

Extraction of Graphene and Synthesis using Microwave

Imad ul Iman Chikkodi¹

Student, Electronics and Communication,

KLE Dr. M.S. Sheshgiri College of Engineering & Technology, Belgaum, India¹

Abstract: Scientists have theorized about graphene for decades. It has likely been unknowingly produced in small quantities for centuries, through the use of pencils and other similar applications of graphite. It was originally observed in electron microscopes in 1962, but only studied while supported on metal surfaces. The material was later rediscovered, isolated and characterized in 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester. Research was informed by existing theoretical descriptions of its composition, structure and properties. High-quality graphene proved to be surprisingly easy to isolate, making more research possible. This work resulted in the two winning the Nobel Prize in Physics in 2010 "for groundbreaking experiments regarding the two-dimensional material graphene." The global market for graphene is reported to have reached \$9 million by 2012, with most of the demand from research and development in semiconductor, electronics, battery energy and composites.

Keywords: Microwave heating, Graphene, Graphene Extraction, Graphite

I. INTRODUCTION

"Graphene" is a combination of "graphite" and the suffix -ene, named by Hanns-Peter Boehm, who described single-layer carbon foils in 1962. The term *graphene* first appeared in 1987 to describe single sheets of graphite as a constituent of Graphite Intercalation Compounds (GICs); conceptually a GIC is a crystalline salt of the intercalant and graphene. The term was also used in early descriptions of carbon nanotubes, as well as for epitaxial graphene and polycyclic aromatic hydrocarbons. Graphene can be considered an "infinite alternant" (only six-member carbon ring) Polycyclic Aromatic Hydrocarbon (PAH).

The IUPAC compendium of technology states: "previously, descriptions such as graphite layers, carbon layers, or carbon sheets have been used for the term graphene... it is incorrect to use for a single layer a term which includes the term graphite, which would imply a three-dimensional structure. The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed."

Geim defined "isolated or free-standing graphene" as "graphene is a single atomic plane of graphite, which – and this is essential – is sufficiently isolated from its environment to be considered free-standing." This definition is narrower than the IUPAC definition and refers to cloven, transferred, and suspended graphene. Other forms of graphene, such as graphene grown on various metals, can become free-standing if, for example, suspended or transferred to Silicon Dioxide (SiO₂) or silicon carbide.

In 2016, Brown University introduced a method for 'crumpling' graphene, adding wrinkles to the material on a nano scale. This was achieved by depositing layers of graphene oxide onto a shrink film, then shrunken, with the film dissolved before being shrunken again on another sheet of film. The crumpled graphene became superhydrophobic, and, when used as a battery electrode, the material was shown to have as much of a 400% increase in electrochemical current density.

II. PROPERTIES

Graphene has a theoretical Specific Surface Area (SSA) of 2630 m²/g. This is much larger than that reported to date for carbon black (typically smaller than 900 m²/g) or for Carbon NanoTubes (CNTs), from ≈100 to 1000 m²/g and is similar to activated carbon.

A. Structure

Graphene is a crystalline allotrope of carbon with 2-dimensional properties. Its carbon atoms are densely packed in a regular atomic-scale chicken wire (hexagonal) pattern. Each atom has four bonds, one σ bond with each of its three neighbors and one π -bond that is oriented out of plane. The atoms are about 1.42 Å (Angstrom) apart.

Graphene's hexagonal lattice can be regarded as two interleaving triangular lattices. This perspective was successfully used to calculate the band structure for a single graphite layer using a tight-binding approximation.

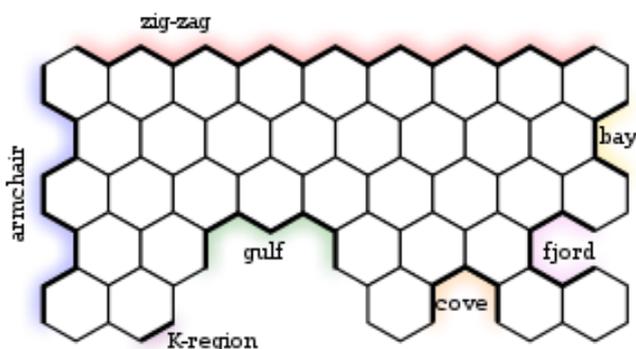
Graphene's stability is due to its tightly packed carbon atoms and a sp^2 orbital hybridization – a combination of orbitals s , p_x and p_y that constitute the σ -bond. The final p_z electron makes up the π -bond. The π -bonds hybridize together to form the π -band and π^* -bands. These bands are responsible for most of graphene's notable electronic properties, via the half-filled band that permits free-moving electrons. Recent quantitative estimates of aromatic stabilization and limiting size derived from the enthalpies of hydrogenation (ΔH_{hydro}) agree well with the literature reports.

Graphene can self-repair holes in its sheets, when exposed to molecules containing carbon, such as hydrocarbons. Bombarded with pure carbon atoms, the atoms perfectly align into hexagons, completely filling the holes.

The atomic structure of isolated, single-layer graphene was studied by transmission electron microscopy (TEM) on sheets of graphene suspended between bars of a metallic grid. Electron diffraction patterns showed the expected honeycomb lattice. Suspended graphene also showed "rippling" of the flat sheet, with amplitude of about one nanometer. These ripples may be intrinsic to the material as a result of the instability of two-dimensional crystals, or may originate from the ubiquitous dirt seen in all TEM images of graphene. Atomic resolution real-space images of isolated, single-layer graphene on SiO_2 substrates are available via scanning tunneling microscopy. Photoresist residue, which must be removed to obtain atomic-resolution images, may be the "adsorbates" observed in TEM images, and may explain the observed rippling. Rippling on SiO_2 is caused by conformation of graphene to the underlying SiO_2 , and is not intrinsic.

B. Chemical

Graphene is the only form of carbon (or solid material) in which every atom is available for chemical reaction from two sides (due to the 2D structure). Atoms at the edges of a graphene sheet have special chemical reactivity. Graphene has the highest ratio of edge atoms of any allotrope.



Defects within a sheet increase its chemical reactivity. The onset temperature of reaction between the basal plane of single-layer graphene and oxygen gas is below $260\text{ }^\circ\text{C}$ (530 K). Graphene burns at very low temperature (e.g., $350\text{ }^\circ\text{C}$ (620 K)). Graphene is commonly modified with oxygen- and nitrogen-containing functional groups and analyzed by infrared spectroscopy and X-ray photoelectron spectroscopy. However, determination of structures of graphene with oxygen and nitrogen functional groups requires the structures to be well controlled.

In 2013, Stanford University physicists reported that single-layer graphene is a hundred times more chemically reactive than thicker sheets.

C. Electronics

Graphene is a zero-gap semiconductor, because its conduction and valence bands meet at the Dirac points. The Dirac points are six locations in momentum space, on the edge of the Brillouin zone, divided into two non-equivalent sets of three points. The two sets are labeled K and K' . The sets give graphene a valley degeneracy of $g_v = 2$. By contrast, for traditional semiconductors the primary point of interest is generally Γ , where momentum is zero. Four electronic properties separate it from other condensed matter systems.

However, if the in-plane direction is no longer infinite, but confined, its electronic structure would change. They are referred to as graphene nanoribbons. If it is "zig-zag", the bandgap would still be zero. If it is "armchair", the bandgap would be non-zero

D. Thermal Conductivity

Thermal transport in graphene is an active area of research, which has attracted attention because of the potential for thermal management applications. Early measurements of the thermal conductivity of suspended graphene reported an exceptionally large thermal conductivity of approximately $5300\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, compared with the thermal conductivity

of pyrolytic graphite of approximately $2000 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room temperature. However, later studies have questioned whether this ultrahigh value had been overestimated, and have instead measured a wide range of thermal conductivities between $1500 - 2500 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for suspended single layer graphene. The large range in the reported thermal conductivity can be caused by large measurement uncertainties as well as variations in the graphene quality and processing conditions. In addition, it is known that when single-layer graphene is supported on an amorphous material, the thermal conductivity is reduced to about $500 - 600 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room temperature as a result of scattering of graphene lattice waves by the substrate, and can be even lower for few layer graphene encased in amorphous oxide. Likewise, polymeric residue can contribute to a similar decrease in the thermal conductivity of suspended graphene to approximately $500 - 600 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for bilayer graphene.

Potential for this high conductivity can be seen by considering graphite, a 3D version of graphene that has basal plane thermal conductivity of over a $1000 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ (comparable to diamond). In graphite, the c-axis (out of plane) thermal conductivity is over a factor of ~ 100 smaller due to the weak binding forces between basal planes as well as the larger lattice spacing. In addition, the ballistic thermal conductance of graphene is shown to give the lower limit of the ballistic thermal conductances, per unit circumference, length of carbon nanotubes.

Despite its 2-D nature, graphene has 3 acoustic phonon modes. The two in-plane modes (LA, TA) have a linear dispersion relation, whereas the out of plane mode (ZA) has a quadratic dispersion relation. Due to this, the T^2 dependent thermal conductivity contribution of the linear modes is dominated at low temperatures by the $T^{1.5}$ contribution of the out of plane mode. Some graphene phonon bands display negative Grüneisen parameters. At low temperatures (where most optical modes with positive Grüneisen parameters are still not excited) the contribution from the negative Grüneisen parameters will be dominant and thermal expansion coefficient (which is directly proportional to Grüneisen parameters) negative. The lowest negative Grüneisen parameters correspond to the lowest transverse acoustic ZA modes. Phonon frequencies for such modes increase with the in-plane lattice parameter since atoms in the layer upon stretching will be less free to move in the z direction. This is similar to the behavior of a string, which, when it is stretched, will have vibrations of smaller amplitude and higher frequency. This phenomenon, named "membrane effect," was predicted by Lifshitz in 1952.

E. Biological

In 2015 researchers used graphene to create sensitive biosensors by using epitaxial graphene on silicon carbide. The sensors bind to the 8-hydroxydeoxyguanosine (8-OHdG) and is capable of selective binding with antibodies. The presence of 8-OHdG in blood, urine and saliva is commonly associated with DNA damage. Elevated levels of 8-OHdG have been linked to increased risk of developing several cancers.

The Cambridge Graphene Centre and the University of Trieste in Italy conducted a collaborative research on use of Graphene as electrodes to interact with brain neurons. The research was recently published in the journal of ACS Nano. The research revealed that uncoated Graphene can be used as neuro-interface electrode without altering or damaging the neural functions such as signal loss or formation of scar tissue. Graphene electrodes in body stay significantly more stable than modern day electrodes (of tungsten or silicon) because of its unique properties such as flexibility, biocompatibility, and conductivity. It could possibly help in restoring sensory function or motor disorders in paralysis or Parkinson patients.

III. EXTRACTION

Isolated 2D crystals cannot be grown via chemical synthesis beyond small sizes even in principle, because the rapid growth of phonon density with increasing lateral size forces 2D crystallites to bend into the third dimension. However, other routes to 2d materials exist. The early approaches of cleaving multi-layer graphite into single layers or growing it epitaxially by depositing a layer of carbon onto another material have been supplemented by numerous alternatives. In all cases, the graphite must bond to some substrate to retain its 2d shape.

A. Exfoliation

An extreme case of intercalation is the complete separation of the layers of the material. This process is called exfoliation. Typically aggressive conditions are required involving highly polar solvents and aggressive reagents. Intercalation is the reversible inclusion or insertion of a molecule (or ion) into materials with layered structures. Examples are found in graphite and transition metal dichalcogenides.

● **Graphite Oxide Reduction**

P. Boehm reported producing monolayer flakes of reduced graphene oxide in 1962. Rapid heating of graphite oxide and exfoliation yields highly dispersed carbon powder with a few percent of graphene flakes. Reduction of graphite

oxide monolayer films, e.g. by hydrazine with annealing in argon/hydrogen also yielded graphene films. Later the oxidation protocol was enhanced to yield graphene oxide with an almost intact carbon framework that allows efficient removal of functional groups, neither of which was originally possible. The measured charge carrier mobility exceeded 1,000 centimetres (393.70 in)/Vs. Spectroscopic analysis of reduced graphene oxide has been conducted.

Burning a graphite oxide coated DVD produced a conductive graphene film (1738 siemens per meter) and specific surface area (1520 square meters per gram) that was highly resistant and malleable.

Dispersing graphite in a liquid medium can produce graphene by sonication followed by centrifugation, producing concentrations 2.1 mg/ml in N-methylpyrrolidone. Using a suitable ionic liquid as the dispersing liquid medium produced concentrations of 5.33 mg/ml. Restacking is an issue with this technique.

Adding a surfactant to a solvent prior to sonication prevents restacking by adsorbing to the graphene's surface. This produces a higher graphene concentration, but removing the surfactant requires chemical treatments.

Sonicating graphite at the interface of two immiscible liquids, most notably heptane and water, produced macro-scale graphene films. The graphene sheets are adsorbed to the high energy interface between the materials and are kept from restacking. The sheets are up to about 95% transparent and conductive.

With definite cleavage parameters, the box-shaped graphene (BSG) nanostructure can be prepared on graphite crystal.

● **Carbon Dioxide Reduction**

A highly exothermic reaction combusts magnesium in an oxidation–reduction reaction with carbon dioxide, producing carbon nanoparticles including graphene and fullerenes.

● **Microwave-assisted Oxidation**

Microwave energy synthesizes graphene in one step. This approach avoids use of potassium permanganate in the reaction mixture. Microwave radiation assistance, graphene oxide with or without holes can be synthesized by controlling microwave time. Microwave heating dramatically shortens the reaction time from days to seconds.

IV. MICROWAVE SYNTHESIS

Microwave heats materials directly through dielectric loss rather than heat convection as in the conventional heating method, and hence can enable fast heating and selective heating. It is regarded to be promising in shortening the reaction time and yielding hot spots with extraordinary high temperature. As such, material scientists have devoted much effort to explore the potential application of microwave in overcoming the current problems and facilitating the fabrication of high-quality rGO in large-scale. To this end, we present an up-to-date critical survey of literature relevant to MW-assisted production of rGO. This brief review is organized as follows. First, techniques for characterizing quality of as-obtained rGO are discussed. Next, we provide a comprehensive summary of microwave-assisted chemical reduction of graphene oxide, microwave-assisted thermal reduction of graphene oxide, and microwave-assisted simultaneous thermal exfoliation and reduction of graphite oxide, respectively. Strong reducing reagents have been widely used to reduce graphene oxide. However, the reduction process is very slow. For example, hydrazine hydrate enabled reduction of graphene oxide in the oil bath for 12 h and 24 h resulted in a C/O ratio about 5. and 10.3, respectively. Microwave irradiation was found to be capable of accelerating the reducing rate significantly. For example, reported microwave assisted hydrazine hydrate reduction of graphene oxide. After microwave treatment for 2 × 30 s (on for 10 s, off and stirring for 20 s), the ID/IG in Raman spectra was 0.1–0.12, indicating a high reduction degree even after such a short treating time. This was confirmed by the improved thermal stability, showing no significant mass loss up to 750°C. Obtained Pd/Fe₃O₄ nanoparticles supported on graphene nanosheets by a one-pot microwave heating with the existence of hydrazine hydrate. After microwave irradiation for 2 min, the C/O of rGO was determined to be 8.1. reported microwave-enhanced chemical reduction of graphene oxide using HI/CH₃COOH as reducing reagent. They found the effect of 4 h microwave irradiation was comparable to 48 h conventional reaction process.

Since strong reducing reagents are very much expensive and hazardous, organic solvents have also been explored to reduce graphene oxide. reported MW-assisted reduction of graphene oxide in dimethyl sulfoxide (DMSO), a solvent with high microwave absorbing capability. The reduction degree of the sample prepared from 2 min MW irradiation at 1,200 W is even much higher than that of the sample derived from 7 h conventional heating treatment. After 2 min of MW irradiation in DMSO, the color of the product changed to black, and the XRD pattern showed no characteristic peak (10.9°) of GO, indicating that most of the GO has been converted into rGO. In contrast, under conventional heating at 180 °C, an apparent peak located at 10.9° was found even after 7 h treatment. It was not until 12th h that the GO was completely reduced, as can be seen from the disappearance of the peak at 10.9° in the XRD pattern and the color change of the sample to black. reported the microwave-enhanced chemical reduction of graphene oxide to rGO in a mixed solution of N, N-dimethylacetamide (DMAc) and water without any additional reductant under nitrogen purge. The XRD pattern of the graphene oxide showed a wide peak, indicating the damage of the regular crystalline pattern of

graphite during the oxidation. After microwave treatment for $2 \text{ min} \times 5 \text{ times}$ (2.45 GHz, 800 W), no peak was observed indicating microwave-assisted formation of single-layered graphene. XPS results showed that C/O ratio changed from 2.09 to 5.46, confirming that the removal of oxygen containing groups happened. However, the ID/IG in Raman spectra changed from 0.95 to 0.96, suggesting that the reduction led to an increase of aromatic domains of smaller overall size in graphene. Similarly, also reported an increase of the product's ID/IG in Raman spectra from 0.80 to 0.94 after being treated by microwave at 750 W for 2 min in N, N-dimethylacetamide (DMF) solution. applied DMF to reduce graphite oxide under microwave irradiation at 100 W for 30 min. The XPS results showed that C/O ratio rose from 2.13 to 6.13 while Raman results showed that ID/IG remained almost unchanged.

V. CONCLUSION

The basic building blocks of all the carbon nanostructures are a single graphitic layer that is covalently functional sp^2 bonded carbon atoms in a hexagonal honeycomb lattice which forms 3D bulk graphite. Raw graphene is heated to 350dC in a 3D bulk graphite. Raw graphene is heated to 350dC in Microwave assisted chamber to achieve reduced graphene with resistance less than 10 ohms.



The graphene is placed in alumina crucible K-type thermocouple is being used to measure the temperature. Soaking time is 20 mins under 350 degree Celcius. The resultant graphene will be less in mass as the moisture present in the graphene is evaporated due to heat. To avoid oxidation the sample is processed under Argon Gas.

The processed graphene is non-crystallized in nature and boast extreme electrical and thermal conductivity.

The D band around $1,350 \text{ cm}^{-1}$ in Raman spectra could reflect the disorder degree of the crystal structure of carbon while the G band around $1,580 \text{ cm}^{-1}$ represents a first-order scattering E_{2g} vibration mode for characterizing the sp^2 bond structure of carbon. ID/IG is the ratio of D band intensity to G band intensity, which could be used to evaluate the

quality of the graphene structure. The higher ID/IG is, the more defects of C atom crystal there are. In the Raman spectrum of graphene, the D-band peak could not be observed. However, the ID/IG of graphene oxide could be as high as ~0.8–1

Besides, the number of rGO layers can be estimated by observing the shape and position of the 2D peak in Raman spectra which is the second-order two-phonon process. For example, single-layer graphene exhibits a single, sharp 2D band located below 2,700 cm^{-1} , while bilayer sheets have a broader 2D peak around 2,700 cm^{-1} , and sheets more than five layers have a broad 2D peak above 2,700 cm^{-1}

REFERENCES

- [1]. Tse V. Chow Ting ,Howard C. Reader., Understanding Microwave Heating Cavities, Artech House Publishers.
- [2]. Microwave Engineer's Handbook, Two Volumes, Theodore Saad, Editor.
- [3]. The RF and Microwave Circuit Design Handbook, Stephen A. Mass.
- [4]. Heating Systems, "www.enerzi.co/heating"
- [5]. Wen, C., Zhao, N., Zhang, D. W., Wu, D., Zhang, Z.-B., and Zhang, S.-L. (2014). Efficient reduction and exfoliation of graphite oxide by sequential chemical reduction and microwave irradiation. *Synthetic Met.* 194, 71–76. doi: 10.1016/j.synthmet.2014.04.023
- [6]. Narayan, R., Kim, J. E., Kim, J. Y., Lee, K. E., and Kim, S. O. (2016). Graphene oxide liquid crystals: discovery, evolution and applications. *Adv. Mater.* 28, 3045–3068. doi: 10.1002/adma.201505122
- [7]. Shao, Y., Wang, J., Wu, H., Liu, J., Aksay, I. A., and Lin, Y. (2010). Graphene based electrochemical sensors and biosensors: a review. *Electroanalysis* 22, 1027–1036. doi: 10.1002/elan.200900571
- [8]. Stobinski, L., Lesiak, B., Malolepszy, A., Mazurkiewicz, M., Mierzwa, B., Zemek, J., et al. (2014). Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods. *J. Electron Spectrosc.* 195, 145–154. doi: 10.1016/j.elspec.2014.07.003
- [9]. Thostenson, E. T., and Chou, T. W. (1999). Microwave processing: fundamentals and applications. *Compos. Part A Appl. Sci. Manufact.* 30, 1055–1071. doi: 10.1016/s1359-835x(99)00020-2
- [10]. Wan, J., Huang, L., Wu, J., Xiong, L., Hu, Z., Yu, H., et al. (2018). Microwave combustion for rapidly synthesizing pore-size-controllable porous graphene. *Adv. Funct. Mater.* 28:382. doi: 10.1002/adfm.2018 00382
- [11]. Gao, X., Jang, J., and Nagase, S. (2010). Hydrazine and thermal reduction of graphene oxide: reaction mechanisms, product structures, and reaction design. *J. Phys. Chem. C* 114, 832–842. doi: 10.1021/jp909284g
- [12]. L. T., Ervin, M. H., Qiu, H., Fuchs, B. E., and Lee, W. Y. (2011). Graphene supercapacitor electrodes fabricated by inkjet printing and thermal reduction of graphene oxide. *Electrochem. Commun.* 13, 355–358. doi: 10.1016/j.elecom.2011.01.023
- [13]. Hur, S.H, & Park, J.-N.(2013). Graphene & its app in fuel cell catalysis: a review. *Asia Pac. J. Chem. Eng.* 8, 218–233. doi: 10.1002/apj.1676
- [14]. Bak, S., Kim, D., and Lee, H. (2016). Graphene quantum dots and their possible energy applications: a review. *Curr. Appl. Phys.* 16, 1192–1201. doi: 10.1016/j.cap.2016.03.026
- [15]. Kaur, M., Kaur, M., and Sharma, V. K. (2018). Nitrogen-doped graphene and graphene quantum dots: a review on synthesis and applications in energy, sensors and environment. *Adv. Colloid Interfac.* 59, 44–64. doi: 10.1016/j.cis.2018.07.001
- [16]. Kumar, D., Raghavan, C. M., Sridhar, C., Shin, J. H., Ryu, S. H., Jang, K., et al. (2015). Microwave-assisted synthesis, characterization of reduced graphene oxide, and its antibacterial activity. *B. Korean Chem. Soc.* 36, 2034–2038. doi: 10.1002/bkcs.10394
- [17]. Kappe, C. O. (2004). Controlled microwave heating in modern organic synthesis. *Angew. Chem. Int. Edit.* 43, 6250–6284. doi: 10.1002/anie.200400655
- [18]. X., Rui, M., Song, J., Shen, Z., and Zeng, H. (2015). Carbon and graphene quantum dots for optoelectronic and energy devices: a review. *Adv. Funct. Mater.* 25, 4929–4947. doi: 10.1002/adfm.201501250
- [19]. Gannavarapu, K. P., Azizhannad, S., Muthukumar, S., Mitra, S., and Dandamudi, R. B. (2018). Microwave-assisted biogenic synthesis of metal-decorated reduced graphene oxide and their electrochemical properties. *ChemistrySelect* 3, 13438–13441. doi: 10.1002/slct.201803420
- [20]. Pokharel, P., Truong, Q. T., and Lee, D. S. (2014). Multi-step microwave reduction of graphite oxide and its use in the formation of electrically conductive graphene/epoxy composites. *Compos. Part B Eng.* 64, 187–193. doi: 10.1016/j.compositesb.2014.04.013
- [21]. Mattevi, C., Kim, H., and Chhowalla, M. (2011). A review of chemical vapour deposition of graphene on copper. *J. Mater. Chem.* 21, 3324–3334. doi: 10.1039/c0jm02126a
- [22]. H. Hou, S. Wang, Q. Jiang, W. Jin, L. Jiang, G. Sun, Durability study of KOH doped polybenzimidazole membrane for air-Q.F. Li, H.C. Rudbeck, A. Chromik, J.O. Jensen, C. Pan, T. Steenberg, M. Calverley, N.J. Bjerrum, J. Kerres, Properties, degradation and high temperature fuel cell test of different types of PBI and PBI blend membranes, *J. Membr. Sci.* 347 (2010) 260–270.
- [23]. breathing alkaline direct ethanol fuel cell, *J. Power Sources* 196 (2011) 3244–3248.
- [24]. S.J. Lue, K.P.O. Mahesh, W.-T. Wang, J.-Y. Chen, C.-C. Yang, Permeant transport properties and cell performance of potassium hydroxide doped poly(vinyl alcohol)/ fumed silica nanocomposites, *J. Membr. Sci.* 367 (2011) 256–264.
- [25]. S.H. Aboutalebi, M.M. Gudarzi, Q.B. Zheng, J.-K. Kim, Spontaneous formation of liquid crystals in ultralarge graphene oxide dispersions, *Adv. Funct. Mater.* 21 (2011) 2978–2988
- [26]. L. Staudenmaier, Verfahren zur Darstellung der Graphitsäure (Process for the representation of the graphitic acid), *Ber. Dtsch. Chem. Ges.* 31 (1898) 1481–1487
- [27]. S.J. Lue, Y.-L. Pai, C.-M. Shih, M.-C. Wu, S.-M. Lai, Novel bilayer well-aligned Nafion/graphene oxide composite membranes prepared using spin coating method for direct liquid fuel cells, *J. Membr. Sci.* 493 (2015) 212–223.
- [28]. Y. Hong, Z. Wang, X. Jin, Sulfuric acid intercalated graphite oxide for graphene preparation, *Sci. Rep.* 3 (2013) 3439.