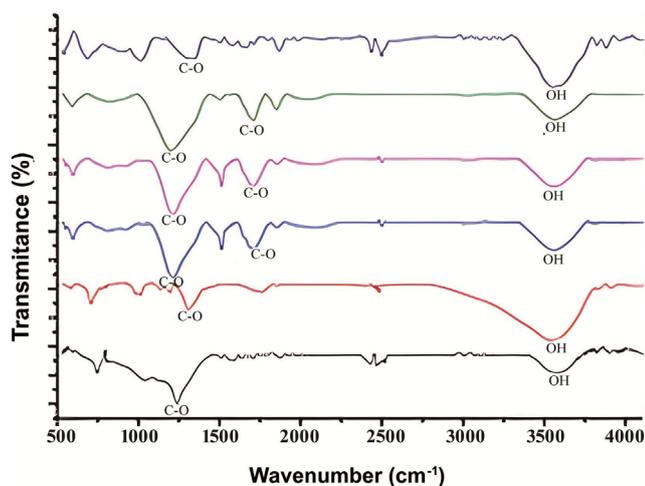


Fig. 1 The FTIR spectra of RGO with time variations: graphite (black spectra); GO (red spectra); RGO 15 minutes (blue spectra); 20 minutes (pink spectra); 25 minutes (green spectra); a few layers of graphene tube (deep blue spectra)

However, the absorption peak of the aromatic C = C bond was increased compared to that of the GO carbon sample.

After undergoing oxidation, GO was dominated by oxide groups. In the GO spectra, there was a peak at the wavenumber 3415 cm^{-1} , the wavelength of the O-H stretching bond, and a peak at the wavenumber 1625 cm^{-1} , the wave number of the C = C aromatic bond vibration. The oxidation results also gave rise to several wave peaks identified as C-O bonds with a wavelength of 1183.5 cm^{-1} [34]. This absorption peak corresponded to the C-O stretching vibration of the C-O-C vibration. The presence of these oxygen-containing groups revealed that the graphite had been oxidized [35].

As a comparison, the results of FTIR few-layer graphene tubes showed that the absorption peak of the O-H and C-O functional groups was near the 2342 cm^{-1} and 1186 cm^{-1} waves. There should be no or at least a small number of these clusters. This was possible because graphene came into contact with the surrounding environment and reacted and changed its characteristics.

Meanwhile, the process of reducing GO to graphene with mass variations can be seen in Fig. 2. The observation shows that GO has been reduced quite well. This is indicated by the decreasing mass of GO. The absorption peak in the OH bond decreased at wave number 3430 cm^{-1} . Then the absorption peak of the C-O bond near the wavenumber 1060 cm^{-1} did not decrease significantly. However, the absorption peak of the C = C bond appeared in all three variations around the 1575 cm^{-1} .

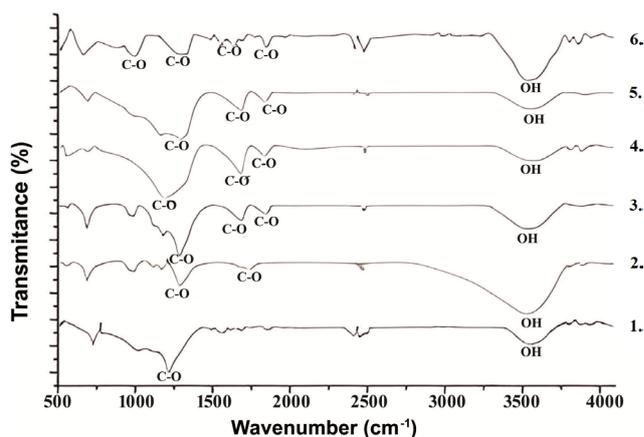


Fig. 2 The FTIR spectra of RGO with mass variations; 1. Graphite; 2. GO; 3. RGO 0.05 g; 4. RGO 0.1 g; 5. RGO 0.15 g; 6. few layers of graphene tube

As a comparison, the results of FTIR few-layer graphene tubes showed that the absorption peak of the O-H and C-O functional groups was near the 2342 cm^{-1} and 1186 cm^{-1} . Graphene should show no peaks in this wavenumber area. This may occur due to the reaction of graphene with other compounds that cause changes in properties.

3.2 UV-Vis analysis

The peaks were observed between 220 nm to 300 nm. The absorption peak at 230 nm was related to the $\pi-\pi^*$ transition of the C = C bond and the shoulder at 300 nm was related to the $n-\pi^*$ transition of the C-O bond [36].

Observation of GO and RGO samples of time variations (the treatment time) can be seen in Fig. 3. The GO observations showed an absorption peak at 232 nm and 252 nm wavelengths. Then the observation of the RGO sample showed that over time, the absorption at the 300 nm wavelength associated with the C-O bond was increasingly shifting. This was indicated by the GO sample, which had been reduced for 25 minutes giving rise to a broad absorption peak between 270 nm – 300 nm because the wavelength around 300 nm showed an electronic transition $n-\pi^*$, which is the electronic transition character of GO. The absence of peaks at the electronic transition wavelength $n-\pi^*$ indicated that GO material had been reduced to RGO [34].

Furthermore, the UV-Vis results from RGO mass variation can be seen in Fig. 4. The absence of a wavelength peak around 300 nm of the three RGO samples indicated that the sample had slowly been reduced. This was indicated by the appearance of peaks at a wavelength of 255 nm in the 0.15 g and 0.1 g RGO samples. Meanwhile, the absorption from the 0.05 g RGO sample appeared at a wavelength

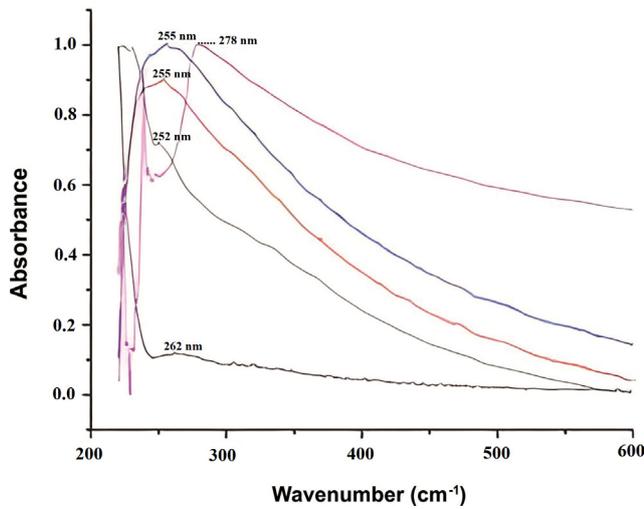


Fig. 3 The UV-Vis spectra of time variations, black line means GO; brown line means RGO 15 min; orange line means RGO 20 min; blue line means RGO 25 min; and red line means few layers of graphene tube

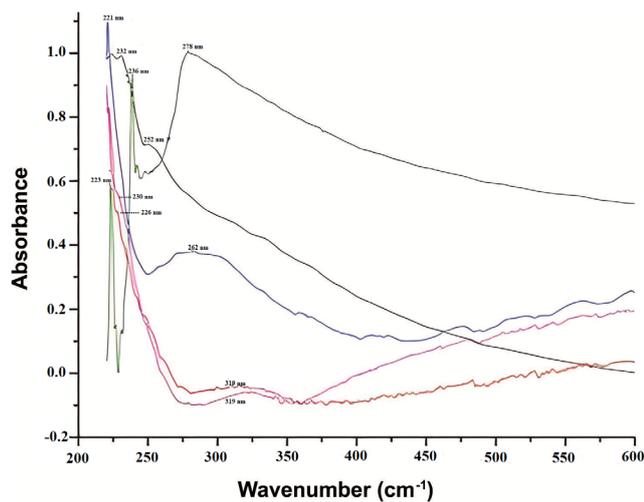


Fig. 4 UV-Vis spectra of RGO with mass variation; black line means GO; brown line means RGO 0.05 g; orange line means RGO 0.1 g; dark blue line means RGO 0.15 g; red line means few layers of graphene tube

of 262 nm. Meanwhile, graphene, a few layers of the tube as a comparison material, reached an absorption peak at a wavelength of 278 nm. In addition, it also gave rise to absorption at 223 nm and 238 nm wavelengths.

3.3 Morphological analysis using SEM/EDX

SEM-EDX test aimed to determine the morphological form and quantitative calculations of the elemental composition of the compounds contained in the sample. Three samples were analyzed: RGO without leaching, RGO with leaching, and a few layers of graphene tubes as comparison materials. The morphology of the RGO material without leaching can be seen in Fig. 3. Based on observations, the results showed that the morphology of RGO without leaching was

still in the form of layered flakes, and the surface structure was not uniform or rough, meaning that it was not thoroughly exfoliated yet [10]. Meanwhile, the EDX spectra in Table 1 showed the presence of many Mn impurities. The metal might have come from the built-in graphite impurities or from the residue of the oxidizing agent KMnO_4 , which had not been completely removed. Then the morphology of RGO with leaching is shown in Fig. 3. Based on the SEM test analysis, the particle size appeared in the form of thick chunks with a surface that was not uniform (smooth), and the result sheet was also not single-layered. Meanwhile, the EDX RGO analysis with leaching in Table 2 shows the percentage of carbon elements that increased sharply compared to the carbon element levels of the RGO samples without leaching. The leaching process was very influential in the absence of Mn, although the elemental oxygen content had not been significantly reduced.

The morphology of the few layers of the graphene tube can be seen in Fig. 5 (c), and the element content is shown in Table 3. Based on observations, the samples appeared to sphere-like with different size variations, overlapping their surface area and forming many cavities. This characteristic is similar to that of graphene, which has 8–10 layers and is slightly transparent. The EDX results showed that the carbon atom content acted as the most dominant constituent in the sample.

Besides this, we found that the time exposure to microwave irradiation has positively affected the structure of RGO. Based on SEM analysis, the morphological space on samples of graphite, GO, and RGO with variation times of

Table 1 The element content of RGO what is synthesized using battery waste without the leaching treatment

Atomic number	Atomic symbol	Name of atom	Concentration (weight %)
6	C	Carbon	33.9%
25	Mn	Manganese	27.5%
8	O	Oxygen	23.3%
7	N	Nitrogen	14.2%
19	K	Potassium	1.1%

Table 2 The element levels of RGO leaching

Atomic number	Atomic symbol	Name of atom	Concentration (weight %)
6	C	Carbon	68.5%
8	O	Oxygen	22.06%
7	N	Nitrogen	6.41%
14	Si	Silica	1.12%
16	S	Sulfur	0.96%

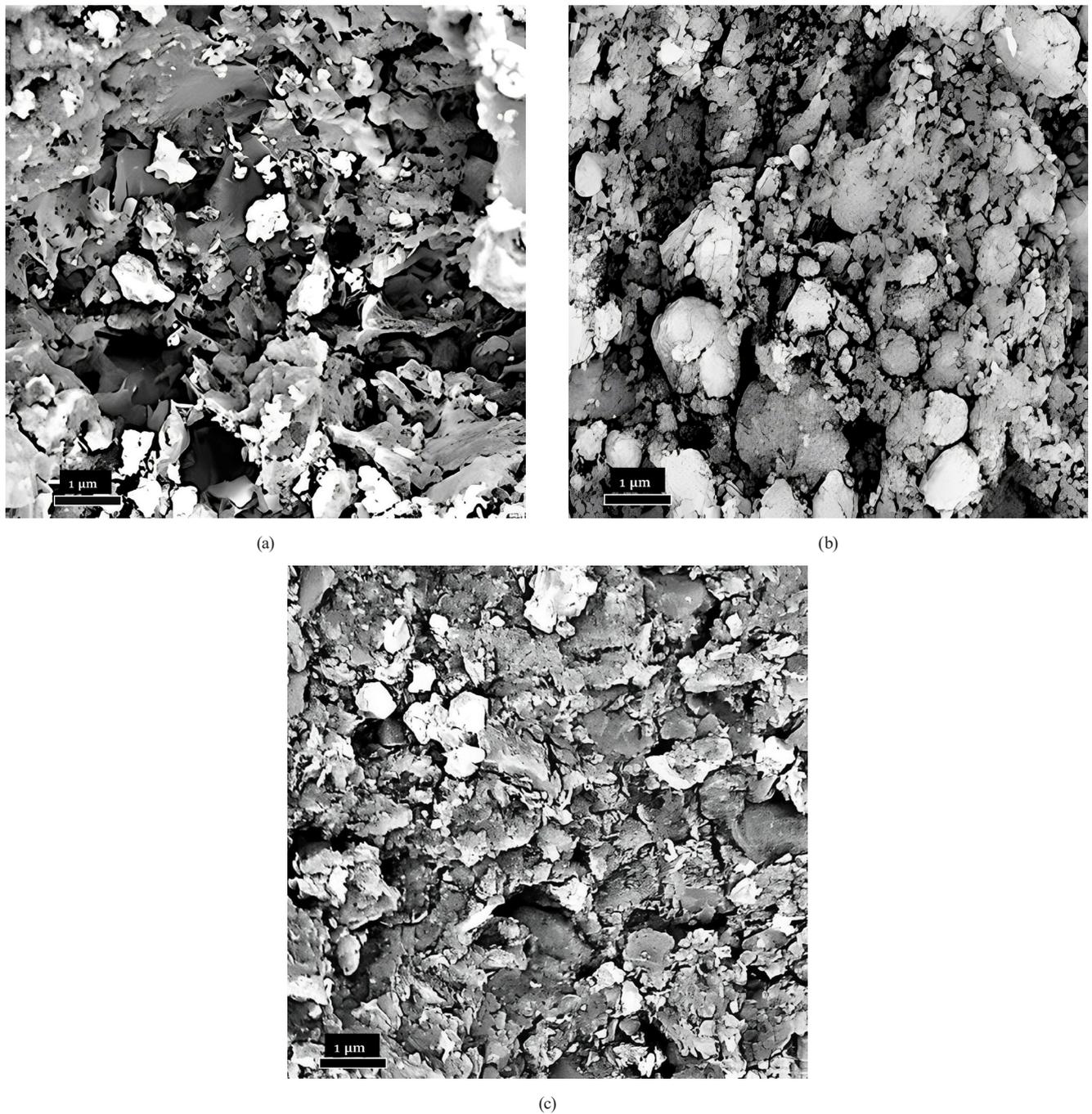


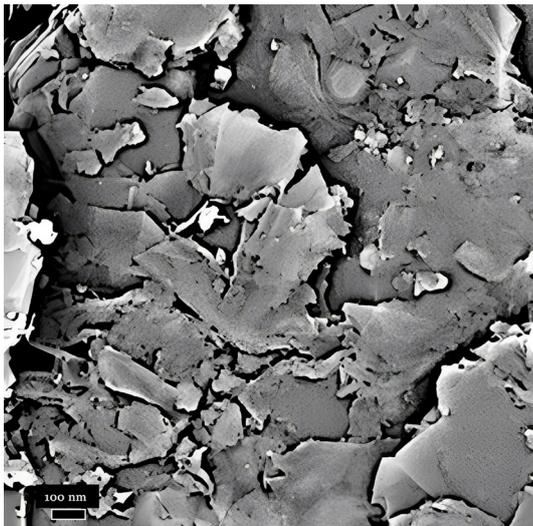
Fig. 5 SEM images of graphene synthesis from batteries waste; (a) without leaching; (b) with leaching; (c) a few layers of graphene tube

Table 3 The element content of a few layers of graphene tube

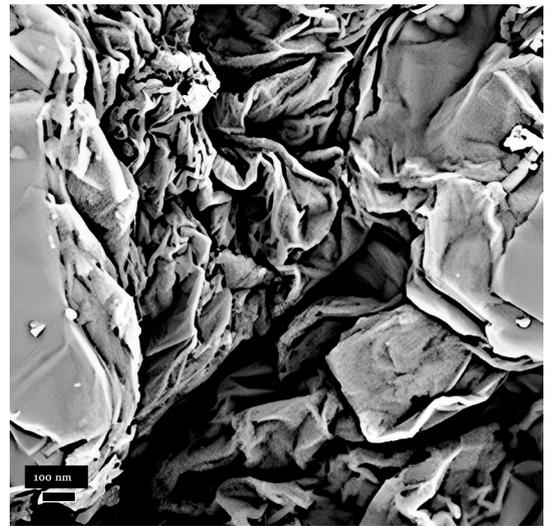
Atomic number	Atomic symbol	Name of atom	Concentration (weight %)
6	C	Carbon	91.16%
18	O	Oxygen	8.13%
13	Al	Aluminum	0.67%
14	Si	Silica	0.04%

15 minutes, 20 minutes, and 25 minutes, with a magnification of each individual of 10000_x, can be shown in Fig. 6.

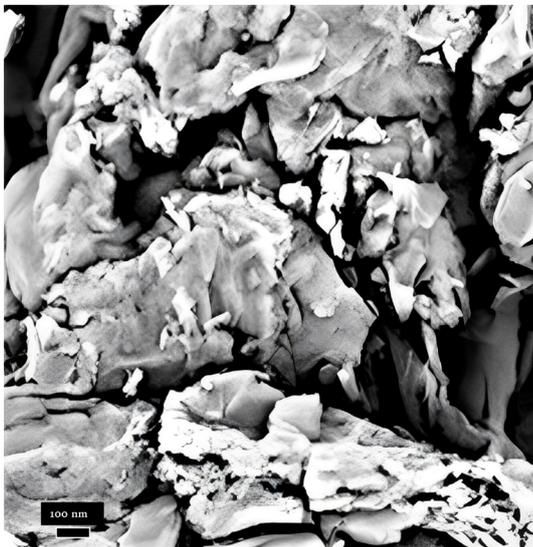
From these SEM images, it can be seen clearly that graphite has structure sheets and SEM images of GO show the sheets were exfoliated. Graphene oxide and graphene are both efficiently exfoliated to form a separate thin sheet. As a comparison, graphene consists of thinner sheets and smaller pores than GO. Fold structure can be found on the surface and edges of RGO (graphene). Fold is the morphology typical of graphene, which may be the formation of the fold, treated at high temperature in a long-time exposure.



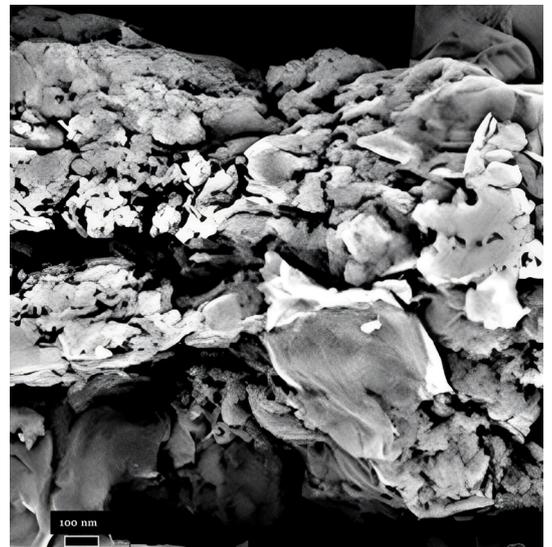
(a)



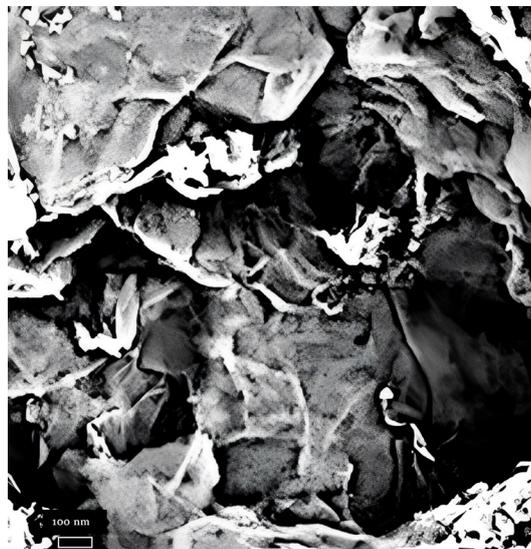
(b)



(c)



(d)



(e)

Fig. 6 SEM characterization results of (a) Graphite; (b) GO; (c) RGO 15 minutes; (d) RGO 20 minutes; (e) RGO 25 minutes

3.4 Capacitance analysis

Finally, Fig. 7 and Table 4 present the outstanding electrochemical performance results of the graphene from the electrode materials described above and then characterized. The capacitive performance of RGO materials was evaluated by CV. The cyclic voltammetry is run at different scan rates in the potential range from 0.6–1.5 V using electrolytes at a constant scan rate. Cyclic voltammetry was used to determine the influence of RGO on the overall charge capacity of the electrode. This study used three scan rates ranging from 20–100 mV/s.

In the test results, there was no redox reaction from pseudo capacitance, which was indicated by the absence of humps in the results of the CV analysis. This indicates

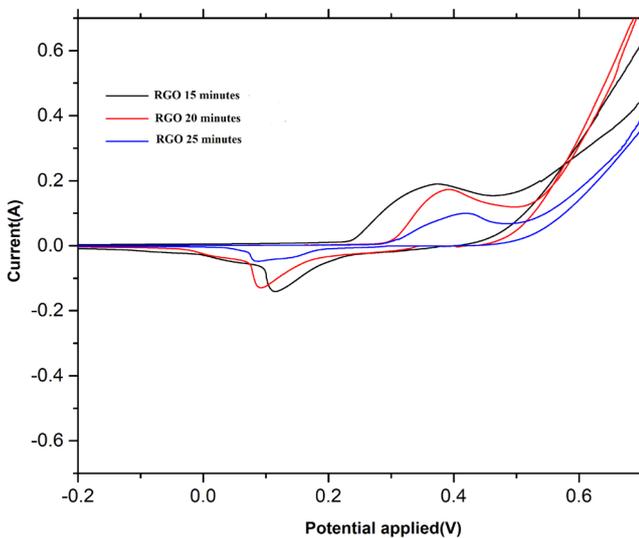


Fig. 7 Cyclic voltammetry of RGO synthesis with irradiation time variation; RGO 15 min (black line); RGO 20 min (red line); RGO 25 min (blue line); the counter electrode is: x axis (V vs Ag/AgCl)

Table 4 Specific capacitance of graphene synthesis with irradiation time variation

No.	Sample	Scan rate (mV/s)	Specific capacitance (F/g)
1	Graphene	20	114.0
		50	51.9
		100	43.2
2	G 15	20	119.9
		50	56.2
		100	50.8
3	G 20	20	137.9
		50	71.5
		100	65.6
4	G 25	20	140.7
		50	79.9
		100	71.2

that the sample tested has double capacitor properties. The absence of mounds indicates that no redox reaction occurs when an oxygen functional group in graphene contributes to pseudo-capacitance. The specific capacitance of graphene with variation time irradiation is shown in Table 4.

From Table 4, there is an increase in the capacitance of the RGO material with the increasing time exposure to microwave irradiation. Increasing irradiation on the hexagonal structure of the carbon skeleton will increase the holes with charge carriers due to the p-type characteristics to modulate the electronic properties by producing excellent conductivity properties [36]. The research data shows that the presence of microwave irradiation can increase the capacitance value of graphene. This is due to the increased active sites that appear in the presence of microwave waves. Microwave irradiation can open the active sites of graphene material better than thermal heating. Table 5 shows the specific capacitance of graphene synthesis with variation mass ratio.

The capacitance shows for all samples that the larger the scan rate used, the smaller the specific capacitance produced in all samples. This happens because the value of the electrode capacitance is affected by the diffusion time of the electrolyte ions. At a high scan rate, the flow rate of ions from the electrolyte to the nickel foam electrode becomes fast, and it only takes a shorter time for the electrolyte ions to diffuse into the nickel foam electrode. Whereas at a low scan rate, the voltage flow rate becomes slow. As a result, the time for the electrolyte ions to diffuse into the nickel foam is longer and forms more double layers [33].

According to [34], the materials that can be used for supercapacitors cannot have specific energy in the range of 0.05 to 20 (Wh/kg) and have a specific power in the

Table 5 Specific capacitance of graphene with mass ratio variation

No.	Sample	Scan rate (mV/s)	Specific capacitance (F/g)
1	Graphene	20	114.0
		50	51.9
		100	43.2
2	G 0.05	20	101.2
		50	48.4
		100	46.8
3	G 0.10	20	119.9
		50	56.2
		100	50.8
4	G 0.15	20	136.6
		50	75.9
		100	70.5

range of 101 to 106 (W/kg). The calculation results using the formula show that the specific energy and specific power each enter the range of materials that can be used as supercapacitors.

4 Conclusion

In this study, GO and RGO from battery waste were synthesized by an easier and more convenient method. Graphene oxide from battery waste was obtained by treating graphite powder with the hummers method and prepared by leaching before synthesized. The obtained GO was reduced to RGO overexposure the microwave irradiation. The preparation of RGO was controlled by reaction time

and mass ratio. This parameter was studied to observe the capacitance characteristic. Both GO and RGO were characterized by FTIR spectroscopy, UV-Vis spectroscopy, CV, and SEM-EDX techniques. The results show that RGO synthesized using microwave irradiation has a better structure than few tube layer graphene, and the time exposure of microwave irradiation has a positive effect on RGO synthesis. The specific capacitance value shows an increase in the synthesized RGO character with an optimum value of 140.7 F/g with a scan rate of 20 mV/s. The advanced synthesis method for graphene and reduced graphene oxide is an alternative approach and could be advantageous for large-scale production.

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