2024SPSBIC0088

Synthesis and Characterisation of Graphene Oxide Nanoparticle

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Abstract

Graphene oxide (GO) is a carbon nanomaterial with two dimensional structure having excellent electronic, optical, mechanical and thermal properties and finds application in biomedicine, electronic devices, energy storage devices, supercapacitors, biosensors and water purification. This study focused on the synthesis and characterisation of GO. Herein, GO was synthesised from graphite powder using the improve Hummers method. Characterisation of the synthesised GO was done using Ultra Violet-visible (UV-vis) spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), High Resolution Scanning Electron Microscopy-Energy Dispersive Spectroscopy (HRSEM-EDS), and X-ray Diffraction (XRD) analysis. The UV-visible spectrum shows absorption peak at maximum wavelength of 228.5 nm. FTIR result shows the presence of functional groups such as O-H, C=O, C-O-C and C-O. HRSEM micrograph reveal the formation of flake-like network having C/O ratio of 1.41, while the XRD spectrum demonstrated the appearance of a wide diffraction peak at 2θ value of 11.6° with crystallite size of 18.1 nm. All the characterisation results confirm the successful synthesis of high-purity graphene oxide which can be useful in wastewater treatment.

Keywords: Graphene oxide, graphite powder, improve Hummers method, characterisation.

1. Introduction

Nanotechnology is the branch of science and engineering which is concerned with manipulating structures of atoms and molecules at the nanoscale (Maitlo *et al.*, 2019, Garg, 2019; Woldeanmanuel *et al*., 2021). Nano materials are materials that are made up of particles in which one or more external dimensions are in the size range of 1-100 nm and they have size related properties that are different from bulk materials (Kumar, *et al*., 2021). These particles exhibit unique physical, chemical and biological properties at nano-scale compared to their respective particles at higher scales due to their relatively large surface area to volume, increased reactivity and stability and increased mechanical strength (Ealias and Saravanakumar, 2017; Ahmad *et al.*, 2021).

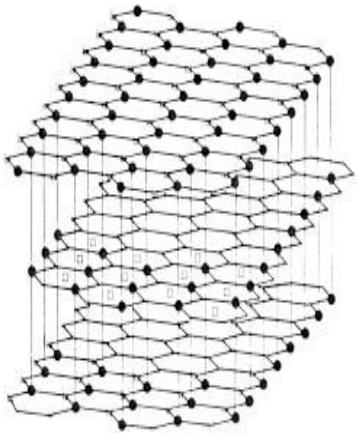
Graphene is a single layer of graphite arranged in a two-dimensional honeycomb lattice. It is one of the allotrope of carbon in the form of a plane of sp^2 hybridised carbon atoms having two dimensional planar surface with thickness of 1 nm. Exhibiting exceptional strength and conductivity, it is said to be the strongest material ever recorded (Jangid and Inbaraj, 2021). This special features make it highly favourable for several environmental applications. Nowadays, there are lots of research on graphene because of its interesting properties such as high mechanical strength, high thermal and electrical properties, fast electron mobility rate and specific surface area (Yin *et al.*, 2018). Because of its unique structure and excellent performance, graphene can be applied in the energy and electronics sectors and also in biomedical fields (Song *et al.*, 2019). However, graphene is hydrophobic, which inhibits its function in water but can be modified into graphene oxide (GO) which is hydophillic.

Graphene oxide (GO) is a layered two dimensional carbon nano-material and a water soluble derivative of graphene having several oxygen containing functional groups such as carboxyl, hydroxyl, epoxy and carbonyls attached to both sides of the layer as well as the edges of the plane (Jirickova *et al.*, 2022). GO can be synthesised using various method which include; Brodie, Staudenmaier and Hummers, but nowadays,

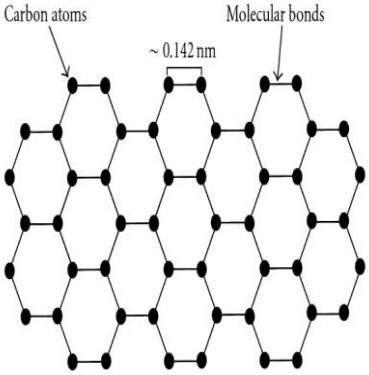
Hummers method is the most commonly used, in which graphite powder or graphite flakes is oxidize into graphite oxide (GTO) followed by the exfoliation of graphite oxide into GO (Caicedo *et al.*, 2020)

Due to the presence of several oxygen containing functional groups, GO can easily be processed and functionalised for various applications and hence has achieved more focus in many areas such as energy storage, biomedical fields and in water and wastewater purification (Falahati *et al.*, 2018)

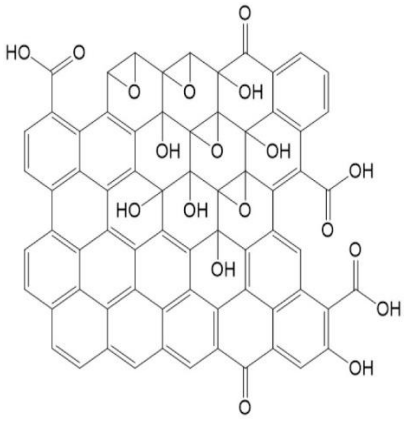
Graphene oxide is a graphene sheet that has been chemically reacted to attach oxygen atoms to the graphene. Graphite on the other hand is a crystal consisting of many sheets of graphene stacked on top of each other. Figure 1 (a-c) show the schematic diagram of graphite, graphene sheet and graphene oxide respectively.



(a)



(b)



(c)

Figure 1: Schematic Diagram of (a) Graphite (b) Graphene sheet (c) Graphene oxide

2 Experimental

2.1. Materials.

Graphite powder was purchased from Merck, Germany, hydrochloric acid (HCl, 37 %), sulphuric acid (H_2SO_4, 98 %), phosphoric acid (H_3PO_4, 98 %) and hydrogen peroxide (H_2O_2, 50 %) were purchased from BDH chemicals, England while potassium permanganate ($KMnO_4$, 98%) was purchased from Lobie Chem, India. All chemicals were used without further purification. Distilled water was used throughout the experiment

2.2 Synthesis of Graphene Oxide. Graphene oxide was synthesised using the improve Hummers method. In a typical synthesis, 360 cm^3 of H_2SO_4 and 40 cm^3 of H_3PO_4 were mixed in a beaker to give 9:1 mixing ratio. 5 g of graphite powder was then added. The mixture was transferred to an ice bath and stirred for 5 mins with the aid of a stirring rod. 20 g of $KMnO_4$ was added and stirred for another 5 mins and was later transferred to a magnetic stirrer and stirred for 4 h at a temperature of 50 ˚C after which 250 cm^3 of distilled water was added followed by the addition of 40 cm^3 of 37 % H_2O_2. The colour of the sample immediately changed to yellow. The mixture was allowed to cool to a room temperature and was then centrifuged. 10 % HCl was used to wash it repeatedly followed by washing with distilled water until a neutral pH is obtained. This gives graphite oxide (GTO). GTO was dispersed in 100 cm^3 of distilled water and sonicated for 1 h using the ultrasonicator for complete exfoliation to graphene oxide (GO). GO solution obtained was then centrifuged again, the supernatant was discarded and the pellet was oven dried at 70 ˚C for 12 h to obtain graphene oxide powder. The schematic diagram of graphene oxide synthesis is shown in figure 2.

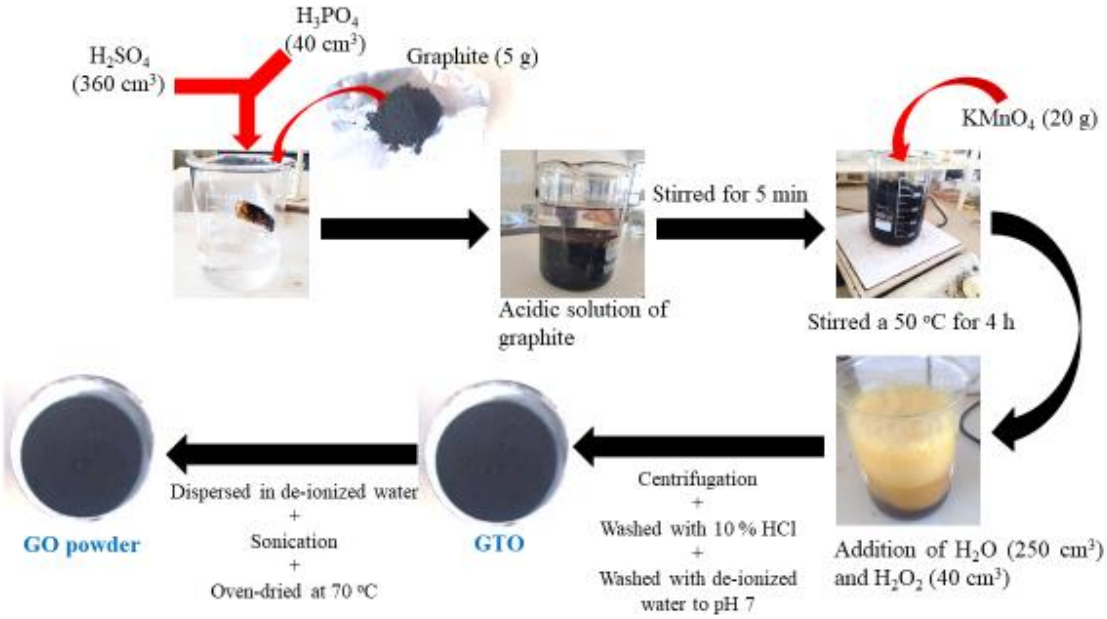


Figure 2: Schematic Diagram of GO Synthesis

2.3 Characterisation

The optical property was investigated using UV–visible (UV-vis) spectrophotometer. Fourier-transform infrared (FTIR) spectroscopy was used to determine the functional group on the surface of the GO, the surface

morphology and elemental composition was studied using high resolution scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (HRSEM/EDS) while the crystallinity was determined using X-ray diffraction (XRD) analysis.

3 Results and Discussion

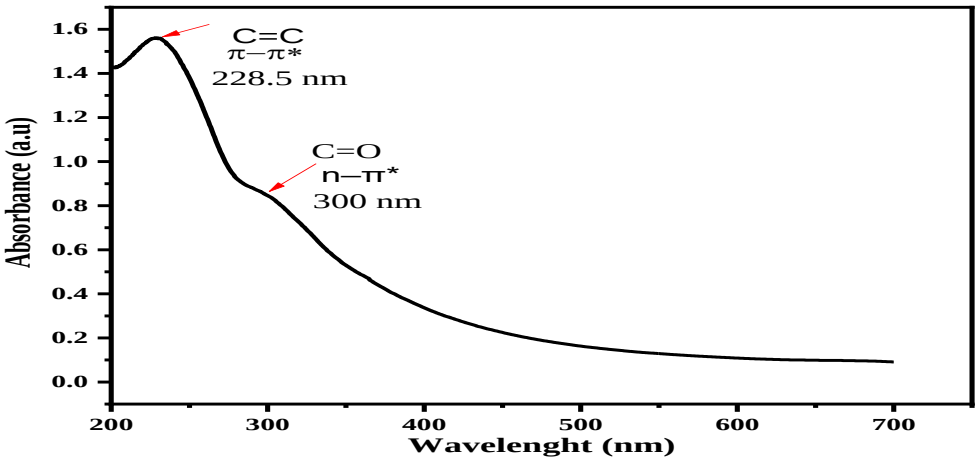


Figure 3: UV-visible Spectrum of GO

UV-vis spectroscopy was used to study the absorption spectra of aqueous GO dispersion for a wavelength range of 200-700 nm and the result is presented in figure 3. A characteristic peak appears at 228.5 nm which corresponds to π-π* transition of C=C bonds implying that pi electron in bonding orbital is excited to corresponding anti bonding orbital. A shoulder peak appeared at 300 nm, indicates the n–π* transition of C=O

According to the Beer-Lambert law, the intensity of the absorbance peak is related to the concentration of π or π * in the carbon framework (Shen *et al.*, 2020)

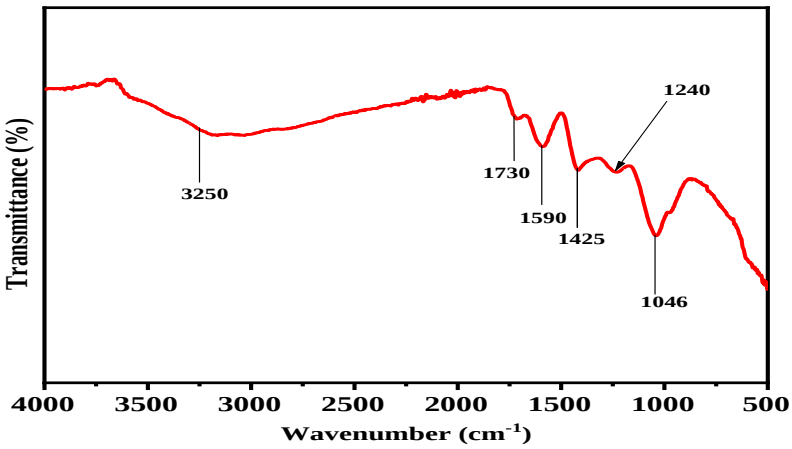


Figure 4: FTIR Spectrum of GO

The functional groups on the surface of GO was identified using FTIR and the result is shown in Figure 4**.** Upon oxidation of graphite to GO, the characteristic peaks of the presence of oxygen in carbon frameworks were observed. A broad peak at 3250 cm^{-1} corresponds to O-H stretching vibration of the surface functional groups as well as absorption of water molecules on the GO layers. The absorption band at 1730 cm^{-1} corresponds to C=O stretching of carbonyl and carboxyl groups, the band at 1590 cm^{-1} can be attributed to aromatic C=C stretching vibration. A band at 1425 cm^{-1} corresponds to tertiary C-OH groups stretching. The band at 1240 cm^{-1} is due to C-O-C stretching vibration of epoxides while the absorption band at 1046^{-1} is associated to C-O stretching vibration of alkoxy group. This observe bands are quite in agreement with what were previously reported by Naeem *et a*l., 2018; Khan *et al.*, 2019 and Marjani *et al.*, 2020. The presence of OH and C=O confirms the presence of COOH group on GO. These polar group especially the surface hydroxyl groups result in the formation of hydrogen bonds between graphite and water molecules which contributes to the good hydrophilic nature of graphene oxide and also confirm that graphite has been successfully oxidized to GO. Also the presence of C=C groups on GO confirms that despite, graphite has been oxidized into GO, the main structure of layered graphite is still retained.

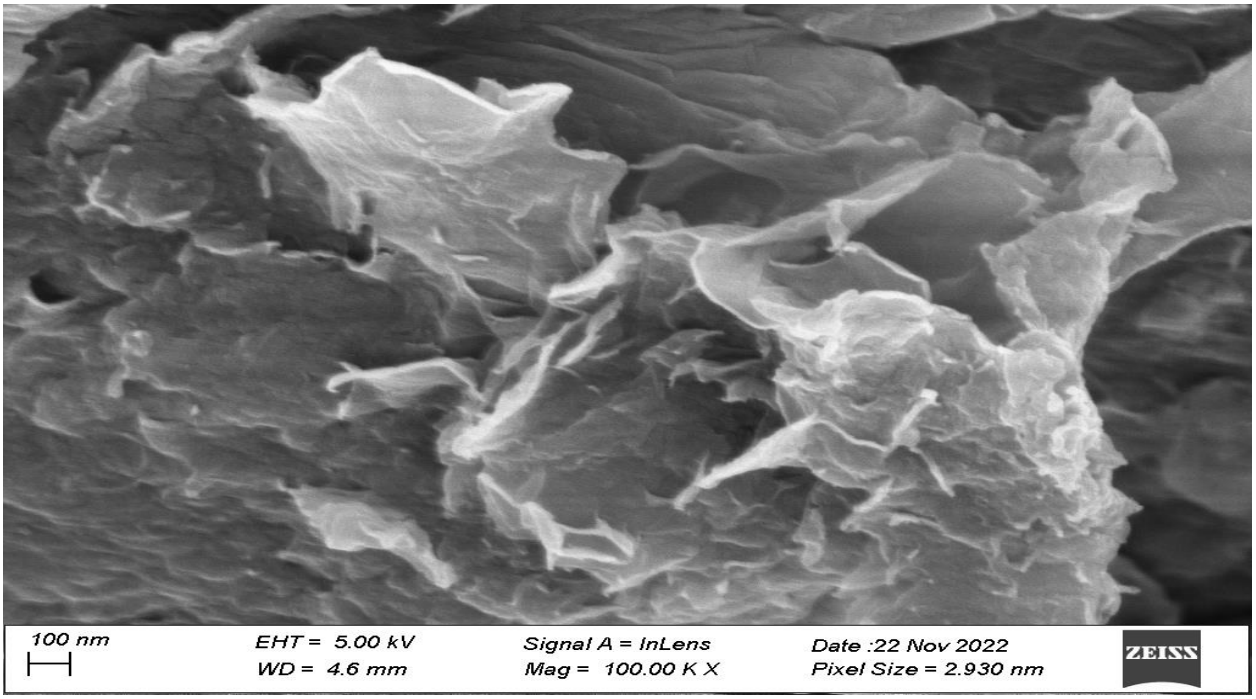


Figure 5: HRSEM Micrograph of GO

The HRSEM morphology of GO in figure 5, shows a uniform thin-layered and flake-like sheet structure with wrinkles and few folds. This wrinkled appearance helps the oxidation process by promoting the addition of functional groups and can further improve graphene oxide already interesting properties. A similar morphology has been reported by Chuah *et al*. (2020) who synthesised GO using Hummers method.

The HRSEM morphology of graphene oxide also shows existence of fewer layers in regular patterns and characteristic stacking which is due to exfoliation of the structure on graphite to form a more open structure similar to a loose sponge due to the porous networking system. The HRSEM morphology of graphite was investigated by Jagiełło *et al.*, 2020 and reported that there is existence of many stacks in the graphite structure indicating that graphite has a layered structure compared to GO with an opened structure.

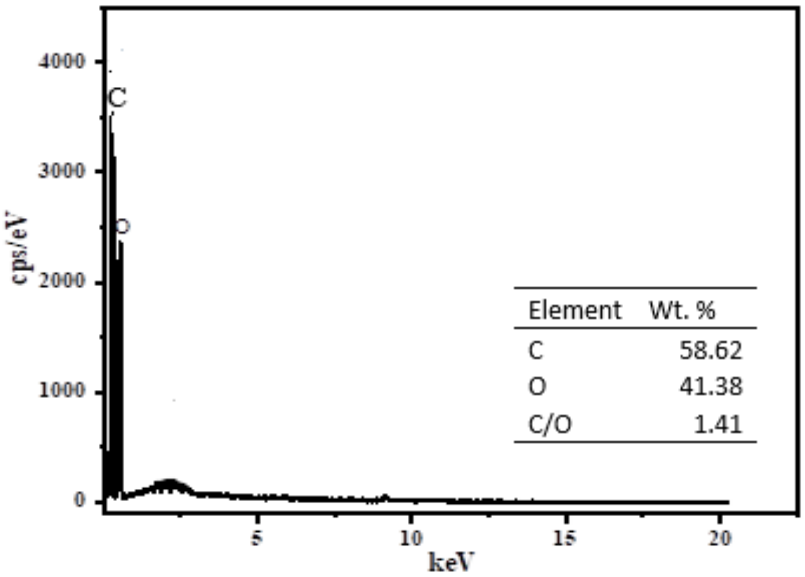
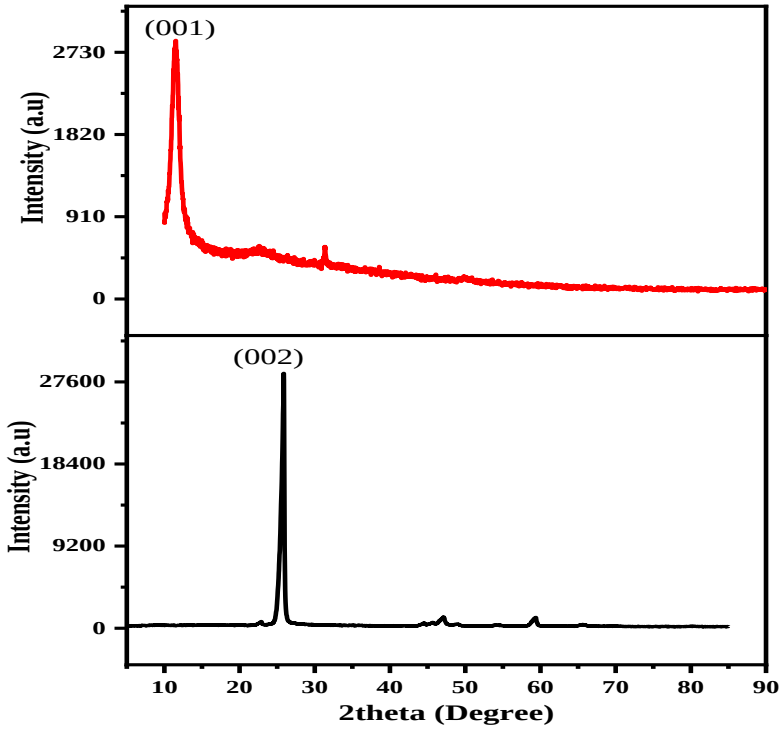


Figure 6: EDS Spectrum and Elemental Composition of GO

Figure 6, presents The EDS spectrum of GO showing peak of carbon and oxygen in composition of 58.62 % and 41.38 % respectively. Absence of any other peak in the spectrum shows that the synthesised GO is relatively pure. From the elemental composition, it can be seen that the C/O ratio of GO is 1.41. The C/O ratio of graphite was reported by Siburian, *et al.*, 2018 and Chuah, *et al.*, 2020 to be 9.81. The low C/O ratio of GO compare to that of graphite confirms the presence of oxygen functional group in GO and also shows that pure graphite is mainly carbon.



(b)

(a)

Figure 7: XRD Pattern of (a) Graphite (b) GO

Figure 7 (a and b) show the XRD patterns of graphite and GO. From figure 7 (a), it can be seen that pristine graphite shows a sharp and very intense diffraction peak at 2θ of 26.5˚ with lattice index of 002 and d-spacing of 0.34 nm. These data confirm the typical crystal structure of graphite and it agrees with the JCPDS (Joint Committee on Powder Diffraction Standards) card number 00-041-1487 of graphite structure with a hexagonal symmetry and a lattice parameter of a = b = 0.25 nm, c = 0.67 nm.

The XRD spectra of GO in Figure 7 (b), shows a wide diffraction peak at 2θ of 11.6° which correspond to 001 plane of pure graphene oxide with the interlayer spacing (d-spacing) of 0.75 nm. Similar result was reported by Khan *et al.* (2019) who reported a peak position of 11.6° for GO synthesised by modified Hummers method. It can be observed that, the peak position of graphite shifts to a lower angle after oxidation and also the interlayer spacing increased from 0.34 nm to 0.74 nm after the oxidation of graphite to GO. This increase in interlayer spacing maybe attributed to the presence of oxygen functional groups such as carboxyl, hydroxyl, carbonyl and epoxy groups that have been introduced into graphitic sheet during oxidation and also due to intercalation of water molecules into the carbon layered structure (Naeem *et. al.*, 2018). These additional groups have the effect of expanding the spacing between the individual layers (Siburian *et al*., 2018). Furthermore, it may also be related to the weak van der Waals bonding formed. These observations confirm the successfully oxidation of graphite to GO. According to Zaaba *et al.* (2017), interlayer spacing, d of graphene oxide is usually in the range of 0.6-1.0 nm and it is controlled by the degree of oxidation of graphite and amount of water molecules intercalated into graphite structure.

The crystallite size was calculated to be 18.1 nm using the Debye Scherrer equation;

$D = K\lambda / \beta Cos\theta$

where D is the crystalline size (nm), K represents the Scherrer constant (0.98), λ denotes the wavelength (0.154 nm), β denotes the full width at half maximum peak (FWHM) and θ is the diffraction angle

The interplaner spacing (d-spacing) is calculated using the Bragg's equation; $n\lambda = 2d \sin(\theta)$,

Where "n" is an integer, λ is the x-ray wavelength, d is the spacing of the diffracting planes, and θ is the angle between the incident rays and the diffracting planes, otherwise known as the Bragg's angle.

REFERENCES

Ahmad, W., Pandey, A., Rajput, V., Kumar, V., Verma, M. & Kim, H. (2021). Plant Extract Mediated Cost-Effective Tin Oxide Nanoparticles: A Review on Synthesis, Properties, and Potential Applications. *Current Research in Green and Sustainable Chemistry*, *4*, 100211.

Caicedo, F. M. C., Lopez, E. V., Agarwal, A., Drozd, V., Durygin, A., Hernandez, A. F. & Wang, C. (2020). Synthesis of Graphene Oxide from Graphite by Ball Milling. *Diamond and Related Materials*, *109*, 108064.

Chuah, R., Gopinath, S. C., Anbu, P., Salimi, M. N., Yaakub, A. R. W. & Lakshmipriya, T. (2020). Synthesis and Characterization of Reduced Graphene Oxide using the Aqueous Extract of Eclipta prostrata. *Biotech*, *10*(8), 364.

Ealias, S. A. M. & Saravanakumar, M. P. (2017). A Review on the Classification, Characterisation, Synthesis of Nanoparticles and their Application. *IOP Conference Series: Materials Science and Engineering* 263(3).

Falahati, F., Baghdadi, M. & Aminzadeh, B. (2018). Treatment of Dairy Wastewater by Graphene Oxide Nanoadsorbent and Sludge Separation using In-situ Sludge Magnetic Impregnation (ISSMI). *Pollution*, *4*(1), 29-41.

Garg, D. (2019). A Literature Review of Nanotechnology. *Journal of Emerging Technologies and Innovative Research*, 6(1), 69-73.

Jagiełło, J., Chlanda, A., Baran, M., Gwiazda, M. & Lipińska, L. (2020). Synthesis and Characterization of Graphene Oxide and Reduced Graphene Oxide Composites with Inorganic Nanoparticles for Biomedical Applications. *Nanomaterials*, *10*(9), 1846.

Jangid, P. & Inbaraj, M. P. (2021). Applications of Nanomaterials in Wastewater Treatment. *Materials Today: Proceedings*, *43*, 2877-2881.

Jirickova, A., Jankovsky, O., Sofer, Z. & Sedmidubsk, D. (2022). Synthesis and Applications of Graphene Oxide. *Materials*, *15*(3), 920.

Khan, S. A., Arshad, Z., Shahid, S., Arshad, I., Rizwan, K., Sher, M., & Fatima, U. (2019). Synthesis of TiO_2/Graphene Oxide Nanocomposites for their Enhanced Photocatalytic Activity against Methylene Blue Dye and Ciprofloxacin. *Composites Part B: Engineering*, *175*, 107120.

Kumar, P. P., Bhatlu, M. L. D., Sukanya, K., Karthikeyan, S. & Jayan, N. (2021). Synthesis of Magnesium Oxide Nanoparticle by Eco-friendly Method. A Review. *Materials Today: Proceedings*, *37*, 3028-3030.

Maitlo, H. A., Kim, K. H., Kumar, V., Kim, S. & Park, J. W. (2019): Nanomaterials-based Treatment Options for Chromium in Aqueous Environments. *Environment International*, 130.

Marjani, A., Nakhjiri, A. T., Adimi, M., Jirandehi, H. F. & Shirazian, S. (2020). Effect of Graphene Oxide on Modifying Polyethersulfone Membrane Performance and its Application in Wastewater Treatment. *Scientific Reports*, *10*(1), 2049.

Naeem, H., Ajmal, M., Muntha, S., Ambreen, J. & Siddiq, M. (2018). Synthesis and Characterization of Graphene Oxide Sheets Integrated with Gold Nanoparticles and their Applications to Adsorptive Removal and Catalytic Reduction of Water Contaminants. *RSC advances*, *8*(7), 3599-3610.

Shen, Y., Zhang, S., Sun, Y., Hai, C., Li, X., Zeng, J., ... & Zhou, Y. (2020). Structure and Property Evolution of Graphene Oxide Sheets during Low-Temperature Reduction on a Solid Substrate. *The Journal of Physical Chemistry C*, *124*(26), 14371-14379.

Siburian, R., Simanjuntak, C., Supeno, M., Lumbanraja, S. & Sihotang, H. (2018). New Route to Synthesize Graphene Nano Sheets. *Oriental Journal of Chemistry*, 34(1), 182-187.

Song, S., Shen, H., Wang, Y., Chu, X., Xie, J., Zhou, N., & Shen, J. (2019). Biomedical Application of Graphene: From Drug Delivery, Tumor Therapy, to Theranostics. *Colloids and Surfaces Biointerfaces*, *185*, 110596.

Woldeamanuel, K. M., Kurra, F. A. & Roba, Y. T. (2021). A Review on Nanotechnology and its Application in Modern Veterinary Science. *International Journal of Nanomaterials, Nanotechnology and Nanomedicine*, *7*(1), 026-031.

Yin, Y., Jiang, B., Zhu, X., Meng, L. & Huang, Y. (2018). Investigation of Thermostability of Modified Graphene Oxide/Methylsilicone Resin Nanocomposites. Eng. Sci. 5, 73–78.

Zaaba, N. I., Foo, K. L., Hashim, U., Tan, S. J., Liu, W. W. & Voon, C. H. (2017). Synthesis of Graphene Oxide using Modified Hummers Method: Solvent Influence. *Procedia engineering*, *184*, 469-477.