

## Synthesis and characterization of high-quality multi layered graphene by electrochemical exfoliation of graphite

Bisma Ali, Adnan Qayoum, Shahid Saleem, Fasil Qayoum Mir

Online Publication Date: 15 Apr 2022

URL: <http://www.jresm.org/archive/resm2022.384na0121.html>

DOI: <http://dx.doi.org/10.17515/resm2022.384na0121>

Journal Abbreviation: *Res. Eng. Struct. Mater.*

### To cite this article

Ali B, Qayoum A, Saleem S, Mir FQ. Synthesis and characterization of high-quality multi layered graphene by electrochemical exfoliation of graphite. *Res. Eng. Struct. Mater.*, 2022; 8(3): 447-462.

### Disclaimer

All the opinions and statements expressed in the papers are on the responsibility of author(s) and are not to be regarded as those of the journal of Research on Engineering Structures and Materials (RESM) organization or related parties. The publishers make no warranty, explicit or implied, or make any representation with respect to the contents of any article will be complete or accurate or up to date. The accuracy of any instructions, equations, or other information should be independently verified. The publisher and related parties shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with use of the information given in the journal or related means.



Published articles are freely available to users under the terms of Creative Commons Attribution - NonCommercial 4.0 International Public License, as currently displayed at [here](http://creativecommons.org/licenses/by-nc/4.0/) (the "CC BY - NC").



## Synthesis and characterization of high-quality multi layered graphene by electrochemical exfoliation of graphite

Bisma Ali<sup>1, a</sup>, Adnan Qayoum<sup>\*1, b</sup>, Shahid Saleem<sup>1, c</sup>, Fasil Qayoom Mir<sup>2, d</sup>

<sup>1</sup>Mechanical Engineering Department, National Institute of Technology Srinagar, J&K, India-190006.

<sup>2</sup>Chemical Engineering Department, National Institute of Technology Srinagar, J&K, India-190006

### Article Info

#### Article history:

Received 11 Jan 2022

Revised 16 Mar 2022

Accepted 07 April 2022

#### Keywords:

Graphite;  
Electrochemical  
exfoliation;  
Graphene;  
Intercalation;  
Synthesis

### Abstract

Graphene is an emerging carbon material, with wide range of practical applications on a large scale. The yield and quality control of the resultant graphene are significant trade-offs in graphene production. The research is focused on fabricating high quality multi layered graphene using an electrochemical exfoliation approach by adjusting the electrolysis parameters, such as type, composition, concentration of electrolyte and DC Voltage. An aqueous solution of 0.3M (H<sub>2</sub>SO<sub>4</sub>) and 30% KOH has been used as an electrolyte. A constant DC voltage supply of +10 V has been incorporated for the electrolysis for investigation of the relationship between characterization and synthesis parameters. The structure, chemical properties and morphology of the synthesized graphene material were investigated using XRD, FTIR, Raman, UV-vis spectroscopy, FESEM, AFM and TEM/HRTEM techniques. FTIR spectrum showed the appearance of C-O and C-OH functional groups, along with C=C stretching of hexagonal network of graphene. The electronic transition of  $\pi-\pi^*$  and  $n-\pi^*$  are visible in UV-vis spectra of graphene. XRD pattern of graphene sample exhibits a characteristic peak at  $2\theta = 26.45$ , corresponding to a 3.412 Å interlayer distance. The development of multi-layered graphene was demonstrated by the shape and location of the 2D band in the Raman spectra. These studies reveal a comprehensive and detailed morphology showing the wrinkled layered surface with crumpled edges of few layer graphene. Further, this study reinforces the tremendous potential of electrochemical exfoliation for fabricating huge amounts of relatively perfect graphene structures for applications of practical importance.

© 2022 MIM Research Group. All rights reserved.

## 1. Introduction

To achieve Graphene, a single layer form of sp<sup>2</sup> hybridized carbon atoms arranged in a two dimensional hexagonal honeycomb crystal lattice, has gained huge interest owing to its intriguing properties in various applications [1]. The exceptional electrical, mechanical, thermal and optical properties make graphene use in multiple technological applications [2-5]. Graphene has a number of distinct physical and chemical properties such as, high intrinsic carrier mobility (200,000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>), specific surface area of the order of 2630 m<sup>2</sup>g<sup>-1</sup>, an excellent mechanical strength (1,100Gpa), superior thermal conductivity (5,000 Wm<sup>-1</sup>K<sup>-1</sup>), high electrical conductivity (10<sup>-6</sup> Ω cm) and is nearly transparent to visible light (97.7%) [5-8]. Graphene show promising application in several fields such as solar cells [9-10], sensors [11-12], optical devices [13], super capacitors [14-15], bioscience/biotechnologies [16-17] and electronic devices [18] etc. A. K Geim and K. S. Novoselov discovered graphene in 2004 using a scotch tape method via mechanical exfoliation [7]. This method was reported to produce high-quality graphene

\*Corresponding author: [adnan@nitsri.ac.in](mailto:adnan@nitsri.ac.in)

<sup>a</sup> orcid.org/0000-0003-1124-0934; <sup>b</sup> orcid.org/0000-0002-4894-3425; <sup>c</sup> orcid.org/0000-0001-6998-0324;

<sup>d</sup> orcid.org/0000-0002-3211-2395

DOI: <http://dx.doi.org/10.17515/resm2022.384na0121>

Res. Eng. Struct. Mat. Vol. 8 Iss. 3 (2022) 447-462

with excellent mobility. The major limitations of this approach are its time consuming and low manufacturing yield [19]. Producing graphene without collateral damage to its structure on large scale with desirable properties, and with few functional groups is still a significant challenge.

Various methods for producing graphene with a huge surface area and exceptional quality have been identified in recent years. Some prominent methods are chemical vapor deposition (CVD) [20], mechanical exfoliation [21], liquid phase exfoliation [22-23], epitaxial growth [24], chemical exfoliation [25-26] and electrochemical exfoliation [27-28]. Mechanical exfoliation and epitaxially grown graphene results in highly controllable and perfect structured graphene layers [21-29] but are not suitable for high-yield production. CVD is a scalable method using catalytic metal substrates for producing large area and relatively perfect structure graphene [30-31]. The requirement of elevated temperature, sacrificial metal, and multistep transfer operations onto the appropriate substrates is, however, a key disadvantage of this approach. The transition of graphene from the fabrication process to the end-use substrate frequently introduces defects that severely damage the properties of synthesized graphene.

Chemical exfoliation methods based on Hummer's approach, involves oxidizing graphite to thin hydrophilic graphite oxide accompanied by thermal or chemical reduction, has come as new area of research anticipated by the beneficial cost effective and solution treated synthesis [32-33]. The oxidation method may induce significant structural defects and inevitably introduces several functional groups severely damaging the honey comb pattern of graphene, resulting in poor electric conduction. Although the Liquid phase exfoliation process can manufacture multi layer graphene, yet the production of fabricated graphene remains moderate [34], and the utilization of elevated boiling point organic solvents posing a significant challenge.

However, majority of these methods go through a series of limitations, such as lower yield, attached functional groups, agglomerated sheets and higher defect densities etc. To control above-mentioned drawbacks, research has been carried to develop a novel, green, economic, scalable and highly productive route for graphene synthesis for large-scale graphene synthesis. Electrochemical exfoliation of graphite has recently developed as a viable method for producing graphene using mild chemical processes on an industrial scale with less defect and an economical hierarchical structure with minimal impact on environmental pollution [11, 19, 27]. The electrochemical method relies on the expansion of the interlayer gap among graphite layers through ion intercalations. Ion intercalations are mainly influenced by the type, composition, concentration and nature of electrolyte used in an electrochemical process [35-36].

Various electrolytes, including, ionic liquids [37-38], acidic liquids and elevated temperature molten salts [27-39] were utilized in the electrochemical process. In ionic liquids, electrochemical exfoliation produces graphene with a low yield and small lateral dimensions. Acidic electrolytes, on the other hand, can produce better-quality graphene. Acidic nature results not only severe exfoliation but also ungovernable exfoliation due to incomplete intercalation. Therefore, it is important to determine the experimental conditions with proper electrolyte system for obtaining the better quality for bulk fabrication of graphene material.

In the past, chemical intercalation of formic acid or sulfuric acid aided in the expansion of graphite, followed by subsection of high heat. Graphite was rapidly expanded due to the formation of gaseous species released from the intercalant [40-41]. However, higher concentration of sulfuric solution affects exfoliation of graphite into much thinner graphene sheets because of the presence of  $\text{SO}_4^{2-}$  [42], while the high acidity of sulfuric

acid results in structural disorder which is highly undesirable. As such, KOH is added to suppress oxidation of graphene layers, on account of its possible reducing effect [43].

Present study reports the H<sub>2</sub>SO<sub>4</sub>-KOH solution system to fabricate graphene via highly efficient electrochemical exfoliation route by reducing the utilization of corrosive and toxic chemicals. By controlling synthesis parameters such as applied electric potentials, composition of electrolyte, concentration and type of electrolyte, graphene material with few layers number with less defect and with large lateral size has been obtained. The study involves tuning of the parameters for synthesis leading to better quality of graphene. Furthermore, the quality of produced graphene has been assessed using a variety of techniques including XRD, FTIR, UV-vis, Raman, FE-SEM, TEM/HRTEM, and AFM.

## 2. Experimental Procedure

### 2.1. Materials

A high purity graphite foil (measuring 0.3×300×300 mm and of purity of 99.9%) was purchased from AST Works. The commercially available reagents Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and Potassium Hydroxide (KOH) were procured from AVANTOR, India ltd. Platinum wire (measuring 0.5mm×100mm) was purchased from Polymet Galvanotech, Germany.

### 2.2. Synthesis of Graphene

For the fabrication of graphene, a two-electrode arrangement was employed, with graphite foil as the electrode material and supply of natural graphite, and platinum as the counter electrode. As illustrated in the Figure (1a, 1b and 1c), the anode and cathode are made of pure graphite foil and platinum wire, which are separated by 4 cm in the electrolyte. Both sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and potassium hydroxide (KOH) are combined as electrolytes. Using Sulphuric acid alone as electrolyte produce graphene with high structural defects due to intense oxidation [44]. As a result, Potassium hydroxide (KOH) is utilized to counteract reduce the acidic electrolyte's oxidative effects [45]. The experimental setup for electrochemical exfoliation process is depicted in Figure 1.

Wires were used to connect the electrodes to the DC power source, and immersed in the electrolyte solution. Table 1 shows the various parameters investigated for better graphene production via electrochemical exfoliation of graphite. These parameters include voltage and concentration of the electrolytes. It has been observed that the electrolyte solution with the concentration of 0.3M (H<sub>2</sub>SO<sub>4</sub>) and 30% KOH at a DC supply of +10 V provides best exfoliation efficiency. The electrochemical exfoliation was conducted at room temperature with a constant Voltage of +10 until the anode was exhausted.

The gradual exfoliation of the graphite electrode is initiated by applying a +10 V DC voltage across the cathode and anode electrodes. In the electrolyte solution, the graphitic flakes begin to expand, dissociate substantially, and spread (Figure 1c). The graphene powder is extracted from the beaker using vacuum filtration and rinsed with DI water multiple times to eliminate any remaining salts. The graphene powder is collected and dispersed in ethanol. Further sonication is carried for 30 minutes. The mixture has been found to be stable for several weeks without apparent agglomeration (Figure 1d). The suspension was also centrifuged for 20 minutes at a low speed of 1000 rpm to remove any remaining salt ions from the dispersion. After drying the sample at 60°C in an oven to remove any traces of water, dry graphene powder is obtained. Figure 2 depicts a schematic of the entire electrochemical process.

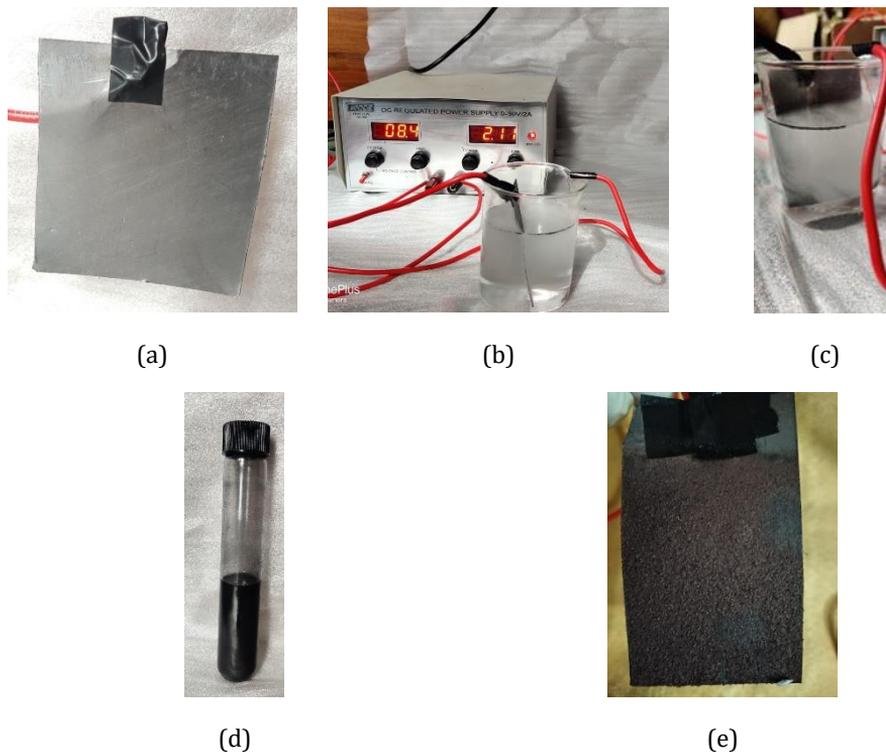


Fig. 1 (a) Optical image of graphite foil before electrochemical exfoliation, (b) Experimental set-up of the electrochemical exfoliation process, (c) Graphene flakes floating on top of electrolyte, (d) Synthesized graphene material dispersed in ethanol and (e) Image of graphite foil obtained after exfoliation process

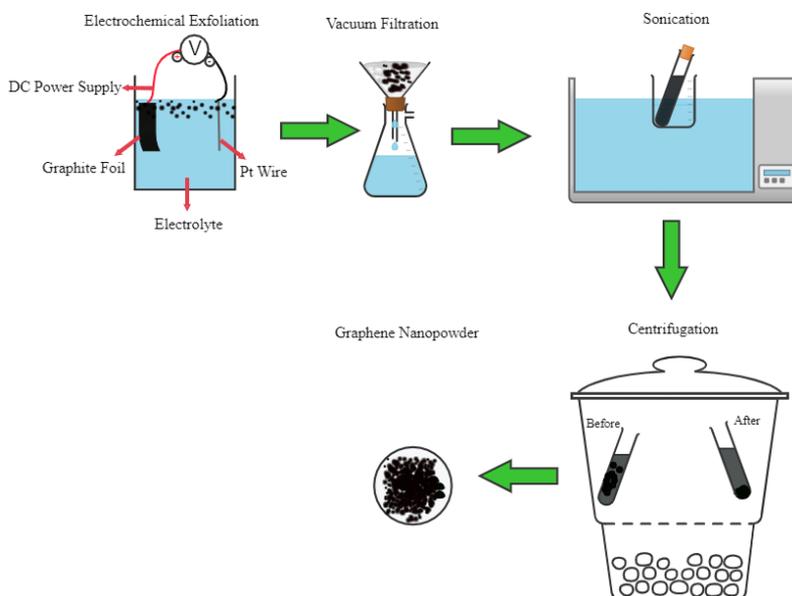


Fig. 2 Schematic illustration of the electrochemical exfoliation process of graphene

Table 1. Experimental parameters for the electrochemical exfoliation

Voltage	Concentration of H <sub>2</sub> SO <sub>4</sub>	Concentration of KOH
10	0.3M H <sub>2</sub> SO <sub>4</sub>	30 % KOH
10	0.3M H <sub>2</sub> SO <sub>4</sub>	35 % KOH
12	0.3M H <sub>2</sub> SO <sub>4</sub>	40% KOH

### 2.3. Material Characterization of Electrochemically Exfoliated Graphene

Fourier transform infrared (FTIR) spectra recorded on Perkin Elmer (UATR Two) spectrometer with a typical wavenumber of 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> were used to investigate the presence of functional groups and bond stretch interactions of the synthesized graphene sample. The optical properties of exfoliated graphene were examined by Ultraviolet-visible (UV-vis) absorption spectrum obtained on a Shimadzu ISR-603 spectrometer. UV-vis spectra were recorded in the range of wavelength from 200 nm to 850. X-Ray diffraction (XRD) using Cu K-beta radiation ( $\lambda = 1.541858$ ) was used to investigate structural parameters and phase analysis using a Rigaku diffractometer. With a step width of 0.200 degree and a scan speed of 21.6746 degrees per minute, XRD patterns were obtained at 40 kV, 30mA with angles  $2\theta$  ranging from 10 to 70. The degree of disorder in the crystal structure was examined using Raman spectroscopy. At a wavelength of ( $\lambda = 532$  nm), the Raman spectra were obtained using a Renishaw inVia Raman spectrometer with an Argon-Krypton laser. The surface morphology and microstructures of graphite anode was investigated by field emission scanning electron microscope (FESEM, ZEISS GeminiSEM 500). The morphology was acquired on graphene material via atomic force microscope (AFM, MFP3D-BIO) and a (TEM, Jeol JEM-1400) was used for Transmission electron microscope analysis at an accelerating voltage of 120 kV.

## 3. Results and Discussion

### 3.1. Mechanism Adopted for Electrochemical Exfoliation of Graphite Foil Anode Into Multi Layered Graphene Sheets

In this study, an electrolyte solution of H<sub>2</sub>SO<sub>4</sub> and KOH has been employed for the electrochemical exfoliation of graphite. When positive potential +10 V is applied, the oxidation occurs at the plane periphery or grain structure of the graphite foil anode. Under the electric effect, the solvated ions intercalate into graphite interlayer's in a sequence of well-defined steps. The internal stress induced by the intercalated ions aids the expansion of graphite anode by weakening the Vander wall forces between the successive graphite layers. OH<sup>-</sup> ions generated during the electrolysis process, on the other hand, open the edges due to electrostatic contact. The co-intercalation of SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, and H<sub>2</sub>O contribute to the more effective intercalation, thereby allowing more particle insertion into graphite layers and thereby expanding graphite layer more rapidly by destroying the long-range morphology related to the c-axis. Finally, on account of the voltage these gases overcome numerous Vander wall forces within graphite layers, and thus facilitate entire exfoliation of graphite anode to be separated as isolated graphene sheets.

### 3.2 Morphological Changes in Different Exfoliation Time

Figure 3 presents the structural morphology changes at different exfoliation times using SEM. These changes confirm with the procedure carried during the present study. The morphology changes of graphite foil anode for a time span of (1-5 min) at various scales have been captured. It is observed that as soon as a voltage of + 10 V is supplied to graphite foil the morphology at sides and edges changes abruptly within 1 min (see

Figure 3a and 3d). The structure exhibits irregular and non-uniform microstructures including network of ripples and corrugated nets mostly on the edges of graphite anode, on account of the deformation due to exfoliation and restacking processes. Due to the visible gas evolution leading to the rapid expansion and rippling of the graphite layers, cracks, bulges, and crumples appear on the surface and boundaries of the graphite anode within 1 minute (Figure 3b and 3e). A significant amount of graphene has left the anode and diffused in the electrolyte solution as the time passes from 3 to 5 minutes. Curled morphology with thin, wrinkled tissue-like features has been achieved. These observations strongly lend credibility to the logic corners and surface of graphite electrode oxidize throughout the electrochemical process, opening the sites of oxidation, promoting intercalation into graphite and subsequently towards the exfoliation of graphene sheets.

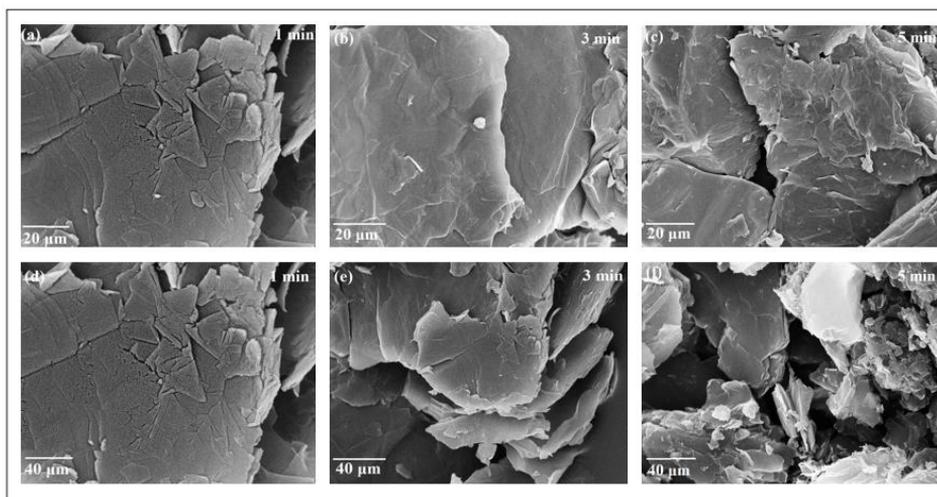


Fig. 3 SEM images of the graphite foil electrode after applying a DC voltage +10 V for 1 min (a, d), 3 min (b, e) and 5 min (c, f) in solution respectively. Scale bar: (a-c) 20 $\mu$ m, (d-f) 40 $\mu$ m

### 3.3. Structural Characterization of Electrochemically Exfoliated Graphene

#### 3.3.1. X-ray Diffraction (XRD) Analysis

The XRD pattern obtained for both natural graphite and electrochemically treated graphite is illustrated in Figure 4. XRD provides the crystalline structure of the natural graphite foil and electrochemically exfoliation graphene powder. The pattern of the graphite exhibits a well-defined diffraction pattern at  $2\theta = 26.7^\circ$  for the plane (002) with the interlayer d-spacing of 3.347 Å and a less significant and wide diffraction peak at  $2\theta = 54.8^\circ$  with a d spacing of 1.6736 Å, as determined by Bragg's law.

$$n\lambda = 2d\sin\theta \quad (1)$$

where  $n = 1$ ,  $\lambda$  is the wavelength,  $d$  is the interlayer distance of the lattices and  $\theta$  is the Bragg's angle. This is in accordance with the interlayer distance of graphite according to JCPDS Card data base (00-041-1487). The synthesized graphene exhibits a significant peak centered at  $2\theta = 26.45^\circ$  corresponding to the (002) plane and has an interlayer spacing of 3.412 Å. After the exfoliation of the graphene sheets, the diffraction peak reduces to a substantial order of magnitude, suggesting that the hexagonal lattice ring

may expand during exfoliation. This is a prerequisite to successful exfoliation of graphene [46, 47]. The XRD characterization indicates that the long-chain morphology of natural graphite around the *c*-axis has been successfully modified and results in the generation of few layer graphene. Using Scherrer's equation, the crystallite size of the sample is estimated from the full width half maximum (FWHM) of the diffraction peak corresponding to the 002 plane.

$$L = \frac{k\lambda}{B \cos\theta} \quad (2)$$

where, *L* is crystallite size (5.32 nm,) *k* is constant (*k*=0.89), *B* is FWHM.

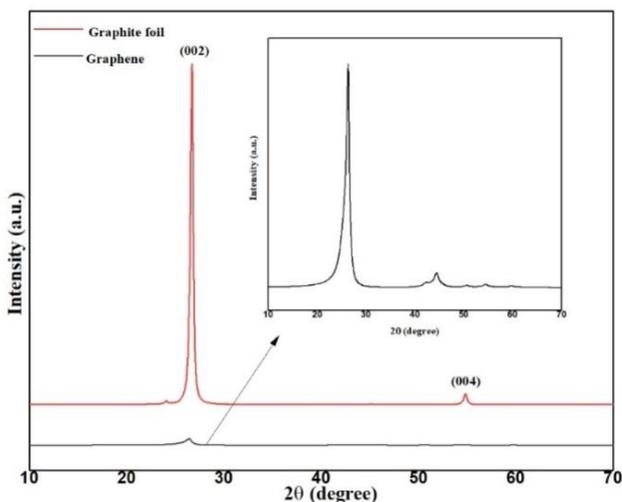


Fig. 4 XRD patterns of graphite foil and synthesized graphene powder

### 3.3.2. Ultra Violet-Visible Absorption (UV-vis) Analysis

Figure 5 depicts the UV-vis spectra of synthesized graphene. The absorption peaks in the spectra of exfoliated graphene are observed at two different wavelengths. The presence of characteristic peak at 250 nm is attributed to the electronic transition from  $\pi$ - $\pi^*$  molecular orbital of aromatic C=C bond present in  $sp^2$  domains of exfoliated graphene structure [13]. A broad peak shoulder around 320-350 nm is associated with  $n$ - $\pi^*$  electronic transitions of C=O bonds present in the  $sp^3$  network of hexagonal structure of exfoliated graphene [48]. Similar findings have been reported in the literature as well [49-50]. As shown in the inset of Figure 5, the optical band gap for the graphene sample is determined using a Tauc plot with a linear extrapolation. An approximate band gap observed ranges over 2.9-3.9 eV, showing an intrinsic semiconductor like characteristics [51] and making it suitable for electronic and optoelectronic applications.

### 3.3.3. Fourier Transform Infrared (FTIR) Analysis

FTIR spectroscopy were used to examine the functional groups and bond stretch interaction of the exfoliated graphene. Figure 6 displays a prominent and powerful peak at  $1070 \text{ cm}^{-1}$  in the FTIR spectra of produced graphene. This is due to the stretching vibration of C-O bond suggesting the presence of oxygen functional groups introduced through the electrochemical process of graphene [45-52]. The C=C bond stretching is

responsible for the peak at  $1572\text{ cm}^{-1}$ [13]. The broad peak with a reduced intensity appears at  $3178\text{ cm}^{-1}$  refers to the development of C-O-H stretching vibration and clearly shows the presence OH radicals in conjunction with exfoliated graphene [43]. The FTIR result indicates that the exfoliated graphene is of good quality with rare functional groups and the peaks obtained are characteristics of the graphene.

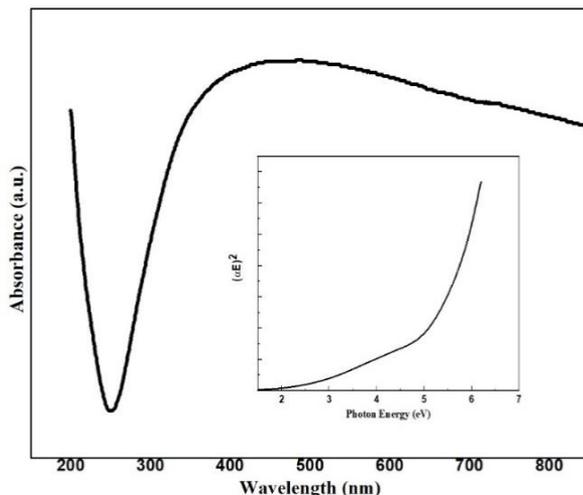


Fig. 5 UV-vis spectra of graphene with inset Tauc plot

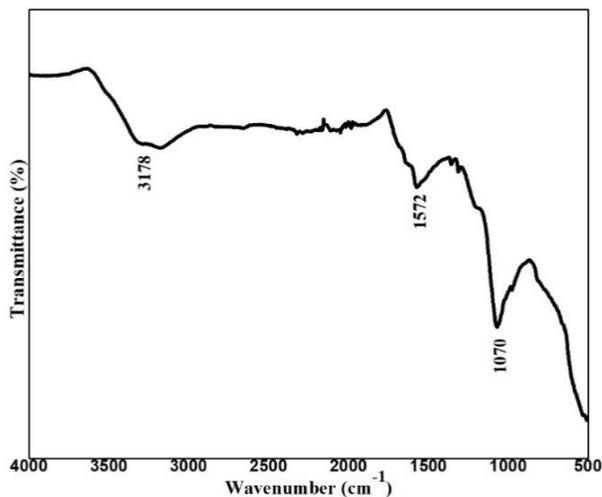


Fig. 6 FTIR spectrum of synthesized graphene

### 3.3.4. Raman Analysis

Figure 7 exhibits a Raman spectrum for the exfoliated graphene sample. The D, G, and 2D peaks in the Raman spectra of graphene material are three characteristic peaks [45-53]. The significant D band at  $1350\text{ cm}^{-1}$  is due to structural disorders, edges, and graphitic surface oxidation, and is connected with the breathing mode of the  $\text{sp}^2$  bound carbon atoms [38]. The G band at  $1588\text{ cm}^{-1}$  arises from Stokes Raman scattering. The optical

phonon ( $E_{2g}$ ) near the Brillouin zone centre is caused by the radial stretching of the C-C bond of  $sp^2$  bonded Carbon [54]. The  $I_D/I_G$  ratio provides information about the degree of defects/disorder of Carbon structures [55]. The graphene material has an  $I_D/I_G$  ratio of 0.8, indicating the presence of structural defects. The G peak at  $1588\text{ cm}^{-1}$  is more pronounced than the D peak at  $1350\text{ cm}^{-1}$ , confirming that the synthesized material has a low defect content, lower than chemically or thermally reduced graphene [44-45]. The results obtained are in agreement with that obtained from the FTIR analysis which shows the presence of oxygen functionalities formed during the exfoliation process. These functional groups are related to the defects in the graphene material and cause partial disorder at the edges. The number of layers of graphene is determined by the shape and intensity of its 2D peak [39-56]. A double-resonant transition excites the 2D band, resulting in the formation of two phonons with opposite momentum. The presence of a 2D band at  $2699\text{ cm}^{-1}$  and an intensity ratio of  $I_{2D}/I_G = 0.147$  indicate that the synthesized material is made up of a few layers of graphene. This is also supported by the widening of the 2D band, as illustrated in Figure 7.

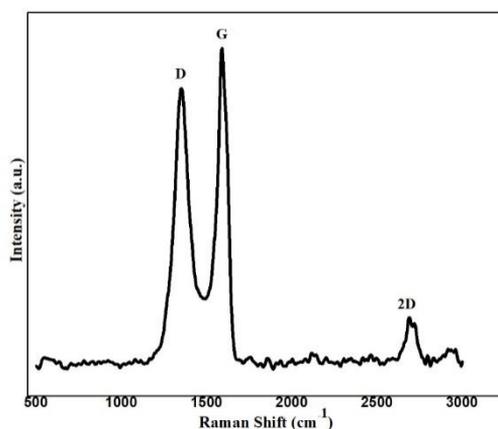


Fig.7 Raman spectrum of synthesized graphene

### 3.4. Morphological Characterization of Electrochemically Exfoliated Graphene

#### 3.4.1. Scanning Electron Microscope (SEM) Analysis

The micromorphology of the surface of exfoliated graphene sample has been characterized by FESEM, AFM and TEM. Figure 8 displays FE-SEM micrograph of graphene deposited on a gold substrate. FE-SEM image reveals that the graphene comprises of haphazardly aggregated, thin crumpled/ruptured sheets and has wrinkled paper like morphology with well-arranged stacked sheets. Crumpling and scrolling are inherent characteristics of graphene sheets, as previously stated [45].

#### 3.4.2. Transmission Electron Microscope (TEM) Analysis

Transmission electron microscope (TEM) images of graphene material is displayed in Figure 9a and 9b. Figure 9a depicts a typical low magnification TEM image of graphene material. The sample for TEM was prepared by suspending graphene in ethanol and sonicating it, after which a few drops of dispersion were dropped on a carbon coated copper TEM grid and dried at room temperature. A high magnification TEM image clearly shows a homogeneous wrinkled film-like structure (Figure 9b). Most of the sheets are

stacked multilayers. HR-TEM images were taken to determine the number of layers in a graphene sample. Figure 9c and 9d display the high-resolution TEM (HR-TEM) micrographs of the material, indicate that the electrochemically exfoliated material is preferably few layered graphene. The estimated d- spacing is 0.35 nm, which is consistent and similar with measurements given in the literature for graphene material and greater than regular graphite (0.335 nm). Exfoliated graphene was subjected to a selected area electron diffraction pattern, and the resulting SAED pattern is shown in Figure 9e. The hexagonal diffraction spots are seen in SAED pattern, originating from the  $sp^2$ -bonded carbon frameworks, indicating that the synthesized material mainly contains few layer graphene and presence of few defects. These defects arise mainly due to the insertion of oxygen functionalities during the electrochemical process as observed in FTIR and Raman spectroscopy. The intensity of the spots with Bravais-Miller ( $hkl$ ) indices (1-210) plane and then from the (0 101) plane show a typical 6-fold symmetric diffraction in the specified area electron diffraction, confirming the strong crystallinity of graphene [57]. Furthermore, the inner and outer spots' relative intensities were found to be  $< 1$ , indicating multi-layered graphene [52, 58]

### 3.4.3. Atomic Force Microscope (AFM) Analysis

Drop casting graphene dissolved in ethanol on a mica substrate was used to create the graphene sample. Figures 10(a) and 10(b) show 2D and 3D AFM images of an exfoliated graphene sample. The graphene on the mica substrate is irregularly distributed, as shown by the height profile in Figure 10c. The topographic heights of the sheets, as determined by the cross-sectional contour, range from 1.8-5.67 nm, indicating few layer graphene. In this study, the electrochemically exfoliated graphene corresponds to a few layers of graphene. AFM indicated the appearance of irregularly formed graphene sheets with lateral dimensions reaching to a few nanometers and a non-uniform thickness.

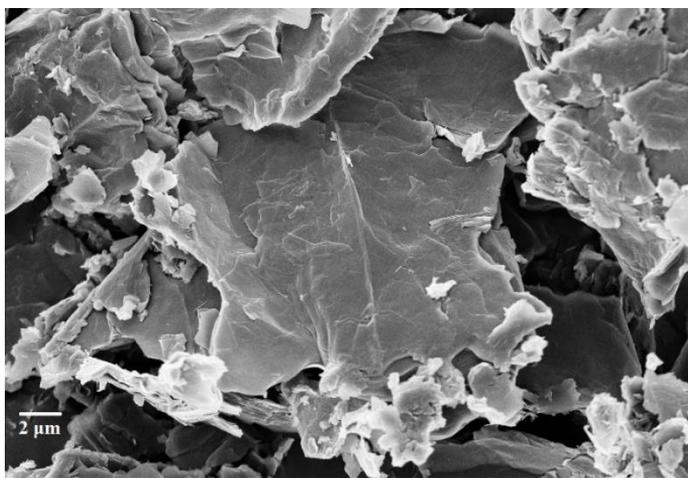


Fig. 8 SEM image of exfoliated graphene coated over a gold substrate

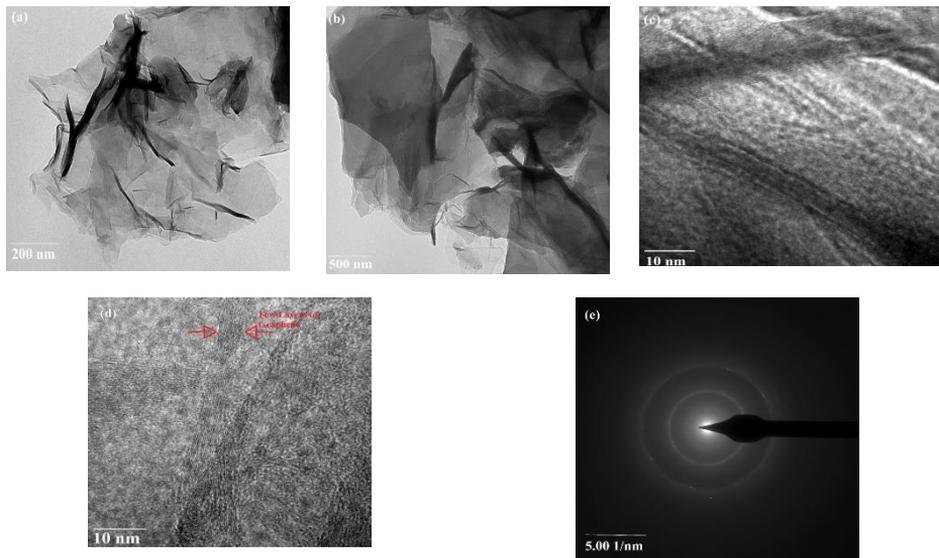
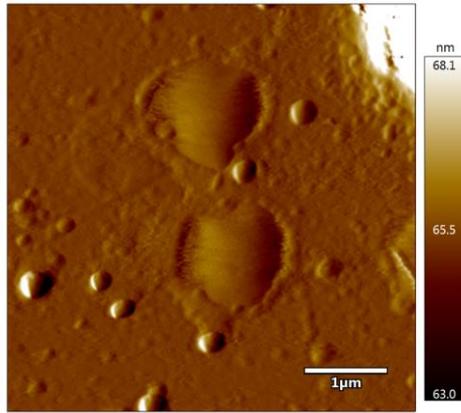


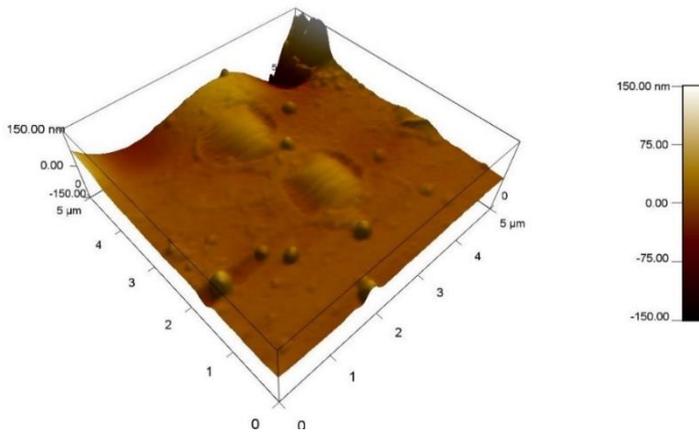
Fig. 9 (a, b) Typical TEM images of stacked graphene at low and high magnification (c, d) Typical HR-TEM images of exfoliated graphene (e) SAED pattern obtained for exfoliated graphene

#### 4. Conclusions

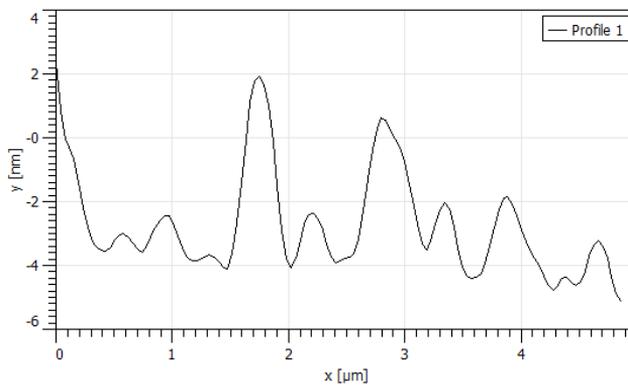
The current study uses a Sulfuric acid/ Potassium Hydroxide/ Water ( $\text{H}_2\text{SO}_4/\text{KOH}/\text{H}_2\text{O}$ ) electrolyte system to demonstrate a simple, easy, green controlled, and environmental friendly technique for the industrial-scale production of graphene. This approach leads to low-cost large-scale production of multi layered graphene, with few defects and low degree of contamination at ambient reaction conditions. The study involves tuning of the parameters for synthesis leading to better quality of graphene. Exfoliation occurs due to the complicated interaction between anodic oxidation of  $\text{SO}_4^{2-}$  and  $\text{OH}^-$  ions. The exfoliated graphene has been characterized using XRD, UV-vis, Raman, FTIR, FE-SEM, AFM and TEM/HRTEM. The synthesized graphene exhibits a significant peak centered at  $2\theta = 26.45$  corresponding to the (002) plane and has an interlayer spacing of  $3.412 \text{ \AA}$ . The  $\pi-\pi^*$  and  $n-\pi^*$  transitions are represented in the UV-vis absorption spectra by a strong peak at  $250 \text{ nm}$  and an adjacent band at  $320-350 \text{ nm}$ , respectively. Raman spectroscopy shows an electrochemically exfoliated graphene exhibits a lower  $I_D/I_G = 0.8$  degree of defect, lower than chemically derived graphene. The G peak at  $1588 \text{ cm}^{-1}$  is more pronounced than the D peak at  $1350 \text{ cm}^{-1}$ , confirming that the synthesized material has low defect content, lower than chemically or thermally reduced graphene. From morphological studies, the layers with wrinkled surface and crumpled edges morphology of few layer graphene are seen. Further, the morphological change in different exfoliated time has been studied from FE-SEM. Raman and AFM analysis confirms that the graphene material is exfoliated successfully into multi layer graphene. The topographic heights of the sheets, as determined by the cross-sectional contour, range from  $1.8-5.67 \text{ nm}$ , indicating few layer graphene. The adopted method resulted in the synthesis of structurally controlled graphene material provides an important insight for scaling up the synthesis of graphene for industrial applications of practical importance.



(a)



(b)



(c)

Fig. 10 (a) 2D AFM image of exfoliated graphene deposited on mica substrate (b) Typical 3D AFM image of exfoliated graphene (c) Height profile of exfoliated graphene

## Nomenclature

JCPDS	: Joint committee on powder diffraction standards
XRD	: X-ray diffraction
FE-SEM	: Field emission scanning electron microscope
TEM	: Transmission electron microscope
FTIR	: Fourier transform infra-red
AFM	: Atomic force microscope
HRTEM	: High resolution transmission electron microscope
CVD	: Chemical vapor deposition
SAED	: Selected area electron diffraction
KOH	: Potassium hydroxide
H <sub>2</sub> SO <sub>4</sub>	: Sulfuric acid
FWHM	: Full width half maximum
d	: Interlayer distance
L	: Crystallite size

## Greek Symbols

$\theta$	: Diffraction angle
$\lambda$	: Wavelength (Angstrom)

## References

- [1] Shao Y, Wang J, Engelhard M, Wang C, Lin Y. Facile and controllable electrochemical reduction of graphene oxide and its applications. *J Mater Chem*, 2010; 20: 743-748. <https://doi.org/10.1039/B917975E>
- [2] Bolotin KI, Sikes KJ, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P, Stormer HL. Ultrahigh electron mobility in suspended graphene. *Solid State Commun*; 2008; 146: 351-355. <https://doi.org/10.1016/j.ssc.2008.02.024>
- [3] Chabot V, Kim B, Sloper B, Tzoganakis C, Yu A. High yield production and purification of few layer graphene by Gum Arabic assisted physical sonication. *Sci Rep*, 2013; 3:. <https://doi.org/10.1038/srep01378>
- [4] Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, Lau CN. Superior thermal conductivity of single-layer graphene. *Nano Lett*, 2008; 8:902-907. <https://doi.org/10.1021/nl0731872>
- [5] Geim AK, Novoselov KS. The rise of graphene. *Nanosci Technol A Collect Rev from Nat Journals*, 2009; 11-19.
- [6] Allen JM, Vincent TC, Richard KB. (2010) Honeycomb carbon : A Review of Graphene What is graphene? *Chem Rev*, 2010; 110:132-145 <https://doi.org/10.1021/cr900070d>
- [7] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA. Electric field effect in atomically thin carbon films. *Science*. 2004 Oct 22; 306 (5696): 666-9. <https://doi.org/10.1126/science.1102896>
- [8] Geim AK. Graphene: Status And Prospects A. K. Geim Manchester Centre for Mesoscience and Nanotechnology, University of Manchester, Oxford Road M13 9PL, Manchester, UK. *Prospects*, 2009; 324: 1-8.
- [9] Wang X, Zhi L, Tsao N, Tomovic Z, Li J, Mullen K. Transparent Carbon Films as Electrodes in Organic Solar Cells. *Angew Chemie*, 2008; 120: 3032-3034. <https://doi.org/10.1002/ange.200704909>
- [10] Wu J, Becerril HA, Bao Z, Zunfeng Wu, Yongsheng C, Peter P. Organic solar cells with solution-processed graphene transparent electrodes. *Appl Phys Lett*, 2008; 92:. <https://doi.org/10.1063/1.2924771>

- [11] Li SJ, Deng DH, Shi Q, Liu SR. Electrochemical synthesis of a graphene sheet and gold nanoparticle-based nanocomposite, and its application to amperometric sensing of dopamine. *Microchim Acta*, 2012; 177: 325-331. <https://doi.org/10.1007/s00604-012-0782-9>
- [12] Brownson DAC, Banks CE. Graphene electrochemistry: An overview of potential applications. *Analyst*, 2010; 135: 2768-2778. <https://doi.org/10.1039/c0an00590h>
- [13] Parveen N, Ansari MO, Cho MH. Simple route for gram synthesis of less defective few layered graphene and its electrochemical performance. *RSC Adv*, 2015; 5: 44920-44927. <https://doi.org/10.1039/C5RA06404J>
- [14] Liu J, Xue Y, Zhang M, Dai L. Graphene-based materials for energy applications. *MRS Bull*, 2012; 37: 1265-1272. <https://doi.org/10.1557/mrs.2012.179>
- [15] Zhang LL, Zhou R, Zhao XS. Graphene-based materials as supercapacitor electrodes. *J Mater Chem*, 2010; 20: 5983-5992. <https://doi.org/10.1039/c000417k>
- [16] Chen H, Müller MB, Gilmore KJ, Wallace GG, Li D. Mechanically strong, electrically conductive, and biocompatible graphene paper. *Adv Mater*, 2008; 20: 3557-3561. <https://doi.org/10.1002/adma.200800757>
- [17] Liu Z, Robinson JT, Sun X, Dai H. Pegylated nanographene oxide for delivery of water-insoluble cancer drugs. *J Am Chem Soc*, 2008; 130: 10876-10877. <https://doi.org/10.1021/ja803688x>
- [18] Hass J, De Heer WA, Conrad EH. The growth and morphology of epitaxial multilayer graphene. *J Phys Condens Matter*, 2008; 20: <https://doi.org/10.1088/0953-8984/20/32/323202>
- [19] Pingale AD, Owhal A, Katarkar AS, Belgamwar SU, Jitendra SR. Facile synthesis of graphene by ultrasonic-assisted electrochemical exfoliation of graphite. *Mater Today Proc*, 2021; 44: 467-472. <https://doi.org/10.1016/j.matpr.2020.10.045>
- [20] Ruan M, Hu Y, Guo Z, Dong R, Palmer J, Hankinson J, Berger C, De Heer WA. Epitaxial graphene on silicon carbide: Introduction to structured graphene. *MRS Bull*, 2012; 37: 1138-1147. <https://doi.org/10.1557/mrs.2012.231>
- [21] Chen J, Duan M, Chen G. Continuous mechanical exfoliation of graphene sheets via three-roll mill. *J Mater Chem*, 2012; 22: 19625-19628. <https://doi.org/10.1039/c2jm33740a>
- [22] Liang B, Liu K, Liu P, Qian L, Zhao G, Pan W, Chen C. Organic salt-assisted liquid-phase shear exfoliation of expanded graphite into graphene nanosheets. *J Mater*, 2021; 1-9. <https://doi.org/10.1016/j.jmat.2021.03.007>
- [23] Hernandez Y, Nicolosi V, Lotya M, Fiona MB, Zhenyu S, Sukanta D, I.T M, Brendan H, Michele B. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat Nanotechnol*, 2008; 3: 563-568. <https://doi.org/10.1038/nnano.2008.215>
- [24] Yang W, Chen G, Shi Z, Liu CC, Zhang L, Xie G, Cheng M, Wang D, Yang R, Shi D, Watanabe K, Taniguchi T, Yao Y, Zhang Y, Zhang G. Epitaxial growth of single-domain graphene on hexagonal boron nitride. *Nat Mater*, 2013; 12: 792-797. <https://doi.org/10.1038/nmat3695>
- [25] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, Wu Y, Nguyen SBT, Ruoff RS. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* N Y, 2007; 45: 1558-1565. <https://doi.org/10.1016/j.carbon.2007.02.034>
- [26] Park S, Ruoff RS. Erratum: Chemical methods for the production of graphenes, *Nature Nanotechnology*. 2010; 5: 309.
- [27] Wu J, Wang H, Qiu J, Shao J, Zhang K, Yan L. Electrochemical exfoliation for few-layer graphene in molybdate aqueous solution and its application for fast electrothermal film. *Prog Nat Sci Mater Int*, 2020; 30: 312-320. <https://doi.org/10.1016/j.pnsc.2020.05.007>
- [28] Paredes JI, Munuera JM. Recent advances and energy-related applications of high quality/chemically doped graphenes obtained by electrochemical exfoliation

- methods. *J Mater Chem A*, 2017; 5: 7228-7242. <https://doi.org/10.1039/C7TA01711A>
- [29] Berger C, Song Z, Li X, Wu X, Brown N, Naud C, Mayou D, Li T, Hass J. Electronic confinement and coherence in patterned epitaxial graphene. *Science*, 2006; 312: 1191-1196. <https://doi.org/10.1126/science.1125925>
- [30] Hawaldar R, Merino P, Correia MR, Bdikin I, Gracio J, Mendex J, Martin-Gago JA, Singh MK. Large-area high-throughput synthesis of monolayer graphene sheet by Hot filament thermal chemical vapor deposition. *Sci Rep*, 2012; 2: 2-10. <https://doi.org/10.1038/srep00682>
- [31] Yoon JC, Lee JS, Kim SI, kwang H.K, Ji HJ. Three-dimensional graphene nano-networks with high quality and mass production capability via precursor-assisted chemical vapor deposition. *Sci Rep* 2013; 3:.
- [32] Gao W, Alemany LB, Ci L, Ajayan PM. New insights into the structure and reduction of graphite oxide. *Nat Chem*, 2009; 1: 403-408. <https://doi.org/10.1038/nchem.281>
- [33] Li D, Müller MB, Gilje S. Processable aqueous dispersions of graphene nanosheets. *Nat Nanotechnol*, 2008; 3: 101-105. <https://doi.org/10.1038/nnano.2007.451>
- [34] Biswas S, Drzal LT. A novel approach to create a highly ordered monolayer film of graphene nanosheets at the liquid-liquid interface. *Nano Lett*, 2009; 9: 167-172. <https://doi.org/10.1021/nl802724f>
- [35] Singh R, Charu Tripathi C. Electrochemical Exfoliation of Graphite into Graphene for Flexible Supercapacitor Application. *Mater Today Proc*, 2018; 5: 1125-1130. <https://doi.org/10.1016/j.matpr.2017.11.192>
- [36] Liu F, Wang C, Sui X. Synthesis of graphene materials by electrochemical exfoliation: Recent progress and future potential. *Carbon Energy*, 2019; 1: 173-199. <https://doi.org/10.1002/cey2.14>
- [37] Lu J, Yang J, Wang J, Lim A, Wang S, Loh KP. One-Pot Synthesis of Fluorescent Carbon Graphene by the Exfoliation of Graphite in Ionic Liquids. *ACS Nano*. 200. *ACS Nano*, 2009; 3: 2367-2375 <https://doi.org/10.1021/nn900546b>
- [38] Mao M, Wang M, Hu J. Simultaneous electrochemical synthesis of few-layer graphene flakes on both electrodes in protic ionic liquids. *Chem Commun*, 2013; 49: 5301-5303. <https://doi.org/10.1039/c3cc41909f>
- [39] Jibrael RI, Mohammed MKA. Production of graphene powder by electrochemical exfoliation of graphite electrodes immersed in aqueous solution. *Optik (Stuttg)*, 2016; 127: 6384-6389. <https://doi.org/10.1016/j.jileo.2016.04.101>
- [40] Variable I, Tal S, Garcia T. (2011) (12) United States Patent (10) Patent No. : 2:
- [41] Kang F, Leng Y, Zhang TY. Influences of H<sub>2</sub>O<sub>2</sub> on synthesis of H<sub>2</sub>SO<sub>4</sub>-GICs. *J Phys Chem Solids*; 1996 57: 889-892
- [42] Jung SM, Mafra DL, Te LC, Young JH, Kong J. Controlled porous structures of graphene aerogels and their effect on supercapacitor performance. *Nanoscale*, 2015; 7: 4386-4393. <https://doi.org/10.1039/C4NR07564A>
- [43] Tripathi P, Patel CRP, Shaz MA, Srivastava ON. Synthesis of High-Quality Graphene through Electrochemical Exfoliation of Graphite in Alkaline Electrolyte
- [44] Parvez K, Li R, Puniredd SR, Hernandez Y, Hinkel F, Wang S, Feng X, Mullen K(2013) Electrochemically exfoliated graphene as solution-processable, highly conductive electrodes for organic electronics. *ACS Nano*, 2013; 7 :3598-3606. <https://doi.org/10.1021/nn400576v>
- [45] Wang G, Wang B, Park J, Wang Y, Sun B, Yao J. Highly efficient and large-scale synthesis of graphene by electrolytic exfoliation. *Carbon N Y*, 2009; 47: 3242-3246. <https://doi.org/10.1016/j.carbon.2009.07.040>
- [46] Kumar N, Srivastava VC. Simple Synthesis of Large Graphene Oxide Sheets via Electrochemical Method Coupled with Oxidation Process. *ACS Omega*, 2018; 3: 10233-10242. <https://doi.org/10.1021/acsomega.8b01283>

- [47] Chen K, Xue D, Komarneni S. Nanoclay assisted electrochemical exfoliation of pencil core to high conductive graphene thin-film electrode. *J Colloid Interface Sci*, 2017; 487: 156-161. <https://doi.org/10.1016/j.jcis.2016.10.028>
- [48] Thema FT, Moloto MJ, Dikio ED, Nyangiwe N.N, Kotsedi L, Maaza M, Khenfouch M. Synthesis and characterization of graphene thin films by chemical reduction of exfoliated and intercalated graphite oxide. *J Chem*, 2013; 3:.
- [49] Zhou M, Tang J, Cheng Q, Xu G, Cui P, Chang QL. Few-layer graphene obtained by electrochemical exfoliation of graphite cathode. *Chem Phys Lett*, 2013; 572: 61-65. <https://doi.org/10.1016/j.cplett.2013.04.013>
- [50] Kuila T, Khanra P, Kim NH, et al. Effects of sodium hydroxide on the yield and electrochemical performance of sulfonated poly(ether-ether-ketone) functionalized graphene. *J Mater Chem A*, 2013; 1: 9294-9302. <https://doi.org/10.1039/c3ta11014a>
- [51] Sahoo SK, Ratha S, Rout CS, Mallik A. Physicochemical properties and supercapacitor behavior of electrochemically synthesized few layered graphene nanosheets. *J Solid State Electrochem*, 2016; 20: 3415-3428. <https://doi.org/10.1007/s10008-016-3304-6>
- [52] Mir A, Shukla A. Bilayer-rich graphene suspension from electrochemical exfoliation of graphite. *Mater Des*, 2018; 156:62-70. <https://doi.org/10.1016/j.matdes.2018.06.035>
- [53] Sahoo SK, Behera AK, Chandran R, Mallik A. Industrial scale synthesis of few-layer graphene nanosheets (FLGNSs): an exploration of electrochemical exfoliation approach. *J Appl Electrochem*, 2020; 50: 673-688. <https://doi.org/10.1007/s10800-020-01422-3>
- [54] You A, Be MAY, In I. Synthesis of few layer graphene by direct exfoliation of graphite and a Raman spectroscopic study, 2017; 027116.
- [55] Yang S, Brüller S, Wu Z, Parvez K, Dong R, Richard F, Samori P, Liu Z. Organic radical-assisted electrochemical exfoliation for the scalable production of high-quality graphene Organic radical-assisted electrochemical exfoliation for the scalable production of high-quality graphene, 2015. <https://doi.org/10.1021/jacs.5b09000>
- [56] Gurzęda et al. - 2016 - Graphene material prepared by thermal reduction of the electrochemically synthesized graphite oxide-annotated.pdf <https://doi.org/10.1039/C6RA10903A>
- [57] Wang J, Manga KK, Bao Q, Loh KP. High-Yield Synthesis of Few-Layer Graphene Flakes through Electrolyte. *J Am Chem Soc*, 2011; 133: 8888-8891 <https://doi.org/10.1021/ja203725d>
- [58] Zhou H, Yu WJ, Liu L, Cheng R, Cheng C. Chemical vapour deposition growth of large single crystals of monolayer and bilayer graphene. *Nat Commun*, 2013; 4: 1-8. <https://doi.org/10.1038/ncomms3096>