

A Review of the Effect of Different Electrolytes on the Synthesis of Graphene Sheets by Electrochemical Exfoliation

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ABSTRACT

Graphene oxide (GO) possess some excellent properties that fulfil various applications. Hummers' method has been used in GO synthesis for years but some issues such as high-cost GO synthesis, the use of toxic chemicals and low yield of GO are still remains and concerned. In addition, this method spends very long time to be completed and subjected to thorough cleaning process to remove toxic chemicals. On the other hand, the electrochemical method saves time, has no explosion risk, releases no toxic gases, and keep safe environmental. The demand of GO supply is crucial particularly important in applications such as energy storage in automobiles thus, a large scale and cheap production of GO is needed. It is reported that the electrochemical synthesis of GO has more benefits such as rapid synthesis, low cost and environmentally friendly than Hummers' method, therefore, the impact of different electrolytes is important to be studied. Herein, various research works about the electrochemical synthesis of GO are reviewed, precisely involving the anodic exfoliation of graphite, exfoliation mechanism and effects of exfoliation parameters.

Keywords: Graphene, Electrochemical exfoliation, Graphene Oxide

1. INTRODUCTION

Since the discovery of graphene, it has initiated the progression of comprehensive research due to its distinctive properties [1]. Graphene is commonly synthesized as a mixture of irregular shapes of monolayers, bi-layers and multilayers [2]. Besides, graphene can appear in 0D buckyballs (fullerenes) or 1D nanotubes as well. Nevertheless, the main obstacle in the synthesis of large amounts of graphene is to overcome the high exfoliation energy within the p-stacked layers of graphite, which is known as cohesive van der Waals energy (5.9 kJ mol^{-1} carbon) that contributes to the bonding between the graphite layers [3][4]. From the past until recently, there are many methods to form graphene have been reported including mechanical exfoliation of graphite [5], epitaxial growth of graphene using chemical vapor deposition[6], solvothermal fabrication and pyrolysis[7], wet-chemical preparation using graphite particles [8], exfoliation in liquid-phase [9], graphite oxidation [10] and thermal treatment of silicon carbide wafer in a highly vacuumed environment [11], but yet these techniques have failed to fulfil the objectives to synthesize graphene in large amount or at an acceptable cost.

Meanwhile, the electrochemical technique has some benefits such as involving a single step process, simple, eco-friendly (if ionic liquid or aqueous surfactants are used as electrolytes) and can be carried out at room temperature.

Lately, graphene flakes in milligram and gram amounts were prepared successfully by some research groups using electrochemical techniques [13][14]–[18]. The electrochemical cell design and engineering have been used to increase the production effortlessly [19]. The synthesis process spends from few minutes to several hours to finish and the outcomes are inspiring scientists to conduct rapid synthesis of bulk quantities of graphene [11]. In the electrochemical technique, electrolyte solution and an electrical current are used to force the graphite layers to be intercalated by anions and water molecules which caused expansion and followed by exfoliation of a graphite rod, plate or wire into graphene flakes [14]. A monopolar, single electrolysis cell is used as the experimental configuration in this technique. The output, efficiency and properties of graphene sheets can be modified by customizing the parameters of electrolysis and electrolytes [16].

2. ANODIC EXFOLIATION

The anions present in the electrolyte would insert into the structure of anode due to the presence of positive potentials. The intercalation and the quality of exfoliated graphene sheets are significantly influenced by few factors such as applied voltage, the types of anions, amount and pH of electrolyte.

Due to the oxidation reaction which induced by the positive potential at anode, some active radicals which formed during the reaction oxidised the exfoliated the two-dimensional (2D) graphene sheets [20].

2.1. Exfoliation Mechanism

In Figure 1, the exfoliation mechanism of graphene sheets is explained in three important steps: 1) the formation of hydroxyl ions (OH^-) from electrolysis of water caused the oxidation of anode, 2) the anode was intercalated by anions, 3) expansion and exfoliation of the graphite layers into graphene nanosheets by the molecule gases resulted from electro-oxidation at the anode [21], [22], [23].

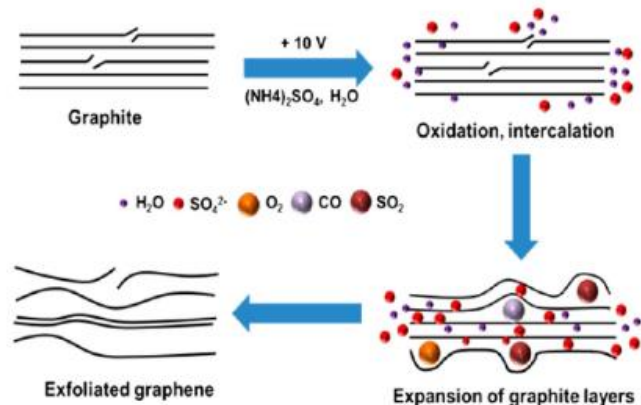


Figure 1 Schematic illustration of electrochemical exfoliation mechanism. Reprinted with permission from ref [21]. Copyright 2014 ACS Publications.

Many types of electrolyte solutions such as nitric acid, perchloric acid, sulphuric acid sodium saccharin, sodium citrate, sodium benzoate, triethylmethylammonium methylsulfate (TEMAMS), 1butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄], and others are capable to intercalate and exfoliate the graphite at anode into graphene sheets [24], [25], [11], [26]. The quality of graphene and efficiency of exfoliation are affected by the types of electrolytes. For instant, better exfoliation efficiency and high defect concentration of exfoliated nanosheets can be retained in H_2SO_4 electrolyte, meanwhile, higher amount of oxygen of graphene (C/O ratio of 4.0) can be retained by using HClO_4 electrolyte [27], [28]. Strong oxidizing of SO_4^- which produced from the $\text{S}_2\text{O}_8^{2-}$ anions contributed to the higher oxygen or quantum carbon dots content in graphene nanosheets [29], [30]; same goes to the oxidation of graphene oxide (GO) nanosheets by using sodium citrate. On the other hand, pure graphene or less oxidized graphene nanosheets can be obtained by using tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$), phytic acid or benzoate [31], [32], [33]. In addition, few layers of graphene sheets with lower amount of oxygen can be synthesized in 5 min by using glycine-bisulfate which much faster than exfoliation rate in diluted H_2SO_4 [34]. Besides, graphene sheets which formed in sulphuric acid are thinner as compared to the graphene exfoliated by using hydrogen peroxide or nitrate-containing electrolyte [15].

The presence of hydroxyl and oxygen radicals could oxidize and degrade the structure of exfoliated 2D

nanosheets. However, some electrolyte act as sacrificial agents to reduce the oxidation or structure defects formation of the graphene nanosheet. As an example, sodium benzene 1,3-disulfate or sodium naphthalene 1,5-disulfate aqueous solution showed the performance to exfoliate and produce high purity graphene [35]. Meanwhile, the addition of reduction agents such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) can react instantly with the OH radicals to protect the graphene from oxidation. Hence, high quality graphene sheets with high carbon to oxygen ratio (~ 25.3) were synthesized using ammonium sulphate aqueous electrolyte in this method [36]. Melamine was added to the sulfuric acid as additives to enhance the exfoliation efficiency and to prevent the oxidation of graphene in order to synthesize defect free and few layers graphene [37]. Furthermore, the amount of oxygen functional groups on graphene can be reduced by adding hydrogen peroxide to the ammonium sulphate due to higher nucleophilicity of O_2^{2-} as compared to OH^- ion in the electrolyte [38].

2.2. Effects of Exfoliation Parameters on the Amount and Quality of Graphene

Furthermore, pre-treatment of graphite anode could protect the exfoliated nanosheets from oxidation. For example, oxidation of graphene can be avoided by doing cathodic pre-treatment of graphite and, then proceed to anodic intercalation [15]. Graphene with low defect and low oxygen content could be exfoliated efficiently through anodic pre-treatment of graphite in sodium hydroxide electrolyte [39].

The pH value of the electrolyte could affect the oxidation performance of the electrolyte and the intermediate molecules which formed from electrolysis, hence, the defect density and amount of oxygen of the exfoliated nanosheets can be affected as well. For example, oxidation degree of graphene can be reduced by tuning the pH value of the aqueous sulphuric acid electrolyte [40]. If sulphate ions replaced the sulphuric acid as electrolyte, the exfoliated graphene sheets exhibited lower oxidation degree and defects [27], [38]. Moreover, the addition of NaOH in ClO_4^- , increased the pH value of the electrolyte which reduced the quantity of defects and oxidation of the exfoliated graphene [41].

The quality of exfoliated graphene nanosheets and its exfoliation efficiency can also be affected by the concentration of electrolyte. Basically, the degree of oxidation increases with the increasing of the concentration of electrolyte. For instant, by increasing the concentration of sulphuric acid as electrolyte, the oxidation of exfoliated graphene sheets was increased significantly [42], [43]. Same phenomena can be noticed when concentration of perchloric acid was increased [44], where defects and amounts of oxygen of graphene sheets were increased. In another report, the use of high concentration of perchloric acid at 8M induced the oxidation of graphite anode fully, even when lower voltage was supplied [45].

Besides, high temperature could affect the exfoliation efficiency of graphite by enlarging the distance between

the layers of graphite and strengthen the thermal vibration of the intercalating anions [46]. Prashant Tripathi et al. [38] noticed that production of graphene nanosheets in sulphate electrolyte was significantly increased up to ca. 70% by increasing the reaction temperature from room temperature to 80 °C. Moreover, higher temperature reduced the defect density of exfoliated graphene sheets in sulphate electrolyte due to the quantity of OH⁻ was reduced [38], meanwhile the defect density was higher when sulphuric acid was used as electrolyte at higher temperature [47].

Apart from all the mentioned factors, bias voltage or current density is a significant factor which affects the oxidation degree and exfoliation efficiency of graphene sheets. Normally, oxidation degree of graphene sheets and exfoliation efficiency are increased with increasing the current density. For example, the quantity of GO was increased significantly when the supplied voltage was increased from 2.2 to 6 V [43]. In addition, higher voltage increased the oxygen content of the graphene nanosheets [48]. Kumar et al. [49] demonstrated that by increasing the potential of the anode, the amount of graphene was raised whereas the thickness was reduced. Besides, they also observed that the quantity of defect of graphene sheets was increased at the beginning and decreased afterwards with the use of saccharin as electrolyte [49].

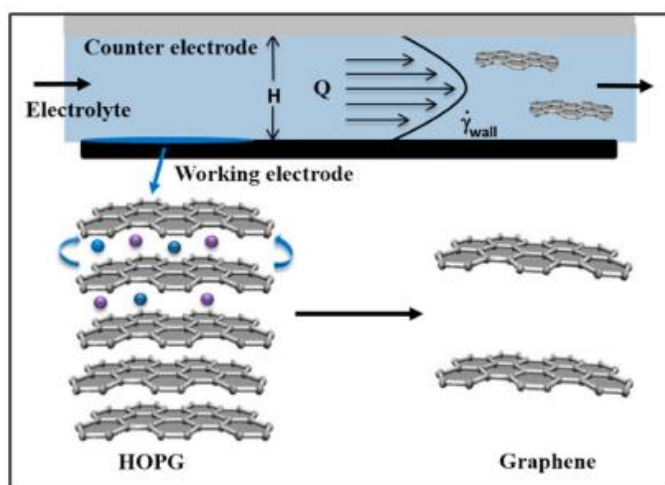


Figure 2 Diagram of electrochemical exfoliation with the aid of shearing force. Reprinted with permission from ref [50]. Copyright 2016 ACS Publications.

The quality of graphene nanosheets or the efficiency of exfoliation can be influenced by the type of anode. For instance, high production of 75% graphene (below 7 layers) was achieved when opened graphite rather than natural graphite and bi-sulfate anions from sulfuric acid were used. Furthermore, the oxygen containing functional groups was slightly more than the exfoliated graphene from natural graphite [51]. When spectroscopic graphite (SG) and HOPG were compared, much lower oxygen content (15.3%) was observed for SG than HOPG during reaction using ammonium persulfate (NH₄)₂S₂O₈ as electrolyte [30]. In addition, pencil core also can be utilised as a suitable graphite precursor to produce few-layers graphene sheets [52].

The exfoliation efficiency and quality of graphene nanosheets can also be enhanced by ultrasonication and shear force. This is an effective technique to synthesize good quality graphene where the exfoliation is facilitated by the shear force. As shown in Figure 2, the presence of shear force due to the electrolyte flow contributed to the formation of big size, low defect structure and few layers graphene sheets even low anodic voltage was supplied [50].

The configuration of the electrochemical cell could also be a factor that affects the efficiency of exfoliation and the quality of the graphene nanosheets. For example, the electrochemical cell was placed vertically as seen in Figure 3 in which the graphite anode was positioned at the bottom whereas the platinum cathode was positioned at the top of the cell. This configuration allows thick and heavy graphite particles to sink at the bottom and the exfoliation was continued until tiny and very light graphene nanosheets were suspended in the solution. This method was able to synthesize ca. 50% of graphene but the amount of oxygen-containing functional groups was higher than exfoliated graphene by using conventional horizontal cell [53].

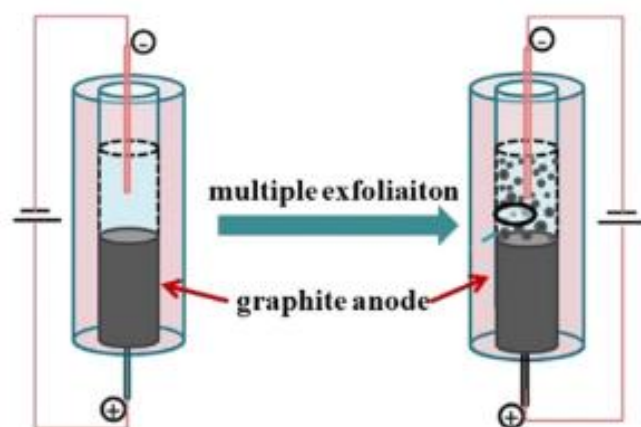


Figure 3 Drawing of vertical electrochemical cell for the purpose of exfoliation of graphite. Reprinted with permission from ref [53]. Copyright 2013 Elsevier Ltd.

4. CONCLUSION

The low-cost synthesis of graphene sheets in large quantities with a negligible impact to the environment is a significant concern for us. The graphene flakes are predicted to be more promising than silicon-based electronics when its desired electrical properties and large quantities of production have been achieved successfully, contributing to upcoming electrical gadgets with increased speed, chemical inertness, eco-friendliness and enhanced functionality.

The main disadvantage of the electrochemical method is the requirement of continuous voltage supplied to the graphite precursor where usually graphite rod, graphite foil or highly oriented pyrolytic graphite was used in the reported methods.

Ideally, electrochemical exfoliation happens on the outermost layer of graphite anode, eventually removing the graphene layers off the precursor, separately. However, the intercalation and exfoliation of anions occurs at whole surface of graphite that immersed in the electrolytes, thus contributing to the formation of few-layered or multi-layered graphene sheets. Moreover, this non-uniform exfoliation effect will be more noticeable when a bigger size of graphite precursor is used because of larger surface area is exposed to the electrolyte. Therefore, it is essential to redesign the electrochemical configuration in order to improve the driving force of electrochemical to the graphite precursor. Thus, by overcoming this obstacle, the advantages of electrochemical approach can be fully utilized.

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