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Graphene Synthesis Methods for Graphene based Supercapacitors used in solar cell energy systems

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A B S T R A C T

In the last decade, graphene as one of the novel engineering materials with unique properties has been strongly considered by researchers. Graphene based supercapacitors and transistors are one the most recent subjects in the case of solar energy systems modification fields. In this study, five main methods of producing graphene (micro-mechanical cleavage, Liquid-phase exfoliation, Graphene via graphite oxide, Graphene from mechanical milling of graphite, Electrochemical exfoliation of graphite) which are in the challenge of engineering and economics justifiable in using for supercapacitors, has been investigated. Subsequently, Liquid-phase exfoliation has been chosen as the best method of producing graphene for using in supercapacitors in the industry scale based on the investigations and comparison throughout advantages and limitations of the preceding methods.

1. Introduction

Free standing graphene was exfoliated by Geim and Konstanitin Novoselov in 2004 but attempts to study and acquisition of graphene return back to 1859[1,2].Since then researchers and industrial companies focoused on production methods and investigations for modifing properties of two dimensional exfoliated grphene[3]. Graphene is a thin layer of carbon atoms that seperated of graphit material and atoms are bounded in hexagonal lattice and seems like seprated blocks of graphite[4].Unique properties such as high surface area, excellent thermal conductivity, high stifness, electron mobility and high light transmittance makes graphene a multifunctional material that used in a wide range of industrial and academical fields so its not surprising to call graphene a miracle material[5]. the most improtant aspect of graphene that makes it precious is stability that caused by minimizing the surface energy[6]. So researchers has mainly focused on its applications in electronics, catalysis, sensors, energy conversion and storage, etc. For these purposes, low costs are one of the basic requirements to fabricate graphene sheets in extend and large scales [7].

Graphite is used as raw material to reach graphene. Graphit is an alotropic form of carbon in which carbon sheets are held together by van der waals weak forces. So the first step to reach graphene material is to overcome these weak van der waals forces[8].

Some of the methods (graphite base and other methods)are indicated in Fig.1.

In solar cell energy systems graphene acts a significant role to produce graphene based supercapacitors which helps to save the higher amounts of energy due to numerical seprated layers and minimizing the energy consumption[7].

In this paper we are going to make an overall investigation for graphene fabrication main methods (in these methods graphene sheets are exfoliated from raw graphite) which are justifiable economically and engineering wise in using for supercapacitors and comparison throughout advantages and limitations of the preceding methods.

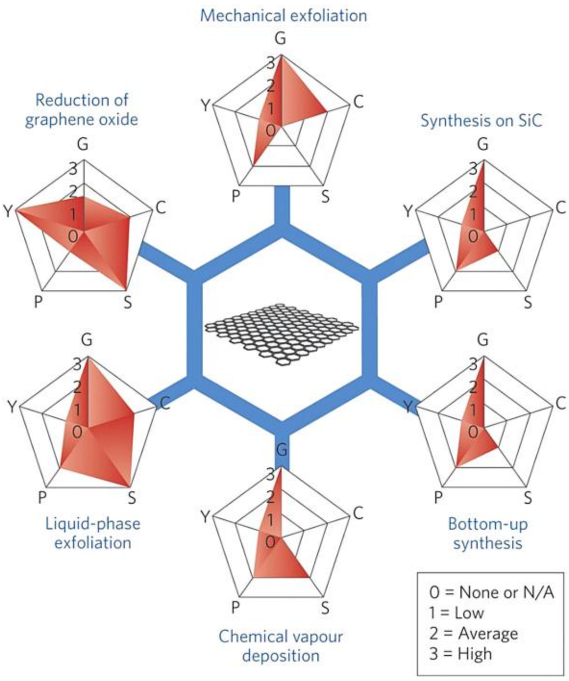

Figure 1. Some methods of graphene fabrication

Each method has been evaluated in terms of graphene quality (G), cost aspect (C; a low value corresponds to high cost of production), scalability (S), purity (P) and yield (Y) of the overall production process.[27]

1. Graphene synthesis Methods

2.1. Micromechanical-cleavage of graphene

Micromechanical cleavage(MC) is the oldest method of graphene fabrication and it became popular because of its simplicity and purity of exfoliated graphene sheets so it is not surprising to name it the "birth of graphene".Geim et al exfoliated graphene by using scotch tape and a substrate in MC method. They peeled of raw graphite layers with scotch tape continiously and dissoleved tape in acetone solution so graphite layers flaked and sediment on the Si wafer (substrate). They reached lateral sheets size upon 10 µm[1].

Graphene produced by means of this method is pure and free of defects(impurities inclusions and etc materialestic defects) or at least defects are less than other methods in comperession also we can reach thiner layers of graphene but the most important challenge in this method is scalibility which means that MC is not a method for graphene fabrixation in large scales and its not a suitable choice for industrial applications but also it remains as a main method for academical researches and fundimentals[55].

2.2. Liquid-exfoliation method

In liquid-phase exfoliation(LPE) method graphite exfoliation procsess takes place in liquid media via shear forces or ultra sound[9].

To select suitable liquid medium it is important to care the surface energy which means that energy of liquid mdium(solvent) should be in the same range of graphene surface energy(graphene surface energy estimated about $46.7 mNm^{-1}$). N-methylpyrrolidone(NMP) and N-dimethylformamide(DMF) are some of the solvents used successfully to exfoliate and stablize graphene sheets because these media minimize the interfacial tensions between solvent and graphene sheets[10].

The excellences of LPE in comprasion to other methods are simpilicity and large scalibility. In LPE procses growth and collapse of micromtere-sized voids or bubbles which shaped by means of solvent pressure acts to exfoliate graphite layers. The most important challenge in LPE is choosing suitable solvents. Since solvents with surface energy in the range of graphene surface energy are almost expensive and toxic, attemps are made to prepare a solvent media such as aceton methanol or other similar solvents with low boiling points[11].

For solving the surface energy scales of solvents investigations focused on surfactants which helps to stablize the surface energy of solvents. Surfactants almost divided in two main groups: ionic and non-ionic and it is been proven that non-ionic surfactants such as P-123 act better than ionic surfactants to stablize solvents energy systems.

Hydrophobic tail and larger hydrophilic part of non-ionic surfactants creates a steric repulsion between the hydrophilic moieties in water and act to stablize dispressed sheets of graphene [12].

The mechanism shcematically indicated in Fig.2.

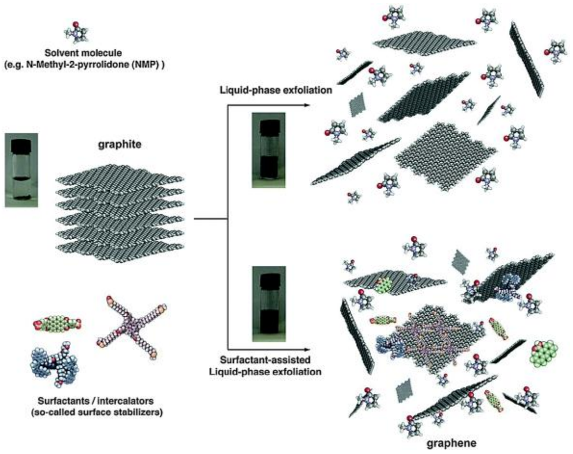

Figure 2.shcematic representation of liquid-exfoliation method. [8]

1.3. Graphene via graphite oxide

The principle of this method is to intercalate functional oxygen groups between graphene sheets and intercaleted oxidants dipress and stablize flakes in water.

There is not a limitation for solvent choice in this method and lots of liquid media can be used for dispresion of graphene sheets. Also low-cost large scalibility and excellent yield are the most important advantages of this method[13].

Tour et al suggested a way to reach graphene oxide(GO) which include three main steps (Fig.2.): first they intercalated graphite with sulfuric acid to reach graphite intercalated compound (GIC) in second step they used potassium permanganate $(KMnO_4)$ and sulfuric acid(H_2So_4) reaction to reach the oxidized form of graphite and subsequently dispersed in water and transforms to graphene oxide(GO)[14].

In graphene via graphite oxide chemical treatments such as potassium per manganate $(KMnO_4)$ and sulfuric acid(H_2So_4) acts to destroy the sp^2 structure of graphite and disperission of layers in water by producing functional oxygen groups like hydroxyl (-OH) and epoxide (C-O-C) on basal plane and carbonyl(C=O) or carboxilyc (-COOH) on the edges[15].

Graphite oxide (basal material in this method) nomally fabricated by so-called hummers method.but it should be noted that in hummers method chemicals like sodium nitride petassium per manganate and sulfuric acid react to produce graphite oxide and turn it to graphene oxide and this chemicals are not envirement friendly and produce toxic gases also the procses is in high tempreture condition and there is great risk of explosion so researchers concentrated investigations on modifing hummers method[16]

As defined graphene via graphite oxide has great potentional to graphene fabrication in large scales but the most important disadvantage of this method is producing oxygen functional groups on graphene planes which acts as inclusions and effect quality parameters some of this defects can resolve by reductional methods but hummers method still need to modify[rev].

2.4. Mechanical milling of graphite

Antisari et al started the mechanical milling technique. They applied milling procses on graphite which dispressed in distilled water for 60 h to reach few layered graphene sheets.The technique continued and modified by Zhao et al where they started to use other liquid media and dispressed graphite in N-dimethylformamide (DMF) and used a low speed planatery ball milling system to reach graphene sheet layers[17].

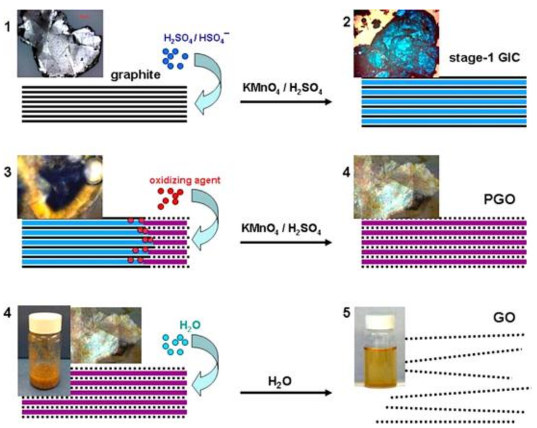

Figure 3. Converting graphite to GO stepsReproduced from Ref. [13]

In this method graphite raw material dispersed in different liquid media and susequently milling procses applies on graphite to peel of flakes so the quantity and quality of fabricated graphene severly depends on procese parameters such as speed of rotation, diameter of milling ball, milling time, type of graphite used, concentration of graphite in the solvent and centrifugation speed[18].

It is clear to know this method can become a useful method with great potentional to graphene fabrication by providing control on wide range of parameteres but also time and energy consumption low graphene yield and defects on the final producted graphene are still problems that researchers faced in this method[19].

2.5. Electromechanical exfoliation of graphite

Electrochemichal technique is an old well-known method which is apply to pruduce aluminum first also its used to produce peroxoacids etc in industrial companies.

Similar to third described method in electromechanical technique also graphite rod is intercalated by compounds and GIC form of graphite is formed. An aqeous or organic electrolyte media required and fabrication compeleted by reduction and oxidation procses Fig.3 illustrated the shcematic form of proceses clearly[20].

An electrode is prepared from graphite material and other electrod is almost platinum rod samples are taken in the electrolyte and a posituve current applied to rods graphitic rod goes under oxidation and negative charge ions intercalated in graphitic rod and caused exfoliation of layers[21].

Unlike hummers method in this method there is not aggressive reactions to form GIC insted of distructive reactions GIC form of graphite is formed due to electrical conductivity property of electrods and electrolyte. An other advantage of method is the potential to mass production of graphene in comparisson mechanical and chemical methods. Unbroken voltage bias to electrodes can be described as an important hinders of application in this method[22].

3. Electrical and mechanical properties of graphene

Among the interesting and surprising properties of graphene, electrical aspects of graphene make this material important for electrical fields and researchers. Novoselov et al indicates the great potential of possibility to varying charge carriers from holes to electrons which is an important factor in transistors fabrication.

The quantum hall effect of graphene to both holes and electrons carriers is another electrical important face of graphene. This effect occurs due to high electron mobility of graphene in various temperature and under exposure to magnetic fields [24].

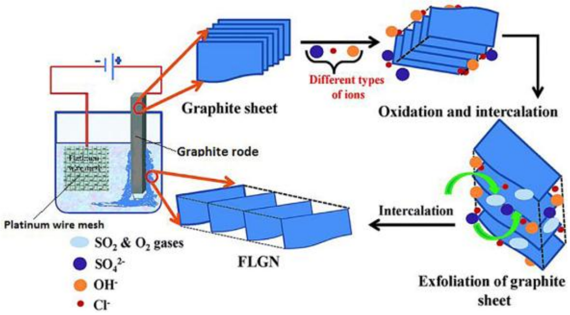

Fig.4.Electromechanical exfoliation of graphene [23].

Also, mechanical properties of graphene are the other important factor which should be pointed to reach suitable product to use in supercapacitors.

Some of these properties are indicated in Table1.

Table 1. mechanical properties of graphene[27].		
Number of layers	Young modulus E(TPa)	Intrinsic strenght σ (GPa)
one	1	130
one	1	131
two three	1.04 0.98	125 101

4. Graphene based supercapacitors

Supercapacitors with properties such as high-power density (time rate of energy transfer) and sufficiency, cyclability in long time applications are one the recent subjects of solar cell energy systems that researchers are concentrated on it.

The key point to design new supercapacitors is to fabricate high performance advance electrode materials so today graphene bolded as an effective material to use in fabrication of next-generation supercapacitors.

Supercapacitors are ideal energy devices in compression conventional batteries for applications such as electric vehicle, forklifts etc [25].

Using graphene as separator and electrode material in supercapacitors enhanced the power density and sores more energy due to thick and numerical layers [26].

5. Conclusion

As it is mentioned recently investigations are focused on graphene based supercapacitors to replace conventional store devices. So by choosing suitable electrodes we can modify the power density and energy storing capability. Today graphene is one best choice to use as electrode due to size scale, layeral structure and amazing electrical properties, and among functional methods to fabricate graphene.After ivestigation on advantages and limitations of mentioned suitable synthesis methods:

1-Graphene based supercapacitors are potentional to use insteed of conventional storing device.

2- we suggest the liquid phase exfoliation method as an econimical and industrial fabrication that makes it possible to produce relativly high quality in large scales.

3-by modifing synthesis methods and improving product quality an evidance promot on supercapacitors efficiency could be reached.

References

[1] Novoselov, K. S. (2011). Nobel lecture: Graphene: Materials in the flatland. *Reviews of Modern Physics*, *83*(3), 837.

[2] Geim, A. K. (2011). Nobel Lecture: Random walk to graphene. *Reviews of Modern Physics*, *83*(3), 851.

[3] Wei, J., Atif, R., Vo, T., & Inam, F. (2015). Graphene nanoplatelets in epoxy system: dispersion, reaggregation, and mechanical properties of nanocomposites. *Journal of Nanomaterials*, *16*(1), 374.

[4] Slonczewski, J. C., & Weiss, P. R. (1958). Band structure of graphite. *Physical Review*, *109*(2), 272.

[5] Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J. W., Potts, J. R., & Ruoff, R. S. (2010). Graphene and graphene oxide: synthesis, properties, and applications. *Advanced materials*, *22*(35), 3906-3924.

[6] Katsnelson, M. I., & Geim, A. K. (2008). Electron scattering on microscopic corrugations in graphene. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, *366*(1863), 195-204.

[7] Vivekchand, S. R. C., Rout, C. S., Subrahmanyam, K. S., Govindaraj, A., & Rao, C. N. R. (2008). Graphene-based electrochemical supercapacitors. *Journal of Chemical Sciences*, *120*(1), 9-13.

[8] Ciesielski, A., & Samorì, P. (2014). Graphene via sonication assisted liquid-phase exfoliation. *Chemical Society Reviews*, *43*(1), 381-398.

[9] Wang, S., Zhang, Y., Abidi, N., & Cabrales, L. (2009). Wettability and surface free energy of graphene films. *Langmuir*, *25*(18), 11078-11081.

[10] Hernandez, Y., Nicolosi, V., Lotya, M., Blighe, F. M., Sun, Z., De, S., … & Boland, J. J. (2008). High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, *3*(9), 563-568.

[11] Du, W., Jiang, X., & Zhu, L. (2013). From graphite to graphene: direct liquid-phase exfoliation of graphite to produce single-and few-layered pristine graphene. *Journal of Materials Chemistry A*, *1*(36), 10592-10606.

[12] Parvez, K., Yang, S., Feng, X., & Müllen, K. (2015). Exfoliation of graphene via wet chemical routes. *Synthetic Metals*, *210*, 123-132.

[13] Li, D., Müller, M. B., Gilje, S., Kaner, R. B., & Wallace, G. G. (2008). Processable aqueous dispersions of graphene nanosheets. *Nature nanotechnology*, *3*(2), 101-105.

[14] Dimiev, A. M., & Tour, J. M. (2014). Mechanism of graphene oxide formation. *ACS nano*, *8*(3), 3060-3068.

[15] Gao, W., Alemany, L. B., Ci, L., & Ajayan, P. M. (2009). New insights into the structure and reduction of graphite oxide. *Nature chemistry*, *1*(5), 403-408.

[16] Marcano, D. C., Kosynkin, D. V., Berlin, J. M., Sinitskii, A., Sun, Z., Slesarev, A., … & Tour, J. M. (2010). Improved synthesis of graphene oxide.

[17] Antisari, M. V., Montone, A., Jovic, N., Piscopiello, E., Alvani, C., & Pilloni, L. (2006). Low energy pure shear milling: a method for

the preparation of graphite nano-sheets. *Scripta Materialia*, *55*(11), 1047-1050.

[18] Zhao, W., Wu, F., Wu, H., & Chen, G. (2010). Preparation of colloidal dispersions of graphene sheets in organic solvents by using ball milling. *Journal of Nanomaterials*, *2010*, 6.

[19] Fan, X., Chang, D. W., Chen, X., Baek, J. B., & Dai, L. (2016). Functionalized graphene nanoplatelets from ball milling for energy applications. *Current Opinion in Chemical Engineering*, *11*, 52-58.

[20] Wendt, H., & Kreysa, G. (1999). *Electrochemical engineering: science and technology in chemical and other industries*. Springer Science & Business Media.

[21] Low, C. T. J., Walsh, F. C., Chakrabarti, M. H., Hashim, M. A., & Hussain, M. A. (2013). Electrochemical approaches to the production of graphene flakes and their potential applications. *Carbon*, *54*, 1-21.

[22] Su, C. Y., Lu, A. Y., Xu, Y., Chen, F. R., Khlobystov, A. N., & Li, L. J. (2011). High-quality thin graphene films from fast electrochemical exfoliation. *ACS nano*, *5*(3), 2332-2339.

[23] Parveen, N., Ansari, M. O., & Cho, M. H. (2015). Simple route for gram synthesis of less defective few layered graphene and its electrochemical performance. *RSC Advances*, *5*(56), 44920-44927.

[24] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov,A.K. Geim, Two-dimensional atomic crystals, Proc. Natl. Acad. Sci. U.S.A. 102(2005) 10451–10453.

[25] Liu, C., Yu, Z., Neff, D., Zhamu, A., & Jang, B. Z. (2010). Graphene-based supercapacitor with an ultrahigh energy density. *Nano letters*, *10*(12), 4863-4868.

[26] Zhang, L. L., Zhou, R., & Zhao, X. S. (2010). Graphene-based materials as supercapacitor electrodes. *Journal of Materials Chemistry*, *20*(29), 5983-5992

[27] Phiri, J., Gane, P., & Maloney, T. C. (2017). General overview of graphene: Production, properties and application in polymer composites. *Materials Science and Engineering: B*, *215*, 9-28..