Synthesis of Graphene-Based Nanocomposites for Environmental Remediation Applications

Subjects: Materials Science, Composites

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The term graphene was coined using the prefix "graph" taken from graphite and the suffix "-ene" for the C=C bond, by Boehm et al. in 1986. The synthesis of graphene can be done using various methods. The synthesized graphene was further oxidized to graphene oxide (GO) using different methods, to enhance its multitude of applications. Graphene oxide (GO) is the oxidized analogy of graphene, familiar as the only intermediate or precursor for obtaining the latter at a large scale. Graphene oxide has recently obtained enormous popularity in the energy, environment, sensor, and biomedical fields and has been handsomely exploited for water purification membranes. GO is a unique class of mechanically robust, ultrathin, high flux, high-selectivity, and fouling-resistant separation membranes that provide opportunities to advance water desalination technologies. The facile synthesis of GO membranes opens the doors for ideal next-generation membranes as cost-effective and sustainable alternative to long existing thin-film composite membranes for water purification applications.

graphene synthesis process polymeric membranes environmental remediation composites

1. Introduction

Graphene is a purified form of graphite that recently gained enormous popularity in the energy [1][2][3], environment [4][5][6][7][8], membranes [1][7], sensor [9][10][11][12], and biomedical fields [13][14][15][16][17][18][19][20][21][22][23][24][25][26]. It is a sp^2 hybridized, hexagonally arranged, chain of polycyclic aromatic hydrocarbon with a honeycomb crystal lattice [27]. It is the most recent element of carbon allotropes and is actually the basic building block of other important carbon allotropes, including 3D graphite, 1D carbon nanotubes (CNTs), and 0D fullerene (C60), as shown in **Figure 1**.

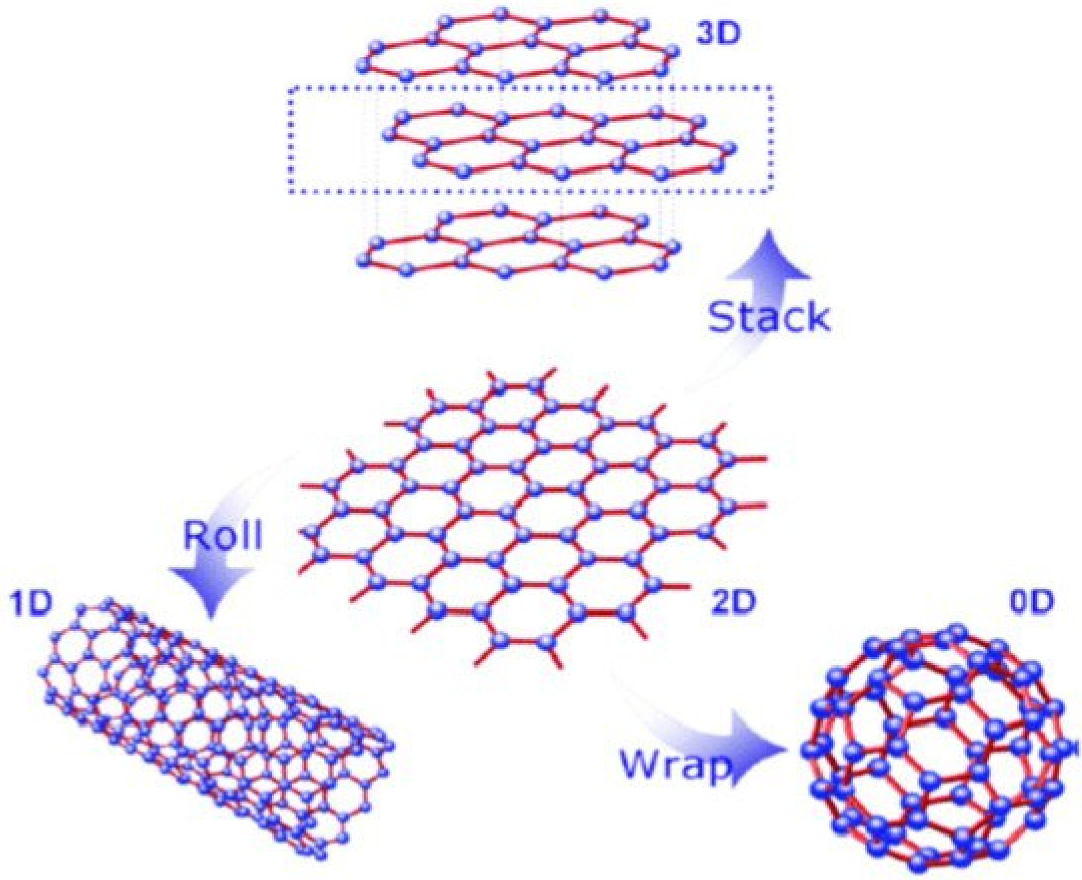

Figure 1. Structural representation of 2D graphene with different dimensions. [Reprinted with permission from ref. [28], Wan, X., Huang, Y., & Chen, Y. (2012). Focusing on energy and optoelectronic applications: a journey for graphene and graphene oxide at large scale. *Accounts of chemical research*, *45*(4), 598–607. Copyright © American Chemical Society].

The name graphene was coined by Boehm in 1986 [1], taking the prefix "graph" from graphite and the suffix "-ene" for sp^2 hybridized carbon, and was finally accepted by the International Union for Pure and Applied Chemistry in 1997 [29][30][31][32][33]. Furthermore, it became famous worldwide in 2004 when Geim and Novoselov obtained a single sheet of graphene on solid support, for which they were honored with the Nobel Prize in Physics in 2010 [34]. The main achievements of graphene in a timeline of history from 1840 to 2018 are shown in **Figure 2**.

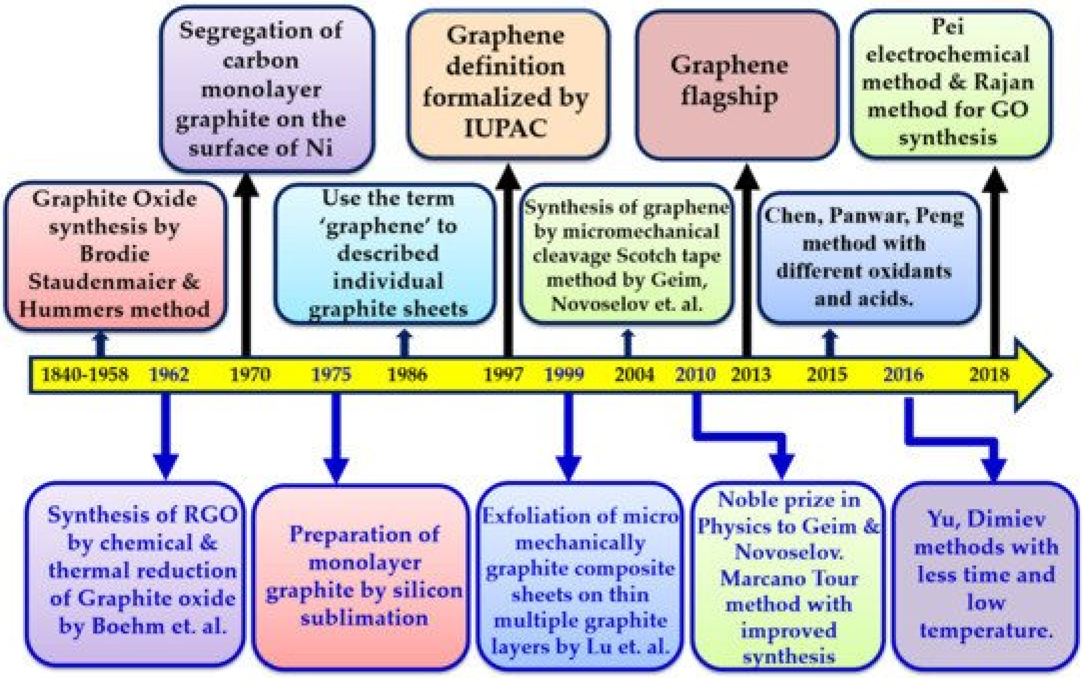

Figure 2. Schematic representation of a graphene timeline.

2. General Methods of Graphene Synthesis

Generally, graphene can be synthesized using two different routes, viz, bottom-up and top-down [33][35][36], as depicted in **Figure 3**.

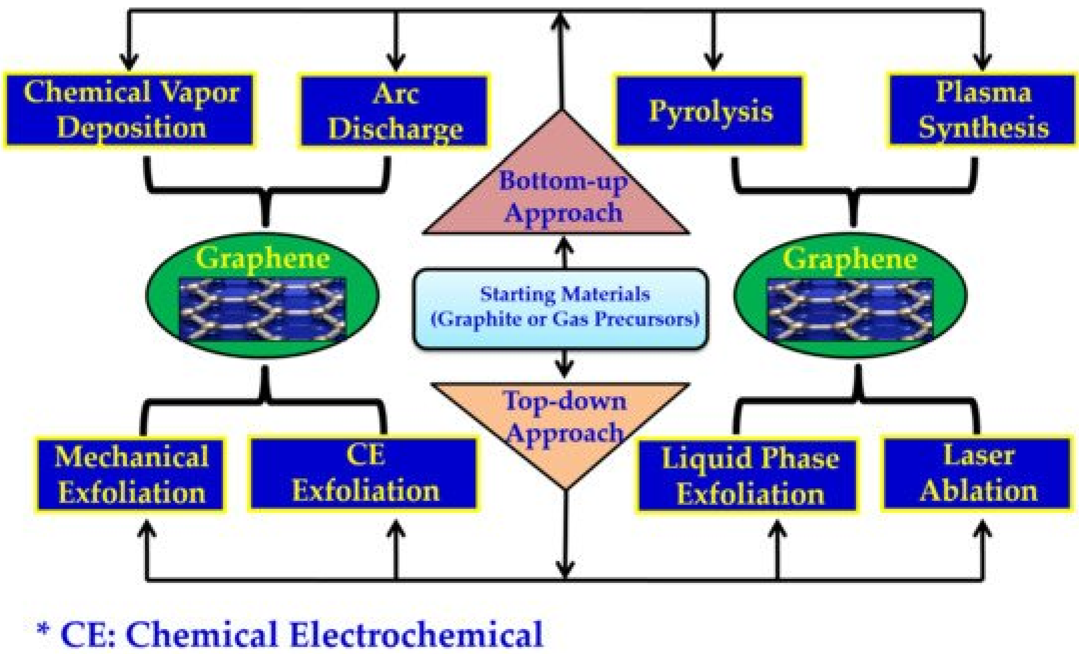

Figure 3. Schematic representation of the general methods for graphene synthesis.

3. Graphene Oxide (GO)

In comparison to graphene, graphene oxide is considered a more versatile and advanced material. GO has a broad range of oxygen containing functional groups such as carboxyl, hydroxyl, epoxy, carbonyl, and keto groups on its surface.

GO has shown great potential in a variety of fields by virtue of its high surface area [37], unique mechanical strength [38], and excellent optical and magnetic properties [39]. In comparison to other carbon-based nanomaterials, GO is considered a green oxidant, as it is enriched with oxygen-containing functional groups [40][41]. Further, GO has an aromatic scaffold, which acts as a template to anchor active species behaving as an organo-catalyst [42][43].

3.1. Synthesis of GO

In 1840, German scientist Schafhacutl was given the first report on the synthesis of graphene oxide and graphite intercalated compounds [44]. For the very first time, he attempted to exfoliate graphite and tried to purify impure graphite "kish" from iron smelters [27]. To date, several methods, as shown in **Table 1**, have been proposed.

Table 1. List of different methods used to synthesize graphene oxide.

Methods	Year	Starting Material	Different Oxidants Used	Reaction Time for GO Synthesis	Temperature °C	Features	References
Brodie	1859	Graphite	$KclO_3$, HNO_3	3–4 days	60	First attempt to synthesize GO	[45]
Staudenmaier	1898	Graphite	$KclO_3$, H_2SO_4, HNO_3	96 h	Room temperature	Improved efficiency	[46]
Hummers	1958	Graphite	$KmnO_4$, H_2SO_4, $NaNO_3$	<2 h	<20–35–98	Water-free, less than 2 h of reaction time	[47]
Fu	2005	Graphite	$KmnO_4$, H_2SO_4, $NaNO_3$	<2 h	35	Validation of $NaNO_3$	[48]
Shen	2009	Graphite	Benzoyl peroxide	10 min	110	Fast and non-acidic	[49]
Su	2009	Graphite	$KmnO_4$, H_2SO_4	4 h	Room temperature	Large-size GO sheets formed	[50]
Marcano and Tour	2010 & 2018	Graphite	$KmnO_4$, H_3PO_4, H_2SO_4	12 h	50	Eco-friendly resulting in a high yield	[51]

Methods	Year	Starting Material	Different Oxidants Used	Reaction Time for GO Synthesis	Temperature °C	Features	References
Sun	2013	Graphite	$KmnO_4$, H_2SO_4	1.5 h	Room temperature-90	High-yield and safe method	[52]
Eigler	2013	Graphite	$KmnO_4$, $NaNO_3$, H_2SO_4	16 h	10	High-quality GO produced	[53]
Chen	2015	Graphite	$KmnO_4$, H_2SO_4	<1 h	40–95	High-yield product	[54]
Panwar	2015	Graphite	H_2SO_4, H3PO_4, $KmnO_4$, HNO_3	3 h	50	Three component acids and high-yield product	[55]
Peng	2015	Graphite	K_2FeO_4, H_2SO_4	1 h	Room temperature	Results in a high-yield and eco-friendly method	[56]
Rosillo-Lopez	2016	Graphite	HNO_3	20 h	Room temperature	Nano-sized GO obtained	[57]
Yu	2016	Graphite	K_2FeO_4, $KmnO_4$ H_2SO_4, H_3BO_3 $(NH_4)_2S_2O_8$	5 h	<5–35–95	Low manganite impurities and high yield obtained	[58]
Dimiev	2016	Graphite	98% H_2SO_4, fuming H_2SO_4 [45]	3–4 h	[46] Room temperature	25 nm thick and ~100%conversion [47] rate	[59]
Pei	2018	Graphite foil	H_2SO_4	<5 min	Room temperature	High efficiency	[60]
Ranjan[45]	2018	Graphite	4 H_2SO_4, H_3PO_4, $KmnO_4$	<24 h 11	<RT-35–95 4 5	Cooled exothermal reaction to make the process safe	[61]

4. From ty of the). In his 60 °C for d mainly lenmaier s from 4 days to 2 days [46]. The nitric acid used in Brodie method was also replaced with sulfuric acid, which further reduced the liberation of toxic gases such as NO_2 or N_2O_4.

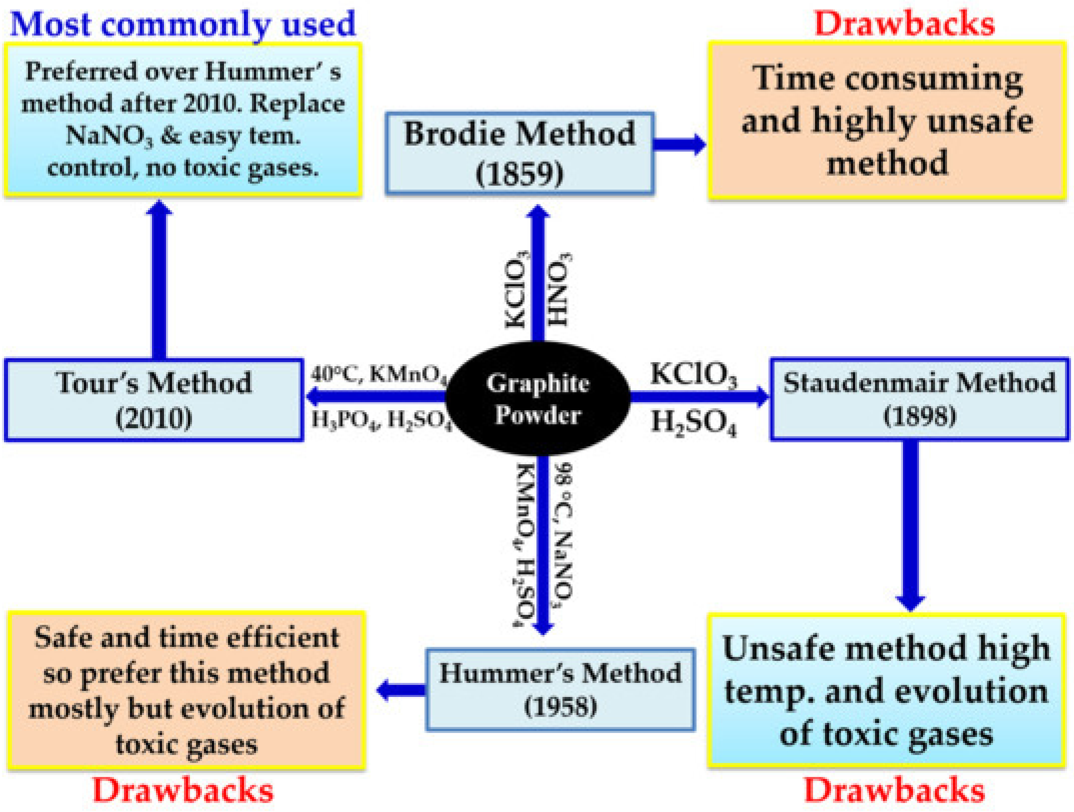

Figure 4. Schematic representation of the synthesis of graphene oxide with different methods.

In 1958, Hummer reduced the reaction time from 2 days to 12 h by using $KmnO_4$ as the oxidizing agent instead of $KclO_4$, followed by the addition of sodium nitrate, but the problem of toxic gases still remains a challenge [47]. Further, in 2010, at Rice University, Tour's group [51] replaced sodium nitrate with phosphoric acid and increased the amount of $KmnO_4$. This improvement made the process eco-friendly, as it completely stops the release of toxic gases such as NO_2, N_2O_4 or ClO_2, along with easy temperature control and better yield [51]. In addition to this, the GO suspension obtained was treated with hydrogen peroxide (H_2O_2) to eliminate all impurities due to permanganate and manganese dioxide.

Furthermore, the final color of the product GO varies from army green to light yellow, depending on the carbon-to-oxygen ratios [62], as depicted in **Table 2**.

Table 2. Effect of acid concentration, reaction temperature, reaction time, and the quantity of the oxidizing agent on the oxidation of graphene [62].

S. No.	Source of Carbon	H_2SO_4 (in mL)	Other Ingredients	Temp. (in °C)	Time (in h)	C:O	Colour of GO Obtained
1	Graphite	15.0	1.0 g $Na_2Cr_2O_7$	30	72	16:1	Black
2	Graphite	15.0	4.0 g $Na_2Cr_2O_7$	30	72	3.4:1	Black
3	Graphite	15.0	15.0 mL 70% HNO_3	30	24	--	Black

S. No.	Source of Carbon	H_2SO_4 (in mL)	Other Ingredients	Temp. (in °C)	Time (in h)	C:O	Colour of GO Obtained
			3.0 g $KmnO_4$,				
4	Graphite	20.0	11.0 g $KclO_3$, 10.0 mL 70% HNO_3	0–60	33	3.1:1	Midnight green
5	Graphite	30.0	3.0 g $KmnO_4$,1.0 g $NaNO_3$	30	2	3.0:1	Bluish green
6	Graphite	30.0	3.0 g $KmnO_4$,1.0 g $NaNO_3$	45	1	--	Green
7	Graphite	22.5	3.0 g $KmnO_4$,1.0 g $NaNO_3$	45	1	--	Brittle yellow
8	Graphite	22.5	3.0 g $KmnO_4$,0.5 g $NaNO_3$	45	1	--	Yellow
9	Graphite	22.5	3.0 g $KmnO_4$,0.5 g $NaNO_3$	45	0.5	2.3:1	Yellow
10	Graphite	22.5	3.0 g $KmnO_4$,0.5 g $NaNO_3$	35	0.5	2.05:1	Bright yellow
11	Graphite	22.5	3.0 g $KmnO_4$, 1.0 g fuming HNO_3	35	1	--	Bright yellow
12	Graphite	22.5	3.0 g $KmnO_4$, 1.0 g $BaNO_3$	45	2	--	Light green

years by the advancement of characterization techniques and technologies. The structural history of GO started in 1936, when Hofmann and Rudolf [63] proposed the first structure of GO in which epoxy groups were unsystematically spotted over the graphene sheets, and then in 1946, Ruess [64] restructured the Hofmann model by introducing hydroxyl moieties and the alternation of the basal plane structure from an sp^2 to an sp^3 hybridized carbon system.

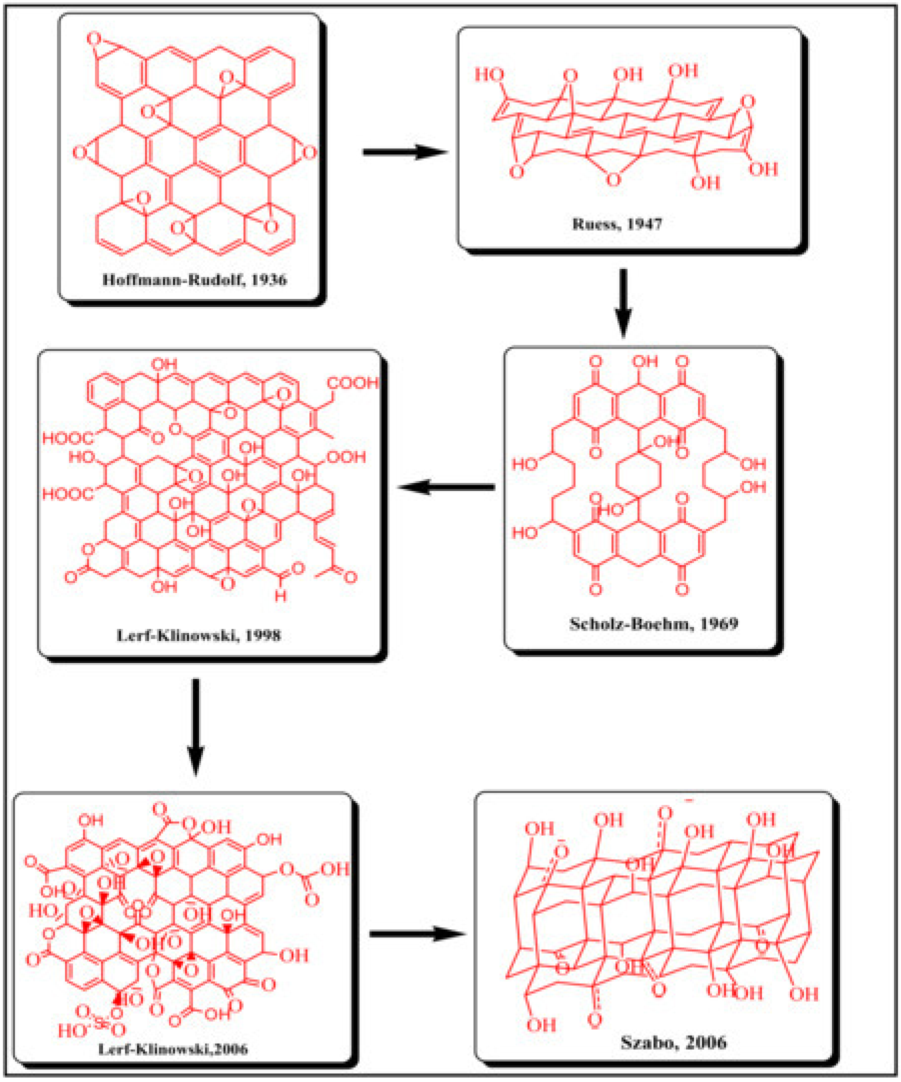

Figure 5. Schematic representation of the year-wise progress in proposed structures of graphene oxide [63][64][65][66][67][68][69][70].

Scholz and Boehm in 1969 [65] proposed a GO structure that was less ordered, having C=C and periodically cleaved C-C bonds within the channeled carbon layers labeled with carbonyl and hydroxyl groups. Further, in 1994, Nakajima and Matsuo [66] presented a graphite intercalation compound (GIC) to look like a lattice framework. Adding to the history, in 1998, Lerf and Klinowski et al. (L–K model) [67][68] proposed a uniform carbon lattice framework GO structure with randomly distributed benzene rings having attached epoxides, carboxyl, and hydroxyl groups. Thereafter, in 2006, Szabó and coworkers [69] put forward a carboxylic-acid-free model comprising two distinct domains: a trans-linked cyclohexyl species interspersed with tertiary alcohols, 1,3-ethers, and a keto/quinoidal species corrugated network. Even closer to the present time, in 2018, Liu et al. [70] experimentally noticed oxygen bonding and evidenced the C=O bonds on the edge and plane of GO, confirming parts of earlier proposed models, especially the L–K model.

Among the above-discussed models from 1936 to 2018, the L–K model has been accepted the most, due to good interpretability over the majority of experimental observations and the ease of further adaption and modification.

3.3. Characterization of GO

In order to authenticate the synthesis of GO and to analyze its chemical configuration, a range of characterization techniques have been employed by numerous research groups. For example, in order to achieve the information of size and surface morphology of graphene oxide, SEM, TEM, and AFM were used abroad [71][72][73][74][75]. With respect to the elemental analysis of graphene oxide, quantitative XPS, EDX, and inductively coupled plasma mass spectrometry (ICP-MS) were utilized generally [76][77][78][79][80][81][82][83][84]. Additionally, Raman spectra, XRD, and FTIR spectra are widely used to point out the graphene oxide chemical structure [84][85][86][87][88].

References

1. Xu, S.; Che, J.; An, Y.; Zhu, T.; Pang, L.; Liu, X.; Li, X.; Lv, M. Research and Preparation of Graphene Foam Based on Passive Ultra-Low Energy Consumption Building New Ultra-Thin External Wall Insulation Material. J. Nanoelectron. Optoelectron. 2021, 16, 1467–1474.
2. Banciu, C.A.; Nastase, F.; Istrate, A.-I.; Veca, L.M. 3D Graphene Foam by Chemical Vapor Deposition: Synthesis, Properties, and Energy-Related Applications. Molecules 2022, 27, 3634.
3. Umar, A.; Kumar, S.A.; Inbanathan, S.S.R.; Modarres, M.; Kumar, R.; Algadi, H.; Baskoutas, S. Enhanced sunlight-driven photocatalytic, supercapacitor and antibacterial applications based on graphene oxide and magnetite-graphene oxide nanocomposites. Ceram. Int. 2022, 48, 29349–29358.
4. Isaeva, V.I.; Vedenyapina, M.D.; Kurmysheva, A.Y.; Weichgrebe, D.; Nair, R.R.; Nguyen, N.P.T.; Kustov, L.M. Modern Carbon–Based Materials for Adsorptive Removal of Organic and Inorganic Pollutants from Water and Wastewater. Molecules 2021, 26, 6628.
5. Pelosato, R.; Bolognino, I.; Fontana, F.; Sora, I.N. Applications of Heterogeneous Photocatalysis to the Degradation of Oxytetracycline in Water: A Review. Molecules 2022, 27, 2743.
6. Huang, H.-H.; Joshi, R.K.; de Silva, K.K.H.; Badam, R.; Yoshimura, M.J. Fabrication of reduced graphene oxide membranes for water desalination. Membr. Sci. 2019, 572, 12.
7. Franco, P.; Cardea, S.; Tabernero, A.; De Marco, I. Porous Aerogels and Adsorption of Pollutants from Water and Air: A Review. Molecules 2021, 26, 4440.
8. Santoso, E.; Ediati, R.; Kusumawati, Y.; Bahruji, H.; Sulistiono, D.O.; Prasetyoko, D. Mater. Today Chem. 2020, 16, 100233.
9. Xiao, C.; Li, C.; Hu, J.; Zhu, L. The Application of Carbon Nanomaterials in Sensing, Imaging, Drug Delivery and Therapy for Gynecologic Cancers: An Overview. Molecules 2022, 27, 4465.
10. Guo, W.; Umar, A.; Alsaiari, M.A.; Wang, L.; Pei, M. Ultrasensitive and selective label-free aptasensor for the detection of penicillin based on nanoporousPtTi/graphene oxide-

Fe3O4/MWCNT-Fe3O4 nanocomposite. Microchem. J. 2020, 158, 105270.

11. Pandey, R.R.; Chusuei, C.C. Carbon Nanotubes, Graphene, and Carbon Dots as Electrochemical Biosensing Composites. Molecules 2021, 26, 6674.
12. Hu, H.; Liang, H.; Fan, J.; Guo, L.; Li, H.; de Rooij, N.F.; Umar, A.; Algarni, H.; Wang, Y.; Zhou, G. Assembling Hollow Cactus-Like ZnO Nanorods with Dipole-Modified Graphene Nanosheets for Practical Room-Temperature Formaldehyde Sensing. ACS Appl. Mater. Interfaces 2022, 14, 13186–13195.
13. Al Fatease, A.; Guo, W.; Umar, A.; Zhao, C.; Alhamhoom, Y.; Muhsinah, A.B.; Mahnashi, M.H.; Ansari, Z.A. A dual-mode electrochemical aptasensor for the detection of Mucin-1 based on AuNPs-magnetic graphene composite. Microchem. J. 2022, 180, 107559.
14. Treerattrakoon, K.; Jiemsakul, T.; Tansarawiput, C.; Pinpradup, P.; Iempridee, T.; Luksirikul, P.; Khoothiam, K.; Dharakul, T.; Japrung, D. Rolling circle amplification and graphene-based sensor-on-a-chip for sensitive detection of serum circulating miRNAs. Anal. Biochem. 2019, 577, 89.
15. Cosma, D.; Urda, A.; Radu, T.; Rosu, M.C.; Mihet, M.; Socaci, C. Evaluation of the Photocatalytic Properties of Copper Oxides/Graphene/TiO2 Nanoparticles Composites. Molecules 2022, 27, 5803.
16. Wang, H.-L.; Wang, Z.-G.; Liu, S.-L. Lipid Nanoparticles for mRNA Delivery to Enhance Cancer Immunotherapy. Molecules 2022, 27, 5607.
17. Gong, Y.; Li, H.; Pei, W.; Fan, J.; Umar, A.; Al-Assiri, M.S.; Wang, Y.; de Rooij, N.; Zhou, G. Assembly with copper(II) ions and D–π–A molecules on a graphene surface for ultra-fast acetic acid sensing at room temperature. RSC Adv. 2019, 9, 30432–30438.
18. Gong, P.; Zhang, L.; Yuan, X.; Liu, X.; Diao, X.; Zhao, Q.; Tian, Z.; Sun, J.; Liu, Z.; You, J. Multifunctional fluorescent PEGylated fluorinated graphene for targeted drug delivery: An experiment and DFT study. Dye. Pigment. 2019, 162, 573.
19. Xu, L.; Gai, L.; Yang, F.; Wu, S. Preparation of Nanographene and Its Effect on the Correlation Between N-Terminal Pro Brain-Type Natriuretic Peptide, Peripheral Blood Copeptin Level and Cardiac Function Grading of Patients with Heart Failure. Sci. Adv. Mater. 2021, 13, 1937–1944.
20. Patil, T.V.; Patel, D.K.; Dutta, S.D.; Ganguly, K.; Lim, K.-T. Graphene Oxide-Based Stimuli-Responsive Platforms for Biomedical Applications. Molecules 2021, 26, 2797.
21. Cirillo, G.; Pantuso, E.; Curcio, M.; Vittorio, O.; Leggio, A.; Iemma, F.; De Filpo, G.; Nicoletta, F.P. Alginate Bioconjugate and Graphene Oxide in Multifunctional Hydrogels for Versatile Biomedical Applications. Molecules 2021, 26, 1355.
22. Bahrami, S.; Solouk, A.; Mirzadeh, H.; Seifalian, A.M. Electroconductive polyurethane/graphene nanocomposite for biomedical applications. Compos. Part B Eng. 2019, 168, 421–431.

23. Wang, W.; Junior, J.R.P.; Nalesso, P.R.L.; Musson, D.; Cornish, J.; Mendonça, F.; Caetano, G.F.; Bártolo, P. Engineered 3D printed poly (ε-caprolactone)/graphene scaffolds for bone tissue engineering. Mater. Sci. Eng. C 2019, 100, 759.

24. Zhang, S.; Zhuang, Y.; Jin, S.; Wang, K. Preparation of Nanoscale Graphene Oxide and Its Application on β-Catenin Expression in Pediatric Osteosarcoma Cells Combine with Probiotics. Sci. Adv. Mater. 2021, 13, 2131–2137.

25. Bai, H.; Guo, H.; Wang, J.; Dong, Y.; Liu, B.; Xie, Z.; Guo, F.; Chen, D.; Zhang, R.; Zheng, Y. A room-temperature NO2 gas sensor based on CuO nanoflakes modified with rGO nanosheets. Sens. Actuators B Chem. 2021, 337, 129783.

26. Hussein-Al-Ali, S.H.; Hussein Alali, S.H.; Al-Ani, R.; Alkrad, J.A.; Abudoleh, S.M.; Abdallah Abualassal, Q.I.; Ayoub, R.; Hussein, M.Z.; Bullo, S.; Palanisamy, A. Betulinic Acid-Graphene Oxide Nanocomposites for Cancer Treatment. Sci. Adv. Mater. 2021, 13, 2138–2148.

27. Singh, J.; Goyat, R. Graphene oxide: Synthesis, characterization and its applications. Res. J. Chem. Environ. 2022, 26, 150–156.

28. Wan, X.; Huang, Y.; Chen, Y. Focusing on energy and optoelectronic applications: A journey for graphene and graphene oxide at large scale. Acc. Chem. Res. 2012, 45, 598–607.

29. Ramu, A.G.; Umar, A.; Ibrahim, A.A.; Algadi, H.; Ibrahim, Y.S.A.; Choi, Y.W.D. Synthesis of porous 2D layered nickel oxide-reduced graphene oxide (NiO-rGO) hybrid composite for the efficient electrochemical detection of epinephrine in biological fluid. Environ. Res. 2021, 200, 111366.

30. Santosh, K.; Sahoo, S.; Wang, N.; Huczko, A. Graphene research and their outputs: Status and prospect. J. Sci. Adv. Mater. Devices 2020, 5, 10–29, ISSN 2468-2179.

31. Aliofkhazraei, M.; Ali, N.; Milne, W.I.; Ozkan, C.S.; Mitura, S.; Gervasoni, J.L. Graphene Science Handbook: Fabrication Methods; CRC Press: Boca Raton, FL, USA, 2016; p. 587.

32. Dasari, B.L.; Nouri, J.M.; Brabazon, D.; Naher, S. Graphene and derivatives–Synthesis techniques, properties and their energy applications. Energy 2017, 140, 766.

33. Toh, S.Y.; Loh, K.S.; Kamarudin, S.K.; Daud, W.R.W. Graphene production via electrochemical reduction of graphene oxide: Synthesis and characterization. Chem. Eng. J. 2014, 251, 422.

34. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric field effect in atomically thin carbon films. Science 2004, 306, 666.

35. Ma, J.; Syed, J.A.; Su, D. Hybrid Supercapacitors Based on Self-Assembled Electrochemical Deposition of Reduced Graphene Oxide/Polypyrrole Composite Electrodes. J. Nanoelectron. Optoelectron. 2021, 16, 949–956.

36. Taghioskoui, M. Trends in graphene research. Mater. Today 2009, 12, 34–37.

37. Chen, Z.; Wang, J.; Cao, N.; Wang, Y.; Li, H.; de Rooij, N.F.; Umar, A.; Feng, Y.; French, P.J.; Zhou, G. Three-Dimensional Graphene-Based Foams with "Greater Electron Transferring Areas" Deriving High Gas Sensitivity. ACS Appl. Nano Mater. 2021, 4, 13234–13245.
38. Wang, C.; Peng, Q.; Wu, J.; He, X.; Tong, L.; Luo, Q.; Li, J.; Moody, S.; Liu, H.; Wang, R.; et al. Mechanical characteristics of individual multi-layer graphene-oxide sheets under direct tensile loading. Carbon 2014, 80, 279–289.
39. Pei, W.; Zhang, T.; Wang, Y.; Chen, Z.; Umar, A.; Li, H.; Guo, W. Enhancement of Charge Transfer between Graphene and Donor-π-Acceptor Molecule for Ultrahigh Sensing Performance. Nanoscale 2017, 9, 16273–16280.
40. Zhang, J.; Li, P.; Zhang, Z.; Wang, X.; Tang, J.; Liu, H.; Shao, Q.; Ding, T.; Umar, A.; Guo, Z. Solvent-free graphene liquids: Promising candidates for lubricants without the base oil. J. Colloid Interface Sci. 2019, 542, 159–167.
41. Chen, Z.; Wang, Y.; Shang, Y.; Umar, A.; Xie, P.; Qi, Q.; Zhou, G. One-Step Fabrication of Pyranine Modified- Reduced Graphene Oxide with Ultrafast and Ultrahigh Humidity Response. Sci. Rep. 2017, 7, 2713.
42. Erickson, K.; Erni, R.; Lee, Z.; Alem, N.; Gannett, W.; Zettl, A. Determination of the local chemical structure of graphene oxide and reduced graphene oxide. Adv. Mater. 2010, 22, 4467–4472.
43. Su, C.; Acik, M.; Takai, K.; Lu, J.; Hao, S.-J.; Zheng, Y.; Wu, P.; Bao, Q.; Enoki, T.; Chabal, Y.J. Probing the catalytic activity of porous graphene oxide and the origin of this behaviour. Nat. Comm. 2012, 3, 1298.
44. Schafhaeutl, C. Ueber die Verbindungen des Kohlenstoffes Mit Silicium, Eisen und Andern Metallen, Welche die Verschiedenen Arten von Gusseisen, Stahl und Schmiedeeisen Bilden. J. Prakt. Chem. 1840, 19, 159–174.
45. Brodie, B.C. On the atomic weight of graphite. Philos. Trans. R. Soc. London 1859, 149, 249–259.
46. Staudenmaier, L. Verfahrenzurdarstellung der graphits äure. Ber. Dtsch. Chem. Ges. 1898, 31, 1481–1487.
47. Hummers Jr, W.S.; Offeman, R.E. Preparation of graphitic oxide. J. Am. Chem. Soc. 1958, 80, 1339.
48. Fu, L.; Liu, H.B.; Zou, Y.; Li, B. Technology research on oxidative degree of graphite oxide prepared by Hummers method. Carbon 2005, 124, 10–14. (In Chinese)
49. Jeong, T.K.; Choi, M.K.; Sim, Y.; Lim, J.T.; Kim, G.S.; Seong, M.J.; Hyung, J.H.; Kim, K.S.; Umar, A.; Lee, S.K. Effect of graphene oxide ratio on the cell adhesion and growth behavior on a graphene oxide-coated silicon substrate. Sci. Rep. 2016, 6, 33835.

50. Su, C.Y.; Xu, Y.; Zhang, W.; Zhao, J.; Tang, X.; Tsai, C.H.; Li, L.J. Electrical and spectroscopic characterizations of ultra-large reduced graphene oxide monolayers. Chem. Mater. 2009, 21, 5674–5680.

51. Marcano, D.C.; Kosynkin, D.V.; Berlin, J.M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L.B.; Lu, W.; Tour, J.M. Improved synthesis of graphene oxide. ACS Nano 2010, 4, 4806–4814.

52. Sun, L.; Fugetsu, B. Mass production of graphene oxide from expanded graphite. Mater. Lett. 2013, 109, 207–210.

53. Eigler, S.; Enzelberger-Heim, M.; Grimm, S.; Hofmann, P.; Kroener, W.; Geworski, A.; Dotzer, C.; Röckert, M.; Xiao, J.; Papp, C.; et al. Wet chemical synthesis of graphene. Adv. Mater. 2013, 25, 3583–3587.

54. Chen, J.; Li, Y.; Huang, L.; Li, C.; Shi, G. High-yield preparation of graphene oxide from small graphite flakes via an improved Hummers method with a simple purification process. Carbon 2015, 81, 826–834.

55. Panwar, V.; Chattree, A.; Pal, K. A new facile route for synthesizing of graphene oxide using mixture of sulfuric–nitric–phosphoric acids as intercalating agent. Phys. E Low-Dimens. Syst. Nanostruct. 2015, 73, 235–241.

56. Peng, L.; Xu, Z.; Liu, Z.; Wei, Y.; Sun, H.; Li, Z.; Zhao, X.; Gao, C. An iron-based green approach to 1-hproduction of single-layer graphene oxide. Nat. Commun. 2015, 6, 5716.

57. Rosillo-Lopez, M.; Salzmann, C.G. A simple and mild chemical oxidation route to high-purity nano-graphene oxide. Carbon 2016, 106, 56–63.

58. Yu, H.; Zhang, B.; Bulin, C.; Li, R.; Xing, R. High-efficient synthesis of graphene oxide based on improved Hummers method. Sci. Rep. 2016, 6, 36143.

59. Dimiev, A.M.; Ceriotti, G.; Metzger, A.; Kim, N.D.; Tour, J.M. Chemical mass production of graphene nanoplatelets in ~100% yield. ACS Nano 2016, 10, 274–279.

60. Pei, S.; Wei, Q.; Huang, K.; Cheng, H.M.; Ren, W. Green synthesis of graphene oxide by seconds timescale water electrolytic oxidation. Nat. Commun. 2018, 9, 145.

61. Ranjan, P.; Agrawal, S.; Sinha, A.; Rajagopala Rao, T.; Balakrishnan, J.; Thakur, A.D. A low-costnon-explosive synthesis of graphene oxide for scalable applications. Sci. Rep. 2018, 8, 12007.

62. Hummers, J.W.S. Preparation of Graphitic Acid. U.S. Patent 2,798,878, 9 July 1957.

63. Hofmann, U.; Holst, R. Über die Säurenatur und die Methylierung von Graphitoxyd. Ber. Dtsch. Chem. Ges. A B 1939, 72, 754–771.

64. Ruess, G. Ber das Graphitoxyhydroxyd (Graphitoxyd). Mon. Fr. Chem. 1947, 76, 381–417.

65. Scholz, W.; Boehm, H.P. Untersuchungen am Graphitoxid. VI. Betrachtungen zur Struktur des Graphitoxids. Z. Anorg. Allg. Chem. 1969, 369, 327–340.

66. Nakajima, T.; Matsuo, Y. Formation process and structure of graphite oxide. Carbon 1994, 32, 469–475.

67. Lerf, A.; He, H.; Forster, M.; Klinowski, J. Structure of graphite oxide revisited II. J. Phys. Chem. B 1998, 102, 4477–4482.

68. Savazzi, F.; Risplendi, F.; Mallia, G.; Harrison, N.M.; Cicero, G. Unravelling some of the structure–property relationships in graphene oxide at low degree of oxidation. J. Phys. Chem. Lett. 2018, 9, 1746–1749.

69. Szabó, T.; Berkesi, O.; Forgó, P.; Josepovits, K.; Sanakis, Y.; Petridis, D.; Dékány, I. Evolution of surface functional groups in a series of progressively oxidized graphite oxides. Chem. Mater. 2006, 18, 2740–2749.

70. Liu, Z.; Nørgaard, K.; Overgaard, M.H.; Ceccato, M.; Mackenzie, D.M.A.; Stenger, N.; Stipp, S.L.S.; Hassenkam, T. Direct observation of oxygen configuration on individual graphene oxide sheets. Carbon 2018, 127, 141–148.

71. Chen, L.; Yu, H.; Zhong, J.; Song, L.; Wu, J.; Su, W. Graphene field emitters: A review of fabrication, characterization and properties. Mater. Sci. Eng. B 2017, 220, 44–58.

72. Chen, X.; Fan, K.; Liu, Y.; Li, Y.; Liu, X.; Feng, W.; Wang, X. Recent advances in fluorinated graphene from synthesis to applications: Critical review on functional chemistry and structure engineering. Adv. Mater. 2022, 34, 2101665.

73. Yin, P.T.; Shah, S.; Chhowalla, M.; Lee, K.B. Design, synthesis, and characterization of graphene–nanoparticle hybrid materials for bioapplications. Chem. Rev. 2015, 115, 2483–2531.

74. Steinert, B.W.; Dean, D.R. Magnetic field alignment and electrical properties of solution cast PET–carbon nanotube composite films. Polymer 2009, 50, 898–904.

75. Jia, R.; Xie, P.; Feng, Y.; Chen, Z.; Umar, A.; Wang, Y. Dipole-Modified Graphene with Ultrahigh Gas Sensibility. Appl. Surface Sci. 2018, 440, 409–414.

76. Sun, Z.; Yan, Z.; Yao, J.; Beitler, E.; Zhu, Y.; Tour, J.M. Growth of graphene from solid carbon sources. Nature 2010, 468, 549–552.

77. Shen, J.; Hu, Y.; Shi, M.; Lu, X.; Qin, C.; Li, C.; Ye, M. Fast and Facile Preparation of Graphene Oxide and Reduced Graphene Oxide Nanoplatelets. Chem. Mater. 2009, 21, 3514–3520.

78. Stankovich, S.; Dikin, D.A.; Piner, R.D.; Kohlhaas, K.A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S.B.T.; Ruoff, R.S. Synthesis of Graphene-Based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide. Carbon 2007, 45, 1558–1565.

79. Zhao, J.; Liu, L.; Li, F. Structural Characterization. In Graphene Oxide: Physics and Applications; Springer: Berlin/Heidelberg, Germany, 2015; pp. 15–29, Chapter 2.

80. Ganguly, A.; Sharma, S.; Papakonstantinou, P.; Hamilton, J. Probing the Thermal Deoxygenation of Graphene Oxide using High-Resolution in Situ X-ray-based Spectroscopies. J. Phys. Chem. C 2011, 115, 17009–17019.

81. Hintermueller, D.; Prakash, R. Comprehensive Characterization of Solution-Cast Pristine and Reduced Graphene Oxide Composite Polyvinylidene Fluoride Films for Sensory Applications. Polymers 2022, 14, 2546.

82. Ahmed, A.; Ibrahim, A.A.; Algadi, H.; Albargi, H.; Alsairi, M.A.; Wang, Y.; Akbar, S. Supramolecularly assembled isonicotinamide/ reduced graphene oxide nanocomposite for room-temperature NO2 gas sensor. Environ. Technol. Innov. 2022, 25, 102066.

83. Bagri, A.; Mattevi, C.; Acik, M.; Chabal, Y.J.; Chhowalla, M.; Shenoy, V.B. Structural Evolution during the Reduction of Chemically Derived Graphene Oxide. Nat. Chem. 2010, 2, 581–587.

84. Schniepp, H.C.; Li, J.-L.; McAllister, M.J.; Sai, H.; Herrera-Alonso, M.; Adamson, D.H.; Prud'homme, R.K.; Car, R.; Saville, D.A.; Aksay, I.A. Functionalized Single Graphene Sheets derived from Splitting Graphite Oxide. J. Phys. Chem. B 2006, 110, 8535–8539.

85. Shahriary, L.; Athawale, A.A. Graphene Oxide Synthesized by using Modified Hummers Approach. Int. J. Renew. Energy Environ. Eng. 2014, 2, 58–63.

86. Wei, N.; Peng, X.; Xu, Z. Understanding Water Permeation in Graphene Oxide Membranes. ACS Appl. Mater. Interfaces 2014, 6, 5877–5883.

87. Zhang, H.-B.; Zheng, W.G.; Yan, Q.; Yang, Y.; Wang, J.W.; Lu, Z.H.; Ji, G.Y.; Yu, Z.Z. Electrically conductive polyethylene terephthalate/graphene nanocomposites prepared by melt compounding. Polymer 2010, 51, 1191–1196.

88. Seekaew, Y.; Lokavee, S.; Phokharatkul, D.; Wisitsoraat, A.; Kerdcharoen, T.; Wongchoosuk, C. Low-cost and flexible printed graphene–PEDOT: PSS gas sensor for ammonia detection. Org. Electron. 2014, 15, 2971–2981.