COMMUNICATIONS IN SCIENCE AND TECHNOLOGY
Homepage: cst.kipmi.or.id

Characterization and electrochemical properties analysis of reduced graphene oxide from corncob carbon as an electrode candidate: Synthesized using modified Hummers method

Eka Anggriani Odja, Indah Raya*, Maming, Muhammad Zakir, Abdul Karim, Djabal Nur Basir,

Department of Chemistry, Hasanuddin University, Makassar 90245, Indonesia

Article history:
Received: 29 December 2023 / Received in revised form: 24 March 2024 / Accepted: 16 May 2024

Abstract

This research aims to synthesize and characterize reduced graphene oxide (RGO), as well as analyse its electrochemical properties. The synthesis of RGO material from corn cobs went through several stages; carbonization, oxidation and reduction. The synthesis of RGO used a modified Hummer method, and was reduced using the reducing agent ascorbic acid. The synthesized RGO was then characterized using Fourier Transform Independent Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Energy Dispersive Spectroscopy (EDS). Electrochemical analysis using the cyclic voltammetry method, the specific capacitance value obtained showed that RGO had a higher capacitance value than GO. The research results showed that carbon from corn cobs, which has not been utilized optimally, can be synthesized as a basic material for making RGO as a quite promising material.

Keyword: Corncob; Reduced Graphene Oxide (RGO); Specific capacitance; Hummers method modified

1. Introduction

Electrical energy is an important need to support human life, especially in the use of electronic devices. In the current digital era, various electronics use batteries as the main component for storing electrical energy. However, batteries have some weaknesses such as low energy storage capacity, long charging speed, and low power density, making the battery less efficient for use over a long time. Efforts to develop emerging energy storage technology can be made to complement the various weaknesses of these batteries, namely by using supercapacitor technology. Today one of the supercapacitor electrode materials that is quite popular in use is graphene [1].

Graphene is a material consisting of sp2 hybridized carbon and is arranged hexagonally in a two-dimensional structure [2]. The hexagonal structure of graphene causes this material to have the characteristics of good thermal stability, high specific surface area, flexibility, excellent electronic properties and conductivity [3]. However, graphene has several weaknesses, one of which is the quite difficult process of synthesizing pure graphene [4]. To overcome the weaknesses of graphene synthesis, of graphene derivatives is carried out, namely graphene oxide (GO, and reduced graphene oxide (RGO) [5].

* Corresponding author.
Email: indahraya@unhas.ac.id
https://doi.org/10.21924/cst.9.1.2024.1365

RGO is a graphene derived material obtained from the reduction of GO, which has properties like pure graphene such as flexibility, electronic properties, excellent conductivity, good dispersion and good thermal stability [7]. Fig. 5 shows the oxidation process of graphite to RGO. RGO materials can be made from biomass waste containing main carbon-based components such as hazelnut shells [8], palm fronds [9], coconut shells [10] and corncobs.

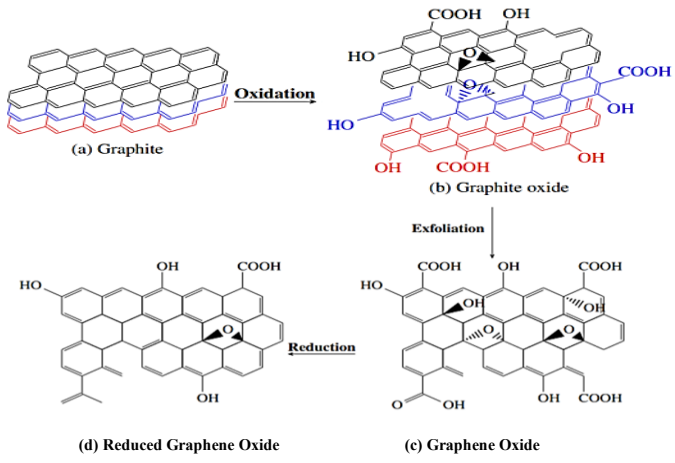

Fig. 1. Graphite oxidation process to become RGO material [6]

Corn cobs are a type of biomass waste that has not been utilized optimally. For this, there is a need for a solution to

utilize and increase the economic value of corn cobs [11]. Corn cobs contain high carbon compounds, including cellulose (41%), hemicellulose (36%) and lignin (6%) [12]. Based on data from the Central Statistics Agency (BPS), corn production in Indonesia reaches 20 million tons/year [13]. High corn production produces waste in the form of corn cobs. Therefore, efforts are being made to reduce corn cob waste, one of which is by using it to synthesize it into RGO material.

According to Dywili, et al [14], reducing GO to RGO by reducing the oxygen content in GO can increase capacitance. In this research, RGO was synthesized from carbon-based materials such as corn cobs, synthesized through an oxidation process using a modified Hummers method and reduced using ascorbic acid as an environmentally friendly reducer. The GO and RGO materials obtained were subjected to electrochemical analysis using the cyclic voltammetry method using distilled water as a comparison, before being analyzed using a Na_2SO_4 electrolyte solution, to determine the specific capacitance value of GO and RGO.

2. Materials and Methods

2.1. Preparation

Corn cobs were cut into small pieces, washed, and dried in the sun for five days. Corncob samples were carbonized at 500 °C for 2 hours. The resulting carbon was then sieved using a 200 mesh sieve to obtain carbon powder.

2.2. Synthesis of reduced graphene oxide (RGO)

5 g of carbon powder was dissolved in 100 mL of 98% H_2SO_4 and stirred for 2 hours at a temperature of 20°C. Then 15 g $KMnO_4$ was added after 2 hours of stirring at a temperature of 10°C. The samples were removed from the ice bath and stirred again for 2 hours at 35°C. After stirring, 100 mL of distilled water was added while stirring for 1 hour. Then 60 mL of 30% H_2O_2 was added and centrifuged at 10,000 rpm for 20 minutes. Samples were washed with distilled water until the pH was neutral. The residue was then dried at 110 °C for 6 hours. After drying, the carbon sample was added to 100 mL of distilled water and sonicated for 2 hours. It was then filtered and dried at a temperature of 110 °C for 6 hours to obtain GO material [15,16]. The GO powder obtained was reduced using the reducing agent ascorbic acid. 1 g GO was dissolved in 50 mL deionized water. Then 0.8 g of ascorbic acid was added and stirred for 1 hour at 80 °C. The samples were centrifuged, filtered and washed with distilled water until the pH was neutral before being and then dried at 110 °C for 6 hours [17].

2.3. Electrode making

An 8cm long copper wire was inserted into the pipette and attached using parafilm. The sample was then mixed with paraffin and stirred on a hot plate until being melted and homogeneous. The paste formed was inserted into the electrode body evenly and densely [18].

2.3.1. Electrochemical measurements

The specific capacitance of the RGO electrode was measured by the cyclic voltammetry method using a Potentiostat. The capacitance measurement of the electrode was carried out with a scanning rate of 50 mV/s using a 1 M Na_2SO_4 electrolyte solution. The specific capacitance can be calculated using the following equation 1:

$$C_{sp} = A/m.k.\Delta V \quad (1)$$

where: Csp is specific capacitance (F/g), A is the curve area, mass (g), k is scan rate (V/s), V is voltage (volts) [19].

3. Result and Discussion

In this research, corn cobs were synthesized into RGO material using a modified Hummers method. The carbon sample was reacted with H_2SO_4 and $KMnO_4$, in this process the color changed from dark green to brownish, indicating that a carbon oxidation process had occurred [20]. H_2SO_4 and $KMnO_4$ are strong oxidizing agents that undergo a chemical reaction. the reaction forms several functional groups. namely epoxy, hydroxyl, carboxyl and carbonyl groups [21]. This functional group is what causes this material to be very hydrophilic and easily exfoliated into GO [20, 22]. The mixture is then diluted by adding H_2O. The oxidation process was stopped by adding H_2O_2, and also to reduce the remaining $KMnO_4$ which was indicated by the color of the solution changing to brownish yellow [23] which is shown in Fig. 2

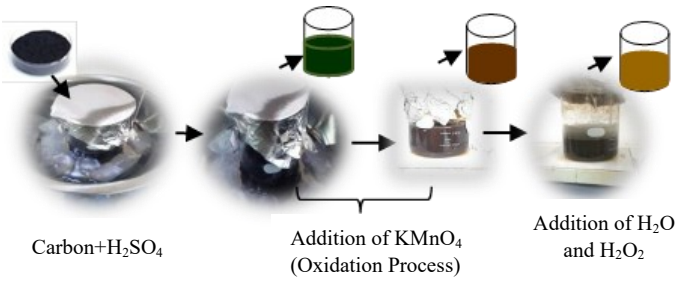

Fig. 2. Oxidation Process

The residue obtained was washed to neutral pH and dried at 110 °C. The sonication process was carried out by dispersing the carbon powder resulting from oxidation into distilled water and sonicating for 2 hours. The exfoliation process of GO sheet occurred due to ultrasonic waves [20,24]. GO reduction in this study used ascorbic acid because it is an environmentally friendly reducer to replace hydrazine as a GO reducer [6].

3.1. Fourier transform infrared (FTIR) analysis

Functional groups were identified using FTIR. Fig. 3 shows theresults of functional group analysis on carbon, GO, and RGO. The broad bands at 3419 cm^{-1} and 3446 cm^{-1} were associated with C–OH stretching vibrations mostly located at the edges [26]. The emergence of wave numbers at 2922 cm^{-1} and 2852 cm^{-1} was caused by symmetric and asymmetric stretching vibrations of CH_2 bonds [27]. The stretching

vibration of the carbonyl group C=O observed between 1701 cm^{-1} and 1705 cm^{-1} indicated the formation of carboxyl groups in GO and RGO [28]. The strong peaks of carbon, GO, and RGO 1581 cm^{-1}, 1575 cm^{-1} and 1585 cm^{-1} corresponded to the aromatic functional group C=C, indicating a conjugated benzene ring [26, 28]. The –OH bending vibration and the C–O stretching vibration of the –COOH group could be observed at 1431 or 1382 cm^{-1} and 1220 or 1230 cm^{-1}, respectively. The C-O strain in GO and RGO was indicated by the wave numbers of 1182 cm^{-1} and 1178 cm^{-1}, and the stretching vibration of the epoxy group C–O–C at 1039 cm^{-1}. After reduction with ascorbic acid, this peak disappeared [26]. Based on the FTIR spectrum results as shown in Table 1, the synthesis of RGO from corncob carbon has been successfully carried out using the Hummers method. This was supported by the appearance of the O-H, C=O, C=C, and –COOH functional groups as the characteristic of RGO and the main constituents of the hexagonal carbon layer structure in RGO.

Table 1. The functional group of carbon, GO, and RGO

Functional Group	Wavenumber (cm^{-1})		
	Carbon	GO	RGO
-OH	3446.79	3619.77	3446.79
$-CH_2$	2922.16	2992.16	2922.16
-C=O	-	1701.22	1705.07
-C=C	1581.63	1575.84	1585.49
-COOH	1382.96	1394.53	1382.96
C-O	-	1182.36	1178.51
C-O-C	-	1039.63	-

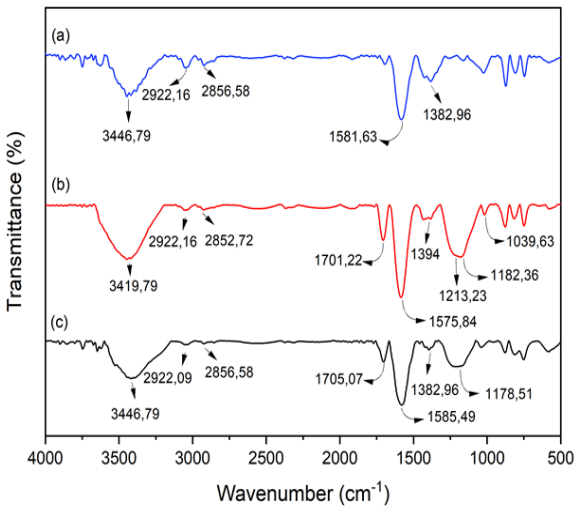

Fig. 3. FTIR spectra of (a) Carbon, (b) GO and (c) RGO

3.2. X-Ray diffraction (XRD) analysis

Fig. 4 show the results of the XRD analysis. The diffractogram pattern of corncob carbon shows a specific area at 2 theta, i.e 22.84° and 44.30° in the (002) and (100) planes, showing the amorphous area of corncob carbon in accordance with the characteristics of carbon [29]. Furthermore, the diffraction pattern of RGO synthesized from corncob carbon showed a broad peak with low intensity in the amorphous region on the (002) plane and a sharp peak on the (100) plane. The intensity of the 2 theta peaks in the diffractogram showed the order of atoms in the thin crystal layer. The higher the intensity value produced, the better the arrangement of the atoms in the layer. The wide peak in the (002) plane indicated that the crystal size decreased due to amorphization. This data then confirmed that the crystal structure of the RGO material was distorted after the oxidation process [21]. Using the Bragg equation, the layer distance between RGO at the 23.30° peak was 0.382 nm. In other words, the presence of oxygen can reduce the distance between graphite oxide layers. The significant decrease in distance is caused by the oxygen functional groups intercalated in the inner layer of RGO.

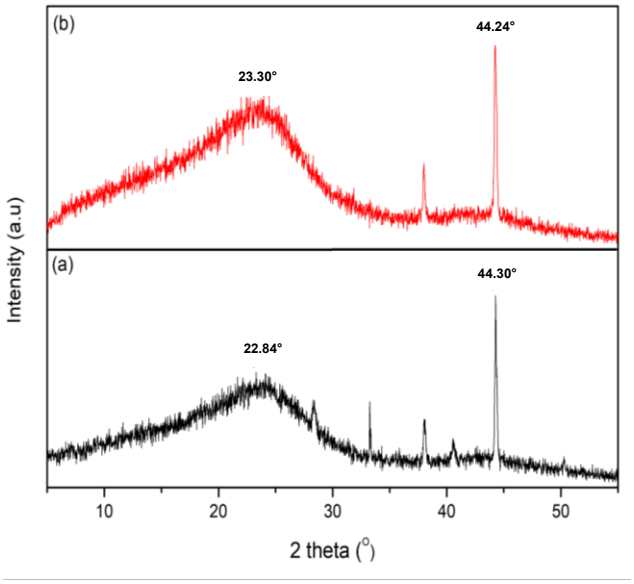

Fig. 4. XRD spectra of (a) Carbon, and (c) RGO

3.3. Scanning electron microscope (SEM) analysis

SEM analysis was used to observe the morphology of carbon, GO and RGO materials. SEM analysis at 3000 and 1300x showed that the carbon consisted of large, irregular, and porous flakes distributed in various sizes and shapes (Fig. 5(a)) [16]. After the carbon underwent the oxidation and sonication process, the morphology of the carbon material shown in Fig. 5(b) resembled a layered sheet, it looked thick, and irregular, and had transparent and overlapping layers [30, 31]. The presence of oxygen functional groups bound to the GO layer causeed thickening on the surface of the material indicating carbon oxidation to form GO. Fig. 5(c) shows that RGO had a thinner sheet shape than GO as the oxygen functional groups were reduced during the reduction process [32,14].

3.4. Energy dispersive spectroscopy (EDS) analysis

EDS analysis was to determine the carbon and oxygen element content after reduction with ascorbic acid. Based on the results of EDS analysis, the corn cob carbon, GO and RGO samples showed a C atomic percentage of 95.88% and an O atomic percentage of 4.12%. The C and O atom contents in GO were 87.88% and 12.12%, respectively. The RGO material obtained had a percentage of 92.90% for C atoms and 7.10% for O atoms. Based on the percentage of EDS analysis results, it can be stated that the reduction process of GO to RGO has been successfully carried out as indicated by a decrease in the O element content and an increase in the O content. element C in RGO [32].

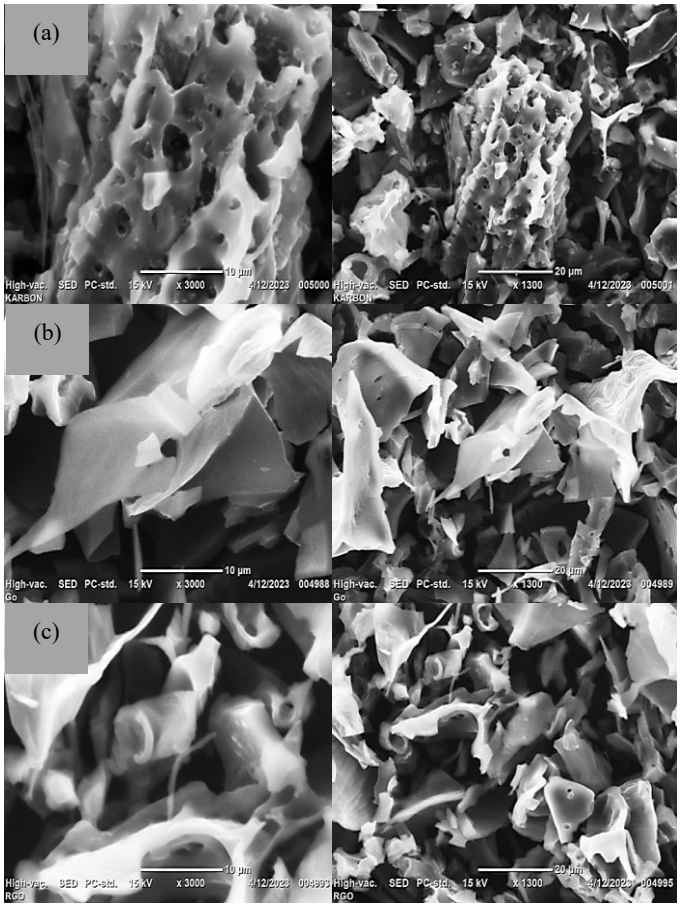

Fig. 5. SEM images of (a) carbon, (b) GO, and (c) RGO

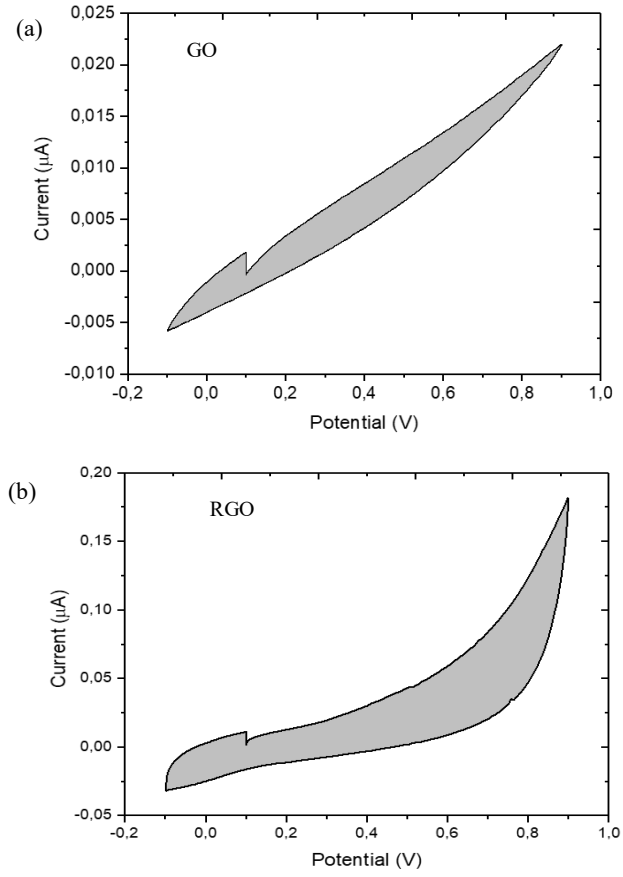

Fig. 6. Cyclic voltammetry curves of GO electrodes (a) and RGO (b)

3.5. Electrochemical measurements

To analyze the electrochemical performance, cyclic voltammetry (CV) measurements were carried out using a 1 M Na2SO4 electrolyte solution. Fig. 6 (a and b) shows the results of CV measurements on GO and RGO. The results of electrochemical analysis show that the capacitance of RGO was higher compared to GO, i.e. 6.2324 F/g and 0.4581 F/g as shown in Table 2. This increase in capacitance indicated showed that GO had a higher oxygen content due to the presence of epoxy functional groups, hydroxyl, and carboxyl, while RGO had a relatively lower oxygen content than GO caused by the reduction of oxygen functional groups during the reduction process, causing an increase in the capacitance value [13]. This is in accordance with research by Yang, et al [33] whose results showed that GO reduction is needed to optimize electrochemical performance thereby increasing specific capacitance.

Table 2. Results of electrochemical analysis at a scan rate of 50 mV/s

Sample	Scan Rate (mV/s)	Specific Capacitance (F/g)
GO	50	0.485
RGO	50	6.232

4. Conclusion

The synthesis of RGO from corncob carbon using a modified Hummers method has been successful. FTIR analysis showed that the functional groups of RGO were O-H, C=O, C=C, and -COOH. The morphological structure of RGO shows a thin and irregular sheet shape. Meanwhile XRD diffractogram showed that RGO was amorphous with a distance between layers in graphite of 0.382 nm. The results of electrochemical analysis showed that the capacitance value of RGO showed an increase in capacitance value of 6.232 F/g, compared to GO with a capacitance of 0.4851 F/g. Therefore, it can be concluded that the process of reducing GO to synthetic RGO from corn cob carbon has been successfully carried out, and showed that the capacitance value of RGO had a higher specific capacitance than GO.

Reference

1. S. Rattanaveeranon and K. Jiamwattanapong. *Effect of CuO/rGO and ZnO/rGO hybrid additional layers on supercapacitor performance.* Trends Sci, 19 15 (2022) 3-9.
2. R. Ding et al. *A brief review of corrosion protective films and coatings based on graphene and graphene oxide*. J. Alloys Compd.. 764 (2018) 1039-1055.
3. A. Osman, A. Elhakeem, S. Kaytbay, and A. Ahmed. *Thermal, electrical and mechanical properties of graphene/nano-alumina/epoxy composites.* Mater. Chem. Phys. 257 (2021) 123809.
4. AEF Oliveira, GB Braga, CRT Tarley, and AC Pereir. *Thermally Reduced Graphene Oxide: Synthesis, Studies and Characterization.* J. Mater. Sci. 53 (2018) 12005-12015.
5. DS Chauhan, MA Quraishi, KR Ansari, and TA Saleh. *Graphene and graphene oxide as new class of materials for corrosion control and protection: Present status and future scenario*. Prog. Org. Coatings. 147 (2020) 105741.
6. P. Cronqvist. Chemistry of Ascorbic Acid Reduction of Graphene Oxide Reduction of Graphene Oxide in Solution and Film. (2019).

7. D. Shahdeo, A. Roberts, N. Abbineni, and S. Gandhi. *Graphene based sensors*. (2020) 175-199.
8. A. Saleh, FA Amhadin, and I. Novianty. *Synthesis of reduced graphene oxide and zinc oxide composite from candlenut shell charcoal (Aleuritas moluccana).* Elkawnie. 8 1 (2022) 1-11.
9. ME Thebora, KN Ningsih, and MI Shalihin. *Sintesis grafena dari limbah pelepah sawit (elaeis sp.) dengan metode reduksi grafit oksida menggunakan pereduksi Zn.* J. Khazanah Intelekt. 3. (2020), 462-476.
10. MBP Honorisal, N. Huda, T. Partuti, and A. Sholehah. *Sintesis dan karakterisasi grafena oksida dari tempurung kelapa dengan metode sonikasi dan hidrotermal.* Tek. J. Sains dan Teknol.16 (2020) 1-11.
11. I. Christica and R. Julia. *Activated carbon utilization from corn cob (zea mays) as a heavy metal adsorbent in industrial waste.* Asian J. Pharm. Res. Dev., 6 (2018) 1-4.
12. R. Farma et al. *Corn cob based activated carbon preparation using microwave assisted potassium hydroxide activation for sea water purification.* J. Phys. Conf. Ser. 1120 (2018) 1-6.
13. Badan Pusat Statistik. *Luas Panen dan Produksi Jagung di Indonesia 2022 (Angka Sementara).* Berita Resmi Statistik, (74) 2023 1-16.
14. N. Dywili, A. Ntziouni, M. M. Ndipingwi, C. Ikpo, A. C. Nwanya, K. Kordatos, and E. Iwuoha. *High Power Asymmetric Supercapacitor Based on Activated Carbon/Reduced Graphene Oxide Electrode System*. Mater. Today Commu. **35** (2023),1-10.
15. S. Wahyuningsih, A. H. Ramelan, M. Fuad, and Q. A. Hanif. *Sintesis grafena oksida tereduksi terdoping nitrogen dan sulfur dari amonium tiosianat sebagai elektroda lawan pada sistem dye sensitized solar cell (DSSC),* ALCHEMY J. Penelit. Kim. 16 (2020) 126-139.
16. K. Rekos, ZC Kampouraki, C. Sarafidis, V. Samanidou, and E. Deliyanni. *Graphene oxide based magnetic nanocomposites with polymers as effective bisphenol–a nanoadsorbents.* Materials (Basel). 12, (2019), 1987.
17. S. Rai, R. Bhujel, M. Khadka, R. L. Chetry, B. P. Swain, and J. Biswas. *Synthesis, characterizations, and electrochemical studies of ZnO/reduced graphene oxide nanohybrids for supercapacitor application.* Mater. Today Chem. 20 (2021) 100472.
18. K. Vytras, I. Svancara, and R. Metelka, 2009, *Carbon Paste Electrodes in Electroanalytical Chemistry*. J. Serb. Chem. Soc. 74 (2009) 1021-1033.
19. RV Tolentino-Hernandez, E. Jimenez-Melero, FJ Espinosa-Faller, C. Guarneros-Aguilar, and F. Caballero-Briones. *One-Step, Low Temperature Synthesis of Reduced Graphene Oxide Decorated with ZnO Nanocrystals using Galvanized Iron Steel Scrap.* Material Research Express, 8 (2021) 1-12.
20. A. Adetayo and D. Runsewe. *Synthesis and fabrication of graphene and graphene oxide: a review.* Open J. Compos. Mater. 09 (2019) 07-229.
21. E. Kusrini, A. A. Suhrowati, A. Usman, D. V. Degirmenci, and M. Khalil. *Synthesis and characterization of graphite oxide, graphene oxide and reduced graphene oxide from graphite waste using modified hummers's method and zinc as reducing agent.* Int. J. Technol. 10 (2019) 1093.
22. A. T. Habte and D. W. Ayele. *Synthesis and characterization of reduced graphene oxide (rGO) started from graphene oxide (GO) using the tour method with different parameters.* Adv. Mater. Sci. Eng. 2019 (2019) 1-9.
23. J. Shen et al. *Facile synthesis and application of Ag-chemically converted graphene nanocomposite.* Nano Res. 3 (2010) 339-349.
24. MJ Fernández-Merino et al. *Vitamin c is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions.* J. Phys. Chem. C. 114 (2010) 6426-6432.
25. E. Aliyev, V. Filiz, MM Khan, YJ Lee, C. Abetz, and V. Abetz. *Structural characterization of graphene oxide: surface functional groups and fractionated oxidative debris. Nanomaterials*. 9 (2019) 1180.
26. M. Bera, Chandravati, P. Gupta, and PK Maji. *Facile one-pot synthesis of graphene oxide by sonication assisted mechanochemical approach and its surface chemistry*. J. Nanosci. Nanotechnol. 18 (2018), 902-912.
27. U. Chasanah, W. Trisunaryanti, Triyono, HS Oktaviano, I. Santoso, and DA Fatmawati. *Study of green reductant effects of highly reduced graphene oxide production and their characteristics*. Commun. Sci. Technol. 7 (2022) 103-111.
28. X. B. Xie et al. *Dielectric parameters of activated carbon derived from rosewood and corncob*. J. Mater. Sci. Mater. Electron. 31 (2020), 18077-18084.
29. B. Gupta, N. Kumar, K. Panda, V. Kanan, S. Joshi, and I. Visoly-Fisher. *Role of oxygen functional groups in reduced graphene oxide for lubrication*. Sci. Rep. 7 (2017) 45030.
30. M. Alpha, U. E. Uno, K. U. Isah, and U. Ahmadu. *Structural and electrochemical properties of Reduced Graphene Oxide (RGO) synthesised using an improved modified hummers method as electrode material for electronics applications*. Niger. J. Technol. 38 (2019) 997.
31. Y. Li, H. Li, A. Du, M. Wang, and J. Zeng. *Morphology and Isothermal Crystallization of Graphene Oxide Reinforced Biodegradable Poly (Butylene Succinate*). Polymer Testing, 59 (2017) 1-9.
32. B. E. Aragaw. *Reduced Graphene Oxide-Intercalated Graphene Oxide Nano-Hybrid for Enhanced Photoelectrochemical Water Reduction*. J. Nano. Chem. 10 (2019) 9-18.
33. L. Yang, L. Zhang, X. Jiao, Y. Qiu, and W. Xu. *The electrochemical performance of reduced graphene oxide prepared from different types of natural graphites*. RSC Adv. 11 (2021) 4042-4052.