RECYCLE AND SYNTHESIS GREEN REDUCE GRAPHENE OXIDE FROM SPENT BATTERY

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RECYCLE AND SYNTHESIS GREEN REDUCE GRAPHENE OXIDE

FROM SPENT BATTERY

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Recycle and Synthesis Green Reduce Graphene Oxide from Spent Battery**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF ABBREVIATIONS

CE	Counter Electrode
CV	Cyclic Voltammetry
DC	Direct Current
ECE	Electrochemical Exfoliation
EDLCs	Electrochemical Double Layer Capacitors
EDX	Energy Dispersive X-ray
FESEM	Field-Emission Scanning Electron Microscope
GCD	Galvanostatic Charge-Discharge
GO	Graphene Oxide
RE	Reference Electrode
rGO	reduced Graphene Oxide
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
USM	Universiti Sains Malaysia
WE	Working Electrode
XRD	X-ray Diffraction

LIST OF SYMBOLS

%	Percentage
°	Degree
Θ	Theta
Δ	Delta
π	pi

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ABSTRAK

Bahan karbon dua dimensi grafena dengan setebal satu atom mempunyai sifat unik yang merangkumi mobiliti pembawa elektron ultra tinggi, luas permukaan yang besar dan lain-lain. Oleh sebab sifatnya yang unik, grafena menjadi semakin popular dalam bidang aplikasi teknologi seperti superkapacitors, bateri, konduktor fleksibel dan lain-lain. Objektif kajian ini adalah untuk menyiasat voltan optimum pengelupasan elektrokimia untuk mensintesis kualiti terbaik grafena oksida tereduksi (rGO) daripada bateri terbuang. Pengenalan kepada grafena dan terbitannya serta konsep kaedah sintesis pengelupasan elektrokimia telah dibincangkan dalam projek ini. Pemeriksaan lanjut mengenai sifat fizikal seperti struktur, fasa, spesies kimia, morfologi dan sifat elektrokimianya yang dicirikan dengan menggunakan voltammetri kitaran (CV) dan nyahcas cas-galvanostatik (GCD) telah diterangkan dan dibentangkan. Pengelupasan elektrokimia telah dijalankan pada pelbagai voltan iaitu 4.0, 4.5, 5.0, 5.5 dan 6.0 V. Sampel 4.5 V telah dipilih untuk menjalankan rawatan pengurangan bagi ciri sifat elektrokimia selanjutnya. Analisis struktur mengesahkan bahawa kewujudan grafit dan grafena oksida. Morfologi dan analisis unsur mengesahkan bahawa lapisan lembaran grafene yang longgar, fleksibel dan berorientasikan bebas wujud dan kehadiran kumpulan berfungsi yang mengandungi oksigen. Ciri elektrokimia telah dilakukan untuk sampel 4.5 V selepas rawatan pengurangan. Dalam CV, rGO mempunyai prestasi terbaik pada kadar imbasan optimum (10 mV s^{-1}) di mana kapasitans spesifiknya ialah 80.40 Fg^{-1}. Dalam GCD, peningkatan dalam ketumpatan arus menghasilkan kapasitans spesifik terendah.

RECYCLE AND SYNTHESIS GREEN REDUCE GRAPHENE OXIDE FROM SPENT BATTERY

ABSTRACT

One atom thick, two-dimensional carbon materials graphene have unique properties which includes ultrahigh carrier mobility, large surface area and others. Due to its unique properties, it become a rising star in the field of technological application such as supercapacitors, batteries, flexible and transparent conductors, fuel cells, solar cells, hydrogen storage, electrochemical sensors, and others. The objective of this work is to investigate the optimum voltage of electrochemical exfoliation to synthesis the best quality of reduced graphene oxide (rGO) from spent battery. An introduction to graphene and its derivatives and the concept of electrochemical exfoliation synthesis method has been discussed in this work. Further examination on physical properties such as structure, phase, chemical species, morphologies and its electrochemical properties characterized by using cyclic voltammetry (CV) and galvanostatic charge- discharge (GCD) have been described and presented. Electrochemical exfoliations were carried out at various voltage which are 4.0, 4.5, 5.0, 5.5 and 6.0 V. 4.5 V sample was selected to performed reduction treatment for further electrochemical properties characterization. The structural analysis confirmed that the existence of graphite and graphene oxide. The morphology and elemental analysis confirmed that loose, flexible and freely oriented graphene sheet layers existed and presence of oxygen containing functional group. Electrochemical characterization was performed for 4.5 V sample after reduction treatment. In cyclic voltammetry (CV), the rGO have the best performance at the optimum scan rate (10 mV s^{-1}) where its specific capacitance is 80.40 Fg^{-1}. In galvanostatic charge-discharge (GCD), increase in current densities results in lowest specific capacitance.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The demand of battery has been sharply increased in recent years for electronic devices such as mobile phones, personal computers and others. However, these non-rechargeable batteries contained chemicals and toxic metals that will decomposing with time and harm to the environment during disposal. The toxicity of primary batteries, abundance and permanence in the environment will cause pollution to surrounding environment. Furthermore, disposal and dumping of these non-rechargeable batteries require large storage availability of landfills or dumpsites. Consequently, the expenses for disposal of spent batteries increases. With the rise of various new technologies, battery can be recycled and its carbon rod can be exfoliated to synthesis graphite and its derivatives. Graphite and its derivatives such as graphene play an essential role in various applications such as supercapacitors, conductors, solar cells and others.

An environmentally friendly and reliable energy storage solutions which is supercapacitor have become ubiquitous power sources for various portable devices used in a wide range of field. Supercapacitor is a device that store electrical energy at the interface between an electrolyte and a solid phase with high power density (10 $kWkg^{-1}$) and long-life cycle (over 10^6 cycles) (Yang et al., 2015). Supercapacitors are well known complements to lithium-ion batteries as power sources for transportation because it meets the high-power demands of vehicle acceleration. The application of supercapacitors includes electric drives, UPS, traction, electric vehicles, SSD's, LED flashlights, etc.

The discovery of graphene with its unique properties is paving the way towards the development of reliable methods for obtaining large quantities of this extraordinary material. Graphene is a two-dimensional single carbon atomic layer, made up of condensed six membered rings (Novoselov et al., 2004). The carbon atoms in graphene are sp^2 bonded and form a hexagonal two-dimensional (2D) lattice (Tkachev et al., 2011). Graphene exhibit high specific surface area, extraordinary strength, higher electron conductivity than graphite, low density, flexibility and ease of chemical processability make it ideal for the application of supercapacitor (Bonaccorso et al., 2015; Raccichini et al., 2015; Simon and Gogotsi, 2013). However, it is difficult to synthesize pristine graphene. Graphene will oxidize to become graphene oxide (GO). Some researchers (Gómez-Navarro et al., 2007; Kudin et al., 2008; Paredes et al., 2009) found that the surface of GO is highly defective due to the oxidation. GO consists of functional groups such as hydroxyl, carboxylic, phenolic and epoxides, *d* spacing increases and the hybridization of the oxidized carbon atoms change from planar sp^2 to tetrahedral sp^3 (Roy et al., 2016). Therefore, the conductivity of GO is poor compared to pristine graphene. However, the reduction of GO preserved the sp^2 hybridized structure and increase its conductivity by up to 4 orders of magnitude (Gilje et al., 2007).

Generally, there are a few methods to synthesis graphene and rGO which includes mechanical exfoliation (Novoselov et al., 2004; Wehling et al., 2008), epitaxial growth (Berger et al., 2006; Land et al., 1992), chemical vapor deposition (CVD) (Eizenberg and Blakely, 1979; Kim et al., 2009), longitudinal “unzipping” of carbon nanotubes (CNTs) (Jiao et al., 2010; Sinitskii et al., 2010) and electrochemical exfoliation (ECE) (Bandi et al., 2019; Tiwari et al., 2017).

However, methods that can be used to exfoliate graphene, GO and rGO from spent batteries consists only plasma exfoliation, liquid phase exfoliation, ECE and Hummer's method. Among all these methods, ECE is the most effective methods to synthesis rGO as it can produce higher yield of rGO, highly processable and cost effective (Tiwari et al., 2017). ECE is a promising bulk method to synthesize graphene from graphite. In this method, an applied voltage drives ionic species to intercalate into graphite where they form gaseous species that expand and exfoliate individual graphene sheets (Achee et al., 2018).

1.2 Problem Statement

Recently, the main challenge of supercapacitor technology is the inability to prove supercapacitor can meet the performance of batteries while cost cutting simultaneously (Béguin et al., 2014; Miller, 2012; Simon and Gogotsi, 2013). Synthesis of new carbon electrode materials are urgently required to enhance the electrochemical performance of supercapacitors (Deschamps et al., 2013; Simon and Gogotsi, 2013; Zhong et al., 2015). At the same time, the disposal of waste battery dramatically increased in recent years cause severe impact to environment due to its toxicity. Consequently, utilization of recycle material, graphene, GO and rGO synthesized from spent batteries provides opportunity to preserve our environment by reducing waste and reuse graphene in other application such as supercapacitor. Graphene has the potential to be used in super capacitor due to its nanostructures and remarkable properties but some properties is still limited. There are various methods that can be used to exfoliate graphene, GO and rGO from spent batteries consists of plasma exfoliation, liquid phase exfoliation, ECE and

Hummer's method. Bandi et al. (2019) has reported that ECE is the most effective methods and able to produce higher yield of rGO, highly processable and cost effective (Bandi et al., 2019). Type of electrolyte, concentration of electrolyte and voltage is the crucial parameters that will affect the quality of rGO synthesized from spent battery. Limited research on ECE voltage parameter with sulphuric acid as electrolyte was done to synthesis rGO from spent battery. Therefore, it is necessary to determine the optimum voltage of electrochemical exfoliation to synthesis the best quality of (rGO) and its electrochemical performance as supercapacitor electrode.

1.3 Research Objectives

The objectives of this study are:

i. To determine the optimum voltage to synthesis the best quality few layered reduced graphene oxide from spent battery via electrochemical exfoliation.
ii. To characterize the chemical structure, surface morphology and internal structure of reduced graphene oxide.
iii. To determine the applicability and evaluate the electrochemical performance of reduced graphene oxide as supercapacitor electrode.

1.4 Thesis Outline

For this research, reduced graphene oxide is synthesized from discharged battery via electrochemical exfoliation at different voltage for supercapacitor application. In this work, there are five chapters to be discussed. For Chapter 1, a brief introduction on supercapacitor, recycle of battery and graphene is presented.

For Chapter 2, a literature review on graphene, GO, rGO, synthesis method, reduction treatment, characterization techniques and supercapacitors are discussed. For Chapter 3, the overall experimental methods and procedures and characterization techniques are presented together with the materials and apparatus used in this research.

In Chapter 4, the optimum voltage to synthesize rGO from spent battery is discussed and the structure, morphology, internal structure analysis is presented. For Chapter 5, the conclusion is presented and future recommendations are suggested.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter briefly discussed fundamental aspects of regarding graphene, graphene oxide, reduced graphene oxide and supercapacitor. A brief introduction to recycle battery, reduced graphene oxide, electrochemical exfoliation and supercapacitor was presented in the earlier topic of this chapter. In this work, several characterization techniques is studied which includes structure analysis, morphology analysis, chemical species analysis and electrochemical characterization for supercapacitors.

2.1.1 Graphene, graphene oxide, reduced graphene oxide

Graphene is a two-dimensional single carbon atomic layer, made up of condensed six membered rings (Novoselov et al., 2004). Graphene oxide (GO) is a single-atomic layered material comprising carbon, hydrogen, and oxygen molecules produced by the oxidation of graphite (Stergiou et al., 2014). Reduced graphene oxide (rGO) is an alternative form of GO which has been processed by various methods which include chemical, thermal, etc. in order to minimize the amount of oxygen as the oxygen content makes GO more unstable (Papageorgiou et al., 2015).

Graphene exhibit high specific surface area, extraordinary strength, higher electron conductivity than graphite, low density, flexibility and ease of chemical processability make it ideal for the application of supercapacitor (Bonaccorso et al., 2015; Raccichini et al., 2015; Simon and Gogotsi, 2013). Graphene has high specific surface

area and low density thus it favors the interaction of electrons and ions (Velasco et al., 2021). Besides, graphene has higher electrical conductivity with high mobilities that enable fast transfer of electrons and ions through various device interfaces and eliminate the use of binder and additives as it can act as an active material and current collector simultaneously (Morozov et al., 2008; Velasco et al., 2021). Furthermore, graphene has extraordinary strength with high Young's Modulus makes it able to maintain a high capacitance resistance (Velasco et al., 2021). Due to all these reasons, graphene has high potential to be used as supercapacitor electrode. Meanwhile, the capacitive performance of graphene-based electrochemical double-layer capacitor (EDLCs) electrode is affected by specific surface area, pore size distribution, interlayer distance, heteroatom doping, surface functionalities and conductivity (Bonaccorso et al., 2015; Gu et al., 2015; Raccichini et al., 2015). Some researchers (Gómez-Navarro et al., 2007; Kudin et al., 2008; Paredes et al., 2009) found that the surface of GO is highly defective due to the oxidation. GO consists of functional groups such as hydroxyl, carboxylic, phenolic and epoxides, *d* spacing increases and the hybridization of the oxidized carbon atoms change from planar sp^2 to tetrahedral sp^3 (Roy et al., 2016). Therefore, the conductivity of GO is poor compared to pristine graphene. However, the reduction of GO preserved the sp^2 hybridized structure and increase its conductivity by up to 4 orders of magnitude (Gilje et al., 2007).

The conductivities of rGO still lack behind the pristine graphene due to the presence of residual functional group remaining after reduction. Thus, reducing GO to produce rGO is a very crucial process as it will affect the quality of the rGO produced and how close rGO like the pristine graphene. Since the specific surface area plays an important role in ion transport and charge storage, agglomeration of rGO synthesized from spent battery must be eliminated to produce porous graphene for application of

supercapacitor electrode. Graphene has high potential to be used in supercapacitor electrode due to its high specific surface area, extraordinary strength, higher electron conductivity than graphite, low density, flexibility and ease of chemical processability.

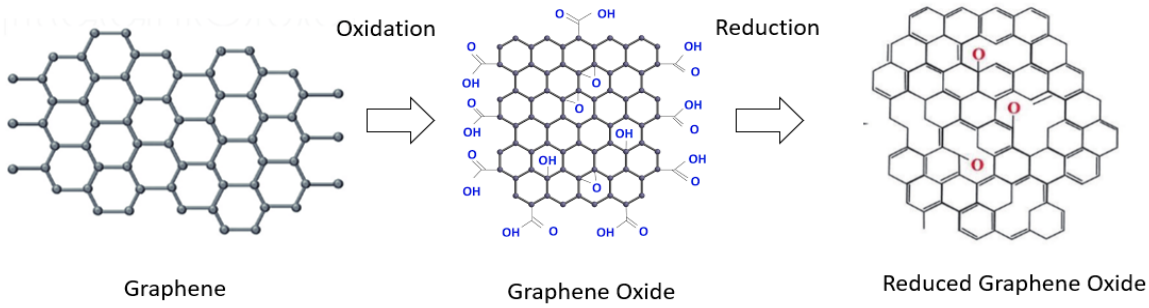

Figure 2. 1: (a) Graphene (Rudrapati, 2020), (b) Graphene oxide (GO) (Kausar, 2021), (c) Reduced graphene oxide (rGO) (Obodo et al., 2019).

2.1.2 Electrochemical Exfoliation Synthesis Method

Generally, there are a few methods to synthesis graphene and reduced graphene oxide which includes mechanical exfoliation (Novoselov et al., 2004; Wehling et al., 2008), epitaxial growth (Berger et al., 2006; Land et al., 1992), chemical vapor deposition (CVD) (Eizenberg and Blakely, 1979; Kim et al., 2009), longitudinal “unzipping” of carbon nanotubes (CNTs) (Jiao et al., 2010; Sinitskii et al., 2010) and electrochemical exfoliation (Bandi et al., 2019; Tiwari et al., 2017). However, methods that can be used to exfoliate graphene, GO and rGO from spent batteries consists only plasma exfoliation, liquid phase exfoliation, electrochemical exfoliation and Hummer’s method.

Among all these methods, electrochemical exfoliation is the most effective methods to synthesis rGO as it can produce higher yield of rGO, highly processable and cost effective (Tiwari et al., 2017). Electrochemical exfoliation is a effective bulk method

to synthesize graphene from graphite. In this method, an applied voltage drives ionic species to intercalate into graphite where they form gaseous species that expand and exfoliate individual graphene sheets (Achee et al., 2018). As voltage is supplied, electrons are flow continuously between anode and cathode graphite rods. Intercalation of negatively charged ion species in the graphite occurs that causes exfoliation of graphene sheets from anode electrode (Yu et al., 2015).

Figure 2.2 shows the schematic diagram of ECE of graphite to synthesis graphene and its derivatives (Yu et al., 2015). When voltage is applied, water will undergo reduction at cathode site which causes generation of hydroxyl ions (OH-) and thus hydrogen gas is evolved (Lu et al., 2009; Parvez et al., 2014). Meanwhile, OH- ions attacks on the graphite rod and cause oxidation at the site (Parvez et al., 2014). Consequently, depolarization and expansion of graphite occurs and facilitates the entrapment of negative ions such as SO_4^{2-} and HSO_4- (Bandi et al., 2019). These negative ions will react with water molecules. Reduction of negative species ions and oxidation of water molecules will bring to formation of functional groups on graphite and generation of gaseous species SO_2, O_2 and others (Beck et al., 1995; Beck et al., 1981). The evolution of gaseous species exerts force to break apart the weakly bonded graphene sheets from graphite rod (Bandi et al., 2019).

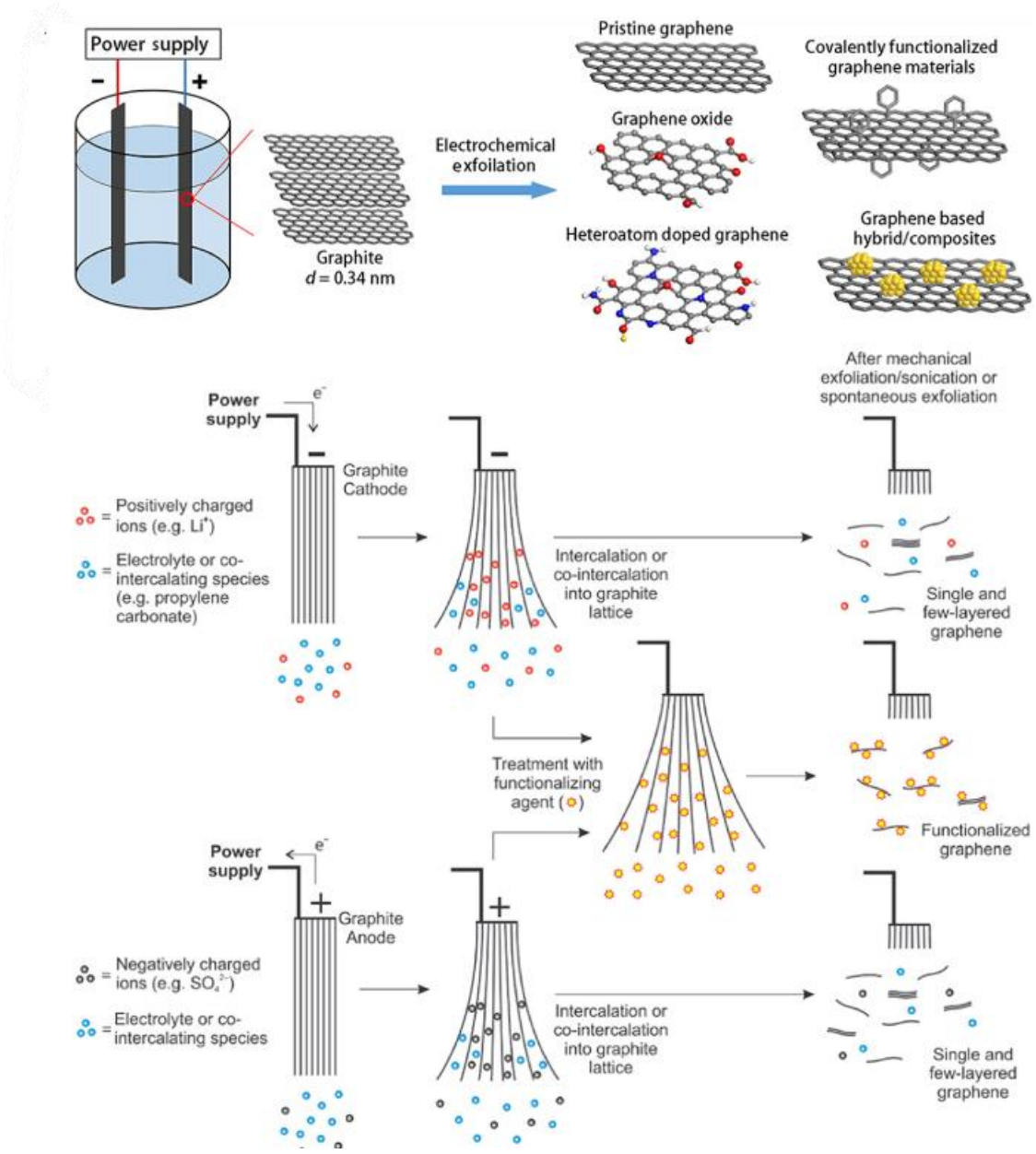

Figure 2. 2: Schematic diagram of ECE of graphite to synthesis graphene and its derivatives (Yu et al., 2015).

Generally, the electrochemical exfoliation was performed at room temperature. First, the graphite rod was extracted out from spent battery and was rinsed with extremely diluted HCl. The graphite rod was then immersed in boiled distilled water remove any

remaining impurities. After that, one graphite rod acts as cathode and another one graphite rod acts as anode (Tiwari et al., 2017).

The electrodes were separated by separator. Both were immersed in H_2SO_4 solutions. Then, ECE was performed by connecting to DC output current at different voltage. Next, big graphite particles are separated by centrifugation. Then the suspension was filtered by a filter paper to collect GO and the others was filtered away. The remaining powder was performed purification process by rinsing with distilled water and ethanol. The GO powder obtained was oven dried overnight at 60° C and weighed. Several researchers found that 4.5 V is the optimum voltage which produced acceptable quality of GO (Tiwari et al., 2017).

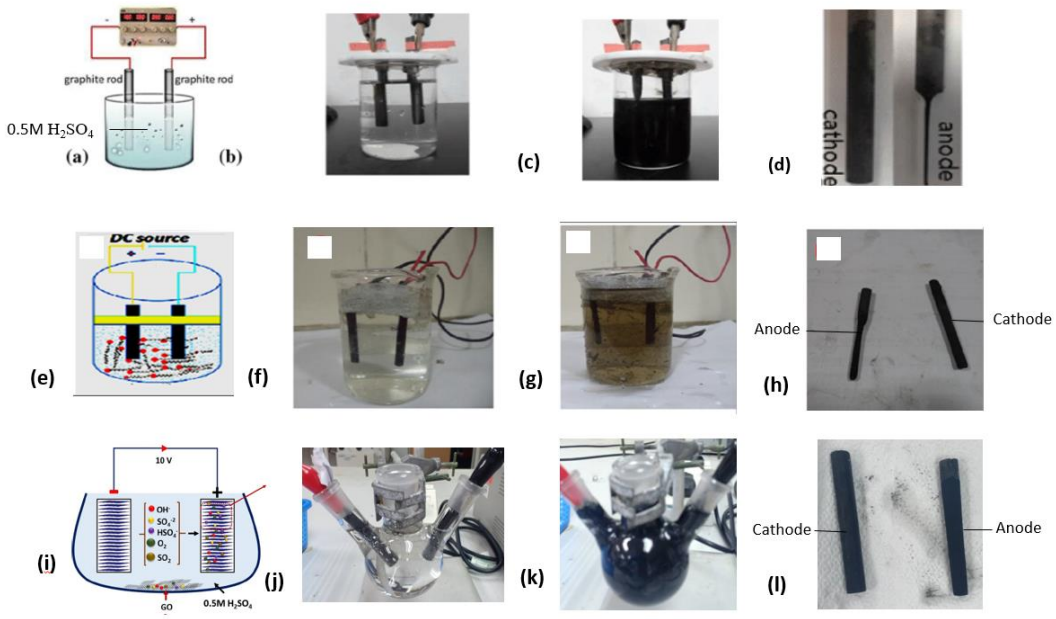

Figure 2. 3: (a, e and i) Setup of ECE for graphite rods (Li et al., 2016, Bandi et al., 2019, Tiwari et al., 2017), (b, f and j) Images of color of electrolyte before ECE (Li et al., 2016, Tiwari et al., 2017), (c, g and k) Images of color of electrolyte after ECE (Li et al., 2016, Tiwari et al., 2017) and (d, h and l) Images of anode and cathode graphite rods after ECE (Li et al., 2016, Tiwari et al., 2017).

2.1.3 Reduction Treatment

Generally, electrochemical exfoliation is the intercalation of negatively charged ion species into the anode and causes chemically derived graphene exfoliated from the anode carbon electrode (Pei and Cheng, 2012; Yu et al., 2015). After GO synthesized from electrochemical exfoliation, reduction treatment has to be carried out in order to get reduced graphene oxide. The main difference between reduced graphene oxide and graphene oxide is the percentage of oxygen functional group over the surface. The thermal reduction should be performed to eliminate the oxygen and other functional group for better electrical conductivity. The thermal reduction treatment can be done by continuous purging of argon in a tubular furnace with graphene oxide placed in the crucible, The reduction treatment will decompose the oxygen containing functional group and convert GO to rGO.

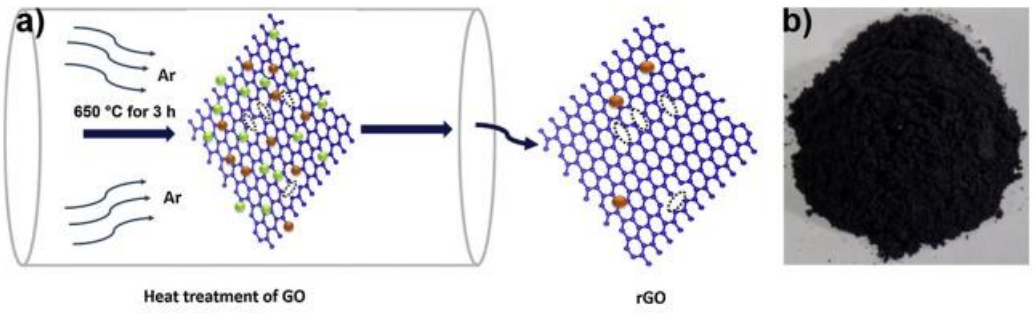

Figure 2. 4: Reduction treatment of GO to rGO (Bandi et al., 2019)

2.2 Physical Characterization of reduced graphene oxide

Graphene, GO and rGO synthesized from spent battery are interesting carbon nanomaterials and therefore its properties such as surface morphology, chemical structure, textural, surface chemistry and other physiochemical attributes have been examined by using different characterization techniques (Lee et al., 2019). There are various methods to characterize graphene and its derivatives which consists of X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Raman spectroscopy. Each methods have its own advantages and limitations.

2.2.1 Structural Analysis

XRD is a nondestructive technique that used to characterize the crystalline materials. The parameters or properties that can be measured are atomic arrangement, crystallinity, and crystal size. The orderly and continuous repeating arrangement in the atomic planes is used to classify a crystalline material (Lee et al., 2019). When X-ray are emitted on a crystalline material, a unique diffraction pattern will form.

Figure 2.5 (a) shows the diffraction pattern of graphite and products obtained at 3 V, 4.5 V and 6 V. Graphite displays a (002) narrow peak at 26.6° with 0.34 nm interlayer spacing. At 3 V electrochemical exfoliation, the peak at 26.8° become wider. As the voltage increases from 3 V to 4.5 V, the peak becomes broader. The disappearance of the sharp peak is due to the exfoliation of layered structured of graphite. The results depict no characteristic peak of graphene derivatives which means that is no oxidation reactions (Tiwari et al., 2017). The sheets are completely separated from each other in the form of few layered graphene when there is absence of any peak at low 2Θ value (Hulicova et al.,

2005, Ohta et al., 2006). At 6 V electrochemical exfoliation, there is a peak at 26° due to fast electrochemical exfoliation which causes lack of time for intercalation of surface molecule inside the graphite and thus multiple stacked graphitic layers exfoliated from the electrode (Tiwari et al., 2017).

Figure 2.5 (b) displays the characteristics peak of GO and rGO. GO shows a (001) narrow peak at 9° with 9.98 Å. After the reduction of GO, (001) plane reflection disappears and (002) planes is shown at 24°. The rGO band is not clear which means that the carbons planes were poorly packaged. The d-spacing for rGO is 3.6 Å. The increase in interspacing layer of GO due to the introduction of oxygen containing functional groups like epoxy, carboxyl and hydroxyl (Jagiełło et al., 2020; Roy et al., 2016).

Figure 2.5 (c) displays the XRD spectra for GO and rGO. GO shows a (001) narrow peak at with 1.45 nm. Meanwhile, rGO shows peak at around 24° with 0.379 nm interlayer spacing. The peak of rGO at 19.6° is broader due to incomplete oxidation. This interlayer spacing of GO is higher due to the presence of oxygen containing functional groups like epoxy, carboxyl and hydroxyl while the interlayer spacing of rGO is smaller due to the removal of oxygen containing functional groups (Achaby et al., 2012; Low et al., 2015).

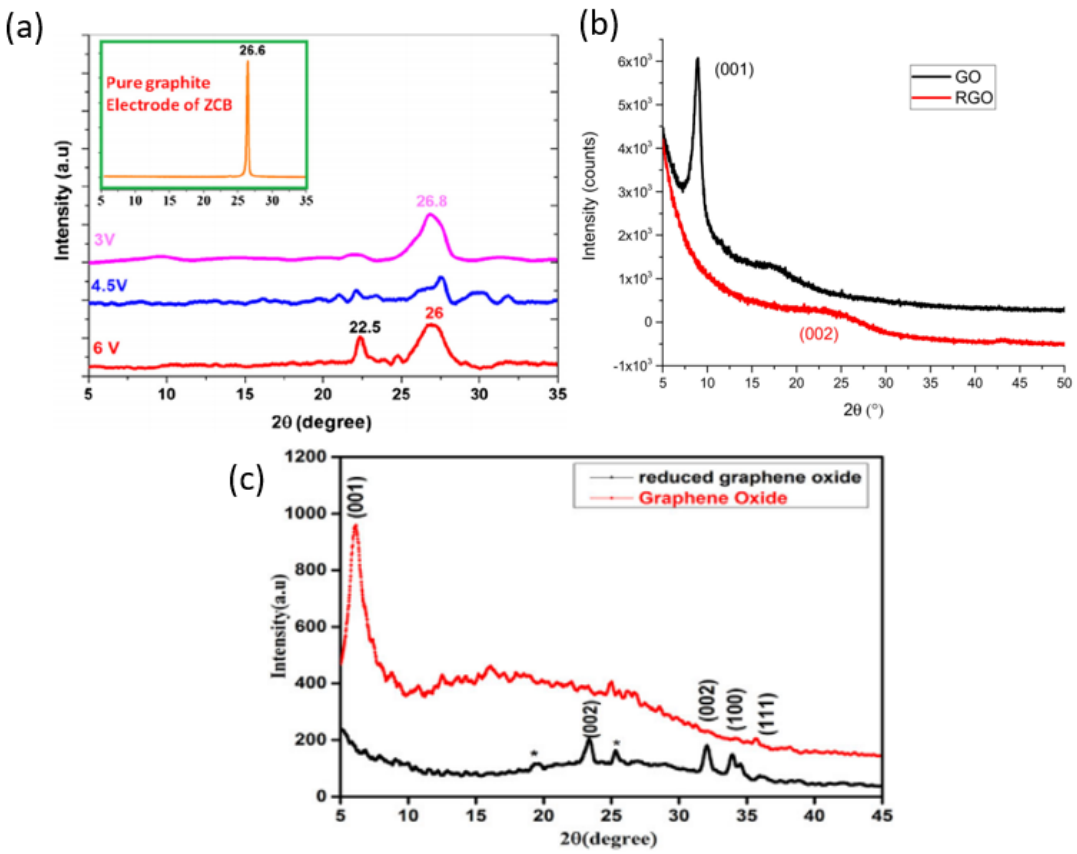

Figure 2. 5: (a) XRD pattern of spent battery materials obtained at different voltage (Tiwari et al., 2017), (b) XRD spectra of GO and rGO (Jagiełło et al., 2020), (c) XRD spectra of GO and rGO samples (Sharma et al., 2017).

XRD can be used to characterize crystalline materials such as graphene of spent batteries. Based on the XRD results, the interlayer spacing of GO is higher than rGO due to the presence of oxygen containing functional groups like epoxy, carboxyl and hydroxyl while the interlayer spacing of rGO is smaller due to the removal of oxygen containing functional groups. Furthermore, too low or too high voltage during electrochemical exfoliation will cause oxidation of graphene. The best quality rGO obtained is 4.5V.

2.2.2 Morphological and Elemental Composition Analysis

SEM is a technique that can be used to determine the surface morphology of graphene synthesized from spent battery (Lee et al., 2019). In this technique, a source of high energy electrons, condenser system and probe lens are used to focus the electron beam into fine probe that impinges on specimen. Image is obtained by scanning the electron probe over surface and to collect image signal. Backscattered electrons image shows phases existed in the sample while secondary electrons show the topography information of the surface. The graphene sample is placed on a silicon wafer for scanning and the number of layers of graphene can be obtained according to the color depth (Dong and Chen, 2010).

Figure 2.6 shows the SEM micrographs of graphite (a and b), GO (d and e) and rGO (g and h). Graphite powders displays tightly stacked graphite layers micrograph (Bandi et al., 2019; Tiwari et al., 2017). The micrograph of GO illustrates large flexible, freely oriented and loosely stacked graphite sheets exfoliated from graphite. Meanwhile, the micrograph of GO and rGO displays similar morphology features. However, the percentage of oxygen containing functional groups is varying. Based on the EDS data, graphite rod showed 6.1% of oxygen presence while GO showed 22.8% of oxygen presence (Bandi et al., 2019). The difference of oxygen percentage can be obtained by the elemental analysis as shown in Figure 2.6. The increase in percentage of oxygen containing functional groups in GO is due to intercalation of oxygen containing groups in the graphitic layers and exfoliation of graphite flakes (Bandi et al., 2019; Roy et al., 2016). Whereas, rGO showed 13.6% oxygen containing group due to the removal of oxygen containing functional groups from GO during reduction heat treatment (Bandi et al., 2019).

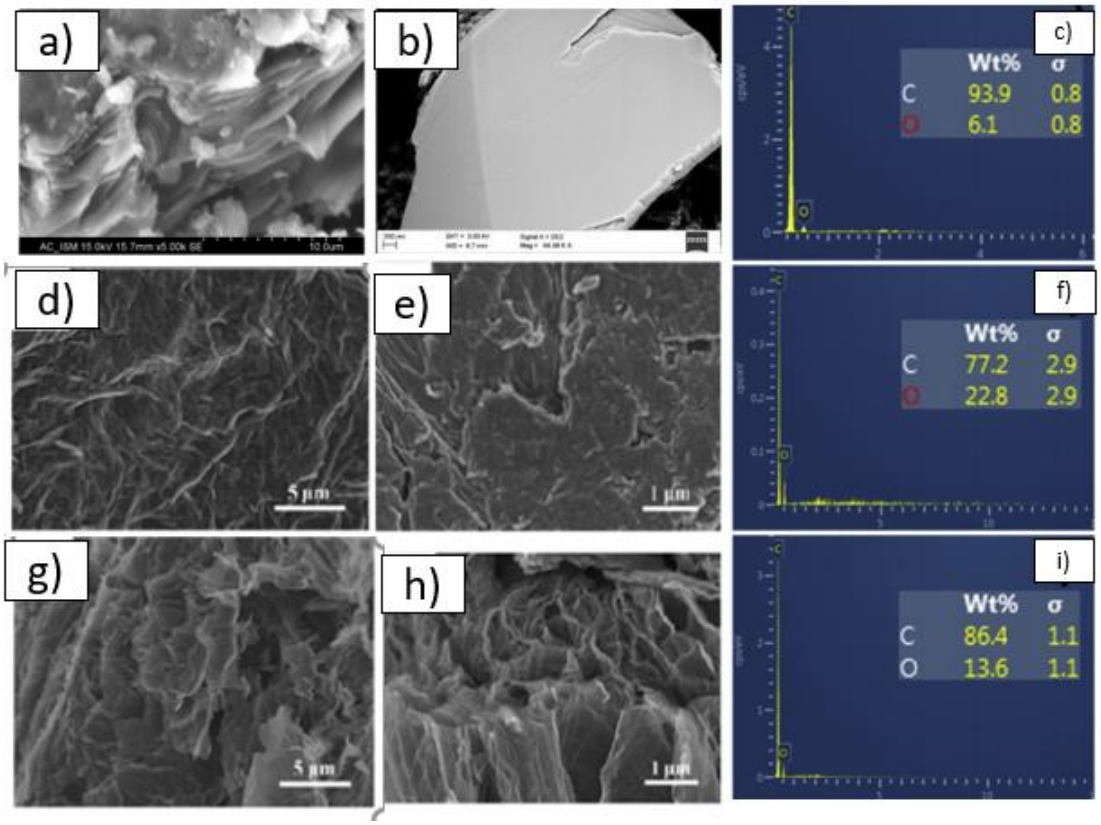

Figure 2. 6: The SEM micrographs of graphite rod (a and b) (Tiwari et al., 2017), GO (d and e) (Gong et al., 2015), rGO (g and h) (Gong et al., 2015) and their respective EDS spectrum (c, f and i) (Bandi et al., 2019).

SEM can be used to characterize graphene and its derivatives by determining the morphology of the graphene and its derivatives obtained from spent batteries. Graphite powders displays tightly stacked graphite layers micrograph. Meanwhile, the micrograph of GO and rGO displays large flexible, freely oriented and loosely stacked graphite sheets morphology features. However, the percentage of oxygen functional groups of GO is higher than rGO due to intercalation of oxygen containing groups in the graphitic layers and exfoliation of graphite flakes.

2.2.3 Chemical Species Analysis

Raman spectroscopy is an optical, vibrational spectroscopic technique that provides detailed information about molecular composition and molecular structure. Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified. There are few characteristics peaks generally described the carbon intercalated compounds in Raman spectroscopic data which includes D band (1350 cm^{-1}), G band (1580 cm^{-1}) and 2D or G ′ band (2700 cm^{-1}) (Ferrari and Robertson, 2000). D band indicates there is a lot of defects in the materials (Ferrari and Basko, 2013). G peak represents the planar configuration sp2 bonded carbon that constitutes graphene (Ferrari and Robertson, 2000). G peak is a characteristic peak in graphite compounds (Ferrari and Basko, 2013). Meanwhile, 2D band is an overtone of the D band. The intensity of peak (I_D) increases with the increase in defects such as presence of oxygen containing functional groups (Bandi et al., 2019). The intensity of G peak (I_G) is estimated to be constant with change in density of defects (Ferrari and Basko, 2013).

Figure 2.7 (a) illustrates the spectroscopic data of graphite, GO and rGO. The G peak of graphite was observed at 1569.4 cm^{-1}. Meanwhile, the G peak was broadened and observed at 1572.82 cm^{-1} for GO. It can be observed that D peak became spectacular at 1345.15 cm^{-1} due to the size reduction of sp2 in-plane domains during the heavy oxidation in exfoliation [9]. The D and G peaks were observed at 1338.96 cm^{-1} and 1571.33 cm^{-1} for rGO. The I_D and I_G calculated for GO and rGO were 0.95 and 1.06. The increase in this value for rGO indicates the reduction of GO to rGO [32].

Figure 2.7 (b) depicts the Raman spectra of graphene obtained from electrochemically exfoliating graphite rods in 0.5 M of PSS concentration at an applied voltage of 8 V and 5 V. It is obvious to see that there are two prominent peaks found in

both samples at around 1357 cm^{-1} (D peak) and 1594 cm^{-1} (G peak). In addition, there is a weak peak at 2694 cm^{-1} which is the 2D peak. The low intensity of 2D peak indicates more defects and disorders in the graphene structure (Bong et al., 2018). The I_D/I_G of Graphene 0.5/8 is 0.95 while the I_D/I_G for Graphene 0.5/5 is 0.86. Lower defect density for Graphene 0.5/5. This is because higher applied voltage during electrochemical exfoliation will accelerate the intercalation and oxidation reactions and thus higher defect of graphene produced (Yang et al., 2013).

Figure 2.7 (c) shows the Raman spectra of products obtained at 3, 4.5 and 6 V electrochemical exfoliation. The G band at 1580 cm^{-1} and 2D band 2710 cm^{-1} which is the typical feature of graphene appears for all three samples exfoliated at different voltages. Meanwhile, 4.5 V and 6 V graphene depicts prominent D band peak at 1350 cm^{-1} but the D band is very weak. Besides, 3 V and 6 V graphene D peak becomes prominent along with decease in intensity of 2D which is an indication of slight oxidation on graphitic layers (Vlassiouk et al., 2011). Therefore, too low and too high exfoliation voltage is not suitable for ECE of graphite.

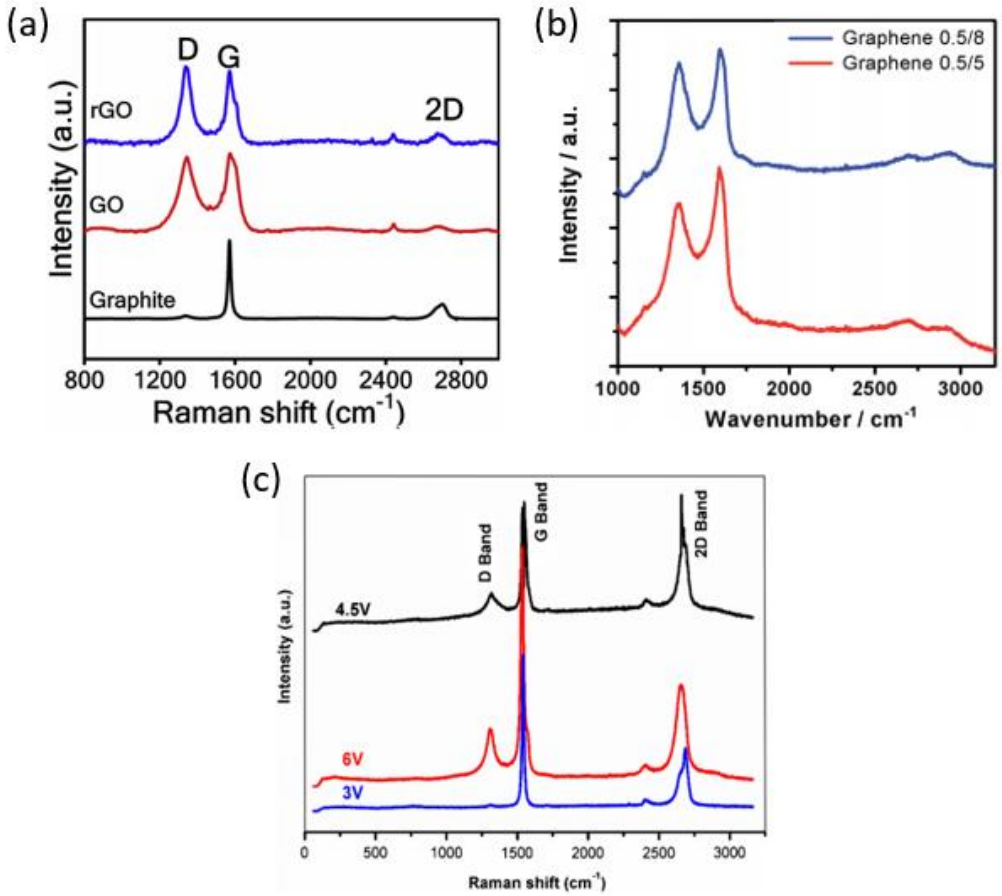

Figure 2. 7: (a) Raman spectra of G, GO and rGO (Bandi et al., 2019), (b) Raman spectra of graphene obtained by electrochemically exfoliating battery waste-derived graphite rods in 0.5 M of PSS concentration at an applied voltage of 8 V (Graphene 0.5/8, blue line) and 5 V (Graphene 0.5/5, red line) (Prakoso et al., 2020), (c) Raman spectra of products obtained at 3, 4.5 and 6 V electrochemical exfoliation (Tiwari et al., 2017).

Raman spectroscopy provides detailed information about molecular composition and molecular structure. Higher I_D/I_G indicates the samples contains higher defect density. GO has higher defect density compared to rGO.

2.2.4 Internal Structure Analysis

TEM is an excellent technique that is widely used to determine and examine the internal structure of materials at nanoscale. TEM has higher resolution compared to FESEM. When an electron beam is pass through a material specimen, TEM micrographs are obtained by the interaction of with the specimen. Thus, TEM micrographs able to reveal the internal structure of nanomaterials in detail. The sample is transparent to allow the electron beam to pass through it.

Figure 2.8 (a and b) displays the TEM images of rGO which revealed the internal structure of rGO. It can be observed that the edge of rGO layers is wrinkled and crumpled. Based on figure 2.8 (b), the darker region indicates multilayered rGO due to aggregation of rGO layer (Coroş et al., 2016). Aggregation behaviour occurs might be due to strong π-π interaction between rGO layer (Wang et al., 2020). Meanwhile, the transparent region indicates one-layer thick rGO layer.

Figure 2.8 (c) illustrates the TEM images of GO which shows the internal structure characteristics of GO. Wavy silk veil structure is observed for GO as shown in figure 2.8 (c). Meanwhile, the transparent region indicates wrinkled thin GO sheets and these GO sheets shows entanglement with each other.

Figure 2.8 (d) depicts the TEM images of graphene which shows the internal structure of graphene nanosheets. The micrograph of graphene shows thin layer of crumpled silk structure. These multilayer graphene sheets are entangled with each other. The transparent region indicates one-layer thick of graphene sheets. At the same time, the edges of graphene sheets show crumpled characteristics due to its intrinsic nature.

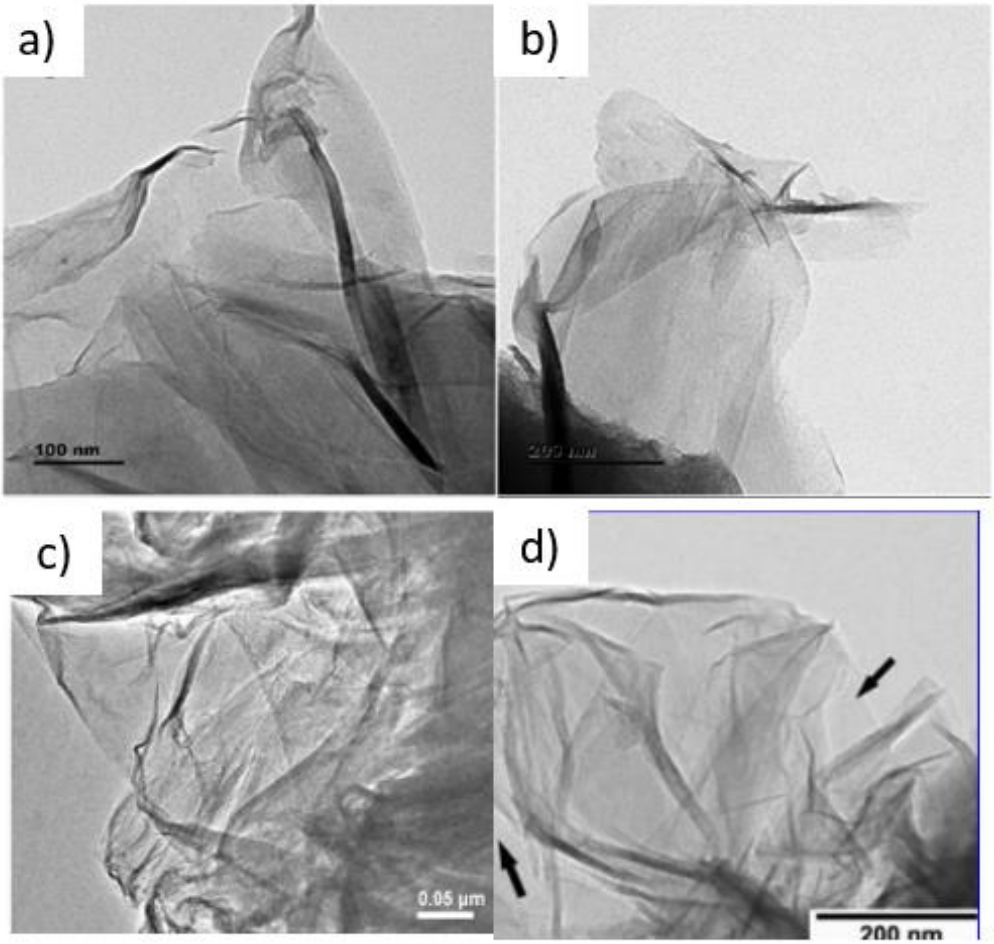

Figure 2. 8:The TEM images of RGO (a and b) (Bandi et al., 2019), GO (c) (Natarajan et al., 2018) and graphene (d) (Wang et al., 2008).

Figure 2.9 (a, b, c and d) shows the HRTEM images of graphene with labelled interlayer spacing value obtained from different synthesis method. It can be clearly seen that the multilayered stacked graphene displays the interlayer spacing in the range of 0.34 nm to 0.35 nm. The lattice fringe indicates multilayered of graphene sheets.

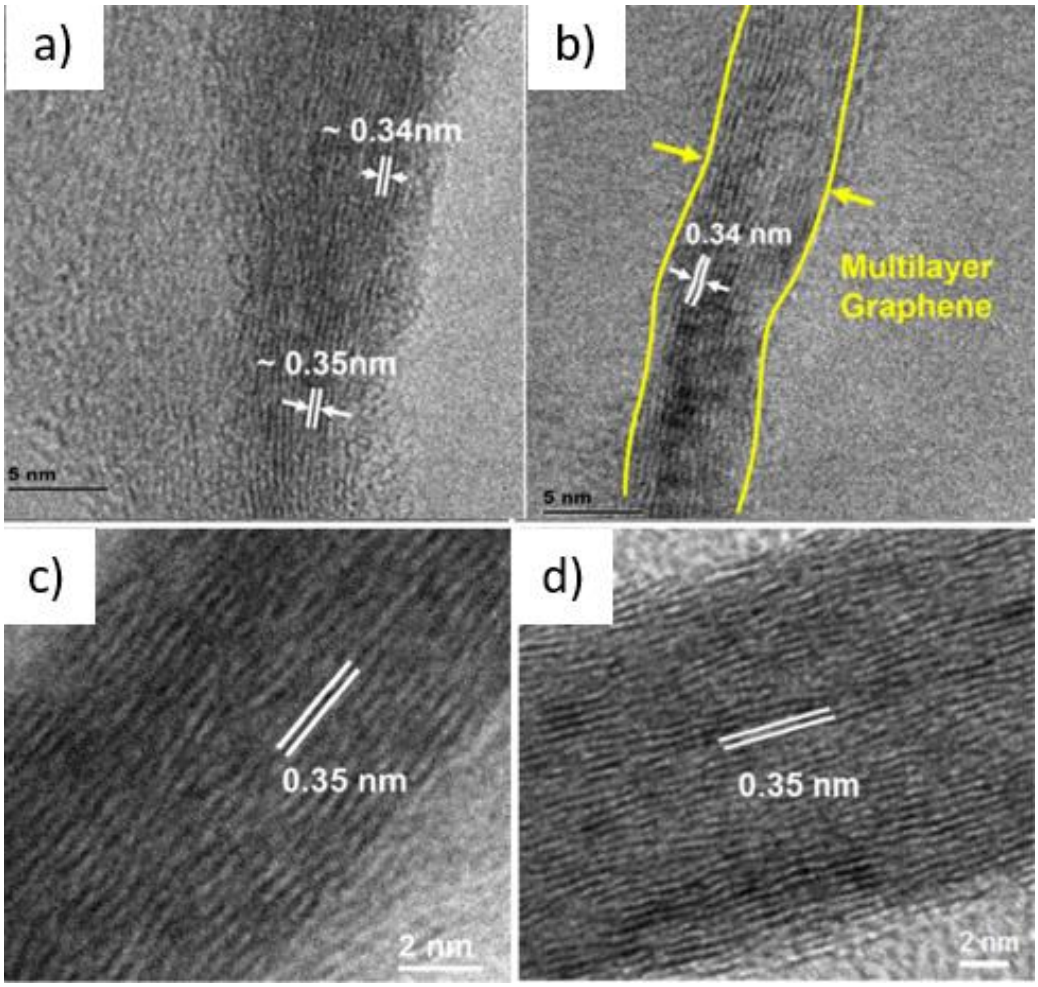

Figure 2. 9: HRTEM images with labelled interlayer spacing (Bandi et al., 2019, Natarajan et al., 2018).

TEM is an effective characterization technique to identify and determine the internal structure of graphene. In addition, the interlayer spacing of graphene can be measured and obtained from the HRTEM images. RGO shows stacked layer of graphene sheets at darker region while the transparent region depicts monolayer of graphene sheets. The interlayer spacing of graphene sheets is approximately 0.34 to 0.35 nm.

2.3 Supercapacitor

Supercapacitor is a device that store electrical energy at the interface between an electrolyte and a solid phase with high power density (10 $kWkg^{-1}$) and long-life cycle (over 10^6 cycles) (Yang et al., 2015). Graphene synthesized from spent battery has potential to be used in supercapacitor. Supercapacitor is made up of two identical electrodes immersed in an electrolyte. The electrodes is the core of the supercapacitor which determines its capacitance, part of its resistance and self-discharge characteristics whereas the electrolyte determines its working windows and power output capability (Inagaki et al., 2010; Yang et al., 2015). They are many types of supercapacitor which includes three major types consisting of electrochemical double-layer capacitors, pseudocapacitors and hybrid capacitors as shown in Figure 2.10.

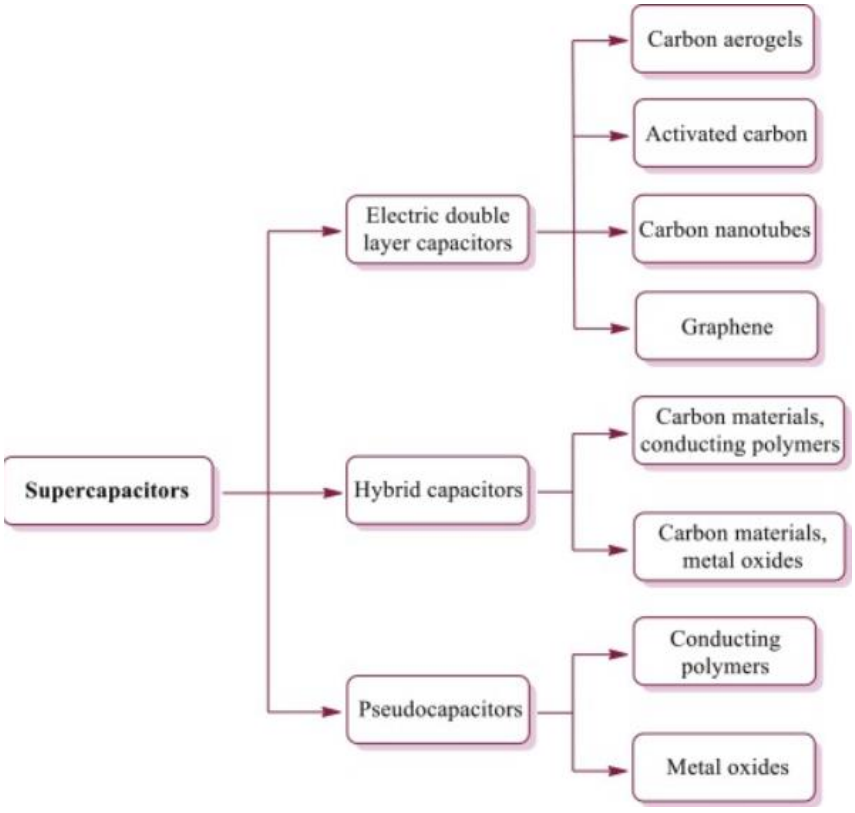

Figure 2. 10: Classification of types of supercapacitors and its electrode materials (Shafiei et al., 2021).